

Advances in Solar Cell Materials and Storage

Photo- Electrochemical Solar Cells



Edited by

Nurdan Demirci Sankir
Mehmet Sankir

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Photoelectrochemical Solar Cells

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Advances in Solar Cell Materials and Storage

Series Editors: Nurdan Demirci Sankir and Mehmet Sankir

Scope: Because the use of solar energy as a primary source of energy will exponentially increase for the foreseeable future, this new series on Advances in Solar Cell Materials and Storage will focus on new and novel solar cell materials and their application for storage. The scope of this series deals with the solution-based manufacturing methods, nanomaterials, organic solar cells, flexible solar cells, batteries and supercapacitors for solar energy storage, and solar cells for space.

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and Mehmet Sankir**



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Preface

Hydrogen has a huge potential as a safe and efficient energy carrier which can be used directly in the fuel cells to obtain electricity, or be used in the chemical industry, fossil fuel processing, or ammonia production. However, hydrogen is not freely available in nature and needs to be produced. Photoelectrochemical (PEC) solar cells produce hydrogen from water using sunlight and specialized semiconductors, which use solar energy to directly dissociate water molecules into hydrogen and oxygen. Hence, it is possible to store solar energy via photoelectrochemical conversion. Besides, PEC systems reduce fossil fuels dependency and curb the exhaust of carbon dioxide. “Advances in Solar Cell Materials and Storage” series aims to provide information on new and cutting-edge materials, advanced solar cell designs and architecture, and new concepts in photovoltaic conversion and storage. *Photoelectrochemical Solar Cells*, which is the second volume of this series, compiles the objectives related to the new semiconductor materials and manufacturing techniques for solar hydrogen generation.

Discussing the underlying basics as well as the advanced details in PEC solar cell designs is highly beneficial for science and engineering students as well as experienced engineers. Additionally, the book has been written to provide a comprehensive approach in the area of the photoactive materials for solar hydrogen generation for the readers with a wide variety of backgrounds. Therefore, the book has been written by distinguished authors with knowledge and expertise about solar hydrogen generation whose contributions can benefit readers from universities and industries. The editors wish to thank the authors for their efforts in writing their chapters.

This book is organized in three parts. Part I (Chapters 1–4) covers the general concepts such as economic targets for hydrogen generation, theory and classification of PEC systems, reactor designs, and the measurements and efficiency protocols in PEC solar cells. Part I also addresses the novel hybrid structures containing inorganic/organic composites, biosensitized semiconductors, and tandem configurations. Part II (Chapters 5–8) is devoted to photoactive materials used in PEC conversion of solar energy

into chemical energy. Hematite materials, design of bismuth vanadate-based materials, copper-based chalcopyrite, and kesterite materials and eutectic composites for solar hydrogen generation are described in this part. Materials selection and photoactive electrode design are very crucial for the production of hydrogen in an efficient and economical route via PEC reaction. Therefore, the main focus of this part is to introduce the diverse range of photoactive materials especially the nanostructured semiconductors for PEC solar cells.

The book concludes with Part III (Chapters 9–11) covering photoelectrochemical-related systems. Implementation of multijunction solar cells in integrated devices for solar hydrogen generation, as well as the promising device design and the future prospects, are extensively summarized in this part. Photoelectrochemical energy and hydrogen production via dye-sensitized systems is also covered in Part III. Finally, photocatalytic formation of composite electrodes for solar cells is given in this book. Fundamentals of the photocatalytic deposition of metal sulfides on the nanostructured metal oxides, which are very promising materials for PEC systems, are summarized in the last section.

To conclude, we would like to emphasize that the second volume of the “Advances in Solar Cell Materials and Storage” series provides an overall view of the new and highly promising photoactive materials and system designs for solar hydrogen generation via photoelectrochemical conversion. Therefore, readers from diverse fields such as chemistry, physics, materials science, and engineering, mechanical and chemical engineering will definitely take advantage of this book to comprehend the impacts of the PEC solar cells.

Series Editors

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Part I

GENERAL CONCEPTS AND PHOTOELECTROCHEMICAL SYSTEMS

Photoelectrochemical Reaction Engineering for Solar Fuels Production

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Abstract

In order for large scale photoelectrochemical (PEC) water splitting devices to be realised, a number of challenges specific to engineering must be studied, understood and overcome. A logical approach requires the deconstruction of the PEC device into a classification framework comprising two parts: the fundamental conceptual design and the engineering PEC device design. This framework was used to study common elements of photoelectrochemical reactor designs and identify the engineering challenges encountered when scaling up PEC devices. A critical review of relevant PEC reactor designs is presented, where the scalability of each is assessed and general trends are identified, indicating improvements made. Innovative reactor designs are discussed in detail and opportunities for future research directions are highlighted. Directions towards technologically and economically feasible PEC water splitting devices are outlined.

Keywords: Photoelectrochemical, engineering, scale-up, water splitting, reactor design, H₂ production

1.1 Introduction

Daily and seasonal intermittency of radiation received from the earth's ultimate energy source, the sun, is driving the search for large capacity and long-term energy storage. Solar fuels are strong candidates that share most of the qualities of conventional fossil fuels, e.g., high energy density, easy distribution and storage, and high power output. In contrast, solar fuels

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can also deliver neutral or negative carbon emissions, hydrogen being the most popular example for the former case. Splitting liquid water to produce hydrogen and oxygen using solar energy requires a minimum of 1.48 V under thermoneutral conditions. Photoelectrochemical (PEC) reactors could produce hydrogen directly using solar energy, but photoelectrode materials are yet to be identified/synthesized that are adequately efficient, durable, and scalable. To date, there is no report of a photoelectrochemical cell with only one photoelectrode capable of achieving spontaneous water splitting satisfactorily with high efficiency [1] and using a wide range of visible light. Consequently, most of the reported systems require an electrical or chemical bias to produce hydrogen at an acceptable rate. When an electrical bias is applied, the electricity can be obtained from the burning of fossil fuels or, preferably, from renewable sources such as hydro, wind, or solar energy, e.g., photovoltaic cells. In the latter case, a photovoltaic cell is integrated with a photoelectrochemical system, buried or external, to harvest the rest of the energy required [2]. Systems with more than one absorber (stacked semiconductors) could be used to supply enough energy to achieve spontaneous water splitting. These configurations are sometimes referred to as internally biased systems [1] or integrated photoelectrochemical devices [3, 4].

The engineering of photoelectrochemical devices is often overlooked, as research has been mainly focused on material development, record efficiencies, and fundamental understanding of the phenomena involved in the photon absorption and charge transfer in semiconductors and catalysts. Hence, the aim of the present work is to summarize recent developments in reactor engineering, focusing on scaled-up photoelectrochemical systems, exposing current gaps in the research literature and contrasting with technical and economic targets. The latter will be discussed briefly below with a short summary of material development, followed by a survey and description of reported designs for theoretical and fabricated photoelectrochemical reactors. In its totality, this chapter aims to define the role of the photoelectrochemical engineering in creating feasible solar fuel devices and the future challenges it will face.

1.1.1 Undeveloped Power of Renewables

The total energy demand worldwide (thermal and electrical) was 18 TW in 2014 [5]. From all renewable energy sources, only solar and wind can provide enough energy for a fully decarbonized society, with technical capacities in the order of 10^3 and 10 TW, respectively [6]. Figure 1.1 summarizes the technical power that can be harvested using current

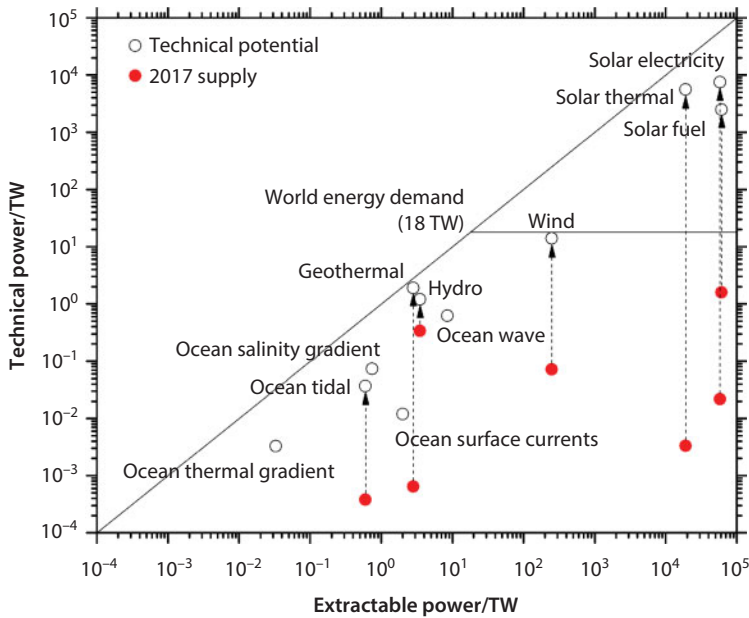


Figure 1.1 Extractable and technical potentials for several renewable sources (adapted from J. Tsao, Solar FAQs [6]).

technologies and updated supply of various renewable energy sources as previously reported by Tsao *et al.* [6] versus the extractable power from the source after chemical conversion. The present conversion and worldwide supply of solar to electricity and thermal is just above 0.02 TW, while solar to fuels dominates with a supply higher than 1 TW [7]. However, biomass is virtually the only source of solar fuels at present with arguable carbon neutrality [8]. The capacity of solar fuels, such as solar hydrogen, is still largely uncharted.

1.1.2 Comparison Solar Hydrogen from Different Sources

To date, only a few reports on the exergy efficiency and cost analysis of hydrogen production from renewable sources can be found. However, photoelectrolysis is usually not properly analyzed [9] or not analyzed at all [10, 11]. Exergy analysis is based on the second law of thermodynamics and considers the quality of the energy and not only a net energy balance. This allows a better comparison of systems that are fundamentally different, e.g., photovoltaic cells and hydroelectric power. From these reports, it was concluded that electrolysis of water using electricity from

hydroelectric power has the highest exergy efficiency (5.6%) and systems using photovoltaic cells has the lowest (1.0%) [10]. Presently, there are no reports with a proper comparison in terms of the exergy efficiency of a photoelectrochemical cell for hydrogen production.

Table 1.1 shows the expected costs of hydrogen production using conventional and already available technologies compared to those still in development [11–14]. Solar methane steam reforming is the most economical process currently deployed. These values have also been summarized by Pinaud *et al.* [14], where an estimated cost of hydrogen produced from steam methane reforming is approximately $\$1.25 \text{ (kg H}_2\text{)}^{-1}$, whereas the cost using photovoltaic technology is higher than $\$4.09 \text{ (kg H}_2\text{)}^{-1}$. In the same report, an estimated cost for hydrogen obtained from photoelectrolysis in particle-based systems was $\$1.60 \text{ (kg H}_2\text{)}^{-1}$, assuming 10% of solar-to-hydrogen (STH) efficiency, $\$4.10 \text{ (kg H}_2\text{)}^{-1}$ for concentrated panel systems with 15% STH efficiency, and as high as $\$10.40 \text{ (kg H}_2\text{)}^{-1}$ for an integrated PEC system with 10% STH efficiency. Recently, slightly higher costs were reported by Shaner *et al.* with PV + PEM (Proton Exchange Membrane) electrolyzer and updated costs for planar PEC devices [13]. It is obvious that the latter systems can barely compete with conventional methods and more development and research is required. The production cost of H_2 using suspended particles is expected to be the lowest among the systems under development; however, low H_2 yields, product (H_2 and O_2) crossover, and uncertain scalability are hindering further progress. Improvements in reactor design and efficiency must be made before these systems can be deployed commercially. Nevertheless, it has been stated that the production of hydrogen by photoelectrolysis is a viable option among carbon-free processes [14].

1.1.3 Economic Targets for Hydrogen Production and PEC Systems

The above prices for hydrogen contrast with the economic targets set by the US Department of Energy for solar hydrogen via photoelectrochemical water splitting as reported in Table 1.2 [16]. At present, the estimated price of hydrogen produced using integrated PEC systems is ca. $\$10 \text{ (kg H}_2\text{)}^{-1}$, the target by 2020 is half this value, and a fifth for the ultimate target, with a hydrogen production rate of $2 \times 10^{-6} \text{ kg H}_2 \text{ m}^{-2} \text{ s}^{-1}$, which corresponds to a minimum current density of 193 A m^{-2} assuming a faradaic efficiency of unity. State-of-the-art photoelectrodes still perform below these values, with a record set at 85 A m^{-2} for an integrated PEC cell (GaAs/InGaP/TiO₂/Ni) [17] and 140 A m^{-2} for a PV+electrolyzer system [18].

Table 1.1 Projected costs (long term) of hydrogen production.

Process	Cost/\$ (kg H ₂) ⁻¹		
Steam reforming (Nov. 2017)	(Lemus, 2010) [15]		
Natural Gas (Market price)	1.2		
Coal (Market price)	1.8		
Designs at small-scale pilot plants	(Koumi, 2012) [11]		
Solar hybrid sulfur cycle	2.3		
Solar sulfur-iodine cycle	2.4		
Solar metal/metal oxide cycle	4.2		
Solar high temperature electrolysis	5.6		
Solar methane cracking	2.1		
Solar methane steam reforming	1.9		
Conventional renewables (Projected)	(Koumi, 2012) [11]	(Acar, 2014) [12]	(Shaner, 2016) [13]
Electrolysis using solar thermal power	3.2	–	–
Electrolysis using wind power	2.8	7.2	–
Electrolysis using photovoltaic power	7.9	9.1	12.1
Electrolysis using nuclear	-	1.3–3.5	–
Biomass gasification	1.3	1.4	–
PEC devices (Projected)	(Pinaud, 2013) [14]		(Shaner, 2016) [13]
Single bed particle suspension	1.6		–
Dual bed particle suspension	3.2		–
Fixed panel array	10.4		11.4
Tracking concentration array	4.0		9.2

Table 1.2 Targets set by US Department of Energy (DoE) [16].

Parameter	Units	2020 Target	Ultimate target
Photoelectrochemical hydrogen cost	$\$ (\text{kg H}_2)^{-1}$	5.70	2.10
Capital cost of concentrator and PEC receiver (noninstalled, no electrode)	$\$ \text{ m}^{-2}$	124	63
Annual electrode cost per tonne H_2 per day	$\$ (\text{t H}_2)^{-1} \text{ d}^{-1} \text{ a}^{-1}$	255 k	14 k
Solar to hydrogen (STH) energy conversion ratio	%	20	25
1-Sun hydrogen production rate	$\text{kg H}_2 \text{ m}^{-2} \text{ s}^{-1}$	1.6×10^{-6}	2.0×10^{-6}

Ultimate targets also set STH efficiencies at 25% and cost of the PEC electrode at \$100 per meter square, and a lifetime of 10 years. These targets prohibit the use of expensive and unstable photoabsorbers. The most inexpensive silicon-based PV modules are currently at $\$0.35 \text{ W}^{-1}$ [19], with an estimated cost of $\$50 \text{ m}^{-2}$ [20]. Perovskites modules are expected to be $\$32 \text{ m}^{-2}$ [21], while CIGS and CdTe are between $\$90$ and $\$80 \text{ m}^{-2}$ ($\$0.9 \text{ W}^{-1}$) [20]. Multijunction, e.g., GaInP/GaAs/S, modules costs are between $\$4.85$ and $\$8.24 \text{ W}^{-1}$ depending on the type of multijunction [22] with an estimated cost between $\$1500$ and $\$3000 \text{ m}^{-2}$.

Studies on photoelectrodes are always constrained by the compromise between efficiency and stability, the former leads to the extensive study of inefficient but scalable and stable materials, e.g., Fe_2O_3 and TiO_2 , while record materials [18, 23, 24] are usually reported without considering in full the costs or scalability of such materials.

1.1.4 Goals of Using Hydrogen

As discussed previously, solar fuels have the advantage to be used for energy storage in a decentralized manner and when higher power output is required. Hence, its use in heavy transportation and heating is most appropriate.

The electrification of heating is constrained by the intense peaks for heat demand at well-defined times during the day, which can be 10 times higher compared to baseline in a typical UK winter day. In contrast, electrical energy peaks are generally observed at twice the baseload [25]. Hydrogen

could supply sufficient power for heating by combustion in a similar manner as natural gas or using fuel cells.

A roadmap from the International Energy Agency on the use of hydrogen in the transport sector has set economical and technical targets for the use of fuel cell electric vehicles (FCEVs) for 2050 in order to meet the decarbonization targets to limit global temperature rise to below 2 °C above the preindustrial level. This involves 25% of passenger light-duty vehicle and 10% of freight road transport running on hydrogen [26]. Studies on the energy supply to off-grid users report smaller footprint by using hydrogen-based systems (electrolyzer, fuel cell, and metal-hydride storage) compared to traditional Li-ion batteries [27]. However, this depends on the consumer needs and time and scale of storage required. In a usually forgotten market, the use of hydrogen-based energy systems for the increasing energy demands of developing countries is a plausible scenario and even regarded as the best option for these markets [28]. Besides the obvious environmental benefits of using renewable energy, solar hydrogen can also enhance the living standards of off-grid populations in developed countries.

In order to supply the hydrogen required to fulfill the demands in the aforementioned future scenarios, a durable, efficient, and inexpensive material has to be developed to be used in PEC systems. Solar-to-hydrogen efficiency is the most commonly used figure of merit, and it has been reported for a wide variety of materials. Figure 1.2 shows the updated learning curves (adapted from Ager *et al.*, 2015 [29]) classified by material for photoelectrochemical cells for spontaneous water splitting. Buried and external PV + electrolyser, with a present record of 30% [18], has dominated research in the last decades. Silicon-based systems have not seen any significant improvement in the last 10 years, mainly due to the stagnating efficiencies for this material. Efficiencies of oxide-based systems remain close to 1% values, while recent improvements on perovskites have allowed researchers at EPFL to reach efficiencies of 12.3% for a PV + electrolyser system [30]. From the materials perspective, it appears that there is less room for improvement in silicon-based PV+PEC devices, while oxides and hybrid systems are evolving fast with an extensive gap to be closed.

1.2 Theory and Classification of PEC Systems

In this section, we aim to formalize the classification of photoelectrochemical designs and terminology. The first part of this section describes the abstract conceptual design (i.e., schematic) which defines the type of system used, while the second part describes the physical structure and layout

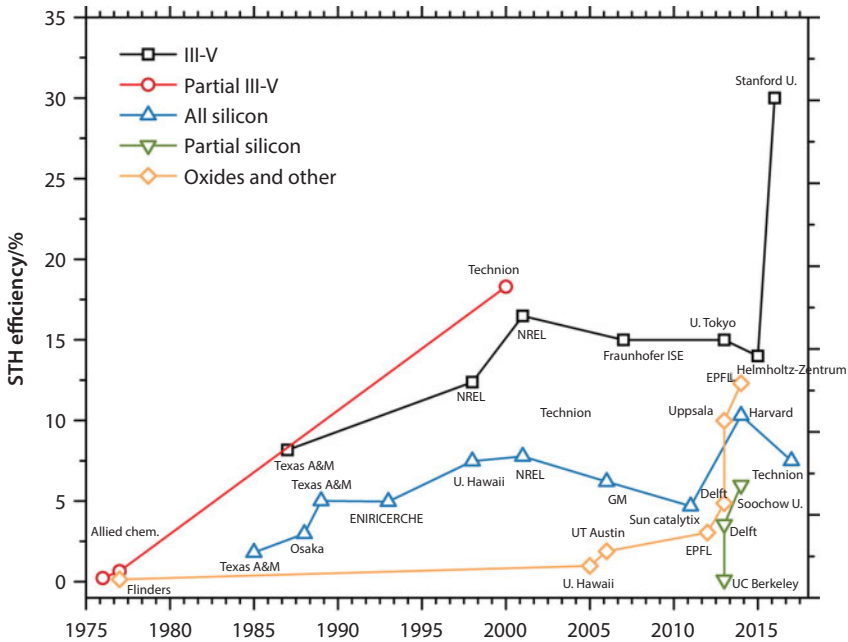


Figure 1.2 Timeline of solar to hydrogen (STH) conversion efficiencies for different materials implemented in photoelectrochemical devices for spontaneous water splitting (adapted from Ager *et al.*, 2015 [29]).

of reactor designs (i.e., engineering drawing). The rationale for this partition is to reduce the complexity in classification and to allow for reactor design grouping. Furthermore, the maximum theoretical efficiency achievable is defined by the conceptual configuration [31–33] and not the reactor design. In this work, we only discuss planar electrode systems as opposed to particulate systems due to the higher record efficiencies reported.

1.2.1 Classification Framework for PEC Cell Conceptual Design

The schematic/conceptual design of PEC systems is categorized in a hierarchical framework. The order in which a PEC system should be classified is as follows:

1. Number of photoabsorbers
2. Electrical configuration of photoabsorbers
3. Optical connection of photoabsorbers and optics of system

Any design will be characterized by these three specifications which are outlined further below.

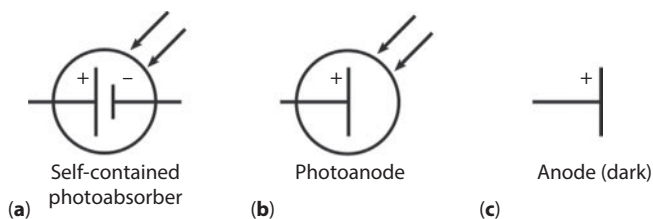


Figure 1.3 Electrical symbols where the polarity of the electrodes is in reference to an electrolytic cell.

Number of Photoabsorbers

The number of photoabsorbers used to drive photoelectrolysis has a great impact on the maximum efficiency of the system [31–33]. Unassisted water splitting with appreciable efficiencies has been achieved only by using multiple photoabsorbers [3] due to the “spectral mismatch” between the energy in the solar spectrum and the energy required to drive water splitting. Commonly, a two-photoabsorber approach is termed “a tandem cell” [34].

Photoabsorbers can be further classified by the conductive nature of the two materials that make up the electrical junction. The junction formed at two electronic conductors is commonly called a solid-state junction or photovoltaic junction, whereas the junction formed between an electronic and an ionic conductor is commonly referred to as a semiconductor–electrolyte junction. It is important to note that the electrolyte may also be a solid-state ionic conductor. An excellent taxonomy was produced by Nielander *et al.* [35], which classified the different architectures and defined a naming scheme which also differentiated between the type of the applied bias source (i.e., whether it was PV or PEC). However, for the conceptual PEC design outlined here, we only differentiate between semiconductor–liquid junction (SCLJ) in contact with the electrolyte, from which the solar fuel is synthesized and self-contained solar cell. This is to group together all systems that can bias the cell, which could include both PEC solar cells, e.g., dye-sensitized solar cells, and PV cells, e.g., multijunction III-V cells. Figure 1.3 introduces the symbols used in the subsequent sections.

Electrical Configuration of Photoabsorbers

The photoabsorbers must be placed within the electrolytic cell electrical circuit. In a generic photoelectrochemical cell, as shown in Figure 1.4, photoabsorbers can be placed at different points within the circuit. Commonly, multiple photoabsorbers are connected in series in order to generate a sufficiently large potential to split water. There is also the possibility of multiple anodes or cathodes utilizing different light absorbers as demonstrated in the work by Kim *et al.* [36].

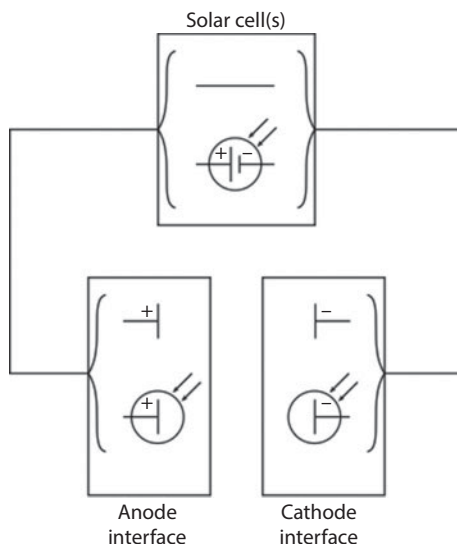


Figure 1.4 Generic schematic of layout of photoelectrochemical cell.

Optical Configuration of Photoabsorbers

For systems employing multiple photoabsorbers, there will be multiple optical configurations. Photoabsorbers can be placed in parallel or in series, which has significant ramifications for the obtainable efficiency and complexity [33]. The main advantage of optical operation in series is that a preceding absorber utilizes a portion of the spectrum and allows other wavelengths to pass through to the next absorber. Higher efficiencies can be obtained using this configuration due to a more complete capture of the spectrum of light while maintaining a more significant proportion of the captured energy of each photon. However, this approach can be complex as the spectrum must be matched to the current density and is often expensive, especially for multijunction solar cells. Optical operation in parallel is often used with photoabsorbers of the same bandgap as each solar cell can receive the portion of the spectrum needed for efficient individual operation. The photoabsorbers are then connected electrically in series in order to generate the required photovoltage for water splitting if one cell is not sufficient.

In order to simplify the classification, we introduced a schematic representation of the optical pathway of light in Figure 1.5. It is important to note that at each junction where light splits (or merges), the diagram makes no assumptions about the fraction of the split and/or the spectral dependence of this. This means that complex optics such as spectral splitters (dichroic mirrors) could achieve high efficiencies through greater utilization of the

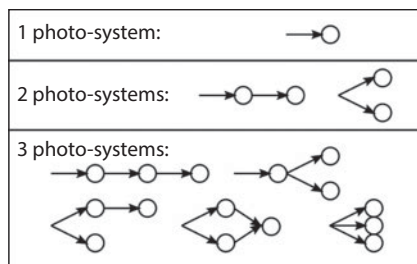


Figure 1.5 Optical configurations for 1, 2 and 3 photoabsorbers.

spectrum (similar to series configuration) while the photoabsorbers are optically in parallel.

Example Conceptual Designs

In order to demonstrate the versatility of the previously described conceptual schematic, a number of example systems from literature are presented. This methodology attempts to be a universal abstraction of the photoelectrolysis process and so can easily represent complex designs using one set of schematic rules.

The examples in Table 1.3 have been chosen to show the broad range of device architectures and the utility of the conceptual design framework outlined previously. As the number of photoabsorbers, electrical, and optical connection defines the maximum theoretical efficiency achievable, this allows for designs to be compared even though the physical implementation and materials used may differ significantly.

In this framework, photo-assisted electrolysis systems, which employ an electrical bias from an external power source (e.g., PV + transformer/inverter, wind turbine, etc.), have not been included; however, they could be easily implemented. As the mode of the external power source is irrelevant from a PEC conceptual design viewpoint, it could simply be included as a power source symbol.

1.2.2 Classification Framework for Design of PEC Devices

For a conceptual PEC cell design to be engineered into a physical device, a number of considerations must be made as to the placement of components within the cell. The framework outlined below classifies each device design.

1. Conceptual design (see previous section)
2. Electrode construction

Table 1.3 Example conceptual designs.

Paper	No. of photoabsorbers	Electrical configuration	Optical configuration	Information about photoabsorbers
Han <i>et al.</i> 2014 [37]	3			1) W:BiVO ₄ 2) a-Si:H 3) nc-Si:H
Khaselev and Turner 1998 [38]	2			1) GaAs 2) GaInP ₂
Jia <i>et al.</i> 2016 [18]	3			1) InGaP 2) GaAs 3) GaInNAs
Jacobsson <i>et al.</i> 2013 [39]	3			1) CIGS 2) CIGS 3) CIGS
Kim <i>et al.</i> 2016 [36]	2			1) BiVO ₄ 2) Fe ₂ O ₃

3. Physical placement of electrodes and photoabsorbers
4. Electrolyte and reaction environment
5. Optical design of reactor
6. Product separation and collection
7. Electrolyte (and evolved gas) fluid mechanics

Electrode Construction

Conventional electrodes studied in water splitting are commonly planar and contain, at a minimum, an electrochemically active surface and mechanical support. A photoabsorber can be incorporated into the electrode by a SCLJ or a “buried junction” where an external solar cell is integrated in a layer below a transparent catalytic layer. As the buried junction spatially separates the electrochemical reaction and the charge excitation, semiconductor materials, which are not stable in the electrolyte due to corrosion, can be used if shielded by a protective “window” layer (such as a TiO_2 thin film), though the efficacy of this approach is an active research topic. All buried junctions, by design, are optically in series to any photoabsorber at the interface.

In order to allow charge to flow through the electrode, an electrical connection must be made to the interface. For dark electrodes (no photoabsorber), metal supports are used. For photoelectrodes, the semiconducting material needs to be placed on a compatible conductive substrate which can be either a metal (e.g., Ti, Fe) or a transparent conductive oxide film on glass (e.g., fluorine-doped tin oxide).

Physical Placement of Electrodes and Photoabsorbers

Electrode placement can be broadly classified into two configurations, examples of which are shown in Figure 1.6. The first of which involves the electrode interfaces stacked (back to back) with any buried/external junctions “sandwiched” in-between them. This integrated configuration is referred to as a monolithic stack or a bipolar electrode. The second has spatially distinct electrodes where the surface orientation of the interfaces is not constrained. Common terms for this configuration is “wired” or monopolar electrode.

It is also possible to classify the placement of the electrode according to whether the current over the surface of the electrode is collected and transferred via a conductor to the opposing electrode (i.e., wired), or whether current flows perpendicular from the surface of one electrode then directly through conductive substrate/PV material onto the other electrode (i.e., wireless). The latter requires each stacked layer to be electrically bonded to one another.

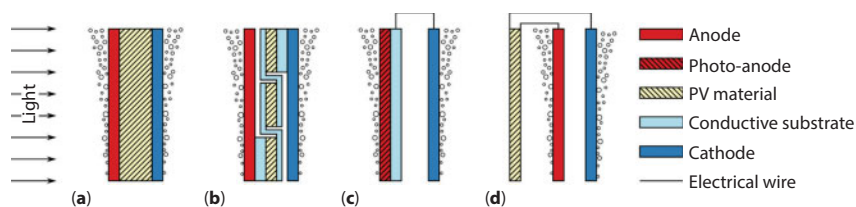


Figure 1.6 Example electrode placement. (a) Wireless monolithic. (b) Wired monolithic. (c) Monopolar with integrated photoabsorber. (d) Monopolar external PV bias.

Here, the terms “wired” and “wireless” are not used to describe the electrode configuration as it is feasible to construct a monolithic device which is wired as shown in Figure 1.6(b). From a reactor design perspective, designs (a) and (b) in Figure 1.6 are identical and therefore the distinction between monolithic bipolar and monopolar is used as this has the greatest impact on the overall design.

Figure 1.6(d) demonstrates an approach which is commonly referred to as “PV + electrolysis” as the external PV is providing the power to drive electrolysis. This external solar cell can be either placed inside the reactor in the electrolyte (which likely requires encapsulation of the PV) or outside. From an engineering perspective, scaling up a PV + electrolysis system is less complex in comparison to integrated PEC designs where light absorption and charge excitation are integrated in an electrochemical reactor.

The current concentration ratio F , as defined by Dumortier *et al.* [40], is the ratio of the geometric projected electrode area to the photoabsorber area. For most integrated PEC systems, this will be constrained to unity. For PV + electrolysis systems, gains in efficiency and speculative cost (due to reduced cost of catalyst) can be made by respectively increasing and decreasing F [4, 41].

Electrolyte and Reaction Environment

The electrolyte used can influence the design of the PEC reactor in a number of ways. The electrolyte must be conductive and is therefore either an acidic or basic solution or one that contains a pH buffer. Near-neutral electrolytes may require flow (see fluid mechanics section below) in order to mitigate the issue of developing pH gradients [42].

The phase of the electrolyte is most commonly liquid, but there have been examples of higher temperature integrated systems with a solid electrolyte and gaseous reactants [43, 44] similar to the membrane electrode assembly seen in fuel cell systems.

In some cases, the oxygen evolution reaction (OER) has been replaced with an alternative oxidation reaction [45, 46], which may be beneficial due to a decrease of the required thermodynamic electric potential or kinetic improvements. Use of such “hole scavengers” must be energetically justified (through a complete life cycle analysis), and therefore such reactants may be waste streams from another chemical process. This may alter the design of the reactor as dilute reactants may suffer mass transport issues, and some hole scavengers may absorb useful portions of the solar spectrum, which will alter the optical design of the reactor.

Optical Design of Reactor

A reactor must physically contain the electrolyte and gaseous products from the surroundings. In order to get light into such a system, at least part of this structure must be optically transparent. The optical design of a reactor can be classified into the number of optical apertures. The vast majority of designs use one window, but there are examples that use two windows [47, 48, 62].

There is a vast array of nonimaging optical designs for capturing solar energy [49], which can include a range of optics such as lenses, mirrors, and spectral splitters. Optical concentration of light can be quantified through the irradiation concentration ratio, C , which is defined as the ratio of the geometrical area of the concentrating optics to the photoabsorber area. There are several examples in literature of novel optical designs such as the use of optical fiber [50–52] and spectral splitters [53, 54].

$$C = A_{conc} / A_{photo} \quad (1.1)$$

Product Separation and Collection

The products from water splitting, hydrogen and oxygen, must be collected and removed from the system. If the products are allowed to mix, then the subsequent separation of gases is energetically expensive and an explosive mixture may occur. The lower flammability limit of H_2 in O_2 is approximately 4 vol%, and due to the low activation energy of combustion, a detonation could very easily be triggered. Furthermore, if products are allowed to “crossover” into the opposite section of cell, the reduction of O_2 and the oxidation of H_2 at the respective electrodes can lower the faradaic efficiency.

Product separation can be achieved by one of the three methods:

1. Ion-selective transport membrane—e.g., AEM or PEM
2. Porous separator—asbestos or polymer diaphragm (such as the type conventionally used in the chloralkali process)

3. Membrane-less separation—achieved through hydrodynamic control of dissolved species and/or bubbles

Currently, the majority of feasible large-scale solar fuel designs employ ion-selective membranes such as Nafion®. This is due to the proven safety record in polymer electrolyte membrane (PEM) electrolysis and low product crossover, although these membranes can be expensive. The consequence of the formation and subsequent detonation of an explosive mixture of gases would be catastrophic. Hence for relatively unexplored membrane-less systems, extended demonstration of operation within safe limits and a hazard and operability study (HAZOP) is required to demonstrate an acceptably low risk before these technologies can be implemented. While porous separators may be relatively inexpensive and potentially significantly more ionically conductive, care must be taken to ensure acceptable levels of dissolved gas crossover [55] as gases can diffuse at significantly higher rates than in ion-selective membranes. These issues are not insurmountable as the use of porous separators (e.g., asbestos diaphragms) is an established technology in alkaline electrolysis.

The membrane separates the cell into two compartments and must be placed in the cell so as to allow light to reach the photoabsorbers inside the reactor. The position in the cell therefore depends on which electrodes (if at all) require illumination. The example designs in Figure 1.7 demonstrate the common locations of the membrane.

Ohmic losses through the membrane are minimized as current densities flowing through the membrane are decreased. Therefore, it may be useful to define a current density ratio between membranes and electrodes, M , which can be defined as the membrane area to the electrode area where larger values lead to lower membrane-resistive losses.

$$M = A_{\text{membrane}} / A_{\text{electrode}} \quad (1.2)$$

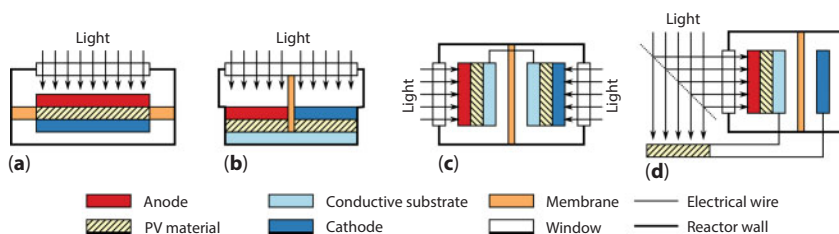


Figure 1.7 Example optical designs demonstrating reactor designs with one (a, b, d) or two windows (c). Example d uses a dichroic mirror to split the light into two paths, leading to more efficient utilization of the spectrum.

Electrolyte (and Evolved Gas) Fluid Mechanics

The majority of laboratory-scale experiments using photoelectrochemical cells are performed in batch. However, the concentration of electrolyte in a batch system will change over time, and reactants and products will have to be added and removed periodically. If large quantities of hydrogen are to be produced, it is far more feasible to envisage a continuous system where electrolyte is pumped through the cell and products removed before recirculation of the electrolyte. Furthermore, electrolyte flow also benefits the process through higher mass transfer rates, removal of gas bubbles, and by ensuring operation that is approximately isothermal.

1.2.3 Integrated Device vs PV + Electrolysis

Jacobson *et al.* [56] demonstrated a gradual transition in design between a fully integrated system and PV + electrolysis. This concept of classification is also mentioned by Rongés *et al.* [57] and can be seen in Figure 1.8. Although a useful abstraction, it can be hard to place every possible reactor design on this one dimensional scale, e.g., particulate systems or systems with multiple light absorbers.

1.3 Scaling Up of PEC Reactors

The engineering of PEC reactors scaled up from the laboratory scale is a nontrivial exercise. At present, there is a multitude of distinct reactor designs described in literature, and no consensus has been established for a standardized design. This is mainly due to the focus on fundamental material science and absence of the “holy grail”: high efficiency, stable, scalable, and inexpensive material. As shown in the sections below, for the vast combination of conceptual PEC systems, a suitable reactor design will differ. However, there are many underlying aspects of electrochemical

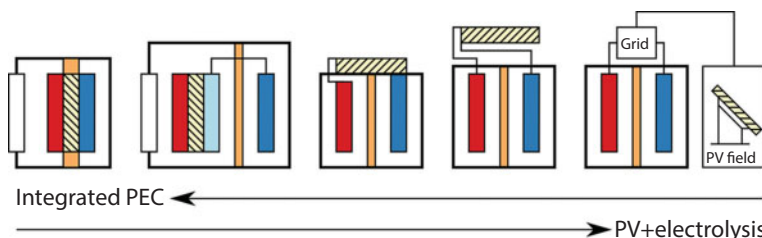


Figure 1.8 Demonstrating the transition between integrated PEC and PV + electrolysis.

engineering to consider when scaling up a PEC device, which is common to all designs. These aspects have been grouped together by their relevant conserved quantity. For example, a change in pH, which is caused by the change in concentration of hydronium or hydroxide ions in solution, falls under mass transfer as the ions must move to accumulate or disperse.

Table 1.4 outlines each aspect grouped by its respective conserved quantity. It is important to note that one cannot tackle each aspect separately as there are many interacting factors between them. Universal to nearly all engineering design challenges, compromises and trade-offs will have to be made between competing design aspects to optimize for the desired objective function, which is often to minimize the total delivered cost of H_2 (\$ kg⁻¹).

It is therefore instructive to acknowledge which reactor design goals are in competition with one another. A similar analysis of the trade-offs for the semiconductor material properties can be made [71, p. 57].

- Minimizing potential losses across membrane $\leftrightarrow$ acceptable levels of product crossover (safety)
- Minimization of the current density distribution nonuniformity $\leftrightarrow$ fabrication of a device of reasonable dimensions
- Electrolyte conductivity $\leftrightarrow$ compatibility with materials (material stability)
- Placement of membrane $\leftrightarrow$ light pathway to photoabsorber
- High production rate $\leftrightarrow$ mass transfer limitations

1.4 Reactor Designs

As mentioned earlier, there are a number of issues that must be overcome in order to allow for successful operation of PECs cells in scaled-up systems. There have been a number of reactor designs proposed and developed in the field throughout the years. However, typically each reactor design proposed would attempt to tackle or solve only a single or a couple of issues at hand. Table 1.5 includes schematics for various designs, and Table 1.6 compares selected implementations of these designs in literature, while identifying the main issues resolved. In both cases, this is not an exhaustive list but gives an overview of the current trends in PEC reactor design. PEC reactor designs specifically for testing the performance of materials have been excluded from this analysis.

Solar-to-hydrogen efficiency is widely used to compare the performance of unassisted water splitting systems (Figure 1.2), and it is defined in Eq. 3

Table 1.4 Engineering considerations when scaling up PEC reactors.

Charge transfer	
Substrate conductivity	Low conductivity substrates such as FTO and ITO may lead to large electrical potential losses [58, 59]. If a transparent conductive oxide is used, the electrical contact to it may lead to potential losses.
Electrolyte conductivity	Must be conductive enough to reduce ohmic losses (e.g., 1M alkaline or acids are often used). Neutral solutions must be buffered in order to be conductive. Bubbles at the electrode interface may cause a decrease in local conductivity [60].
Membrane conductivity	Membranes might cause a large drop in performance due to the electric potential lost over the membrane which subsequently must be provided by the solar cell [61].
Current density distribution	This must be minimized as it can lead to inactive electrode area [62, 63].
Charge transfer within the light absorber and at the interface	This is primarily a semiconductor material consideration and its fundamental principles can be found elsewhere [64–66].
Photon transfer	
Window material	Reflectance and transmittance of the window material must be considered. Transmittance of various relevant glasses and polymers can be found in Miller <i>et al.</i> [67].
Gas evolution	Bubbles reflect and scatter light away from the photoabsorber.
Electrolyte attenuation	Electrolyte absorbs a significant amount of light, especially at larger wavelengths [68]. Dissolved species, which absorb light more strongly, may also be present, such as aqueous redox mediators or hole scavengers. Commonly, membranes are not transparent enough for light transfer through them to be considered.
Heat accumulation	Especially when using concentrated sunlight, the temperature of the reactor must be considered (water absorbs the infrared portion of spectrum strongly).

(Continued)

Table 1.4 Cont.

Mass transfer	
pH and concentration gradients	Especially for neutral pH operation and for batch operation, unacceptable pH gradients or depletion of electrochemical species can occur [42, 60].
Species crossover	Crossover of products can lead to a decrease in product collection efficiency, faradaic efficiency, and explosive mixtures of H ₂ and O ₂ and this is commonly minimized with a membrane or separator. Membrane-less systems without flow could suffer significantly from crossover issues [60], while with careful hydrodynamic control, they could be theoretically possible [69].
Mass transfer-limiting current	This may only be applicable when operating at higher photon intensities. Mass transfer-limited current densities in concentrated electrolytes are ca. 10 ⁴ A m ⁻² [62], compared to theoretical current densities of 81 A m ⁻² at 1 sun and 10% STH. If redox mediators are used or dilute organic waste is oxidized, the current may become mass transfer limited.
Momentum transfer	
Electrolyte and gas fluid mechanics	CFD is a useful tool to evaluate electrolyte fluid mechanics and flow patterns [42, 58, 70]. When gas bubbles are formed, complex two-phase flow must be considered [71].

where Φ_{H_2} is the molar rate of H₂ evolution per area, $G_{H_2}^f$ is the Gibbs free energy of formation for H₂, η_F is the faradaic efficiency, and P_{solar} is the illumination power per area.

$$\eta_{STH} = \frac{\Phi_{H_2} G_{H_2}^f \eta_F}{P_{solar}} \quad (1.3)$$

However, as STH efficiencies are strongly affected by the implementation of feasible reactor designs, care must be taken when making comparisons. Typically, systems with a membrane show a reduced efficiency, but systems without separators and coevolution of H₂ and O₂ would not be able to operate safely. An example of this is in the collated record efficiency

Table 1.5 Schematics for the design of various PEC devices found in literature.

Design 1	Design 2	Design 3
Design 4	Design 5	Design 6
Design 7	Design 8	Design 9
Design 10	Design 11	Design 12
Design 13	Design 14	
Legend		
Anode	Conductive substrate	Membrane
PV material	Cathode	Electrical wire
	Window	Reactor wall

table by Ager *et al.* [3], where most of the top efficiencies are constrained to small electrode areas and membrane-less operation.

All of the examples reported that achieve STH efficiencies $>10\%$ use multiple junctions, of which one or more are buried junctions or external PVs [30, 38, 39, 73]. This is indicative of the future direction of PEC devices with sufficient efficiency to be economically viable, and hence, many of the implementations of reactor designs outlined in Table 1.6 are based on multijunctions (and buried junctions).

With respect to light management, reactor designs fall into three categories. A number of designs illuminate the photoabsorber through the electrochemical junction from the side of the electrolyte (“front-side” illumination) [17, 55, 58, 62, 74–77] (Designs 1–10, 14). Others illuminate a PV junction externally and so circumvent the issue of getting light through the electrolyte, bubbles, and any catalytic layer [78] (Designs 11–13). Only a couple of designs suggest illuminating multiple photoabsorbers from two different optical ports in the reactor by the means of mirrors [47, 48, 63] (Design 4 & 8).

For monopolar configurations, which use a SCLJ or buried PV, an unobstructed path is required for the light to the electrode. For example, in the case of Design 1, the membrane material absorbs a significant fraction of the light. Design 2 circumvents this but compromises the current density uniformity. A membrane-less design (Design 13) allows for unobstructed front-side illumination but then requires a transparent cathode (or semi-transparent photocathode). Design 2 could reduce the issue of current density distribution through perforations; Design 3, though, this may reduce the photoactive area.

In an attempt to resolve the mass transfer issue of product separation, a number of researchers utilized membranes in their designs to separate the evolved oxygen and hydrogen gases. The membranes were in the form of anion-exchange membranes (AEMs) [17], proton-exchange membranes (PEMs) such as Nafion[®] [43, 47, 58, 80], porous glass frits [81] or a Teflon diaphragm [82].

The evolution of bipolar monolithic designs has tended to involve small repeating units or “perforated” electrodes due to the need to minimize the current density distribution [55, 58, 75, 78]; however, this may have the drawback of a loss of photoactive area due to the membrane [86]. The “louvered” design introduced by Walczak *et al.* [63], number 8 in Table 1.6, circumvents this issue: the unit electrode size was relatively large (16 mm) while the current density was found to be highly uniform. However, this may have been due to the low current densities observed (ca. 0.32 mA cm^{-2}), and therefore, operation at higher current densities ($<8 \text{ mA cm}^{-2}$) would

Table 1.6 Comparison of selected reactor designs in literature where (t) indicates a theoretical design, (e) is an experimental demonstration and (p) is a patent concept. Each design is ranked against various scaled-up considerations using the following symbols: +: resolved, -: unresolved, o: considered but isn't conclusive, NA: not applicable.

Design number	Author	Category	Reference	Charge				Photon				Mass			Momentum
				Substrate conductivity	Electrolyte conductivity	Membrane conductivity	Current density distribution	Window material	Gas evolution	Electrolyte attenuation	Heat accumulation	pH and conc. gradient	Species crossover	Limiting mass transfer	Fluid mechanics
1	C. Carver 2012	t	[58]	o	+	-	+	o	-	-	+	+	+	+	+
2	T. Lopes 2014	e	[47]	+	+	o	-	o	-	+	o	+	+	+	-
2	Y. Li, 2011	e	[74]	+	+	-	-	o	-	+	+	+	+	+	+
2	M. Graetzel, 2005	p	[76]	-	o	-	-	o	-	-	-	o	+	NA	-
3	A. Hankin 2017	t	[61]	+	+	-	+	o	-	+	-	+	+	+	-

(Continued)

Table 1.6 Cont.

4	T. Lopes 2014	t	[47]	-	+	o	-	o	-	o	-	+	+	o	+	+	+	+	-
4	Q. Fan, 2007	p	[48]	+	o	-	-	o	-	o	-	+	+	-	+	+	+	NA	-
5	E. Verlage, 2015	e	[17]	+	+	o	-	o	-	o	-	-	-	-	-	+	+	+	-
6	E. Selli, 2007	e	[73]	+	+	-	-	o	-	o	-	-	-	-	-	+	+	NA	-
6	E.L. Miller, 2003	t	[81]	+	o	-	-	o	-	o	-	-	o	-	+	+	+	+	+
7	S. Haussener, 2012 (b)	t	[55]	+	+	+	+	o	-	o	-	-	+	-	+	+	+	+	-
7	T. Bosserez, 2016	e	[82]	+	+	NA	+	NA	+	NA	+	-	-	-	+	-	+	+	-
7	F. Bedoya, submitted	t	-	+	+	o	+	o	+	o	o	o	o	o	+	+	+	+	-
8	K. Walczak, 2015	e	[62]	+	+	o	o	o	o	o	-	-	+	o	+	+	+	+	-
9	X. Deng, 2010	p	[75]	+	+	-	+	+	+	o	+	+	-	o	+	+	+	NA	+
10	S. Haussener, 2012 (a)	t	[55]	+	+	+	+	+	+	o	-	-	+	-	+	+	+	+	-
11	S. Haussener, 2012 (a)	t	[55]	+	+	+	+	+	+	o	-	+	+	-	+	+	+	+	-
11	B. Turan, 2016	e	[77]	+	+	NA	o	+	+	+	+	+	+	-	+	+	+	+	-
12	A. Landman, 2017	e	[72]	+	+	NA	+	+	+	+	+	+	+	-	+	+	+	+	-
13	N Kelly, 2008	e	[83]	+	+	NA	-	-	-	-	-	-	-	-	+	+	+	+	-
13	J. Becker, 2017	e	[84]	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+	+
13	S. Tembhurne, 2016	t	[43]	+	+	+	+	NA	+	+	+	+	+	+	+	+	+	-	-
14	I. Holmes-Gentle, 2017	t	[68]	-	+	NA	+	+	+	o	+	+	+	o	+	+	+	+	+

require miniaturization of this design. As one travels toward the limit of miniaturization of bipolar monolithic designs, one moves from “perforated electrode” designs to membrane-embedded semiconductors such as the ca. μm size Si microwires proposed by Nathan Lewis *et al.* [87, 88].

Some authors have considered implementation of electrolyte flow in and out of the cell [58, 63, 69, 75, 89], but the vast majority did not. As outlined previously, continuous systems would be required for large-scale production of hydrogen, where electrolyte flow could also help to alleviate issues around concentration gradients [42] and facilitate bubble removal [90].

Overall, many PEC designs perform well at tackling a particular scaling-up issue (see Table 1.4), but none of them simultaneously meet all the requirements. Therefore, PEC reactor design constitutes a complex optimization problem in order to balance reactor performance, cost, and operability. When the light absorber system is decoupled from the electrochemical system, i.e., PV + electrolysis, each component can be optimized separately and complexity of scaling up such system becomes significantly less complex than for integrated PEC designs.

A comparison of reactor designs using a descriptive ranking scale is made in Table 1.6, and an overall trend with time can be observed if each row is summed to obtain a “net number of resolved issues.” This analysis can be seen in Figure 1.9, which demonstrates two clear trends: Firstly, the number of descriptions of PEC reactors in literature has increased in the period from 2003 to 2018. Secondly, more engineering challenges have been considered, addressed, or indeed solved as we move toward 2018. While this analysis is not exhaustive and only a qualitative assessment, the trend clearly demonstrates both the interest and progress made in the field of solar water splitting reactors.

1.5 System-Level Design

System-level design is the final stage required for the scaling up of PEC devices. All the relevant unit processes, such as fuel production, processing, storage, and transport, must be analyzed. While system-level analysis has been conducted extensively for electrolyzers coupled with a renewable source of electricity, such as PV, and various demonstrator systems have been built [91–94], there have been fewer studies regarding the system design of a PEC device and a lack of large-scale (area ca. $1 + \text{m}^2$) demonstrations. Many parallels can be drawn between studies on PV + electrolysis and PEC systems, such as on the available solar resource, land cost, gas processing, and H_2 storage, etc., as these are independent of whether the light

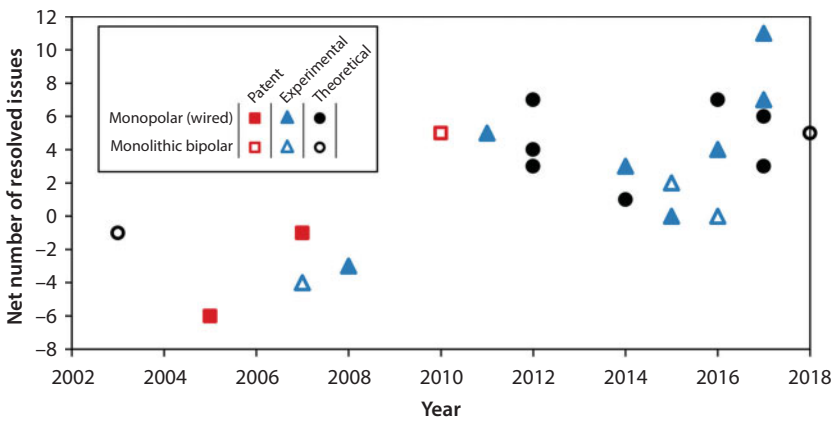


Figure 1.9 Learning curve for selected PEC reactor design from literature. Net number of resolved issues from Table 1.6 where +, o, – are summed as +1, 0, –1, respectively.

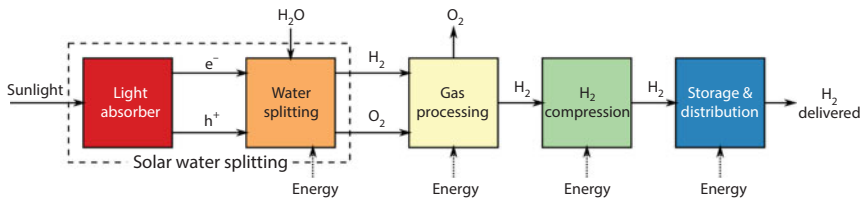


Figure 1.10 Flow diagram of solar hydrogen production process (adapted from Modestino *et al.* 2016 [94]).

absorber and electrochemical system are integrated. Figure 1.10 shows a flow diagram of all the key unit processes in a solar hydrogen plant.

Due to complexities of hydrogen pressurization and storage and favorable economies of scale, research has mainly focused on large centralized systems as opposed to a distributed fuel production system. Rongé *et al.* [57] compared the benefits of centralized vs distributed H₂ production, and it was noted that for distributed systems, a hydrogen storage pressure of 8 atm was more practical than 700 atm. Perhaps the most comprehensive system-level study, a US Department of Energy commissioned report on the detailed technoeconomic analysis of solar hydrogen, was discussed by Pinaud *et al.* [14]. The economic sensitivity analysis concluded that efficiency had the biggest impact on hydrogen-delivered cost. Zhai *et al.* [96] performed a life cycle assessment (LCA) on the energy balance and described the key relationship between primary energy requirement, efficiency, and lifetime. Shaner *et al.* [13] used a system-level design to guide

future research on various solar to hydrogen technologies. Interestingly, they noted that the cost associated with the transport of low pressure hydrogen could be more favorable than the transportation (via high power transmission lines) of low power PV electricity. Furthermore, they also found that system efficiency is key to delivered H_2 cost and hence suggested that the target should be a system efficiency of ca. 25% and a lifetime of 7–10 years in order to be competitive with fossil fuel-derived H_2 .

When considering the final system design, the fundamental STH efficiency will not represent the complete system efficiency (η_{system}). For this, external energy from pumps and other necessary equipment ($P_{external}$), or electrical energy used to bias the PEC system ($P_{electrical}$), must be included [97].

$$\eta_{system} = \frac{\Phi_{H_2} G_{H_2}^f \eta_F}{P_{solar} + P_{electrical} + P_{external}} \quad (1.4)$$

1.6 Outlook

1.6.1 Future Reactor Designs

1.6.1.1 Perforated Designs

As seen in Table 1.5 as Design 7, perforated monolithic electrodes have been the focus of recent studies on the engineering of PEC systems [55, 61, 82]. After careful study, we may find that Design 7 is preferred over other designs as it focuses on the improvement of homogeneous current density distribution over the electrode area while minimizing product crossover [62] and ohmic losses in the perforations [83]. The geometric properties of such monolithic photoelectrodes must be judiciously estimated to achieve a maximum hydrogen yield with a minimum presence of oxygen and potential losses. This can be done with the help of multiphysics models, which must incorporate photon, charge, and mass transfer, and additionally momentum transfer for membrane-less systems [42, 69] and heat transfer for high photon fluxes. Membranes [58] and porous separators [55] have been proposed, since the first description of Design 7, to prevent product crossover; however, there is no clear consensus on which of these two options would be the more suitable for photoelectrochemical reactors operating at relatively low current densities. Only recently, the geometric dimensions of the perforation were investigated by Bosserez *et al.* [83] inspired by a similar study using Si microwire arrays [88], and independently by Bedoya-Lora *et al.* (submitted) accounting for bubble generation and diffusion and desorption of dissolved gas. It was concluded that

perforations at microscale are indeed necessary to achieve a good balance between ohmic losses, product crossover, and current density distribution. Nevertheless, a deficiency of experimental studies to corroborate the suitability of membranes over porous separators at microscale is still hindering the development of microstructured photoelectrodes.

1.6.1.2 Membrane-Less and Microfluidic Designs

Product separation through the buoyancy of the gas bubbles has been proposed and investigated, although significant rates of product crossover have been observed [61]. Scaled-up designs, such as those by Kelly and Nelson [84], do not employ any separators and hence are likely to have significant issues of dissolved product crossover.

Holmes-Gentle *et al.* [69] proposed a membrane-less PEC design where product separation was controlled through hydrodynamic control of the electrolyte. The advantage of removing the requirement of a membrane is threefold: (1) no electrical potential loss associated with the membrane, (2) removal of an expensive component, and (3) the ability to implement new structures that minimize the path length between electrodes and stack cells optically. Furthermore, for alkaline operating conditions, anion exchange membranes will be required, which currently suffer from low conductivities and long-term stability issues [98].

Membrane-less designs have been investigated for water electrolysis [99–101] and fuel cell/redox batteries [102–105] but are relatively understudied for PEC reactors. For membrane-less systems, the required electric potential to drive water splitting will be reduced (potential losses may be in the order of 50–100 mV [106] for a membrane), which subsequently reduces the required photovoltage. This is significant as the conceptual design choices, such as the number of photoabsorbers, materials (i.e., bandgap energy), and electrical structure, are driven by the requirement to provide sufficient photovoltage.

There are still significant safety issues to be overcome as membrane-less systems will not be as intrinsically safe compared to their counterparts. In many ways, membrane-less systems substitute one issue with another, requiring further research and a full economic analysis in order to determine the technologies feasibility.

1.6.1.3 Redox-Mediated Systems

The water splitting reaction can also be divided into two redox reactions linked together with a reversible redox shuttles such as IO_3^-/I^- . For

particulate systems, aqueous (soluble) redox mediator systems have been studied in order to separate the evolution of hydrogen and oxygen to different sites and perform the water splitting reaction into two-step photo-excitation, which mimics the so-called “Z-scheme” in photosynthesis [107, 108]. The benefit of such system is that it allows particulate systems to more easily implement a tandem photoabsorber system and therefore capture and use more of the solar spectrum. Furthermore, two-bed photocatalyst reactor designs can circumvent the coevolution of a dangerous mixture of gases by separating the chambers with a membrane [109], which is a distinct scale-up issue for particulate systems [72, 108]. However the key disadvantage of aqueous redox mediators is selectivity. If a membrane is not used to separate the oxidizing and reducing environments of the system, the backward reaction of the redox mediator may occur and this will lead to significant faradaic losses [108, 109].

For planar electrode systems, solid-state redox mediators have also been investigated as a method to remove membranes from the PEC device. Two interesting examples of a solid-state redox mediator system utilized the reversible reaction of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ [73, 110]. In the work by Chen *et al.* [110], the water splitting occurred in a two-step process where first H_2 was evolved while $\text{Ni}(\text{OH})_2$ was converted to NiOOH , then O_2 was evolved while NiOOH was converted to $\text{Ni}(\text{OH})_2$. Landman *et al.* [73] used two auxiliary electrodes (AEs) where the $\text{NiOOH}/\text{Ni}(\text{OH})_2$ redox reaction occurs. This allowed for the simultaneous generation of H_2 and O_2 while one AE “charged” and the other “discharged.” Once fully charged or discharged, the AE are either physically swapped or the polarity is reversed. Essentially, the redox system replaces the membrane and allows for spatially separated gas evolution without the need to manage the ionic path length between the O_2 evolving anode and the H_2 evolving cathode. The electric potential drop over the membrane is replaced by the overpotentials required to drive the redox reaction. However, further study is required to determine whether the replacement of a membrane with a redox system is ultimately superior.

Concomitantly, decoupling the gas evolution steps allows the evolution of H_2 to be performed under pressure which may reduce the required downstream gas compression energy costs (as liquid compression is typically more efficient). Recent work by Rausch *et al.* [111] demonstrated decoupled H_2 evolution system using silico tungstic acid as a redox mediator. They were motivated by protecting the membrane from high pressure (due to increased degradation) whilst also evolving hydrogen at high pressure. Furthermore, with this system, a reduced Pt loading was required when compared with a polymer electrolyte membrane electrolysis.

1.6.2 Avenues for Future Research

1.6.2.1 Intensification and Waste Heat Utilization

To effectively utilize the generated hydrogen, it must be initially compressed, which would normally be achieved by the use of external gas compressors. However, by designing a PEC reactor that operates at high pressures, e.g., 10 bar, it would be possible to generate or supply pressurized hydrogen directly or simply reduce the amount of pressurization required via an external gas compressor postproduction representing a possible cost reduction [111]. Intensification by solar concentration could also result in reduced device costs as demonstrated in the literature. This allows for the use of more efficient and expensive materials by significantly reducing the area of the cell, i.e., lower system costs [14, 40].

A significant portion of the solar energy (in the form of low energy photons) is wasted as heat. The photoabsorber materials in a PEC cell can only capture a certain amount of the energy from the solar spectrum and effectively use it to split water. In order to increase the efficiency of the process, this wasted heat energy could be used to electrically bias the PEC cell by means of a heat engine (e.g., Organic Rankine Cycle) coupled with electricity generation or directly via a thermoelectric generator. Furthermore, there are a number of uses for low-grade heat (35 °C–50 °C) such as space heating, maintaining the temperature of green houses, desalination, drying biomass and ammonia production, etc. [112].

1.6.2.2 Usefulness of Oxidation and Coupled Process with Hydrogen Generation

Even though water oxidation is considered the kinetic bottleneck of water splitting, and significant effort has been focused on the photoanode material, e.g., Fe_2O_3 , TiO_2 , BiVO_4 ; the use of oxygen, or in general oxidation processes, is usually overlooked as hydrogen is considered the ultimate and most important product of water splitting [113]. However, due to the high costs involved in the production of solar hydrogen (see Table 1.1), it is necessary to couple the forgotten half of photoelectrochemical reactors with other valuable processes. High-purity oxygen should be considered a useful by-product; however, it competes with mature and inexpensive technologies, e.g., absorption and membrane separation processes. Chlorine, a useful chemical commodity, can be produced with an electrolyte containing Cl^- ions (e.g., NaCl , HCl), as the evolution of chlorine is kinetically favorable over oxygen [113, 114].

On waste treatment, replacing the energetically demanding oxygen evolution reaction with hydrogen sulfide oxidation can decrease the thermodynamic energy requirement for hydrogen production by ca. 80% while recovering sulfur from undesirable hydrogen sulfide emissions, e.g., from hydrodesulfurization processes or sour water treatment. First mentioned by Gratzel in 1983 [115], and later by Licht [116] and Bockris [117], a few successful studies have been reported where hydrogen sulfide oxidation was coupled with water reduction using photoelectrochemical reactors [118, 119], while stable hematite photoanodes have been studied for direct oxidation of hydrogen sulfide ions [45, 120], with relatively low efficiencies.

Oxidation processes can also be used for water treatment and decomposition of organic compounds [46]; however, most of these efforts are limited to oxidation of short carbon chain and already useful compounds such as methanol [121]. Oxidation of some complex organic compounds may require high-energy photons and a prolonged quest for a suitable photoabsorber that can deliver enough potential, while being stable and efficient is still hindering further research on these processes.

1.7 Summary and Conclusions

For the potential of solar fuels (and solar-derived chemical feedstocks) to be realized, we need to transition from laboratory-scale demonstrations to large-scale (m^2 to km^2) implementations of the technology. In order for this to occur, the engineering of scaled-up reactor designs must be considered.

In this chapter, we have provided a classification system for PEC designs, from the conceptual system to the physical engineering design. It was found that while many reactor designs perform better in one or more areas, few designs simultaneously meet all the requirements. For planar electrode systems, three design trends stand out. Firstly, for a bipolar monolithic configuration, a trend toward porous monoliths is observed. Secondly, for monopolar configurations, the front-side illumination of the interface is complicated by the placement of components in order to allow photons to reach the photoelectrodes, while minimizing the current density distribution. The use of membrane-less designs or perforation of the photoactive electrode could remove the complexities of obtaining an unobstructed light path. Thirdly, that the PV + electrolysis system is undoubtedly easier to design from an engineering scale-up perspective, than a PEC reactor. Nevertheless, the challenges associated with scale-up of PEC reactors have been increasingly studied in recent years, and many convincing solutions have been proposed and demonstrated.

System-level analyses, such as life cycle and technoeconomic assessments, heavily depend on the reactor design. Therefore, the key performance metrics of the design's feasibility, such as the total system efficiency, delivered solar fuel cost and energy-return-on-energy-invested may rest on the innovative engineering of the PEC reactor.

References

1. Minggu, L.J., Wan Daud, W.R., Kassim, M.B., An overview of photocells and photoreactors for photoelectrochemical water splitting. *Int. J. Hydrogen Energy*, 35, 5233–5244, 2010.
2. Bolton, J.R., Solar photoproduction of hydrogen: A review. *Sol. Energy*, 57(1), 37–50, 1996.
3. Ager, J.W., Shaner, M.R., Walczak, K.A., Sharp, I.D., Ardo, S., Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. *Energy Environ. Sci.*, 8(10), 2811–2824, 2015.
4. Modestino, M.A., Haussener, S., An integrated device view on photoelectrochemical solar-hydrogen generation. *Annu. Rev. Chem. Biomol. Eng.*, 6(1), 13–34, 2015.
5. International Energy Agency, Key world energy statistics, 2017.
6. Tsao, J., Lewis, N., Crabtree, G., *Solar FAQs*, US Dep. Energy, 2006.
7. World Energy Council, World Energy Resources, 2016.
8. Johnson, E., Goodbye to carbon neutral: Getting biomass footprints right. *Environ. Impact Assess. Rev.*, 29(3), 165–168, 2009.
9. Joshi, A.S., Dincer, I., Reddy, B.V., Exergetic assessment of solar hydrogen production methods. *Int. J. Hydrogen Energy*, 35(10), 4901–4908, 2010.
10. Christopher, K., Dimitrios, R., A review on exergy comparison of hydrogen production methods from renewable energy sources. *Energy Environ. Sci.*, 5(5), 6640, 2012.
11. Koumi Ngoh, S., Njomo, D., An overview of hydrogen gas production from solar energy. *Renew. Sustain. Energy Rev.*, 16(9), 6782–6792, 2012.
12. Acar, C., Dincer, I., Comparative assessment of hydrogen production methods from renewable and non-renewable sources. *Int. J. Hydrogen Energy*, 39(1), 1–12, 2014.
13. Shaner, M.R., Atwater, H.A., Lewis, N.S., McFarland, E.W., A comparative technoeconomic analysis of renewable hydrogen production using solar energy. *Energy Environ. Sci.*, 9(7), 2354–2371, 2016.
14. Pinaud, B.A., *et al*, Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ. Sci.*, 6(7), 1983, 2013.
15. Lemus, R.G., Martínez Duart, J.M., Updated hydrogen production costs and parities for conventional and renewable technologies. *Int. J. Hydrogen Energy*, 35(9), 3929–3936, 2010.

16. DOE EERE, Fuel Cells Technologies Program: Multi-Year Research, Development and Demonstration Plan: 3.1 *Hydrogen Production*, 2015.
17. Verlage, E., *et al*, A monolithically integrated, intrinsically safe, 10% efficient, solar-driven water-splitting system based on active, stable earth-abundant electrocatalysts in conjunction with tandem III–V light absorbers protected by amorphous TiO_2 films. *Energy Environ. Sci.*, 8(11), 3166–3172, 2015.
18. Jia, J., *et al*, Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nat. Commun.*, 7, 13237, 2016.
19. Fu, R., Feldman, D.J., Margolis, R.M., Woodhouse, M.A., Ardani, K.B., US solar photovoltaic system cost benchmark: Q1 2017, 2017.
20. International Renewable Energy Agency, Renewable energy technologies: Cost analysis series-solar photovoltaics, 2012.
21. Song, Z., *et al*, A technoeconomic analysis of perovskite solar module manufacturing with low-cost materials and techniques. *Energy Environ. Sci.*, 10(6), 1297–1305, 2017.
22. Essig, S., *et al*, Raising the one-sun conversion efficiency of III–V/Si solar cells to 32.8% for two junctions and 35.9% for three junctions. *Nat. Energy*, 2(9), 2017.
23. Verlage, E., *et al*, A monolithically integrated, intrinsically safe, 10% efficient, solar-driven water-splitting system based on active, stable earth-abundant electrocatalysts in conjunction with tandem III–V light absorbers protected by amorphous TiO_2 films. *Energy Environ. Sci.*, 8(11), 3166–3172, 2015.
24. May, M.M., Lewerenz, H.-J., Lackner, D., Dimroth, F., Hannappel, T., Efficient direct solar-to-hydrogen conversion by *in situ* interface transformation of a tandem structure. *Nat. Commun.*, 6, 8286, 2015.
25. Dodds, P.E., Hawkes, A., *The role of hydrogen and fuel cells in providing affordable, secure low-carbon heat*, London, UK, 2014.
26. International Energy Agency, Technology roadmap: Hydrogen and fuel cells, 2017.
27. Gray, E.M., Webb, C.J., Andrews, J., Shabani, B., Tsai, P.J., Chan, S.L.I., Hydrogen storage for off-grid power supply. *Int. J. Hydrogen Energy*, 36(1), 654–663, 2011.
28. Veziroğlu, T.N., Barbir, F., Initiation of hydrogen energy system in developing countries. *Int. J. Hydrogen Energy*, 17(7), 527–538, 1992.
29. Ager, J.W., Shaner, M.R., Walczak, K.A., Sharp, I.D., Ardo, S., Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. *Energy Environ. Sci.*, 8(10), 2811–2824, 2015.
30. Luo, J., *et al*, Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts. *Science*, 345(6204), 1593–1596, 2014.
31. Bolton, J.R., Strickler, S.J., Connolly, J.S., Limiting and realizable efficiencies of solar photolysis of water. *Nature*, 316(6028), 495–500, 1985.
32. Fountaine, K.T., Lewerenz, H.J., Atwater, H.A., Efficiency limits for photoelectrochemical water-splitting. *Nat. Commun.*, 7, 13706, 2016.

33. Seitz, L.C., Chen, Z., Forman, A.J., Pinaud, B.A., Benck, J.D., Jaramillo, T.F., Modeling practical performance limits of photoelectrochemical water splitting based on the current state of materials research. *ChemSusChem*, 7(5), 1372–1385, 2014.
34. Prévot, M.S., Sivula, K., Photoelectrochemical tandem cells for solar water splitting. *J. Phys. Chem. C*, 117(35), 17879–17893, 2013.
35. Nielander, A.C., Shaner, M.R., Papadantonakis, K.M., Francis, S.A., Lewis, N.S., A taxonomy for solar fuels generators. *Energy Environ. Sci.*, 8(1), 16–25, 2015.
36. Kim, J.H., *et al*, Hetero-type dual photoanodes for unbiased solar water splitting with extended light harvesting. *Nat. Commun.*, 7, 13380, 2016.
37. Han, L., *et al*, Efficient Water-Splitting Device Based on a Bismuth Vanadate Photoanode and Thin-Film Silicon Solar Cells. *ChemSusChem*, 7(10), 2832–2838, 2014.
38. Khaselev, O., Turner, J., A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. *Science*, 280(5362), 425–427, 1998.
39. Jacobsson, T.J., Fjällström, V., Sahlberg, M., Edoff, M., Edvinsson, T., A monolithic device for solar water splitting based on series interconnected thin film absorbers reaching over 10% solar-to-hydrogen efficiency. *Energy Environ. Sci.*, 6(12), 3676, 2013.
40. Dumortier, M., Tembhurne, S., Haussener, S., Holistic design guidelines for solar hydrogen production by photo-electrochemical routes. *Energy Environ. Sci.*, 8(12), 3614–3628, 2015.
41. Rodriguez, C.A., Modestino, M.A., Psaltis, D., Moser, C., Design and cost considerations for practical solar-hydrogen generators. *Energy Environ. Sci.*, 7(12), 3828–3835, 2014.
42. Singh, M.R., Xiang, C., Lewis, N.S., Evaluation of flow schemes for near-neutral pH electrolytes in solar-fuel generators. *Sustain. Energy Fuels*, 1(3), 458–466, 2017.
43. Tembhurne, S., Haussener, S., Integrated Photo-Electrochemical Solar Fuel Generators under Concentrated Irradiation I. 2-D non-isothermal multi-physics modeling. *J. Electrochem. Soc.*, 163(10), H988–H998, 2016.
44. Tembhurne, S., Haussener, S., Integrated photo-electrochemical solar fuel generators under concentrated irradiation II. Thermal management a crucial design consideration. *J. Electrochem. Soc.*, 163(10), H999–H1007, 2016.
45. Bedoya-Lora, F., Hankin, A., Kelsall, G.H., Photo-electrochemical hydrogen sulfide splitting using SnIV-doped hematite photo-anodes. *Electrochem. commun.*, 68, 19–22, 2016.
46. Li, T., Kasahara, T., He, J., Dettelbach, K.E., Sammis, G.M., Berlinguette, C.P., Photoelectrochemical oxidation of organic substrates in organic media. *Nat. Commun.*, 8(1), 6–10, 2017.
47. Lopes, T., Dias, P., Andrade, L., Mendes, A., An innovative photoelectrochemical lab device for solar water splitting. *Sol. Energy Mater. Sol. Cells*, 128, 399–410, 2014.

48. Fan, Q., Onischak, M., Liss, W.E., Solar cell electrolysis of water to make hydrogen and oxygen, US7241950 B2, 2007.
49. O'Gallagher, J.J., *Nonimaging optics in solar energy*, vol. 2, no. 1. Morgan & Claypool Publishers, 2008.
50. Weintraub, B., Wei, Y., Wang, Z.L., Weintraub, B., Wei, Y., Wang, Z.L., Optical fiber/nanowire hybrid structures for efficient three-dimensional dye-sensitized solar cells. *Angew. Chemie – Int. Ed.*, 48(47), 8981–8985, 2009.
51. Kandilli, C., Ulgen, K., Review and modelling the systems of transmission concentrated solar energy via optical fibres. *Renew. Sustain. Energy Rev.*, 13, (1), 67–84, 2009.
52. Marinangeli, R.E., Ollis, D.F., Photo-assisted heterogeneous catalysis with optical fibers. Part III: Photoelectrodes. *AIChE J.*, 28(6), 945–955, 1982.
53. Bicer, Y., Dincer, I., Experimental investigation of a PV-Coupled photoelectrochemical hydrogen production system. *Int. J. Hydrogen Energy*, 42 (4), 2512–2521, 2017.
54. Mojiri, A., Taylor, R., Thomsen, E., Rosengarten, G., Spectral beam splitting for efficient conversion of solar energy – A review. *Renew. Sustain. Energy Rev.*, 28, 654–663, 2013.
55. Haussener, S., Xiang, C., Spurgeon, J.M., Ardo, S., Lewis, N.S., Weber, A.Z., Modeling, simulation, and design criteria for photoelectrochemical water-splitting systems. *Energy Environ. Sci.*, 5(12), 9922, 2012.
56. Jacobsson, T.J., Fjällström, V., Edoff, M., Edvinsson, T., Sustainable solar hydrogen production: from photoelectrochemical cells to PV-electrolyzers and back again. *Energy Environ. Sci.*, 7(7), 2056–2070, 2014.
57. Rongé, J., Bosserez, T., Huguenin, L., Dumortier, M., Haussener, S., Martens, J.A., Solar Hydrogen Reaching Maturity. *Oil Gas Sci. Technol. – Rev. d'IFP Energies Nouv.*, 70(5), 863–876, 2015.
58. Carver, C., Ulissi, Z., Ong, C.K., Dennison, S., Kelsall, G.H., Hellgardt, K., Modelling and development of photoelectrochemical reactor for H₂ production. *Int. J. Hydrogen Energy*, 37(3), 2911–2923, 2012.
59. Holmes-Gentle, I., Agarwal, H., Alhersh, F., & Hellgardt, K. (2018). Assessing the scalability of low conductivity substrates for photo-electrodes via modelling of resistive losses. *Physical Chemistry Chemical Physics*, 20(18), 12422–12429.
60. Vogt, H., The incremental ohmic resistance caused by bubbles adhering to an electrode. *J. Appl. Electrochem.*, 13(1), 87–88, 1983.
61. Jin, J., Walczak, K., Singh, M.R., Karp, C., Lewis, N.S., Xiang, C., An experimental and modeling/simulation-based evaluation of the efficiency and operational performance characteristics of an integrated, membrane-free, neutral pH solar-driven water-splitting system. *Energy Environ. Sci.*, 7, (10), 3371–3380, 2014.
62. Hankin, A., Bedoya-Lora, F.E., Ong, C.K., Alexander, J.C., Petter, F., Kelsall, G.H., From millimetres to metres: the critical role of current density distributions in photo-electrochemical reactor design. *Energy Environ. Sci.*, 10(1), 346–360, 2017.

63. Walczak, K., *et al*, Modeling, simulation, and fabrication of a fully integrated, acidstable, scalable solar-driven water-splitting system. *ChemSusChem*, 8(3), 544–551, 2015.
64. Nozik, A.J., Memming, R., Physical chemistry of semiconductor-liquid interfaces. *J. Phys. Chem.*, 100(31), 13061–13078, 1996.
65. Memming, R., *Semiconductor electrochemistry*, 2. ed. Wiley-VCH-Verl, Weinheim, 2015.
66. Rajeshwar, K., Fundamentals of Semiconductor Electrochemistry and Photoelectrochemistry. *Encycl. Electrochem.*, 6, 1–53, 2007.
67. Miller, D.C., Kempe, M.D., Kennedy, C.E., Kurtz, S.R., Analysis of transmitted optical spectrum enabling accelerated testing of multijunction concentrating photovoltaic designs. *Opt. Eng.*, 50(1), 13003, 2011.
68. Döschner, H., Geisz, J.F., Deutsch, T.G., Turner, J.A., Sunlight absorption in water – efficiency and design implications for photoelectrochemical devices. *Energy Environ. Sci.*, 7(9), 2951–2956, 2014.
69. Holmes-Gentle, I., Hoffmann, F., Mesa, C.A., Hellgardt, K., Membrane-less photoelectrochemical cells: product separation by hydrodynamic control. *Sustain. Energy Fuels*, 1(5), 1184–1198, 2017.
70. Farivar, F., CFD simulation and development of an improved photoelectrochemical reactor for H₂ production. *Int. J. Hydrogen Energy*, 41(2), 882–888, 2015.
71. Torras, C., Lorente, E., Hernández, S., Russo, N., Salvadó, J., Hydrodynamics and oxygen bubble characterization of catalytic cells used in artificial photosynthesis by means of CFD. *Fluids*, 2(2), 25, 2017.
72. van de Krol, R., Grätzel, M., *Photoelectrochemical hydrogen production*, vol. 102. Springer, 2012.
73. Landman, A *et al*, Photoelectrochemical water splitting in separate oxygen and hydrogen cells. *Nat. Mater.*, 16(6), 646–651, 2017.
74. Selli, E., Chiarello, G.L., Quartarone, E., Mustarelli, P., Rossetti, I., Forni, L., A photocatalytic water splitting device for separate hydrogen and oxygen evolution. *Chem. Commun.*, 47, 5022–5024, 2007.
75. Li, Y., Yu, H., Song, W., Li, G., Yi, B., Shao, Z., A novel photoelectrochemical cell with self-organized TiO₂ nanotubes as photoanodes for hydrogen generation. *Int. J. Hydrogen Energy*, 36, 14374–14380, 2011.
76. Deng, X., Xu, L., Integrated photoelectrochemical cell and system having a liquid electrolyte. US7750234 B2, 2010.
77. Graetzel, M., Augustynski, J., Tandem cell for water cleavage by visible light, US6936143 B1, 2005.
78. Turan, B., Becker, J.-P., Urbain, F., Finger, F., Rau, U., Haas, S., Upscaling of integrated photoelectrochemical water-splitting devices to large areas. *Nat. Commun.*, 7, 12681, 2016.
79. Ida, S., Yamada, K., Matsunaga, T., Hagiwara, H., Matsumoto, Y., Ishihara, T., Preparation of p-Type CaFe₂O₄ photocathodes for producing hydrogen from water. *J. Am. Chem. Soc.*, 132, 17343–17345, 2010.
80. Brillet, J *et al*, Highly efficient water splitting by a dual-absorber tandem cell. *Nat. Photonics*, 6(12), 824–828, 2012.

81. Murphy, A.B *et al*, Efficiency of solar water splitting using semiconductor electrodes. *Int. J. Hydrogen Energy*, 3114, 1999–2017, 2006.
82. Miller, E.L., Rocheleau, R.E., Deng, X.M., Design considerations for a hybrid amorphous silicon/photoelectrochemical multijunction cell for hydrogen production. *Int. J. Hydrogen Energy*, 28, 615–623, 2003.
83. Bosserez, T., *et al*, Minimization of ionic transport resistance in porous monoliths for application in integrated solar water splitting devices. *J. Phys. Chem. C*, 120(38), 21242–21247, 2016.
84. Kelly, N.A., Gibson, T.L., Solar energy concentrating reactors for hydrogen production by photoelectrochemical water splitting. *Int. J. Hydrogen Energy*, 33, 6420–6431, 2008.
85. Becker, J.-P., *et al*, A modular device for large area integrated photoelectrochemical water-splitting as a versatile tool to evaluate photoabsorbers and catalysts. *J. Mater. Chem. A*, 5(10), 4818–4826, 2017.
86. Rongé, J., *et al*, Monolithic cells for solar fuels. *Chem. Soc. Rev.*, 43(23), 7963–7981, 2014.
87. Lewis, N.S., Developing a scalable artificial photosynthesis technology through nanomaterials by design. *Nat. Nanotechnol.*, 11(12), 1010–1019, 2016.
88. Spurgeon, J.M., Walter, M.G., Zhou, J., Kohl, P.A., Lewis, N.S., Electrical conductivity, ionic conductivity, optical absorption, and gas separation properties of ionically conductive polymer membranes embedded with Si microwire arrays. *Energy Environ. Sci.*, 4(5), 1772, 2011.
89. Lopes, T., Dias, P., Andrade, L., Mendes, A., An innovative photoelectrochemical lab device for solar water splitting. *Sol. Energy Mater. Sol. Cells*, 128, 399–410, 2014.
90. Balzer, R.J., Vogt, H., Effect of electrolyte flow on the bubble coverage of vertical gas-evolving electrodes. *J. Electrochem. Soc.*, 150(1), E11, 2003.
91. Brinner, A., Bussmann, H., Hug, W., Seeger, W., Test results of the hysolar 10 kW PV-electrolysis facility. *Int. J. Hydrogen Energy*, 17(3), 187–197, 1992.
92. Szyszka, A., Ten years of solar hydrogen demonstration project at Neunburg vorm Wald, Germany. *Int. J. Hydrogen Energy*, 23(10), 849–860, 1998.
93. Hollmüller, P., Joubert, J.M., Lachal, B., Yvon, K., Evaluation of a 5 kW photovoltaic hydrogen production and storage installation for a residential home in Switzerland. *Int. J. Hydrogen Energy*, 25(2), 97–109, 2000.
94. Kelly, N.A., Gibson, T.L., Ouwkerk, D.B., A solar-powered, high-efficiency hydrogen fueling system using high-pressure electrolysis of water: Design and initial results. *Int. J. Hydrogen Energy*, 3311, 2747–2764, 2008.
95. Modestino, M.A., Hashemi, S.M.H., Haussener, S. Mass transport aspects of electrochemical solar-hydrogen generation. *Energy Environ. Sci.*, 9(5), 1533–1551, 2016.
96. Zhai, P., *et al*, Net primary energy balance of a solar-driven photoelectrochemical water-splitting device. *Energy Environ. Sci.*, 6(8), 2380, 2013.
97. Coridan, R.H., *et al*, Methods for comparing the performance of energy-conversion systems for use in solar fuels and solar electricity generation. *Energy Environ. Sci.*, 8(10), 2886–2901, 2015.

98. Merle, G., Wessling, M., Nijmeijer, K., Anion exchange membranes for alkaline fuel cells: A review. *J. Memb. Sci.*, 377(1–2), 1–35, 2011.
99. Gillespie, M.I., van der Merwe, F., Kriek, R.J., Performance evaluation of a membraneless divergent electrode-flow-through (DEFT) alkaline electrolyser based on optimisation of electrolytic flow and electrode gap. *J. Power Sources*, 293, 228–235, 2015.
100. Hashemi, S.M.H., Modestino, M.A., Psaltis, D., A membrane-less electrolyzer for hydrogen production across the pH scale. *Energy Environ. Sci.*, 8(7), 2003–2009, 2015.
101. Esposito, D.V., Membraneless electrolyzers for low-cost hydrogen production in a renewable energy future. *Joule*, 1(4), 651–658, 2017.
102. Braff, W.A., Bazant, M.Z., Buie, C.R., Membrane-less hydrogen bromine flow battery. *Nat. Commun.*, 4, 2346, 2013.
103. Braff, W.A., Buie, C.R., Bazant, M.Z., Boundary Layer Analysis of Membraneless Electrochemical Cells. *J. Electrochem. Soc.*, 160(11), A2056–A2063, 2013.
104. Kjeang, E., Michel, R., Harrington, D.A., Djilali, N., Sinton, D., A microfluidic fuel cell with flow-through porous electrodes. *J. Am. Chem. Soc.*, 130(12), 4000–4006, 2008.
105. Kjeang, E., Proctor, B.T., Brolo, A.G., Harrington, D.A., Djilali, N., Sinton, D., High-performance microfluidic vanadium redox fuel cell. *Electrochim. Acta*, 52(15), 4942–4946, 2007.
106. Hernández-Pagán, E.A., Vargas-Barbosa, N.M., Wang, T., Zhao, Y., Smotkin, E.S., Mallouk, T.E., Resistance and polarization losses in aqueous buffer-membrane electrolytes for water-splitting photoelectrochemical cells. *Energy Environ. Sci.*, 5(6), 7582–7589, 2012.
107. Maeda, K., Domen, K., Photocatalytic water splitting: Recent progress and future challenges. *J. Phys. Chem. Lett.*, 1(18), 2655–2661, 2010.
108. Hisatomi, T., Kubota, J., Domen, K., Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.*, 43(22), 7520–7535, 2014.
109. Bala Chandran, R., Breen, S., Shao, Y., Ardo, S., Weber, A.Z., Evaluating particle-suspension reactor designs for Z-scheme solar water splitting via transport and kinetic modeling. *Energy Environ. Sci.*, 11(1), 115–135, 2018.
110. Chen, L., Dong, X., Wang, Y., Xia, Y., Separating hydrogen and oxygen evolution in alkaline water electrolysis using nickel hydroxide. *Nat. Commun.*, 7, 11741, 2016.
111. Rausch, B., Symes, M.D., Chisholm, G., Cronin, L., Decoupled catalytic hydrogen evolution from a molecular metal oxide redox mediator in water splitting. *Science*, 345(6202), 1326–1330, 2014.
112. Parker, T., Kiessling, A., Low-grade heat recycling for system synergies between waste heat and food production, a case study at the European Spallation Source. *Energy Sci. Eng.*, 4(2), 153–165, 2016.

113. Mei, B., Mul, G., Seger, B., Beyond water splitting: Efficiencies of photo-electrochemical devices producing hydrogen and valuable oxidation products. *Adv. Sustain. Syst.*, 1(1–2), 1600035, 2017.
114. Chinello, E., *et al*, A 25.1% efficient stand-alone solar chloralkali generator employing a microtracking solar concentrator. *Glob. Challenges*, 1(9), 2017.
115. Graetzel, M., Molecular engineering in photoconversion systems, in *Energy resources through photochemistry and catalysis*, pp. 71–98, Academic Press New York, 1983.
116. Licht, S., Hodes, G., Manassen, J., Numerical analysis of aqueous polysulfide solutions and its application to cadmium chalcogenide/polysulfide photo-electrochemical solar cells. *Inorg. Chem.*, 25(15), 2486–2489, 1986.
117. Kainthla, R.C., Bockris, J.O., Photoelectrolysis of H_2S using an n-CdSe photoanode. *Int. J. Hydrogen Energy*, 12(1), 23–26, 1987.
118. Kawade, U.V., *et al*, Environmentally benign enhanced hydrogen production via lethal H_2S under natural sunlight using hierarchical nanostructured bismuth sulfide. *RSC Adv.*, 4, 49295–49302, 2014.
119. Zong, X., *et al*, An integrated photoelectrochemical-chemical loop for solar-driven overall splitting of hydrogen sulfide. *Angew. Chemie – Int. Ed.*, 53(17), 4399–4403, 2014.
120. Natarajan, K., Saraf, M., Mobin, S.M., Visible-light-induced water splitting based on a novel $\alpha-Fe_2O_3/CdS$ Heterostructure. *ACS Omega*, 2(7), 3447–3456, 2017.
121. Reichert, R., Zambrzycki, C., Jusys, Z., Behm, R.J., Photo-electrochemical oxidation of organic C1 molecules over WO_3 films in aqueous electrolyte: Competition between water oxidation and C1 oxidation. *ChemSusChem*, 8(21), 3677–3687, 2015.

The Measurements and Efficiency Definition Protocols in Photoelectrochemical Solar Hydrogen Generation

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Abstract

With the increase of world's population, more energy is demanded. The power consumption of mankind in 2016 is already up to 18 TW according to the BP Statistical Review of World Energy published in July 2017. Fossil fuel is nonrenewable energy and will be unable to meet the increasing demand for energy. Hydrogen obtained from water splitting by using solar energy is a clean and renewable energy that can be widely used in future. Photoelectrochemical (PEC) water splitting is an important method used for hydrogen evolution. In this chapter, the PEC water splitting measurements will be introduced firstly. Up to now, many efficiency values were reported for PEC water splitting. The use of proper efficiencies has become necessary. The definition of various efficiencies and their application conditions in PEC water splitting are introduced in detail. These introductions could serve as guidelines in future research.

Keywords: IPCE, APCE, light harvesting efficiency; charge separation efficiency, charge injection efficiency

2.1 Introduction

The PEC measurement was usually carried out in three-electrode configuration under light illumination [1–3]. The basic experimental setup in a

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three-electrode configuration for PEC photocurrent measurements consists of a PEC cell with a flat surface, a light source (a solar simulator or a xenon lamp with filters), and a potentiostat. Conducting and optically transparent substrates modified with various semiconductors were used as working electrode. The substrate should be conducting to serve as back-contact between semiconductors and potentiostat, while the optically transparent property of the substrate allows the electrode to be illuminated from the back. Transparent conducting oxides with high carrier concentrations and mobilities deposited on glass were usually used as the substrate. The common conducting and optically transparent substrates are Sn-doped In_2O_3 (ITO), F-doped SnO_2 (FTO), Sb-doped SnO_2 (ATO), and Al-doped ZnO (AZO). To simplify the study, a Pt foil electrode is usually used as the counter electrode because of its small overpotential for hydrogen or oxygen evolution. Ag/AgCl or Hg/Hg₂Cl₂ electrode is the most common reference electrode used in the three-electrode configuration to determine the potential of working electrode. Solar simulator or a xenon lamp equipped with a filter, which has the similar spectrum to sunlight and desired value (100 mW/cm², AM 1.5G), is used as light source.

Many factors influence the results of photocurrent in PEC water splitting, which is a common metric to determine the performance of photoelectrode. In order to reduce the influence of researchers themselves to some extent, the measurements must be performed under the exact same conditions. In the front part of this chapter, the most common measurements in the PEC water splitting will be introduced, while the definition of various efficiencies and their application conditions in PEC water splitting will be introduced in the later part of this chapter.

2.2 PEC Measurement

In this section, measurement and characterization methods in PEC water splitting are introduced, including optical properties, polarization curve, photocurrent transients, incident photon-to-current conversion efficiency (IPCE), absorbed photon-to-current conversion efficiency (APCE), Mott-Schottky plot, charge separation efficiency, charge injection efficiency, and gas evolution measurements.

2.2.1 Measurements of Optical Properties

Light absorption is the first step for PEC water splitting. So, it is important to research the optical properties of photoelectrode. The optical properties

of a photoelectrode include light absorption, light reflection, and light transmission. Among them, the light absorption efficiency is a vital parameter in PEC water splitting, which is dependent on the material absorption coefficient and the thickness [4].

Light absorption efficiency is also called light harvesting efficiency (LHE, defined as the ratio of absorbed light to incident light). It can be calculated from the UV-vis absorption spectrum of photoelectrode using the following equation:

$$\text{LHE} = 1 - 10^{-A(\lambda)} \quad (2.1)$$

where $A(\lambda)$ is the absorbance of photoelectrode at a specific wavelength, which can be measured using a diffuse reflectance spectrophotometer. Figure 2.1 gives the typical UV-vis absorption spectrum and light harvesting efficiency as the function of wavelength.

2.2.2 Polarization Curve Measurements

Polarization curve measurements, also known as current-voltage measurements, are the most important technique and common practice to evaluate the performance of a photoelectrode for PEC water splitting. It is usually measured using the linear sweep voltammetry mode at a low scan rate under the standard AM 1.5G illumination (100 mWcm^{-2}). Then the photocurrent at all the given potential is recorded.

From the polarization curve, we can get the information of photocurrent density as a function of applied potential, plateau photocurrent, and onset potential. Figure 2.2 gives the typical polarization curves of an ideal

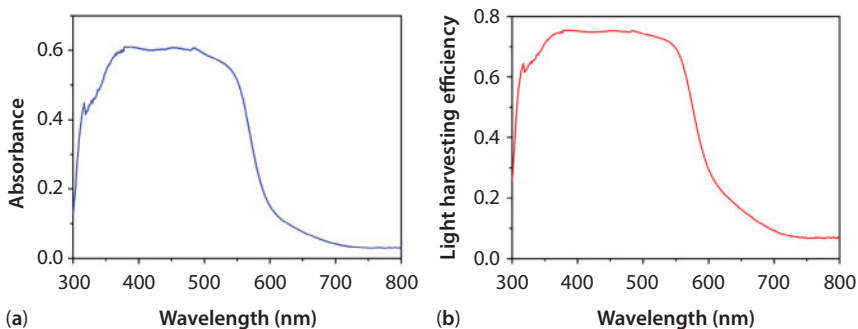


Figure 2.1 (a) UV-vis absorption spectrum of pristine Fe_2O_3 , (b) Light harvesting efficiency of pristine Fe_2O_3 [5].

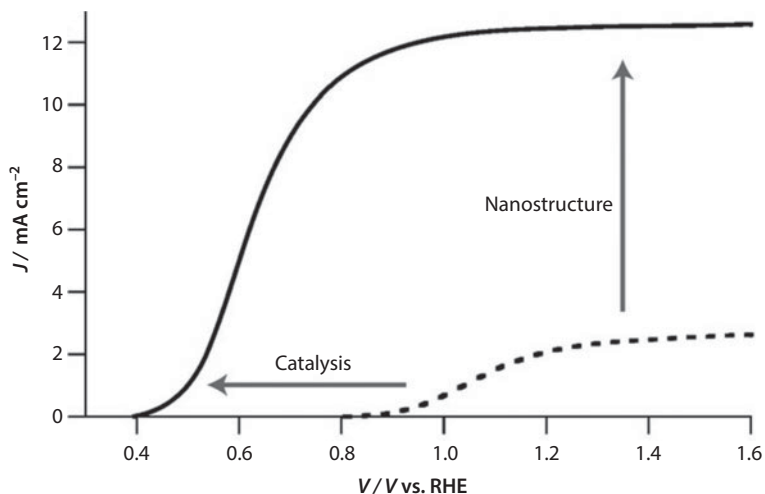


Figure 2.2 Typical polarization curves of photoanode in PEC water splitting. The solid trace indicates the idealized performance of hematite photoanode while the dashed trace indicates the former state-of-the-art hematite photoanode under AM1.5G 100 mWcm⁻² simulated sunlight [6].

hematite and that of the former state-of-the-art hematite photoanode in PEC water splitting. For the state-of-the-art hematite photoanode (dashed trace), the current is close to zero at the potential below 0.9 V vs. RHE, which is called dark current. The dark current begins to increase at ~0.9 V vs. RHE, indicating the start of PEC oxidation of water at this potential. So, the potential of 0.9 V is the onset potential. This onset potential is much more positive than that of an ideal hematite photoanode mainly due to slow oxidation kinetics on the surface of hematite photoanode. The photocurrent increases with the rise of applied voltage until it reaches a plateau value at ~1.3 V vs. RHE. This plateau photocurrent gives the information of how many photogenerated holes are reaching the photoanode.

2.2.3 Photocurrent Transients Measurements

Photocurrent transients are recorded during polarization curve measurement or constant potential I-t measurement by switching the light on and off with a shutter. The anodic photocurrent transients presented as the light is switched on to indicate the accumulation of holes at the electrode/electrolyte interface, while the cathodic photocurrent transients represent the recombination of electrons and accumulated holes when light is turned off [7]. From photocurrent transients curve, the photocurrent onset potential

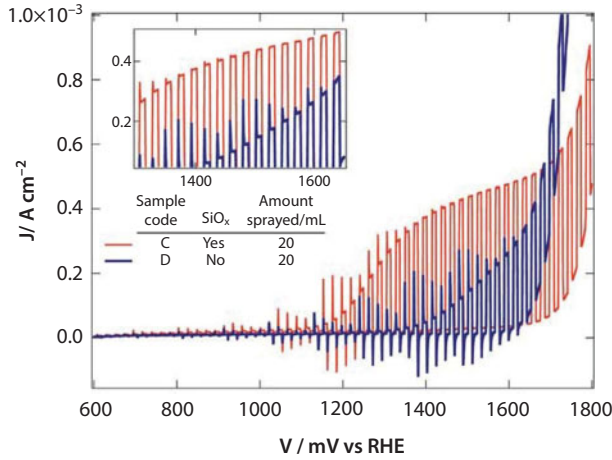


Figure 2.3 Transient photoresponse of Fe_2O_3 photoanodes using a SiO_x/FTO substrate (red) and a control FTO substrate (blue) shown by light chopping current densities J (light on/light off) as a function of the applied potential V , with respect to the RHE [8].

can be accurately determined because even small differences between the dark current and the photocurrent can be easily observed. As shown in Figure 2.3, the photocurrent densities show transient behavior just after light is switched on or off when the voltage was swept from 0.6 to 1.8 V vs. RHE. It can be easily observed that the onset potential of Fe_2O_3 photoanodes using a SiO_x/FTO substrate is negative than that using a FTO substrate.

2.2.4 IPCE and APCE Measurements

IPCE and APCE are the abbreviations of incident photon-to-current conversion efficiency and absorbed photon-to-current conversion efficiency measurement, respectively. They are two important parameters to evaluate the performance of photoelectrode.

The definition of IPCE is the percentage of incident photons (N_e) that are converted into electrons (N_p) as a function of the wavelength of illuminating light. It is also called the external quantum efficiency. According to this definition, an equation (Eq. 2.2) can be deduced to calculate the value of IPCE as follows:

$$IPCE = \frac{N_e}{N_p} = \frac{\frac{J \times A \times t}{F} \times N_A}{\frac{p \times A \times t \times \lambda}{h \times c}} = \frac{1240 \times J}{\lambda \times P}. \quad (2.2)$$

Here, J is the photocurrent density at a special light wavelength, A is the electrode area, t is the test time, N_A is Avogadro number, F is Faraday's constant, P is the power intensity of the incident monochromatic light at a special wavelength, λ is the wavelength of the incident monochromatic light, h is Planck constant, and c is the speed of light.

To gain the value of IPCE at a special light wavelength, the J and P should be measured. Monochromator is needed to provide monochromatic light, whose power intensity (P) is calibrated by an optical power meter after the lamp is warm-up. The J is measured versus time using chronoamperometry mode with or without an applied bias. So, the IPCE is the function of applied bias.

From the IPCE spectrum, an estimate of the total photocurrent under AM1.5G illumination can be obtained by multiplying the IPCE values with the AM1.5G photon flux for each wavelength (ASTM G173-03), followed by integration over all wavelengths [5]. The obtained value of photocurrent should match the photocurrent measured under AM1.5G conditions at the same potential.

The definition of APCE is percentage of absorbed incident photons that are converted into electrons as a function of the wavelength of the illuminating light. It is also called the internal quantum efficiency. According to this definition, the value of APCE can be calculated by dividing the IPCE value by light harvesting efficiency (LHE) of the photoelectrode at the same wavelength (Eq. 2.3). By measuring LHE, J , and P , the APCE value at special wavelength can be obtained.

$$APCE = IPCE / LHE = \frac{1240 \times J}{\lambda \times P} / [1 - 10^{-A(\lambda)}] \quad (2.3)$$

2.2.5 Mott-Schottky Measurements

The charge-carrier density (N_D , for a photoanode) and flat band potential (V_{FB}) are two important factors in semiconductors that affect the charge-transport properties and onset potential, which, in turn, affects their PEC performance. Mott-Schottky plot can be measured to determine the charge-carrier density and flatband potential of a thin-film photoelectrode based on the Mott-Schottky theory according to the following equation (Eq. 2.4, for a photoanode):

$$\frac{1}{C^2} = \left(\frac{2}{\epsilon_0 \epsilon N_D} \right) \left(V_A - V_{FB} - \frac{kT}{e} \right) \quad (2.4)$$

where C is the space charge capacitance (F/cm^2), ϵ_0 is the vacuum permittivity ($8.854 \times 10^{-14} \text{ F}/\text{cm}$), ϵ is the dielectric constant of the semiconductor, e is the electron charge ($1.6 \times 10^{-19} \text{ C}$), V_A is the applied potential (V), k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J}/\text{K}$), and T is the temperature ($kT/e = 0.026 \text{ V}$ at 25°C).

To measure Mott–Schottky plot, a potentiostat with a frequency response analyzer or with EIS capabilities is needed. This can be carried out on an electrochemical workstation using impedance-potential mode. The measurement is performed in the dark at a fixed frequency over a range of potentials, which should be chosen to avoid any faradaic reactions, to determine the potential dependence of the C . The scan rate is usually chosen to be between 1 and 20 mV/s based on the integration time of the frequency response analyzer. The modulation amplitude imposed on the sample should be as low as possible to avoid nonlinearities (usually 5 mV).

According to Equation (2.4), by measuring the C as a function of t , V_A , a straight tangent line can be drawn by using a plot of $1/C^2$ versus V_A , which gives a slope that is proportional to $1/N_D$, while the intercept of the line with the potential axis gives the V_{FB} .

Figure 2.4 gives typical Mott–Schottky plots of pristine Fe_2O_3 - and Mn-doped Fe_2O_3 . The positive tangent slope indicates that the pristine and doped Fe_2O_3 are n-type semiconductors. Furthermore, the smaller the slope, the large the charge-carrier density. The calculated N_D and V_{FB} are listed in Table 2.1.

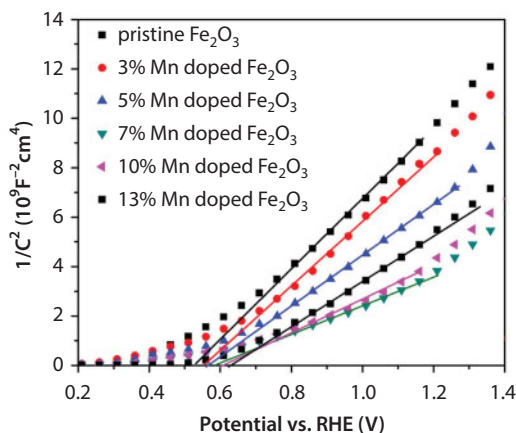


Figure 2.4 Representative Mott–Schottky plots of pristine Fe_2O_3 and $\text{Mn}:\text{Fe}_2\text{O}_3$ [5].

Table 2.1 Semiconductor properties of pristine Fe_2O_3 and $\text{Mn}:\text{Fe}_2\text{O}_3$ [5].

Sample	$N_D \text{ (cm}^{-3}\text{)}$	$V_{\text{FB}} \text{ (V}_{\text{RHE}}\text{)}$
Pristine Fe_2O_3	1.26×10^{20}	0.53
3% Mn-doped Fe_2O_3	1.47×10^{20}	0.55
5% Mn-doped Fe_2O_3	1.71×10^{20}	0.57
7% Mn-doped Fe_2O_3	3.10×10^{20}	0.60
10% Mn-doped Fe_2O_3	2.90×10^{20}	0.61
13% Mn-doped Fe_2O_3	2.01×10^{20}	0.62

2.2.6 Measurement (Calculation) of Charge Separation Efficiency

In a PEC water splitting process, five main processes occur on the photoelectrode: (I) light absorption, (II) charge separation, (III) charge migration, (IV) charge recombination, and (V) redox reactions [9]. When a photoelectrode absorbs the photons with energy greater than the band-gap energy (E_g), electrons are excited to the conduction band, leaving the holes in the valence band. Due to the formation of space-charge layer near the surface of photoelectrode, the photogenerated minority carriers (holes for photoanode and electrons for photocathode) transfer to the surface of photoelectrode where redox reactions occur [10, 11]. However, not all the photogenerated charge carriers can transfer to the surface of photoelectrode and participate in reaction.

The charge separation efficiency ($\eta_{\text{separation}}$) is the ratio of electrons and holes that transport to the photoelectrode/electrolyte interface to the total photogenerated electrons and holes. It can be used to estimate the bulk recombination of photogenerated charge carrier within the photoelectrode [12]. The charge separation efficiency is mainly determined by the property of photoelectrode materials. In addition to this, the morphology, thickness, and junction types of photoelectrode will influence the charge separation efficiency.

The charge separation efficiency is calculated by dividing the photocurrent ($J_{\text{scavenger}}$) for a hole scavenger (for a photoanode, usually H_2O_2 [5] or Na_2SO_3 [13]) oxidation by the J_{abs} (the photocurrent density achievable, assuming 100% absorbed photon-to-current conversion efficiency for photons), namely, $\eta_{\text{separation}} = J_{\text{scavenger}}/J_{\text{abs}}$. In order to calculate J_{abs} , the maximum photocurrent density (J_{max}) achievable assuming 100% IPCE for photons

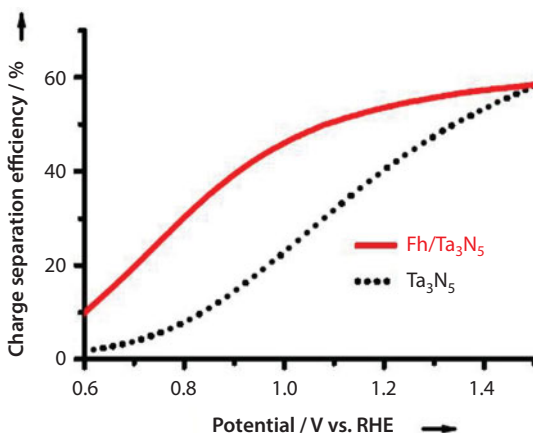


Figure 2.5 Charge separation efficiency versus potential curves of Ta₃N₅ and ferrihydrite-modified Ta₃N₅ (Fh/Ta₃N₅) photoanodes [15].

with energy larger than E_g of photoelectrode should be calculated firstly by converting standard AM 1.5G solar spectral irradiance to solar energy spectrum in terms of number of photons ($\text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{nm}^{-1}$) vs. wavelength (nm) [14]. Then, the number of photons above the bandgap energy of the photoelectrode is calculated using a trapezoidal integration of the spectrum and is converted to the current density ($\text{mA} \cdot \text{cm}^{-2}$). During each step of the trapezoidal integration, the LHE at each wavelength is multiplied to get the value of J_{abs} . This measurement (calculation) method is based on an assumption that the oxidation of hole scavenger is very fast and all the holes reaching the surface of electrode can be captured by hole scavenger; that is, the charge injection efficiency at the surface of electrode is 100%. $J_{\text{scavenger}}$ is usually measured using the linear sweep voltammetry mode at a low scan rate under the standard AM 1.5G illumination in a electrolyte containing hole scavenger. So, the charge separation efficiency is plotted as a function of the applied potential. Typical charge separation efficiency plots of photoanodes vs. potential are shown in Figure 2.5.

2.2.7 Measurements of Charge Injection Efficiency

The charge injection efficiency ($\eta_{\text{injection}}$) represents the yield of holes that are injected into the electrolyte from the photoelectrode surface to oxidize the water at the photoelectrode/electrolyte interface. It is an important parameter for assessing the ratio of holes that participate in the reaction of water oxidation to holes that reach the surface of the electrode. The $\eta_{\text{injection}}$ is also

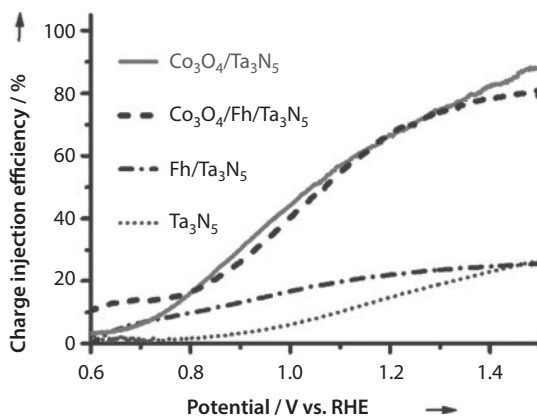


Figure 2.6 Charge injection efficiency versus potential curves of Ta₃N₅, ferrihydrite-modified Ta₃N₅ (Fh/Ta₃N₅), Co₃O₄/Ta₃N₅, and Co₃O₄/Fh/Ta₃N₅ photoanodes [15].

mainly determined by the property of photoelectrode materials. Normally, the $\eta_{\text{injection}}$ can be improved by loading water oxidation or reduction catalyst to lower the overpotential/activation energy of the redox reaction and to avoid the back reactions [16–18].

For a photoanode, the charge injection efficiency is calculated by dividing the photocurrent for water oxidation ($J_{\text{H}_2\text{O}}$) by that for a hole scavenger oxidation ($J_{\text{scavenger}}$), namely, $\eta_{\text{injection}} = J_{\text{H}_2\text{O}}/J_{\text{scavenger}}$. $J_{\text{H}_2\text{O}}$ is usually measured using the linear sweep voltammetry mode at a low scan rate under the standard AM 1.5G illumination. So, the charge injection efficiency is plotted as a function of the applied potential. Typical charge injection efficiency plots of photoanodes vs. potential are shown in Figure 2.6.

2.2.8 Gas Evolution Measurements

Hydrogen and oxygen are the products of PEC water splitting, which are produced at photocathode and photoanode, respectively. The amount of produced hydrogen and oxygen is an important parameter to assess the performance of photoelectrode, including solar-to-hydrogen efficiency and faradaic efficiency. So, it is critical to measure the quantity of produced gases.

Gas chromatograph (GC) or calibrated pressure sensor is usually used to measure the produced gases. The PEC should be gas tightness and deaerated by purging with Ar gas or other inert gas. For a widely used GC, a certain volume of produced gas samples in headspace of PEC cell were

withdrawn by a gas-tight syringe and then analyzed by GC over certain time interval. Before using GC to measure the quantity of produced gases, calibration curves regarding the peak area and quantity of gas should be prepared. After calibration, the gas amount versus evolution time can be plotted.

2.3 The Efficiency Definition Protocols in PEC Water Splitting

In order to make a comparative evaluation, various efficiency definitions in PEC water splitting process have been made. Widely accepted efficiency definition protocols are necessary to help researchers from different groups report their characterization of PEC materials in a way that allows for direct comparison. Solar-to-hydrogen conversion (STH) efficiency, applied bias photon-to-current efficiency (ABPE), incident photon-to-current efficiency (IPCE) or external quantum efficiency (EQE), and absorbed photon-to-current efficiency (APCE) or internal quantum efficiency (IQE) are the four most common efficiencies used in PEC water splitting. Among them, STH efficiency is the single value by which all PEC devices can be reliably ranked against one another [19].

The above four efficiencies are divided into practical system efficiency and demonstrated research efficiency [20]. STH efficiency is the only practical system efficiency by which device performances can be quantifiably compared under the same standard. The other three efficiencies are categorized as demonstrated research efficiency.

The four efficiencies are also classified as benchmark efficiency and diagnostic efficiencies [21]. STH efficiency is the benchmark efficiency, while the other three efficiencies are categorized as diagnostic efficiencies. In this section, the four types of efficiencies will be introduced in detail, including their using conditions and notices.

2.3.1 Solar-to-Hydrogen Conversion Efficiency

Among all the efficiency definitions in PEC water splitting devices, STH efficiency is the most important parameter to characterize a PEC device [21]. It describes the overall efficiency of a PEC water splitting device and is defined as the ratio of the chemical energy stored in the produced hydrogen gas to the solar energy input (100 mW/cm^2 , AM 1.5G) under zero bias. The chemical energy stored in the produced hydrogen gas can be calculated from the product of the rate of hydrogen production (r_{H_2}) and change

in Gibbs free energy (ΔG) per mol of H_2 (237 kJ mol^{-1}), while the solar energy input is incident illumination power density (P , 100 mW/cm^2 , AM 1.5G) multiplied by the illuminated electrode area (S). There is no applied voltage between the working electrode and counter electrode, and all of the energy in the water splitting process is being supplied by sunlight. So, the STH efficiency can be calculated according to the following equation:

$$STH \text{ efficiency} = \frac{r_{H_2} \times \Delta G}{P \times S} \quad (2.5)$$

In the above equation, the chemical energy stored in the produced hydrogen gas can also be expressed as the product of voltage, current, and the faradaic efficiency for hydrogen evolution. So, Equation 2.5 could be given in the below form:

$$STH \text{ efficiency} = \frac{1.23 \times J \times \eta}{P} \quad (2.6)$$

where 1.23 is the thermodynamic water splitting potential, J (mA/cm^2) is the photocurrent density without applied voltage, η is the faradaic efficiency of photocathode, and P is the incident illumination power density (100 mW/cm^2 , AM 1.5G). There is a requirement that the reaction should be carried out in the absence of any sacrificial electron donors or acceptors and the product in photoanode must specifically be O_2 to maintain a sustainable overall reaction in which sunlight and water are the only inputs.

2.3.2 Applied Bias Photon-to-Current Efficiency

No potential bias is stated when using the STH efficiency. However, an external voltage is usually required in PEC water splitting system. The electrical energy has to be subtracted from the energy gain. A new applied bias photon-to-current efficiency (ABPE) is defined and frequently used in the PEC water splitting system with a potential bias. ABPE is defined as:

$$ABPE = \frac{|J| \times (1.23 - V_{bias})}{P} \quad (2.7)$$

where J is the photocurrent density at a specific potential, 1.23 is the thermodynamic water splitting potential, V_{bias} is the applied potential, and P is the incident illumination power density (100 mW/cm^2 , AM 1.5G).

Considering that the faradaic efficiency is below unity in most situations, applied bias-compensated solar-to-hydrogen efficiency (AB-STH) is suggested as a general expression of STH through multiplying ABPE by faradaic efficiency of photoelectrode (η) [9]. The AB-STH efficiency can be calculated according to the following equation:

$$AB-STH \text{ efficiency} = \frac{|J| \times \eta \times (1.23 - V_{bias})}{P} \quad (2.8)$$

The ABPE is defined for using in a two-electrode configuration. For a photoelectrode measured in the three-electrode configuration, hypothetical half-cell solar-to-hydrogen efficiency (HC-STH) is given to characterize the efficiency of photoelectrode [9]. As same as ABPE and AB-STH efficiency, the electrical energy has to be subtracted from the energy gain. For a photoanode:

$$HC-STH \text{ efficiency} = \frac{|J| \times (1.23 - E_{RHE})}{P} \quad (2.9)$$

While for a photocathode:

$$HC-STH \text{ efficiency} = \frac{|J| \times E_{RHE}}{P} \quad (2.10)$$

2.3.3 IPCE and APCE

Incident photon-to-current efficiency (IPCE) is identical to external quantum efficiency (EQE). The definition and measurement of IPCE has been introduced in Section 2.4. In essence, IPCE is an overall process efficiency including light absorption efficiency, charge separation efficiency, and charge injection efficiency. It is worth noting that IPCE describes the ratio of output electrons to incident photons, which unlikes STH efficiency and ABPE that demonstrate the ratio of output energy to incident light energy. For example, if an equivalent number of photons with different energy (wavelength) impinge on a photoelectrode and an equal number of electrons are collected at each wavelength, the IPCE for each wavelength is identical, despite the difference of photon energy. However, the STH efficiency and ABPE at each wavelength is different on this occasion.

IPCE gives the photon-to-current conversion efficiency at each special light wavelength. So, it can be used to estimate the maximum possible STH

efficiency by integrating the IPCE data over the solar spectrum if the IPCE data are collected under zero bias and all generated electrons are used for the evolution of hydrogen. The actual STH efficiency under zero bias also can be calculated by testing the faradaic efficiency of photoelectrode and then multiplying the maximum possible STH efficiency by faradaic efficiency.

In addition to the difference of definition between IPCE and STH efficiency, the using conditions are also different. From the definition of IPCE, it is clear that monochromatic light with detected (or calculated) photon number is necessary for testing IPCE. This is different to STH efficiency measurement, which needs broadband-standard solar-simulated illumination (100 mW/cm^2 , AM 1.5G). Besides, as mentioned in Section 2.4, IPCE is the function of applied bias, while STH efficiency requires zero-bias conditions.

Absorbed photon-to-current efficiency (APCE) is also called internal quantum efficiency (IQE). The definition and measurement of APCE has been introduced in Section 2.4. STH efficiency and IPCE are the total efficiency in the whole PEC water splitting process. APCE is defined to understand the inherent performance of a photoelectrode, eliminating the effect of light absorption efficiency. It includes charge separation efficiency and charge injection efficiency.

2.4 Summary

The common measurements in PEC water splitting system including optical properties, polarization curve, photocurrent transients, IPCE, APCE, Mott–Schottky plot, charge separation efficiency, charge injection efficiency, and gas evolution measurements are introduced firstly. Then STH efficiency, ABPE, IPCE, and APCE used for comparative evaluation and their using conditions and notices are described in detail. These standard measurements and efficiency definitions are useful to guide research works in PEC water splitting.

References

1. Nellist, M.R., Laskowski, F.A.L., Lin, F., Mills, T.J., Boettcher, S.W., Semiconductor–electrocatalyst interfaces: Theory, experiment, and applications in photoelectrochemical water splitting. *Acc. Chem. Res.*, 49, 733–740, 2016.

2. Wang, T., Luo, Z., Li, C., Gong, J., Controllable fabrication of nanostructured materials for photoelectrochemical water splitting via atomic layer deposition. *Chem. Soc. Rev.*, 43, 7469–7484, 2014.
3. Swierk, J.R., Mallouk, T.E., Design and development of photoanodes for water-splitting dye-sensitized photoelectrochemical cells. *Chem. Soc. Rev.*, 42, 2357–2387, 2013.
4. Young, K.M.H., Klahr, B.M., Zandi, O., Hamann, T.W., Photocatalytic water oxidation with hematite electrodes. *Catal. Sci. Technol.*, 3, 1660–1671, 2013.
5. Huang, J., Hu, G., Ding, Y., Pang, M., Ma, B., Mn-doping and NiFe layered double hydroxide coating: effective approaches to enhancing the performance of α -Fe₂O₃ in photoelectrochemical water oxidation. *J. Catal.*, 340, 261–269, 2016.
6. Tilley, S.D., Cornuz, M., Sivula, K., Grätzel, M., Light-induced water splitting with hematite: improved nanostructure and iridium oxide catalysis. *Angew. Chem. Int. Ed.*, 49, 6405–6408, 2010.
7. Dotan, H., Sivula, K., Grätzel, M., Rothschild, A., Warren, S.C., Probing the photoelectrochemical properties of hematite (α -Fe₂O₃) electrodes using hydrogen peroxide as a hole scavenger. *Energy Environ. Sci.*, 4, 958–964, 2011.
8. Le, F., Grätzel, M., Sivula, K., Controlling photoactivity in ultrathin hematite films for solar water-splitting. *Adv. Funct. Mater.*, 20, 1099–1107, 2010.
9. Hisatomi, T., Kubota, J., Domen, K., Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.* 43,, 7520–7535, 2014.
10. Grätzel, M., Photoelectrochemical cells. *Nature*, 414, 338–344, 2001.
11. Walter, M.G., Warren, E.L., McKone, J.R., Boettcher, S.W., Mi, Q., Santori, E.A., Lewis, N.S., Solar water splitting cells. *Chem. Rev.*, 110, 6446–6473, 2010.
12. Zhong, D.K., Choi, S., Gamelin, D.R., Near-complete suppression of surface recombination in solar photoelectrolysis by “Co-Pi” catalyst-modified W:BiVO₄. *J. Am. Chem. Soc.*, 133, 18370–18377, 2011.
13. Huang, J.W., Zhang, Y., Ding, Y., Rationally designed/constructed CoOx/WO₃ anode for efficient photoelectrochemical water oxidation. *ACS Catal.*, 7, 1841–1845, 2017.
14. Kim, T.W., Choi, K.-S., Nanoporous BiVO₄ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. *Science*, 343, 990–994, 2014.
15. Liu, G., Shi, J., Zhang, F., Chen, Z., Han, J., Ding, C., Chen, S., Wang, Z., Han, H., Li, C., A tantalum nitride photoanode modified with a hole-storage layer for highly stable solar water splitting. *Angew. Chem. Int. Ed.*, 53, 7295–7299, 2014.
16. Yang, J., Wang, D., Han, H., Li, C., Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Acc. Chem. Res.*, 46, 1900–1909, 2013.
17. Ran, J., Zhang, J., Yu, J., Jaroniec, M., Qiao, S.Z., Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. *Chem. Soc. Rev.*, 43, 7787–7812, 2014.

18. Roger, I., Shipman, M.A., Symes, M.D., Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.*, 1, 0003, 2017.
19. Khaselev, O., Bansal, A., Turner, J.A., High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production. *Int. J. Hydrogen Energy*, 26, 127–132, 2001.
20. Pinaud, B.A., Benck, J.D., Seitz, L.C., Forman, A.J., Chen, Z., Deutsch, T.G., James, B.D., Baum, K.N., Baum, G.N., Ardo, S., Wang, H., Miller, E., Jaramillo, T.F., Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ. Sci.*, 6, 1983–2002, 2013.
21. Chen, Z., Jaramillo, T.F., Deutsch, T.G., Kleiman-Shwarscstein, A., Forman, A.J., Gaillard, N., Garland, R., Takanabe, K., Heske, C., Sunkara, M., McFarland, E.W., Domen, K., Miller, E.L., Turner, J.A., Dinh, H.N., Accelerating materials development for photoelectrochemical hydrogen production: standards for methods, definitions, and reporting protocols. *J. Mater. Res.*, 25, 3–16, 2010.

Photoelectrochemical Cell: A Versatile Device for Sustainable Hydrogen Production

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Abstract

Photoelectrochemical (PEC) cell has been envisioned as a versatile device for sustainable hydrogen production since its inception in 1972. PEC device mimics the process of natural photosynthesis by absorbing sunlight and channeling the photo-generated electron hole pairs to evolve hydrogen. Natural photosynthesis exhibits quantum coherence, a process by which randomly incident sunlight on chlorophyll molecules is absorbed, transformed, and stored into useful chemical energy bonds. PEC device lacks quantum coherence due to which it exhibits low solar-to-hydrogen conversion efficiency. With the advent of nanotechnology, scientific community is trying to overcome the limitations of PEC cell by either engineering nano-structures or adapting different processes. Further different approaches are being undertaken worldwide to alleviate the solar-to-hydrogen conversion process via PEC cell as it can be a potential contributor in the future of green energy initiative. The first approach involves making novel hybrid nanostructures which contains inorganic/organic composites embedded within one electrode as it can satisfy to some extent the complex bunch of mandatory conditions essential for an ideal semiconductor. The second approach is designing tandem (photovoltaic's cell integrated photoanodes) configurations for realizing efficient stand-alone PEC systems for practical conversion devices. This chapter is a compendium of recent advancements in the area of sustainable hydrogen generation using metal oxides in PEC cells coalesced with novel hybrid nanostructures and tandem systems.

Keywords: Photoelectrochemical cell, solar, hydrogen, photosynthesis

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3.1 Introduction

Developing sustainable energy economy for long term is one of the major goals of research community. Although we have sufficient dwindling fossil fuels reserves and the technology that can fulfill our energy needs for few decades, it will lead to some irreversible cataclysmic impact on the environment. To achieve environmental friendly and cost-effective solutions for developing sustainable energy economy, it is vital to innovate and discover new scientific technologies [1–2]. Novel technologies are needed that can help in sustaining the unprecedented pace of projected energy consumption rate. Worldwide energy consumption report has projected that the global energy consumption will grow by 48 % between 2012 and 2040. Total world consumption of energy will expand from 549 quadrillion British Thermal Units (BTU) in 2012 to 815 quadrillion BTU in 2040 [3]. Global energy consumption rate is projected to double from 13.5 TW in 2001 to 27 TW by 2050 [4].

To overcome and sustain the power consumption rate, hydrogen is one of the most attractive chemical fuels obtained as a product of water electrolysis, which can be stored indefinitely and has the highest energy content per unit mass (120 MJ/Kg, i.e., three times higher than petrol) [5]. Steam reforming is the most dominant technology by which hydrogen is produced currently. The process involves complex reaction between hydrocarbon and steam and is normally based on fossil fuels releasing large quantities of CO_2 in air ($\sim 7 \text{ Kg CO}_2/\text{Kg H}_2$, which is 3 % of industrial CO_2 emission) [6]. There are certain issues which are linked with the generation, usage, and the storage of hydrogen on a very large scale. Despite all the issues and challenges, hydrogen has fascinated a lot of researchers and the interest has been continued making it a prospective fuel for future [7–8]. Among all the developed technologies, photoelectrochemical (PEC) hydrogen production is one of the most promising technologies that can provide cleanest, cheapest, and locally produced energy by harnessing a partial fraction of the $\sim 1,67,000 \text{ TW/year}$ of radiation incident on the earth's surface [9]. The inception and first demonstration of PEC cell by Fujishima and Honda in 1972 has allured many researchers, and a series of investigations have been carried out since then [10]. Khaslev and Turner [11] demonstrated a complex monolithic PEC device with solar-to-hydrogen conversion efficiency of 12.4 %, which could effectively harness the solar energy and perform photoelectrolysis of water. PEC device harvests, transforms, and then converts solar energy into chemical energy using photoelectrode, when immersed in an electrolyte of suitable pH. On the generation front of hydrogen, prime focus of the research community has

been on synthesizing cost-effective photoelectrodes for efficient PEC cells. Photoelectrode is the heart of PEC cell, and for efficient water-splitting process, it has to satisfy a complex set of mandatory conditions. An ideal material should have requisite band characteristics, high quantum efficiency, and long term anticorrosive nature [12–13].

The search for an ideal semiconductor material is commonly known as “holygrail in semiconductor photoelectrochemistry” [14]. A large variety of semiconductor materials such as metal oxides and metal sulfides have been investigated, but the search for an ideal semiconductor is still on its way [15–17]. Metal oxides are considered as the most promising PEC material because they are often stable and have low cost [18]. However, metal oxides have low carrier mobility compared to silicon and other III-V semiconductor. The biggest challenge is overcoming the limitation exhibited by metal oxide and taking advantages of their high stability and low cost. One of the approaches adapted by the researchers is designing novel hybrid nanoarchitectures for realizing efficient photoelectrodes. These hybrid nanoarchitectures contain inorganic/organic composites embedded within one electrode as they complement each other and can satisfy the stringent set of conditions essential for an ideal semiconductor to some extent [19–21]. Another approach is designing tandem (multijunction, monolithic, etc) devices for realizing efficient stand-alone PEC devices [22–25]. In this chapter, we will discuss and throw light on the recent advancements in the area of hydrogen generation where metal oxides are used in PEC cell.

3.2 Photoelectrochemical (PEC) Cells

Hydrogen production via PEC cells is one of the most attractive methods which utilize abundantly available renewable resources, i.e., solar light and water. A basic PEC cell consisting of semiconductor photoelectrode, metal counter electrode, and electrolyte together with band diagrams and cell mechanism is shown in Figure 3.1. In this system, the semiconductor photoelectrodes having either n-or p-type conductivity serves as working electrode, and the function of the counter electrode is performed by Pt (or other materials). To investigate the mechanism of half cell reaction in the PEC cell, a reference electrode is also employed. There are several physicochemical mechanisms which take place at the semiconductor, semiconductor/electrolyte interface during photoelectrolysis of water. This includes (1) efficient light absorption, (2) charge segregation, (3) charge migration, (4) charge recombination, and (5) redox reaction at the surface.

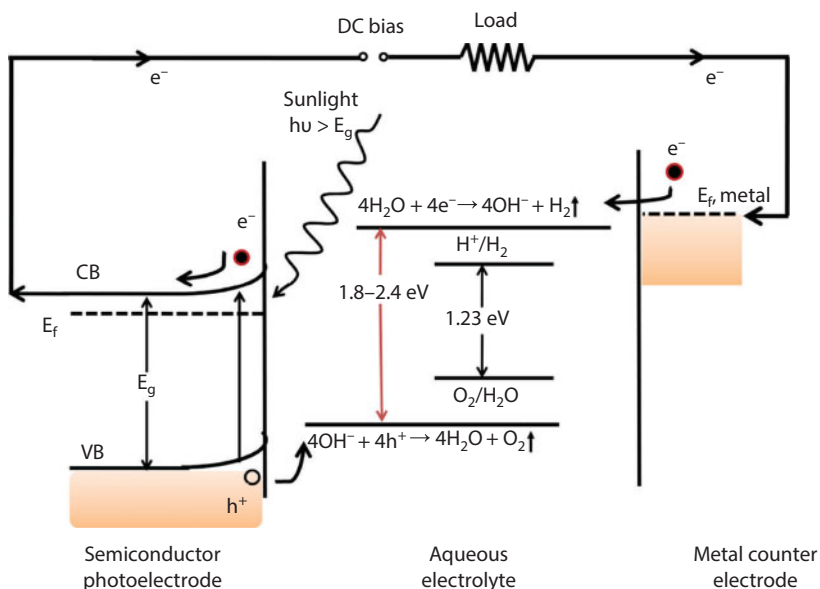
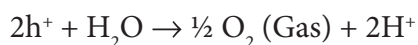
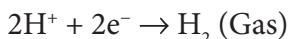


Figure 3.1 Schematic diagram of a basic photoelectrochemical cell.

When a semiconductor is illuminated with photons having energy greater than the bandgap energy of semiconductor, the electrons are excited to the conduction band and the holes are left behind in the valence band. The segregated electron and holes move through the semiconductor photoelectrodes to the interface of semiconductor electrolyte, where redox reactions take place and solar energy is converted into chemical energy. In case of photoelectrode having n-type nature, holes react with water molecule at the semiconductor surface which results in O_2 evolution whereas electrons are transferred to the counter electrode via substrate where they reduce H^+ into H_2 . On the other hand in the p-type semiconductor photoanodes, O_2 and H_2 evolution takes place at counter- and semiconductor electrode, respectively.

This means that fast transfer of electrons toward the electrolyte compared to holes leads to flow of cathodic photocurrent, whereas fast hole transfer toward the electrolyte results into a strong anodic photocurrent in the PEC water-splitting process [9, 26–27]. The basic reaction for PEC cell is as follows:





When a semiconductor photoelectrode is immersed in an electrolyte solution, transfer of charge carriers takes place until the Fermi energy of the electrons in the semiconductor is equal to the redox potential of the electrolyte. The transfer of charge carriers associated with electric field on both the sides of junction produces a region which is known as space charge region. A familiar electrostatic double layer is present on the electrolyte side, which consists of compact Helmholtz layer (composed of oriented water molecule dipoles and adsorbed electrolyte ions) accompanied by diffused Gouy-Chapman layer. On the semiconductor side, band bending takes place and also depends on the positions of the Fermi level in the semiconductor. The bands are flat if the Fermi level of the semiconductor is equal to the flat band potential, i.e., excess charge is absent on both the sides of the junction. In an n-type semiconductor photoanodes, the position of Fermi level is typically higher than the redox potential of the electrolyte, so electrons migrate from the photoanode to the electrolyte solution leaving behind a positive charge in the space charge region which is normally depicted by upward band bending. In a p-type semiconductor, the Fermi level is present at position which is lower than the redox potential of electrolyte, therefore electrons move from electrolyte to the semiconductor photoelectrode in order to achieve equilibrium. In this process, downward band bending takes place because of the negative charge present in the space charge region in PEC water-splitting process. Upon illuminating the semiconductor photoelectrode, a photovoltage is generated due to segregation of photogenerated charge carriers in the band bending region. These photogenerated charge carriers are separated by the transport mechanism, mainly (1) drift and (2) diffusion. Drift is defined as the motion of charge carriers in response to the applied electric field present across the semiconductor, whereas diffusion is associated with the gradient related to the concentration of the charge carriers. The water-splitting reaction will proceed if the photoelectrode is capable enough to provide sufficient driving force required for the water-splitting reaction to occur (energy obtained by photoelectrode from sunlight or by external power sources). The presence of light causes the H^+/H_2 redox potential to lower down, whereas application of external bias raises Fermi energy level of counter electrode above H^+/H_2 redox potential. This facilitates smooth transfer of electron to H^+ ions for the evolution of hydrogen. The applied external bias also provide the over-potential to the cathode, which is necessary for sustaining the current flow and increasing the band bending, which in turn drives charge separation. However, in photoelectrolysis of water, the prime objective is development

of a robust, efficient, reliable, stable, and cost-effective PEC system, which has sunlight and water as the main energy inputs.

From the last four decades, various metal oxide (TiO_2 , ZnO , Fe_2O_3 , BiVO_4 , WO_3 , etc.) and nonoxide (GaAs , CdS , InP , etc.) semiconductors have been utilized as photoelectrode material in PEC cell [15–18]. For an efficient photoelectrode material, the semiconductor should satisfy a set of complex conditions. (1) Foremost the material should have high visible light absorption, which depends on the bandgap of the semiconductor material and which in turn determines the solar-to-hydrogen (STH) efficiency (discussed in the next section) of a PEC cell. To have high STH efficiency, semiconductor should have a small bandgap, so that it can absorb the entire spectrum of sunlight efficiently. Thermodynamically water splitting is an uphill reaction ($\Delta G = 237 \text{ KJ/mol}$) and to generate hydrogen and oxygen by this process, a thermodynamic potential of 1.23 eV is required [10]. Considering all the thermodynamic losses and the overpotential required for the fast reaction kinetics, the semiconductor should have an inherent bandgap of $\sim 1.8 \text{ eV}$. To achieve 10% STH efficiency, a target set by the US Department of Energy, a photoelectrode should exhibit a minimum photocurrent density of $\sim 8 \text{ mA cm}^{-2}$, which corresponds to maximum bandgap of $\sim 2.4 \text{ eV}$ [27]. Therefore, the optimum value of the bandgap should be in between 1.8 and 2.4 eV. (2) The photoelectrodes should have suitable band energetics, i.e., the conduction and valence band must straddle well with the water redox potential. The position of conduction band must be more negative than H_2 generation potential and the valence band position should be more positive relative to oxygen generation potential. This way the photogenerated charge carrier will have enough driving force in performing the redox reaction of water. (3) The transfer of photogenerated charge carriers across the semiconductor/electrolyte interface should be relatively fast to avoid charge accumulation and recombination. This property is often determined by intrinsic (electron hole mobility) and extrinsic properties (presence of defects) of semiconductor photoelectrodes [15]. (4) The semiconductor electrode must be chemically stable in the electrolyte. The general rule for material stability in PEC is, for n-type semiconductor the oxidation potential of the material in the electrolyte should be lower than the oxygen evolution potential, while for p-type semiconductor the reduction potential should be higher than H_2 evolution potential [28]. Last but not the least; the material should be inexpensive, abundantly available, and most important it should be environmental friendly. These are the important parameters on which a photoelectrode is evaluated, but it is benchmarked on the most important parameter which is known as efficiency. Different types of efficiency measurements have been described in literature and the important ones are summarized as follows [29].

3.2.1 Solar-to-Hydrogen (STH) Conversion Efficiency

(to report stand-alone water-splitting capability of PEC cell): STH determines the overall efficiency of a PEC device with illumination of AM 1.5G and without bias conditions. STH efficiency is a ratio of chemical energy produced to that of input solar energy. The chemical energy generated is defined as the product of hydrogen produced with the change in Gibbs free energy per mole of hydrogen at room temperature, whereas input solar energy is defined as the product of incident illumination intensity with illuminated area of the photoelectrode.

$$\text{STH} = [(\text{mmol H}_2/\text{s}) \times (237 \text{ kJ/mol})] / [P_{\text{total}} (\text{mW/cm}^2) \times \text{Area} (\text{cm}^2)]_{\text{AM1.5G}} \quad (3.1)$$

Alternatively, another equation can be used to describe the STH efficiency.

$$\text{STH} = [J_{\text{ph}} (\text{mA/cm}^2) \times (1.23 \text{ V}) \times \eta_{\text{F}}] / [P_{\text{total}} (\text{mW/cm}^2)]_{\text{AM1.5G}} \quad (3.2)$$

where J_{ph} is photocurrent density and (η_{F}) is the Faradaic efficiency for hydrogen evolution.

3.2.2 Applied Bias Photon-to-Current Efficiency (ABPE) (to measure and understand the intricate nature of semiconductor/electrolyte interface)

The efficiency measurements recorded in the presence of external bias are known as ABPE. It is not a true STH estimate as external bias is being used but the magnitude of photocurrent generated plays an important role in achieving higher efficiency in PEC process.

$$\text{ABPE} = [J_{\text{ph}} (\text{mA/cm}^2) \times (1.23 - |V_{\text{b}}|) (\text{V})] / [P_{\text{total}} (\text{mW/cm}^2)]_{\text{AM1.5G}} \quad (3.3)$$

3.2.3 External Quantum Efficiency (EQE) or Incident Photon-to-Current Efficiency (IPCE)

IPCE is defined as the ratio of electrons out to the photons in. It is the amount of photocurrent collected per incident photon flux as a function of incident monochromatic wavelength.

$$\text{IPCE} (\lambda) = \text{electrons cm}^{-2} \text{ s}^{-1} / \text{photons cm}^{-2} \text{ s}^{-1}$$

$$\text{EQE}(\lambda) = \frac{[|J_{\text{ph}}|(\text{mA}/\text{cm}^2) \times 1240 (\text{V} \times \text{nm})]/[P_{\text{mono}} (\text{mW}/\text{cm}^2) \times \lambda(\text{nm})]}{(3.4)}$$

3.2.4 Internal Quantum Efficiency (IQE) or a Absorbed Photon-to-Current Efficiency (APCE)

IQE of a PEC cell is defined as the ratio of collected photocurrent to the absorbed photons. In other terms, APCE is a relationship between maximum photon absorption with least effective charge carrier movement within the semiconductor photoelectrode material.

$$\text{IQE}(\lambda) = \frac{[|J_{\text{ph}}|(\text{mA}/\text{cm}^2) \times 1240 (\text{V} \times \text{nm})]/[P_{\text{mono}} (\text{mW}/\text{cm}^2) \times \lambda(\text{nm}) \times (1 - 10^{-A})]}{(3.5)}$$

where A is the absorbance of the photoelectrode determined by UV-Vis spectroscopy and it is the logarithmic ratio of measured output light intensity (I) vs. input light intensity (I_0).

Several attempts have been made to advance the design and synthesis of semiconductor photoelectrode materials. It is reported that efficiency of PEC reaction is greatly affected by the charge transfer process, band-gap energy, and band structure of the semiconductor photoelectrodes. The semiconductor photoelectrodes which are visible spectrum active can be changed/alterd using different strategies such as doping, dye sensitization, mixed oxides, semiconductor-semiconductor heterojunction, etc., which are discussed in the later section of this chapter. Although a large number of reviews are available on PEC water-splitting process, none of them have covered the entire range of technical and scientific issues along with the recent advancements in metal oxides. This chapter is a compendium of recent advancements in hydrogen generation using hybrid metal oxides and their tandem systems.

3.3 Monometal Oxide Systems for PEC H_2 Generation

In 1972, Fujishima and Honda [10] have demonstrated the overall process of PEC water-splitting reaction utilizing single crystalline TiO_2 as photoanode and Pt as cathode under UV-Vis irradiation (assisted by electric bias). Since then, different types of materials have been scrutinized as semiconductor materials for the synthesis of photoelectrodes. In this section, our prime focus will be on the use of single component metal oxide systems as photoelectrodes for designing efficient PEC cell. The impediments and the

recent new developments in using single component metal oxides for PEC water splitting are highlighted as follows.

3.3.1 Titanium Dioxide (TiO_2)

TiO_2 is the most comprehensively studied and reviewed metal oxide system which exists in two phases, i.e., anatase and rutile phase. Anatase and rutile phases exhibit a bandgap energy of 3.18 and 3.03 eV, respectively [30]. The minority hole diffusion length in anatase and rutile phases is ~ 70 and ~ 10 nm, respectively [31–32]. TiO_2 is the most stable and abundantly available metal oxide which has appropriate energy levels which straddle well with the water redox potentials. The biggest drawback of TiO_2 is its weak absorption capability in the visible region. Anatase and rutile phases of TiO_2 exhibit a very low theoretical STH efficiency of 1.3 and 2.2%. Both the phases of TiO_2 show PEC efficiency of $\sim 1\%$ with visible light source [33]. Anatase TiO_2 has better charge mobility and prolonged charge carrier lifetimes. It also exhibits larger depletion width and strong band bending. Due to upward band bending, the spatial charge segregation is dominated by the surface hole trapping. Rutile TiO_2 has a 10 times faster recombination rate than that of anatase. Moreover, anatase TiO_2 has a higher conduction band which makes it suitable for water reduction reaction. The composite mixture of both the phases (i.e., anatase and rutile) of TiO_2 exhibits much higher photoactivity than individual phase of TiO_2 [33]. At the interface of both the phases, a space charge layer is developed which leads to band bending. At the interface of both the phases, the presence of electric field promotes charge segregation and restrains charge recombination process. The photogenerated electrons can migrate from anatase to rutile phase and reverse pathway is followed by holes.

Normally, single- and polycrystalline materials are often utilized for realizing photoelectrodes. Single-crystalline materials have high charge mobility and low recombination rate characteristics compared to polycrystalline materials [34]. The presence of grain boundaries in polycrystalline materials impedes the process of charge transportation and acts as charge recombination sites. The biggest advantage of using single crystals is their inherent capability of exhibiting selective crystal facets on the surface [35]. The photocatalytic activity is enhanced when the offset of the band energy levels present between the different facets alleviate the charge transfer process. Nowadays, high-dimensional nanostructures have caught the attention as they exhibit enhanced charge transport characteristics. The photoresponse of nanostructured 1D- TiO_2 thin films was approximately twofold times more than the mesoporous TiO_2 thin films [36–38].

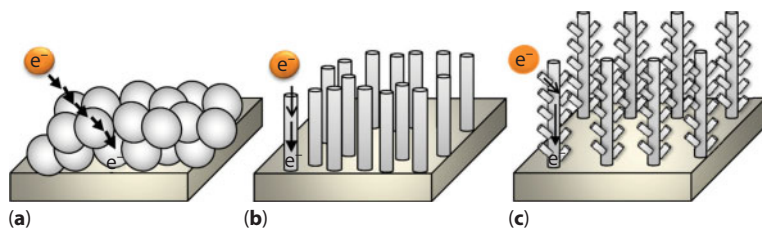


Figure 3.2 Different morphologies for enhanced PEC response.

Similarly, highly ordered TiO_2 nanotube arrays have shown improved PEC response, and recent focus is on developing new synthesis strategies by which morphology and density of TiO_2 nanorod arrays can be tailored for PEC applications. Figure 3.2(a) shows the mesostructured nanoporous thin film, while Figure 3.2(b) and (c) depicts the nanorods and branched nanorods with enhanced charge transport properties.

Cho *et al.* [37] have reported single-crystalline branched TiO_2 nanorods as nanostructure photoanode for efficient PEC devices. Under AM 1.5G illumination (100 mW cm^{-2}), the ABPE for nanoparticles, nanorods, and branched nanorods are 0.02% (at 0.94 V vs. Pt), 0.17% (at 0.65 V vs. Pt), and 0.49% (0.65 V vs. Pt), respectively. Both nanorod and branched nanorod TiO_2 films had better performance than nanoparticle films because they have enhanced light absorption and improved charge carrier transport. Yang *et al.* [39] have synthesized core shell of TiO_2 nanostructure where the core portion, i.e., nanodendrite array is of rutile TiO_2 and the shell portion consisted of both rutile and anatase TiO_2 nanoparticles. The quasi-single-crystalline structure of TiO_2 nanodendrite array provides fast electron pathway whereas its shell provides high surface area for effectual charge segregation. A photocurrent density and photoconversion efficiency of 2.08 mA cm^{-2} at 1.23 V vs. reversible hydrogen electrode (RHE) and 1.13% at 0.51 V vs. RHE are, respectively, attained using hierarchical TiO_2 nanostructured array PEC cell under illumination of AM 1.5G. A detailed comparison of different TiO_2 nanostructures with other materials and their PEC response has been enlisted in Table 3.1.

3.3.2 Zinc Oxide (ZnO)

ZnO is a versatile metal oxide semiconductor material which has also attracted researchers as it has comparable properties as that of TiO_2 . ZnO has almost the same bandgap ($\sim 3.2 \text{ eV}$) and electron affinities as that of TiO_2 . ZnO has a large exciton binding energy (60 eV), is abundantly

available, is cheap, and is considerably stable against photocorrosion [40–41]. It has a very high electron mobility of $155 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and has much higher electron diffusivity than that of TiO_2 , which makes it a favorable candidate for PEC activity [42]. The crystalline structure of ZnO is conducive to anisotropic growth of nanorods, nanosheets, nanobelts, nanoflowers, etc., making it an ideal candidate for PEC cells. Different types of nanostructures ranging from nanowires to nanorods and nanosheets can be synthesized using ZnO [43]. Since distinct and diverse morphologies are being displayed by ZnO, several novel designs of photoelectrodes can be assembled and realized using it. Wolcott *et al.* [44] have reported the synthesis of ZnO thin films by three different deposition techniques: pulsed laser deposition, pulsed laser oblique-angle deposition, and electron beam glancing deposition. The PEC properties of all the three types of films have been investigated as a function of porosity, charge transport properties, crystal defect concentration, and space charge layer characteristics. Rokade *et al.* [45] have reported the synthesis of ZnO nanorods and nanotubes for designing PEC photoelectrodes, by a very simple electrodeposition technique which is also free from templates and capping agents. ZnO nanotubes exhibited remarkably enhanced PEC response with excellent stability, and many superior characteristics than that of nanorods. These characteristics can be attributed to increased surface area. Babu *et al.* [46] have investigated and reported the synthesis of ZnO nanorods and the effect of diameter change of these rods on the PEC activity. The controlled growth of ZnO nanorods ranging from 45 to 275 nm was carried out on both SiO_2/Si and indium tin oxide substrates by simple hydrothermal method (by varying zinc nitrate and HMTA concentration). The diameter of the nanorods decreases on decreasing the zinc nitrate concentration and the photocurrent density increased with the decrease in the diameter of the nanorods. Photoconversion efficiencies of 45.3 % and 0.42 % were obtained for 45 nm ZnO nanorods on using UV and visible light sources respectively [46]. Hierarchical ZnO nanostructures exhibited interesting novel PEC properties because of the multidimensional shape and nanoarchitectures [47]. The gas evolution kinetics also increased drastically because of the increased surface area and the decreased radius of curvature. The branched 1D nanowire offers direct integration of materials with different functionalities which results in realization of highly efficient photoelectrodes for PEC splitting of water [47]. Although ZnO is considerably stable in aqueous medium, a coating of thin film of metal over photoelectrodes can further improve the stability, minimize the decomposition, and enhance the PEC hydrogen reduction kinetics. Hassan *et al.* [48] have synthesized ZnO nanotetrapod photoanodes by thermal

evaporation method. The reaction time was found to be a critical factor in the synthesis of well-defined tetrapod nanostructures. ZnO nanotetrapod electrodes showed a photocurrent density of 0.4 mA cm^{-2} under AM 1.5G illumination (100 mW cm^{-2} , $0.5 \text{ M Na}_2\text{SO}_4$), a significantly greater photocurrent than the bulk ZnO counterpart electrodes. Sun *et al.* [49] synthesized three-dimensional ZnO nanoforests using hydrothermal method. The unique architecture characteristics endow the willowlike ZnO nanoforest with efficient PEC performances, yielding photocurrent density of 0.92 mA cm^{-2} at $+1.2 \text{ V}$ (vs. Ag/AgCl) along with small charge transfer resistance and long photoelectron lifetime. The performance of different single component ZnO nanoarchitectures with other metal oxides has been shown in Table 3.1.

3.3.3 Tungsten Oxide (WO_3)

A metal oxide which has been the subject of intensive PEC water-splitting research is tungsten oxide (WO_3). WO_3 has an ideal bandgap of $\sim 2.5 \text{ eV}$ which can easily capture almost 12% of the visible light spectrum [50]. WO_3 has a reasonable hole diffusion length, good chemical stability, and can be synthesized by a very easy process [51–52]. WO_3 is stable in acidic aqueous solution [53–54]. Butler has investigated the use of WO_2 as photoelectrodes for PEC splitting of water and had also modeled the charge carrier separation process at the semiconductor/electrolyte interface [55]. In the research work, it was shown that a linear relationship existed in between photocurrent density and light intensity up to 10 air mass showing, that charge carrier dynamics influence the performance of PEC cell. Preparation parameters and the annealing temperatures determine the morphology and the crystallinity of WO_3 photoelectrodes which dictates the PEC properties of PEC cell. WO_3 nanostructures such as nanowires, nanorods, nanodisks, etc. have been used for PEC applications. Ahn *et al.* [56] have reported deposition of WO_3 films on normal substrates by thermal evaporation followed by annealing at different temperatures (300, 500, and 600°C) for 5 h in air. WO_3 films annealed at 500°C exhibited the best PEC response due to improved crystallinity and enhanced light absorption properties. Zhang *et al.* [57] reported synthesis of WO_3 nanoflakes modified by etching and reduction process in a weak acidic medium. Synthesized WO_3 photoelectrodes have a larger coarse surface area in which oxygen vacancies are formed during the etching process. The synthesized photoelectrodes exhibited photocurrent density of $\sim 1.1 \text{ mA cm}^{-2}$ which is approximately twofold time more than the pristine WO_3 nanoflakes (using 1.0 V Ag/AgCl reference electrode).

Table 3.1 Summary of various semiconductor monometal oxide nanostructures used in photoelectrochemical water-splitting cell.

Single material	Fabrication method	Electrolyte	Source intensity	Photocurrent (mA cm ⁻²)	Voltage (V)	Reference
TiO ₂ (nanorods)	Oblique-angle deposition	0.5 M NaClO ₄	100 mW/cm ²	0.02	1 V vs. Ag/AgCl	[36]
TiO ₂ (nanotube)	Anodization	1.0 M KOH	100 mW/cm ²	8.0	0 V vs. Ag/AgCl	[38]
TiO ₂ (branched)	Hydrothermal	1.0 M KOH	88 mW/cm ²	0.83	0.8 V vs. RHE	[37]
TiO ₂ (mesoporous)	Sol-gel, dip coating	1.0 M NaOH	1000 mW/cm ²	3.50	0 V vs. Ag/AgCl	[83]
TiO ₂ (nanowire)	Hydrothermal	1.0 M NaOH	100 mW/cm ²	1.10	1.5 V vs. RHE	[84]
TiO ₂ (3D hierarchical nanostructured array)	Hydrothermal	1 M KOH	100 mW/cm ²	2.08	1.23 V vs. RHE	[39]
Heterostructured TiO ₂ nanorod@nanobowl	Nanosphere lithography and hydrothermal	1 M NaOH	100 mW/cm ²	1.24	1.23 V vs. RHE	[85]
ZnO (thin film)	Pulsed-laser deposition	0.5 M NaClO ₄	100 mW/cm ²	0.14	1.0 V vs. Ag/AgCl	[44]
ZnO (nanotetrapod)	Thermal evaporation method	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.40	0.8 V vs. Ag/AgCl	[48]
ZnO (nanowire)	Electrodeposition	0.1 M LiI	100 mW/cm ²	5.79	-;	[86]

(Continued)

Table 3.1 Cont.

Single material	Fabrication method	Electrolyte	Source intensity	Photocurrent (mA cm ⁻²)	Voltage (V)	Reference
ZnO (nanocoral)	RF magnetron, thermal oxidation	0.5 M Na ₂ SO ₄	125 mW/cm ²	0.25	1.2 V vs. Ag/AgCl	[87]
ZnO (nanoforest)	Hydrothermal	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.92	1.2 V vs. Ag/AgCl	[49]
ZnO (nanotubes)	Electrochemical anodization	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.52	0.25 V vs. SCE	[41]
ZnO (caterpillar-like)	Hydrothermal method	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.72	+1.2 V vs. Ag/AgCl	[88]
ZnO (nanorods)	Vacuum annealed	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.60	1.23 V vs. RHE	[89]
WO ₃ (mesoporous)	Sol-gel	3.0 M H ₂ SO ₄	100 mW/cm ²	2.90	1.23 V vs. RHE	[90]
WO ₃ (mesoporous)	Potentiostatic anodization	1.0 M H ₂ SO ₄	370 mW/cm ²	9.0	1.8 V vs. SCE	[91]
WO ₃ (column)	Sputtering	0.3 m H ₃ PO ₄	100 mW/cm ²	2.70	1.6 V vs. SCE	[92]
WO ₃ (nanobowl)	Anodization	0.5 M Na ₂ SO ₄	0.59 mW/cm ²	3.50	2.0 V vs. Ag/AgCl	[93]
WO ₃ (mesoporous)	Sol-gel dip coating method	1 M KH ₂ PO ₄	300 mW/cm ²	0.60	1.23 V vs. RHE	[94]

WO ₃ (flake wall thin film)	Hydrothermal	0.1 M Na ₂ SO ₄	100 mW/cm ²	2.30	1.2 V vs. Ag/AgCl	[95]
WO ₃ (platelike)	Hydrothermal	1.0 M Na ₂ SO ₄	100 mW/cm ²	0.50	1.45 V vs. Ag/AgCl	[96]
WO ₃ (nanoplate)	Hydrothermal	0.5 M Na ₂ SO ₄	100 mW/cm ²	1.88	1.3 V vs. Ag/AgCl	[97]
WO ₃ (micro-nano architectures)	Ultrafast laser processing hybrid with thermaloxidation	0.1 M H ₂ SO ₄	100 mW/cm ²	1.20	1.0 V vs. Ag/AgCl	[98]
WO ₃ film with (002)-orientation	Hydrothermal method, rubbing, calcination	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.38	+1.0 V vs. Ag/AgCl.	[99]
Fe ₂ O ₃ (mesoporous)	Spraypyrolysis	1.0 M NaOH	50.0 mW/cm ₂	3.70	0.7 V vs. SCE	[100]
Fe ₂ O ₃ (mesoporous)	Solution-based	1.0 M NaOH	100 mW/cm ²	0.56	1.23 V vs. RHE	[101]
Fe ₂ O ₃ (mesoporous)	Ultrasonic spraypyrolysis	1.0 M NaOH	130 mW/cm ²	1.07	1.2 V vs. RHE	[102]
Fe ₂ O ₃ (mesoporous single crystals)	Facial crystallization and etching	1 M NaOH	100 mW/cm ²	0.61	1.23 V vs. RHE	[103]
Fe ₂ O ₃ (nanorods)	Chemical bath deposition	1.0 M NaOH	87 mW/cm ²	0.52	1.2 V vs. RHE	[67]
Fe ₂ O ₃ (wormlike)	Solution-based	0.1 M KH ₂ PO ₄	100 mW/cm ²	4.32	1.2 V vs. RHE	[69]

(Continued)

Table 3.1 Cont.

Single material	Fabrication method	Electrolyte	Source intensity	Photocurrent (mA cm ⁻²)	Voltage (V)	Reference
Fe ₂ O ₃ (ultrathin nanotube)	Chemical bath deposition	1.0 M KOH	87 mW/cm ²	1.41	0.4 V vs. Ag/AgCl	[66]
Fe ₂ O ₃ (nanoplatelets)	Plasma-enhanced chemical vapor deposition	1.0 M NaOH	100 mW/cm ²	1.39	1.55 V vs. RHE	[70]
BiVO ₄ (mesoporous)	Sol-gel, dip coating	1.0 M Na ₂ SO ₃	350 mW/cm ²	2.10	1.2 V vs. RHE	[104]
BiVO ₄ (thin film)	Liquid solid-state reaction	0.1 M K ₂ SO ₄	100 mW/cm ²	1.20	1.5 V vs. Ag/AgCl	[105]
BiVO ₄ (nanowire)	Reactive ballistic deposition	1.0 M Na ₂ SO ₄	100 mW/cm ²	0.90	1.0 V vs. Ag/AgCl	[106]
BiVO ₄ (nanopyramids)	Liquid solid-state reaction, spin coating	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.40	1.0 V vs. Ag/AgCl	[81]
BiVO ₄ (crystalline hydrophilic)	Hydrothermal	0.1 M Na ₂ B ₄ O ₇	100 mW/cm ²	1.04	1.23 V vs. RHE	[107]

3.3.4 Iron Oxide (Fe_2O_3)

Fe_2O_3 is a suitable material for PEC application with an ideal bandgap of ~ 1.9 to 2.2 eV. It is nontoxic, stable, earth abundant, has optical penetration depth of 1180 Å at 5500 Å, and can achieve a STH efficiency of 12.9% [58–59]. The major drawback with Fe_2O_3 is its short minority diffusion length, poor mobility of minority charge carriers, and poor water oxidation kinetics [60–61]. Due to these three factors, holes accumulate at surface and increase the recombination rate. To circumvent these limitations, nanostructures are utilized to enable the migration of holes to the surface [61–62]. In case of thick Fe_2O_3 films, photogenerated charge carriers annihilate due to recombination. The photogenerated carriers generated at far away distance from the semiconductor-electrolyte interface are not able to contribute to the generation of photocurrent. Souza *et al.* [63] have shown that in Fe_2O_3 thick films defects are generated due to stress when a strong interaction takes place between film and the substrate, thereby increasing the rate of electron and hole recombination. Stacked thin films can also be used as an alternative for extending hole transport distance. Complex nanostructures of Fe_2O_3 such as dendrites, mesoporous, and other nanostructures suffer with recombination problems at the grain boundaries [64]. 1D Fe_2O_3 nanostructures such as nanorods, nanotubes, nanowires grown on the substrate facilitate the effectual collection of photogenerated carriers. Vertically aligned, Fe_2O_3 nanorods and nanotubes exhibit strong photocurrent which is assigned to the efficient light harvesting and charge transport property of these 1D nanostructures. These nanostructures help photogenerated charge carriers to move and reach the electrolyte surface and expose the different facets to the electrolyte for oxidation. 1D Fe_2O_3 nanostructures with smaller diameters can provide a short pathway to the holes by which they can diffuse to the electrolyte-semiconductor interface, thereby solving the problem of poor charge migration [65–68]. A Fe_2O_3 photoanode showing a stable, record-breaking performance of 4.32 mA cm^{-2} PEC water oxidation current at 1.23 V vs. RHE under simulated 1-sun (AM 1.5G) irradiation was reported by Kim *et al.* [69]. FeOOH nanorods were grown directly on a transparent conducting oxide glass via an all-solution method followed by insitu two-step annealing at 550 °C and 800 °C. The synthesized hematite adapted a unique single-crystalline “wormlike” morphology. Marelli *et al.* [70] have reported nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoelectrode synthesized through plasma-enhanced chemical vapor deposition. The synthesized $\alpha\text{-Fe}_2\text{O}_3$ films have nanobranches that self-organize in plumlike nanoplatelets of length $350\text{--}700$ nm. The precursor concentration controls the dimension, density, and roughness of the

nanoplatelets. The highest photocurrent density of 1.39 mA cm^{-2} at 1.55 V vs RHE was shown by the photoanodes consisting of platelets.

Iordanova *et al.* [71] have shown Fe_2O_3 lattice consisting of anisotropic planes where conductivity in basal plane is approximately four times higher than the other directions. It is related to hopping mechanism of the valence states of $\text{Fe}^{2+}/\text{Fe}^{3+}$ within the iron layers. Kim *et al.* [72] have first defined Fe arrays lithographically and then synthesized multiwalled nanobeam arrays over them and after that transformed them into iron oxide beam arrays by calcination. These multidiameter nanopillar and nanocone structures allow optical resonances and enhance light intensity inside photoelectrodes. 3-D nanostructures can offset the trade-off between film thickness and the low photon absorption of Fe_2O_3 thin films [73]. They can also enhance the charge collection efficiency and improve their light harvesting properties. Nanospikes have attracted a lot of attention as the antireflection and light trapping properties enable them to absorb majority of solar light incident on them [74]. Thus, hematite hierarchical nanoarchitectures assure good photocurrent performance and appear to be an ideal platform for the construction of customized multilayer architecture for PEC water splitting.

3.3.5 Bismuth Vandate (BiVO_4)

The most important n-type semiconductor that has recently evolved as one of the most promising materials for photoelectrodes in PEC applications is BiVO_4 . It has three different morphologies: (a) tetragonal zirconia structure, (b) monoclinic scheelite, and (c) tetragonal scheelite [75]. The most important morphology is monoclinic scheelite which exhibits a bandgap of $\sim 2.4 \text{ eV}$ which transforms to a maximum photocurrent of 7.5 mA cm^{-2} which translate to STH efficiency of $\sim 9.2\%$ (close to commercialization) under sunlight of AM 1.5 [76]. BiVO_4 monoclinic scheelite phase has optical penetration depth ranging from 100 nm to 500 nm at $\lambda = 420$ to 530 nm and has proper valence and conduction band edges straddling well with the redox levels. These properties make BiVO_4 an attractive candidate for tandem device that can be directly used in PEC applications [77–78]. Kudo *et al.* [79] reported the use of BiVO_4 as a photocatalyst for solar hydrogen production. Earlier work was focused on the suspended BiVO_4 nanoparticles as photocatalysts or photodegradants. BiVO_4 has a majority and minority carrier diffusion lengths of ~ 10 and 100 nm, respectively. In a half cell reaction, the water oxidation reaction involves transfer of protons and the poor oxygen evolution kinetics restrains the BiVO_4 efficiency. The morphological evolution and assembly of polycrystalline BiVO_4 crystals

can also provide an effective way of enhancing PEC properties of BiVO_4 . Luo *et al.* [80] have prepared BiVO_4 electrodes using a modified metal organic decomposition method. The synthesized photoelectrodes consisted of wormlike particles having sizes of 50–200 nm with porous structures with increased electrode/electrolyte junction areas. Photoelectrodes consisting of 1-D nanostructure such as nanowires/nanorod arrays had an enhanced surface area and also provide better charge transport and collection properties. These nanostructures also provide the shortest pathway for the minority charge carriers to move across/over them and reach the electrode/electrolyte interface. Su *et al.* [81] have reported the synthesis of pyramidal shaped BiVO_4 nanowire arrays grown on conductive FTO substrates by using a seed layer in an aqueous suspension of BiVO_4 . These pyramidal shaped BiVO_4 nanostructures were obtained by varying the temperature of the solution using a very simple and mild synthetic process. Hernanadz *et al.* [82] reported that the maximum photocurrent density of a photoelectrode is strongly dependent on its physicochemical properties such as its thicknesses, porosity, light absorption capacity, recombination rate, and most importantly on the operational characteristics of the device. A detailed comparison of various monometal oxide systems and their PEC performance has been enlisted in Table 3.1.

3.4 Complex Nanostructures for PEC Splitting of Water

To improve the performance of mono/single component metal oxide materials for PEC application, complex semiconductor materials have been rationally designed. These complex nanostructures of metal oxides have improved PEC properties due to alteration in the electronic band structures, which modify their optical and electronic properties. Moreover, the PEC properties of complex nanostructures can be modified using different approaches that have been outlined as follows.

3.4.1 Plasmonic Metal Semiconductor Composite Photoelectrodes

The optimal band requirement for single component semiconductor material in PEC application is 1.8 to 2.4 eV. This means sunlight of wavelength greater than 688 nm is ineffectual for the PEC device as it is unable to harvest it. This is a severe limitation exhibited by the single-component PEC device as absorption is an important process and has a cascading effect

on the overall PEC response. The absorption of the metal oxide systems can be improved by incorporating plasmonic metal nanostructure in it, which in turn can alleviate the efficiency of PEC systems. The plasmonic metal nanostructure is strongly related to the surface plasmon resonance (SPR) phenomena. SPR phenomena takes place when the incident light is in resonance with the excited conduction electrons present at the interface of metal and dielectric as shown in Figure 3.3(a). SPR consists of two important processes: surface plasmon polariton and localized surface plasmon resonance. Surface plasmon polaritons are propagating, dispersive electromagnetic waves coupled to the electron plasma of a conductor at a dielectric interface. Localized surface plasmons on the other hand are non-propagating excitations of the conduction electrons of metallic nanostructures coupled to the electromagnetic field [108]. SPR increases the PEC response of single component metal oxide semiconductor systems by three different processes: (i) increasing light absorption by enhancing photon interaction, (ii) direct electron transfer or plasmonics induced resonance energy transfer (PIRET), and (iii) reducing recombination rate [108].

There are different ways by which photonic absorption can be increased in plasmonic embedded complex nanostructures. The processes are strongly dependent on the size of the metal nanostructure [109–110]. If the metal nanostructure is large (i.e., ≥ 100 nm), then light trapping inside the semiconductor materials occurs due to multiple reflections and scattering, thereby effectively increasing the optical path length of incident radiation. The smaller embedded nanoparticles (i.e., ≤ 20 nm) lead to weak light

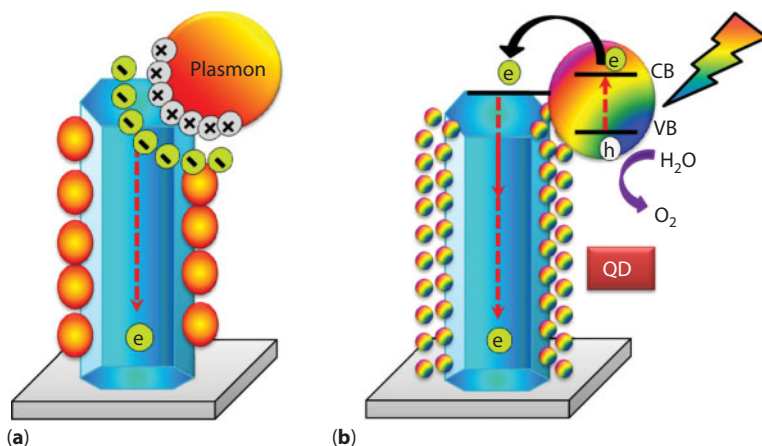


Figure 3.3 Schematic showing the effect of (a) plasmons and (b) quantum dots functionalized photoelectrodes for PEC splitting of water.

scattering, but they can create a strong local electromagnetic field with intensity up to ~ 100 times that of incident light, thereby further increasing the light absorption cross section [110]. On the other hand, a periodic plasmonic nanostructure in a semiconductor can unanimously guide the incident light along the lateral direction and thus help in trapping it. When sunlight is incident on complex nanostructures embedded with plasmonic metals, the conduction electrons in the plasmonic metals are excited to become highly energetic electrons known as hot electrons. These hot electrons can overcome the Schottky barrier and can easily hop to the adjacent semiconductor. The energies of the hot electrons are strongly dependent on the carrier concentration and size, shape of the plasmonic nanostructures [111–112].

In a complex semiconductor material, the coupling between the dipoles of the plasmons and the semiconductor material leads to the PIRET process, which eventually transfers plasmons energy nonradiatively from metal to semiconductor and help in charge separation [113]. In contrast to direct energy transfer, PIRET does not require close contact between plasmons and semiconductor and the efficiency is strongly dependent on the spectral overlap of plasmons and the absorption band of semiconductor. The PIRET process efficiently enhances the PEC response compared to direct energy transfer [114]. The charge carrier lifetime in plasmonic embedded semiconductor is increased by the strong plasmonic field present at the metal semiconductor interface. Zhang *et al.* [115] have synthesized a composite plasmonic metal/semiconductor photoanode by using Au nanoparticle decorated on 3D branched ZnO nanowire arrays. The photoanode exhibited photocurrent density of 1.45 mA cm^{-2} at 1.0 V vs. RHE, which translates to STH conversion efficiency of 0.52%. Recently, $\alpha\text{-Fe}_2\text{O}_3$ thin film electrodes coated with Au nanorods have been used for enhanced PEC water splitting by Wang *et al.* [116]. Using this self-assembled chemical method, a photocurrent density of 0.10 mA cm^{-2} at 0.5 V vs. Ag/AgCl was obtained. Patra *et al.* [117] have shown the effect of Ag-Au bimetallic nanocluster on TiO_2 and reported a quantum yield of 3.3% with hydrogen generation of $718 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$. The improved photocatalytic activity can be partially attributed to hot electrons. Thin layer of Ag over Au particles leads to a core-shell morphology, which increases the visible light absorption in TiO_2 . Moakhar *et al.* [118] had also reported the PEC response of bimetallic nanoparticle, i.e., Au and Pd decorated on ZnO nanorods. The bimetallic decoration sets up a favorable electric field which increases charge carrier transfer and helps in achieving a photocurrent density of 0.34 mA cm^{-2} at 0.4 V vs. Ag/AgCl. Momeni *et al.* [119] have shown highly ordered TiO_2 and $\text{WO}_3\text{-TiO}_2$ nanotubes, when decorated with Au using

photo-assisted deposition process, the total amount of hydrogen evolved by $\text{Au}/\text{WO}_3\text{-TiO}_2$ was three times higher than of bare $\text{WO}_3\text{-TiO}_2$ nanotubes and approximately nine times higher than that of bare TiO_2 nanotubes. Another way of increasing PEC response is by fabricating semiconductor heterojunctions.

3.4.2 Semiconductor Heterojunctions

When different types of inorganic semiconductor materials are combined together, they form a heterojunction which leads to some important change in the properties of semiconductors such as (i) broadens the light absorption, (ii) increases charge separation, (iii) suppresses charge recombination, and (iv) inhibits photocorrosion.

When different materials having adjacent bandgaps form a heterojunction, a change in band-offset takes place whereas the light absorption range remains intact [120–124]. This change in band-offset is responsible for improved charge segregation and restraining charge recombination. One can confirm this from the shift in the Fermi level to the negative potential side, which indicates more charge accumulation. On the other hand, when two semiconductor materials form a p-n junction, a stronger electric field is generated at the interface, which leads to efficient charge separation and reduced charge recombination rate [125–126]. Different types of system which have been synthesized consist of p-type nanoparticles loaded over n-type semiconductor material. For example, p-type NiO and Mg incorporated Fe_2O_3 nanoparticles were grown on n-type Fe_2O_3 film to form photoanodes for PEC water splitting. The presence of p-type layer facilitates hole extraction from Fe_2O_3 and also lowers the barrier for oxygen evolution. When wide gap semiconductor (ZnO , TiO_2 , SrTiO_3 , BaTiO_3) is combined with a narrow bandgap semiconductor material (CdS , CdSe , Fe_2O_3 , BiVO_4) different type of heterojunction is formed [127–128]. The high absorption coefficient ($>10^4 \text{ cm}^{-1}$) narrow band gap material acts as a photosensitizer. Zhang *et al.* [129] reported the design and fabrication of three-dimensional $\text{WO}_3/\text{BiVO}_4/\text{cobalt phosphate (Co-Pi)}$ composites inverse opal electrodes for PEC water splitting by electrodeposition of BiVO_4 layer and Co-Phosphate (Co-Pi) water oxidation catalyst on the WO_3 inverse opal. The continuous and conductive WO_3 inverse opals act as host skeletons for BiVO_4 layer deposition, providing direct and fast electron transport pathways. The void spaces of the inverse opals make an excellent interface contact with large surface area. The as-fabricated $\text{WO}_3/\text{BiVO}_4/\text{Co-Pi}$ photoanode had an excellent PEC performance, with a maximum photocurrent density of 4.5 mA cm^{-2} at 1.4 V versus Ag/AgCl , which is much

better than that of the individual constitute of WO_3 and BiVO_4 , respectively. Li *et al.* [130] have synthesized a novel heterojunction photoanode of $\text{WO}_3/\alpha\text{-Fe}_2\text{O}_3$ nanosheet array. The heterojunction exhibits improved sunlight-harvesting and electron-hole separation/transport efficiency. This heterojunction photoanode exhibits a photocurrent response of 1.66 mA cm^{-2} , a high IPCE of $\sim 73.7\%$ at 390 nm, and an excellent photostability of 100 %, at 1.23 V vs. RHE. Wang *et al.* [131] have rationally designed and fabricated 3D WO_3 nanoplate/ Bi_2S_3 nanorod heterostructures on FTO substrates by combining hydrothermal method, successive ion layer adsorption reaction (SILAR) and chemical bath deposition (CBD) reaction. A seed layer of Bi_2S_3 was utilized before the chemical bath deposition process, leading to the uniform distribution of Bi_2S_3 nanorods on WO_3 and high-quality interfacial contact. The composite photoanode with seed layer exhibited a very high photocurrent density of 5.95 mA cm^{-2} at 0.9 V vs. RHE, which is 35 and 1.4 times higher than that of pristine WO_3 and heterostructure without seed layer, respectively.

Barreca *et al.* [132] reported deposition of hematite nanostructures by plasma-enhanced chemical vapor deposition (PE-CVD) followed by atomic layer deposition of TiO_2 . The fabricated $\text{Fe}_2\text{O}_3\text{-TiO}_2$ photoanodes exhibited attractive performances, i.e., photocurrent density of 2.0 mA cm^{-2} at 1.23 V vs. the reversible hydrogen electrode in 1 M NaOH under simulated 1-sun illumination. Hsu *et al.* [133] have proposed fabrication of $\alpha\text{-Fe}_2\text{O}_3$ as a shell layer on the surface of ZnO nanowires as a core-shell nanoelectrode for application in PEC splitting of water. The optimal PEC activities of ZnO/ Fe_2O_3 core-shell NW as photoanodes are systematically analyzed. This n/n-type heterojunction structure causes a negative shift of the flatband potential and increases the surface band bending, relative to a bare $\alpha\text{-Fe}_2\text{O}_3$ film electrode. These characteristics resulted in doubling of photocurrent and greater PEC stability at a less positive potential for decomposition of water. Bai *et al.* [134] designed and synthesized CdS nanoparticle-sensitized patterned ZnO nanowire arrays using two-beam laser interference lithography, hydrothermal synthesis, and SILAR method. The synthesized photoanodes have a maximum STH conversion efficiency of 0.67 % at -0.4 V vs. Ag/AgCl , which is 22 times that of the nonpatterned ZnO nanowire array photoanodes. Such enhancement is attributed to the patterned ZnO nanowire arrays having ordered nanostructures with increased light-harvesting (due to light scattering effect) and segregated photogenerated electron-hole pairs.

Bard *et al.* [135] introduced the concept of “Z-scheme” derived from the process of natural photosynthesis. In this scheme, dual n-type semiconductors were combined together to overcome the limitations of a single

photoelectrode [136]. Since 1979, several efforts have been made to find a suitable combination of photoelectrodes and redox couples that can match perfectly and be suitable for PEC application. Combinatorial methods have been explored as a quick screening method to find suitable photoanodes for water oxidation which utilize metal oxides, for example, Fe_2O_3 , TiO_2 , BiVO_4 [128, 137–142].

3.4.3 Quantum Dots Sensitized Semiconductor Photoelectrodes

In the past few years, quantum dots (QDs) have evolved as important building blocks of PEC devices [143]. QDs are semiconductor materials whose motion is confined in all three spatial dimensions so tightly that quantum dots are said to be zero-dimensional [144]. The quantized energy levels facilitate the modulation of electronic properties, thereby promoting optimum light harvesting and charge carrier utilization as shown in Figure 3.3(b). To optimize the bandgap of ZnO , TiO_2 , SnO_2 , SrTiO_3 , etc., chalcogenides such as CdSe , CdS , CdTe , PbS , Fe_2O_3 , BiVO_4 and III-V semiconductors such as InAs , GaAs , InP have been extensively studied for PEC application [145–146]. These QDs possess high visible light absorption coefficient and are considerably stable and cost effective which makes them a viable alternative to noble metals.

Normally, semiconductors have low capacity to interact with the incident flux of photons, but the size quantization property exhibited by the QDs makes them capable to interact with the photons. Moreover, the bandgap tunability property of QDs related to composition shape and size can help in building new multigap systems that can cover the entire solar spectrum. The size of the QDs clearly controls the light absorption property [147]. The energetics favoring the electron transfer from conduction band of QD to that of semiconductor can also be modulated to attain thermodynamically feasible charge transfer particularly in large bandgap semiconductors. The conduction band edge is shifted toward negative potential value as the size of the quantum dot decreases. The kinetic studies reveal that the electron transfer rate for smaller QDs is higher than longer QDs. This indicated that smaller QDs can transfer electrons at a much faster pace. Recently, QDs have been used to generate multiple excitons after absorbing a photon [148]. These multiple excitons could generate hot electrons that can in turn amplify the available incident photon flux. Thus, number of electrons can be significantly improved by using QDs. The next advantage provided by QDs is efficient charge separation which helps in decreasing the recombination rate. When the size of the quantum dots is smaller

than the Bohr radius, the charge separation process becomes very simple [145]. The trapping of charge carriers in defects can be avoided by using QDs as they exhibit strong carrier localization. The aggregation of QDs can be taken care of by using ligands in the colloidal dispersions. The ligands stabilize the QDs and also serve as linkers which attach these nanostructures to the semiconductor surface. The choice of the capping agents is also important as they can lead to quenching effects [149]. Zeng *et al.* [150] have deposited PbS and CdS quantum dots onto TiO₂ nanotube arrays in turn via sonication-assisted SILAR method. QDs were uniformly decorated on TiO₂ nanotube arrays, and their aggregation was controlled by adjusting the length of the arrays. Under 1-sun illumination, the QD-sensitized TiO₂ nanotube arrays having length of 2.4 nm exhibit the highest photocurrent density of 4.32 mA cm⁻², which is ~27 times higher than that of the bare TiO₂ nanotube arrays. Incorporation of ZnO interlayer (10 atomic layer deposition cycles of) between TiO₂ nanotube arrays and QDs exhibit the highest photocurrent of 5.24 mA cm⁻² and best photoconversion efficiency of 4.9%. Trevisian *et al.* [151] had deposited PbS/CdS QDs, on mesoporous TiO₂ to harvest visible and near-infrared light. This TiO₂/PbS/CdS heterostructure has been used to realize a “quasi-artificial leaf” which can produce hydrogen at the rate of 4.30 ± 0.25 mL cm⁻² day⁻¹ (under simulated solar illumination)

3.4.4 Synergistic Effect in Semiconductor Photoelectrodes

The efficiency of PEC devices can be alleviated by combining two or more different process which can have a cumulative effect on the PEC response [152–153]. This is known as synergism between different components of a photoelectrode. It has been observed that TiO₂ when doped with nitrogen and sensitized with CdSe quantum dots exhibited much higher efficiency compared to bare TiO₂ which can be attributed to the synergistic effect [154]. Due to N-doping, the hole transfer increases due to increased oxygen vacancy levels; it also facilitates charge migration and reduces recombination rate. The sensitization of metal oxides with multiple photosensitizers can also be used to enhance the PEC response. The cosensitization of ZnO with CdSe and CdS QDs demonstrates that PEC response is improved by this process. ZnO nanotube arrays grown on conducting substrate of indium tin oxide were cosensitized using CdS and CdSe. The novel design had used dense ZnO nanotube arrays as base semiconductor material and cosensitizers as enhancers for visible light activity. The presence of cosensitized double layer structure provides direct interaction between QDs, and nanotubes exhibited strong photocurrent with

enhanced charge collection efficiency [155]. Liu *et al.* [156] have reported the synthesis of Ag/Cu₂O/ZnO tandem photoelectrodes. The photocurrent increased almost 11 times on using Ag/Cu₂O/ZnO photoelectrode compared to Cu₂O thin films. The performance of the synthesized photoanodes is attributed to the optimized design of the tandem triple junction photoelectrode where plasmonic material Ag and heterojunction efficiently absorb the incident light and segregate the electron hole pairs. Primc *et al.* [157] reported the synthesis of titania–hematite photoanodes with subsequent annealing. Photocurrents up to 2.2 mA cm⁻² were obtained at 1.23 V in 1.0 M NaOH under 1.5 AM simulated solar illumination. Hou *et al.* [158] reported the design and fabrication of three-dimensional branched (3DB) hybrid 3DB WO₃-NA (nano arrays)/C₃N₄-NS (nanosheets) heterojunctions decorated with CoOx nanoparticles (3DB WO₃-NA/C₃N₄-NS-CoOx) for efficient PEC water oxidation. The 3DB WO₃-NA/C₃N₄-NS-CoOx photoanode showed the photocurrent density of 5.76 mA cm⁻² at 2.1 V; 1.88 and 1.66 times greater than the photocurrent densities of WO₃-NA and WO₃-NA/C₃N₄-NS, respectively. A highest photocurrent density of 16 mA cm⁻² was obtained under 300 mW cm⁻² light intensity together with methanol as a sacrificial reagent. Hou *et al.* [159] reported the synthesis and characterization of a novel heterojunction array of α-Fe₂O₃/graphene/BiV_{1-x}Mo_xO₄ core/shell nanorod for PEC water splitting. The heterojunction yielded a pronounced photocurrent density of ~1.97 mA cm⁻² at 1.0 V vs. Ag/AgCl and a high photoconversion efficiency of ~0.53% at -0.04 V vs. Ag/AgCl under the irradiation of a Xe lamp. The improved PEC properties were a cumulative result of enhanced light absorption (i.e., “window effect” between the α-Fe₂O₃ cores and BiV_{1-x}Mo_xO₄ shells) and the improved separation of photogenerated carriers (at the α-Fe₂O₃ nanorod/graphene/BiV_{1-x}Mo_xO₄ interfaces). Prasad *et al.* [160] have studied the synergistic of Ag plasmons and reduced graphene oxide on ZnO nanorods (Z-NRs)-based photoanodes for PEC splitting of water. Plasmonic layer of Ag was incorporated either as a base (Ag-Z-NRs) layer or as a top layer (Z-NRs-Ag) in an electrochemically deposited Z-NRs-based photoanodes. A mediator layer of reduced graphene oxide when introduced in Z-NRs-Ag photoanodes synergistically with Ag plasmons enhances the photocurrent density to ~1.3 mA cm⁻² at a bias of 1.4 V/RHE.

Another important method to improve the PEC efficiency of photoelectrodes is surface treatment [161–164]. The surface treatment diminishes the charge segregation states at the surface which act as recombination sites for photogenerated charge carriers. Another way of increasing the overpotential which is necessary for spontaneous PEC water-splitting process is the use of electrocatalysts/cocatalysts [165–169]. Electrocatalysts

can be broadly categorized into two types: (a) water oxidation catalyst and (b) water reduction catalyst. Cocatalyst contains activation sites which evolves hydrogen and oxygen and enhances the reaction kinetics by reducing bias and increasing IPCE. A good cocatalyst should adhere to two basic requirements. First, it should obtain the minimum overpotential required for water reduction/oxidation reaction, i.e., the evolution of hydrogen and oxygen. Thus, the evolution of hydrogen and oxygen should occur as soon as the semiconductor photoelectrodes supply photogenerated electrons and holes to the electrocatalyst. Second but the most important property is that the electrocatalyst must be chemically and optically stable. Recently, CoPi and CoS_x , Co_3PO_4 , etc. have attracted the attention of researchers. These electrocatalysts are recently used in semiconductor materials for enhanced PEC response [170–176]. A detailed comparison of various complex metal oxide systems and their PEC performance has been enlisted in Table 3.2.

3.4.5 Biosensitized Semiconductor Photoelectrodes

The environmentally friendly biomolecules can be used as a sensitizer for the semiconductor surfaces in hybrid bio-inorganic PEC devices [204]. Different types of proteins and natural photoreceptors such as bacteriorhodopsin, phycocyanin, chlorophyll, etc. can be used to sensitize the surface of photoelectrodes [204]. Among all the biomolecules, bacteriorhodopsin is the most important light-harvesting protein obtained from *Halobacterium salinarium* that can be used for PEC splitting of water [205]. Bacteriorhodopsin (bR) contains several transmembrane helical segments and consists of a polypeptide chain composed of amino acids. It undergoes conformational changes when light is incident on it [206]. The retinal chromophore in bR acts as a visible light sensitizer, activating building blocks in photoelectrodes, and as proton pump for hydrogen generation. In a recent experiment, TiO_2 photoanodes were functionalized with the bR for PEC water splitting application as reported by Allam *et al.* [207]. The photocurrent densities reached upto 0.87 mA cm^{-2} when the redox mediator pair iodide/tri-iodide was added to the electrolyte [207]. Bacteriorhodopsin has been used as a photosensitizer by attaching it to the surface of TiO_2 nanotubes using specific chemical linkers (3-mercaptopropionic acid), and it leads to a 50% increase in the photocurrent densities. It is observed that the enhanced photocurrent generation is due to the proton pumping effect of bR and it increases further with the use of the redox electrolyte. Mohammadpour *et al.* [208] investigated the surface adsorption property of bR on TiO_2 photoanodes and their application in PEC cells. Under illumination of simulated AM1.5 sunlight, the

Table 3.2 Summary of various semiconductor complex metal oxide nanostructures used in photoelectrochemical water splitting.

Complex nanostructures	Fabrication methods	Electrolyte	Light intensity	Photocurrent (mA cm ⁻²)	Voltage	Reference
TiO ₂ /CeO ₂ core-shell	Hydrothermal	1 M KOH	100 mW/cm ²	5.30	1.23 V vs. Ag/AgCl	[177]
Au:TiO ₂ /WO ₃	Electrodeposition	1.0 M NaOH	100 mW/cm ²	1.85	1.0 V vs. Ag/AgCl	[119]
TiO ₂ nanotube	Flame and chemical reduction, anodization	-	100 mW/cm ²	0.40	1.23 V vs. RHE	[178]
Co-Pi/BiVO ₄ /TiO ₂	Wet chemical, hydrothermal, CBD	0.5 M Na ₂ SO ₄ with KPi	100 mW/cm ²	2.45	1.7 V vs. RHE	[179]
WO ₃ /TiO ₂ nanotube	Anodization/electrodeposition (ED)	0.1 M H ₂ SO ₄	100 mW/cm ²	0.70	0.8 V vs. Ag/AgCl	[180]
Au@TiO ₂	Doctor blade/spin coating/ED	0.1 M Na ₂ SO ₄	100 mW/cm ²	-4.34	-0.2 V vs. Ag/AgCl	[181]
MWCNT@ZnO nanorods	Hydrothermal/simple solution deposition	0.5 M Na ₂ SO ₄	100 mW/cm ²	0.25	0.0 V vs. Ag/AgCl	[182]
TiO ₂ nanotube/ ZnO/CdS-PbS QD	Anodic oxidation/atomic and ionic layer deposition	0.2 M Na ₂ SO ₃ +0.1 M Na ₂ S	100 mW/cm ²	5.24	-0.3 V vs. SCE	[150]

CdS@ZnO	Hydrothermal/SILAR	0.5 M Na ₂ S	70 mW/cm ²	3.58	0.0 V vs. Ag/ AgCl	[183]
Au-Pd@ZnO nanorods	ED/sputtering	0.1 M Na ₂ SO ₄	100 mW/cm ²	0.34	0.4 V vs. Ag/ AgCl	[118]
CIGS/CdS/ ZnO-Pt	Coevaporation/ED	0.5 M Na ₂ SO ₄ + KOH (pH=9)	100 mW/cm ²	-32.5	-0.7 V vs. Ag/ AgCl	[184]
CdS@3D ZnO nanorods	Hydrothermal / SILAR	0.5 Na ₂ S	100 mW/cm ²	1.18	0.0 V vs. Ag/ AgCl	[134]
BiVO ₄ /Al:ZnO opal network	Evaporation- induced self- assembly/ solution-based method	KH ₂ PO ₄ (pH=7)	100 mW/cm ²	1.50	1.23 V vs. RHE	[185]
ZnFe ₂ O ₄ /Al:ZnO	Hydrothermal/solu- tion-based method	0.1 M Na ₂ SO ₄	100 mW/cm ²	1.72	1.23 V vs. RHE	[186]
1D ZnO/BiVO ₄	Hydrothermal/ SILAR	0.5 M Na ₂ SO ₄	100 mW/cm ²	1.72	1.2 V vs. Ag/ AgCl	[187]
Fe ₂ O ₃ -TiO ₂ nano- heterostructure	PE-CVD/atomic layer deposition (ALD)	1.0 M NaOH	100 mW/cm ²	2.0	1.23 V vs. RHE	[132]
Carbon-coated α-Fe ₂ O ₃	Pyrolysis of ferrocene	1.0 M NaOH (pH=13.6)	100 mW/cm ²	2.10	1.23 V vs. RHE	[188]

(Continued)

Table 3.2 Cont.

Complex nanostructures	Fabrication methods	Electrolyte	Light intensity	Photocurrent (mA cm ⁻²)	Voltage	Reference
IrO ₂ /RuO ₂ /Fe ₂ O ₃	Spray pyrolysis/ED	1 M KOH	100 mW/cm ²	1.52	1.23 V vs. RHE	[189]
FeOOH cocatalyst/ultrafine Ti ⁴⁺ -doped α -Fe ₂ O ₃	CBD/ hydrothermal	1.0 M NaOH	100 mW/cm ²	2.42	1.5 V vs. RHE	[190]
α -Fe ₂ O ₃ /graphene/BiV _{1-x} Mo _x O ₄ core-shell heterojunction	Hydrothermal/ photocatalytic reduction/ spin coating	0.01 Na ₂ SO ₄	100 mW/cm ²	1.97	1.0 V vs. Ag/AgCl	[159]
BiVO ₄ /TiO ₂	Doctor blade method/ sol-gel	0.5 M NaHCO ₃	100 mW/cm ²	5.5	2.0 V vs. RHE	[191]
TiO ₂ /BiVO ₄ /Co-Pi	Hydrothermal/ photodeposition	0.5 M Na ₂ SO ₃	100 mW/cm ²	1.86	1.0 V vs. RHE	[192]
BiVO ₄ /ZnFe ₂ O ₄ /Co ²⁺	ED/ photodeposition	0.1 M KOH	100 mW/cm ²	2.84	1.23 V vs. RHE	[193]
NiO/CoOx/BiVO ₄	Electrodeposition/ solution-based/ ALD	0.5 M K ₃ BO ₃	100 mW/cm ²	2.50	0.6 V vs. RHE	[194]
BiOI/BiVO ₄	ED	KH ₂ PO ₄ (pH=7)	100 mW/cm ²	3.27	1.23 V vs. RHE	[195]

Ti doped WO_3	Hydrothermal	0.1 M Na_2SO_4	100 mW/cm ²	1.13	1.23 V vs. RHE	[196]
Bi_2S_3 nanobelt@ WO_3 nanoplate	Hydrothermal	0.1 M Na_2SO_3 + 0.1 M Na_2S	100 mW/cm ²	8.91	-0.1 V vs. Ag/ AgCl	[197]
Gadolinium- doped WO_3	Hydrothermal	0.2 M Na_2SO_4	100 mW/cm ²	2.28	1.0 V vs. Ag/ AgCl	[198]
Tin dioxide inverse opal/ WO_3	Sol-gel, spin coating, ED	0.5 M Na_2SO_4	100 mW/cm ²	2.82	1.23 V vs. NHE	[199]
BiVO_4 / WO_3 / SnO_2 / triple layer planar heterojunction	Solution-based method	0.5 M KH_2PO_4	100 mW/cm ²	3.10	1.23 V vs. RHE	[200]
WO_3 nanoplates/ Bi_2S_3 nanorods	Hydrothermal, SILAR, CBD	0.1 M Na_2S + 0.1 M Na_2SO_3	100 mW/cm ²	5.95	0.9 V vs. RHE	[131]
Branched WO_3 / C_3N_4 / CoO_x nanoparticle	Hydrothermal, wet impregnation	0.01 M Na_2SO_4	100 mW/cm ²	5.76	2.1 V vs. RHE	[158]
WO_3 /W:BiVO ₄ core-shell nanowires	Flame vapor deposi- tion/drop casting	0.5 M phosphate buffer	100 mW/cm ²	4.0	1.23 V vs. RHE	[201]

(Continued)

Table 3.2 Cont.

Complex nanostructures	Fabrication methods	Electrolyte	Light intensity	Photocurrent (mA cm ⁻²)	Voltage	Reference
WO ₃ /BiVO ₄ -CoPi	Glancing angle/multi-magnetron sputtering	0.5 M Na ₂ SO ₄	100 mW/cm ²	5.1	1.23 V vs. RHE	[202]
3D WO ₃ /BiVO ₄ cobalt phosphate inverse opal	Sol-gel/ED	0.5 M Na ₂ SO ₄	100 mW/cm ²	4.50	1.4 V vs. Ag/AgCl	[129]
Ta-doped TiO ₂ /amorphous FeOOH	Doctor blade/solution-based method	1.0 M NaOH	100 mW/cm ²	2.20	1.23 V vs. RHE	[157]
WO ₃ @ZnWO ₄ @ZnO-ZnO hierarchical nanocactus	Hydrothermal/thermal-ALD	0.35 M Na ₂ S, 0.25 M NaSO ₃	100 mW/cm ²	1.57	1.23 V vs. RHE	[203]
Ag/Cu ₂ O/ZnO	Vacuum evaporation/electrochemical deposition/ALD	0.5 M Na ₂ SO ₄	100 mW/cm ²	1.10	-0.8 V vs. Ag/AgCl	[156]

STH conversion reached up to 0.35%, with an open circuit voltage of 533 mV and photocurrent density of 1 mA cm^{-2} . Balasubramanian *et al.* [209] reported the application of bR assembled on Pt/TiO₂ nanocatalyst for PEC hydrogen generation. The hybrid system produces 5275 $\mu\text{mole of H}_2$ ($\mu\text{mole protein}^{-1} \text{ h}^{-1}$) at pH 7 in the presence of methanol (as a sacrificial electron donor) under white light irradiation. Transient absorption studies indicate efficient charge transfer between bR and TiO₂ nanoparticles. Molaeirad *et al.* [210] utilized a monolayer of bR created by Langmuir-Blodgett method and immobilized it on ZnO nanoporous films. Under AM1.5 irradiation, a short-circuit current of 0.39 mA cm^{-2} , open-circuit voltages of 0.5 V, fill factor of 0.52, and an overall energy conversion efficiency of 0.1 % were reported. Naseri *et al.* [211] synthesized two different morphologies of TiO₂ photoanodes, nanoparticulate, and nanotubular and have modified them with bR. Photoconversion efficiency of TiO₂ photoanodes was increased from 2.9 to 16.5 in bR-TiO₂ nanoparticulate while it increased from 0.5 to 1.9 in nanotubular system. Lu *et al.* [212] fabricated the three-dimensional wormlike mesoporous WO₃-TiO₂ films (with pore size $\sim 7.1 \text{ nm}$) to prepare biophotoelectrodes through direct entrapping of bacteria photosynthetic reaction centers. The well-matched energy levels of WO₃-TiO₂ and reaction centers contributed to the photoelectric performance, especially in the red to near-infrared region. Bora *et al.* [213] have used the phycocyanins which have light-harvesting properties and belong to the phycobilisome protein family. They are present in cyanobacteria, which capture light energy and funnel it to reaction centers during photosynthesis. A hematite-phycocyanin integrated system is assembled by consecutive adsorption and cross-coupling of protein molecules, separated by an agarose layer and a linker molecule, on the top of a mesoporous hematite film. The hematite-phycocyanin assembly shows a twofold increased photocurrent in comparison with pristine hematite film. Wang *et al.* [214] fabricated a hybrid photoanode by imbibing cyanobacterial photosystem II with a hematite film. A direct electron transfer occurs from photosystem II to the excited Ti/Fe₂O₃ electrode under light irradiation, resulting in a substantial improvement of the photocurrent.

Kay *et al.* [215] synthesized colloidal TiO₂ electrodes and photosensitized them with derivatives of chlorophyll and natural porphyrins. Under simulated sunlight illumination, a short circuit current density of 9.4 mA cm^{-2} and an open circuit photovoltage of 0.52 V and were recorded. The overall energy conversion efficiency of the cell is 2.6% under these conditions. The study indicates that free carboxyl groups are essential for adsorption and sensitization of TiO₂. Schrantz *et al.* [216] have shown an optimized enzymatic formation of melanin that can be utilized for

immobilizing the cyanobacterial light-harvesting protein photocomplex on the surface of the hematite photoanode, enhancing the efficiency of the photoanode. Upon addition of tyrosinase to a photocomplex-l-tyrosine mixture on hematite surfaces, a melanin-PC network is formed which is cross-linked with the hematite surface. This modification resulted in an enhancement in PEC performance by a factor of 2. Shah *et al.* [217] had demonstrated a linker-free deposition technique enabled by an electro-spray system, in which photosystem was coupled to 1-D nanostructured TiO_2 thin films to realize photoelectrodes for PEC cell. A maximum current density of 4.15 mA cm^{-2} was measured after 10 min of electrospray deposition, and this is the highest current density reported so far for photosystem-based PEC cells. The high current is attributed to 1D nanostructure of TiO_2 and orientation of the photosystem onto the surface, which allows easy transfer of electrons. Yaghoubi *et al.* [218] reported combination of zinc oxide nanowires with monolayers of photosynthetic reaction centers which are self-assembled, via a cytochrome c linker, as photoactive electrode. In a three-probe biophotovoltaics cell, a photocurrent density of $5.5 \text{ } \mu\text{A cm}^{-2}$ and photovoltage of 36 mV was achieved, using methyl viologen as a redox mediator in the electrolyte. Using ferrocene as a redox mediator, a transient photocurrent density of $8.0 \text{ } \mu\text{A cm}^{-2}$ was obtained, which stabilized at $6.4 \text{ } \mu\text{A cm}^{-2}$ after 20 s. Recently, Prasad *et al.* [219] have reported the synthesis and use of chlorophyll-a/ ZnO nanorod-based hybrid photoanodes for PEC activity. Vertically oriented ZnO nanorod arrays were fabricated via electrodeposition and sensitized with chlorophyll-a. Under AM 1.5 illumination (100 mW cm^{-2}), at 0.75 V bias, the hybrid photoanodes achieved a photocurrent density of 0.67 mA cm^{-2} which is ~ 2.6 times increase over bare ZnO nanorods (0.26 mA cm^{-2}). A detailed comparison of the various biophotoelectrochemical systems has been enlisted in Table 3.3.

3.4.6 Tandem Stand-Alone PEC Water-Splitting Device

A tandem stand-alone configuration is required to realize an efficient PEC device as it can overcome the limitations exhibited by the existing materials used in the water-splitting process. To have an efficient PEC device, the biggest challenge is to achieve an STH efficiency of 10%. Since none of the material can achieve this target alone, to circumvent this problem, three different configurations have been proposed: (i) photovoltaic–electrocatalysts, (ii) photoanode–photocathode, and (iii) photovoltaic–photoelectrochemical. Each of the tandem configurations has its own pros and cons [225–230].

Table 3.3 Summary of various biomolecules embedded complex metal oxides nanostructures used in photoelectrochemical water splitting.

Semiconductor/biomolecules	Light intensity	Electrolyte	Photocurrent density (mA cm ⁻²)	Reference
α -Fe ₂ O ₃ /phycocyanin	100 mW/cm ²	1.0 M KOH	0.49	[213]
TiO ₂ / <i>Halobacterium salinarum</i>	100 mW/cm ²	Electrolyte obtained from Solaronix	0.45	[220]
ITO/TiO ₂ /PSI	100 mW/cm ²	0.1 M KCl (20 mM sodium ascorbate+250 μ M DC PID)	4.15	[217]
bR/TiO ₂	100 mW/cm ²	Iodolyte AN-50	0.28	[221]
TiO ₂ /molecular (photosensitizer+catalyst)	300 mW/cm ²	0.1 M Na ₂ SO ₄	0.48	[222]
TiO ₂ /WO ₃ (photosynthetic center <i>Rb.sphaeroides</i>)	5 mW/cm ²	Tris-HCl + 8 mM Na ₂ SO ₄	0.03	[212]
TiO ₂ /ZnO/PSI	10 ⁴ mW/cm ²	Organic solvent	0.36	[223]
PSII-Ti/Fe ₂ O ₃ hybrid anode	100 mW/cm ²	50 mM phosphate sodium buffer	0.02	[214]
Melanin and C-phycocyanin functionalized Hematite	100 mW/cm ²	1.0 M KOH or PbS	0.36	[216]
Chl-A/ZnO nanorods	100 mW/cm ²	0.5 M Na ₂ SO ₄	0.67	[219]

(Continued)

Table 3.3 Cont.

Semiconductor/biomolecules	Light intensity	Electrolyte	Photocurrent density (mA cm ⁻²)	Reference
bR/TiO ₂	100 mW/cm ²	I ⁻ /I ₃ – redox electrolyte	2.0	[209]
Chlorophyll/natural porphyrins/TiO ₂	100 mW/cm ²	0.5 M KI/40 mM I ₂ in 80% ethylene carbonate+20 % polycarbonate	9.40	[215]
Chl-e6 immobilized TiO ₂	80 mW/cm ²	0.05 M I ₂ /0.5 M KI in ethylene glycol/acetonitrile	1.47	[224]

In photovoltaic–electrocatalysts system, a triple junction Si solar cell is used in conjunction with different O_2 and H_2 evolution electrocatalysts. This configuration was first demonstrated by Delahoy *et al.* [225]. The configuration returns high efficiency values, but its progress is hindered by the complexity associated with the solar cell. In photoanode–photocathode configuration, two photoelectrodes (n- and p-type) are combined together. This is the simplest tandem configuration in which the shorter wavelength of the incident radiation is absorbed by the first photoelectrode and the transmitted light by the second photoelectrode. Highest efficiency reported is 0.22% by combining WO_3 photoanode and Cu_2O/NiO_x composite as photocathode [226]. However, in this configuration, efficiency is less due to low photovoltage and poor stability. In photovoltaic–photoelectrochemical configuration, the semiconductor photoelectrode is combined with PV device in conjunction with H_2 evolution/ O_2 evolution catalyst which serves as counter electrode. Upon illumination, semiconductor photoelectrode absorbs a part of solar spectrum while the transmitted light is absorbed by the PV device which can provide the additional potential required to photo-split the water. This configuration was first shown by Miller *et al.* [227].

Till today, very few stand-alone complete PEC water-splitting devices have been reported. The cost of the PEC device can be brought down by integrating PV components in the PEC device (PV-PEC) itself. Miller *et al.* [227] in 1998 reported the first stand-alone water-splitting device using multijunction a-Si. They have used a-Si photovoltaic cell having 10% efficiency with sputtered films of Co and Ni as hydrogen and oxygen evolving electrocatalysts. This was equivalent to an STH efficiency of 7.8% for a 0.27 cm^2 device immersed in 1 M KOH. Photoelectrodes were considerably stable for over 7200 h. Recently, Recce *et al.* had reported the same device fabricated by Miller *et al.* [228] but with earth abundant elements. It was based on a commercially available triple junction. Silicon device modified by the electrodeposited NiMoZn and Co borate as hydrogen and oxygen evolution electrocatalysts, respectively. Under neutral pH conditions, a record STH efficiency of 4.7 % was achieved.

Working on the same lines of action, Abdi *et al.* [229] have reported that the poor charge carrier-separation efficiency in $BiVO_4$ photoanode can be overcome by implementing a multistep gradient in the W-dopant concentration, resulting in the formation of a series of homojunctions in the bulk of the material. Under AM 1.5G illumination, gradient-doped Co-Pi-catalyzed W: $BiVO_4$ photoanode generates a photocurrent of 3.6 mA cm^{-2} at 1.23 V vs. RHE, representing a ~60% improvement over the same electrode with a homogeneous W-dopant concentration. Combining this

electrode with a 2-jn a-Si solar cell results in a water-splitting device with a $\sim 4.9\%$ STH efficiency. Baek *et al.* [200] demonstrated the synthesis of $\text{BiVO}_4/\text{WO}_3/\text{SnO}_2$ triple-layer planar heterojunction photoanodes, with improved charge transport and transmittance properties. The photoanodes show greatly improved IQE ($\sim 80\%$) and PEC water oxidation performance ($\sim 3.1 \text{ mA cm}^{-2}$ at 1.23 V vs. RHE) compared to the previously reported $\text{BiVO}_4/\text{WO}_3$ photoanodes. The PEC performance was further improved by a reactive-ion etching treatment and CoOx electrocatalyst deposition. Bornozi *et al.* [231] evaluated the feasibility of a $\text{BiVO}_4/\text{Cu}_2\text{O}$ photoanode/photocathode tandem cell for PEC solar water splitting. The photocurrent density of 1.0 mA cm^{-2} was achieved which corresponds to STH conversion efficiency of 0.5% . Chakthranont *et al.* [232] reported the fabrication of a nanostructured Si core and BiVO_4 shell to produce an integrated tandem heterostructure photoanode that can achieve an average STH efficiency of 0.45% under standard AM1.5G illumination in 0.5 M potassium phosphate buffer. Chen *et al.* [233] synthesized a novel silicon nanowire tungsten oxide (Si NWs/ WO_3) core/shell photoanode prepared by a mild and inexpensive metal catalyzed by etching process. In comparison to planar n-Si, Si NWs, and planar Si/ WO_3 , the Si NWs/ WO_3 samples showed significantly enhanced photocurrent over the entire potential sweep range. The as-prepared electrode also has a photocurrent density of 2.7 mA cm^{-2} at 0.61 V versus RHE in $0.5 \text{ M Na}_2\text{SO}_4$ solution under simulated solar light irradiation (100 mWcm^{-2} from 300 W xenon lamp coupled with an AM 1.5G filter). An optimal STH efficiency of about 1.9% was achieved at 0.26 V vs. RHE. Chen *et al.* [234] demonstrated an all-solution-processed tandem water-splitting device composed of a BiVO_4 photoanode and a single-junction $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid perovskite solar cell. Under AM 1.5G illumination, the tandem device in conjunction with an earth-abundant cobalt phosphate catalyst exhibits a STH conversion efficiency of 2.5% at neutral pH. Frites *et al.* [235] fabricated a single chip in which optically transparent Mn-oxide- TiO_2 thin layer was deposited on the front side of a triple junction amorphous Si photovoltaic cell. This single chip water electrolysis cell operates like an artificial leaf and produces hydrogen at the rate of $12.42 \text{ L m}^{-2} \text{ h}^{-1}$, and a STH efficiency of 3.25% was recorded with the device running continuously for 6 h . Han *et al.* [236] fabricated a hybrid PV/PEC water-splitting device with a STH conversion efficiency of 5.2% under AM1.5 illumination. This device consists of W doped BiVO_4 photoanode and a thin film Si solar cell. Kim *et al.* [237] realized a stand-alone, wireless solar water-splitting device without external energy supply which has been realized by combining a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite single junction solar cell with a cobalt carbonate-catalyzed, extrinsic/intrinsic dual-doped

BiVO₄ (hydrogen-treated and 3 at.% Mo-doped). The photoanode recorded one of the highest PEC water oxidation activities (4.8 mA cm⁻² at 1.23 V vs. RHE) under simulated 1-sun illumination. The oxygen evolution cobalt carbonate cocatalyst showed similar performance to best known cobalt phosphate (5.0 mA cm⁻² at 1.23 V RHE) on the same dual-doped BiVO₄ photoanode, but with significantly better stability. This tandem artificial-leaf-type device produced stoichiometric hydrogen and oxygen with an average STH efficiency of 4.3% (wired), 3.0% (wireless) under simulated 1-sun illumination. Kim *et al.* [238] designed a PEC device consisting of modified BiVO₄ and α-Fe₂O₃ as dual photoanodes which shows stable photocurrents of 7.0±0.2 mA cm⁻² at 1.23 V vs. RHE under 1 sun irradiation. This tandem cell (with dual photoanodes and silicon solar cell) exhibited unbiased water splitting efficiency of ~7.7%. Kim *et al.* [239] realized a stand-alone PEC water-splitting system with a tandem scheme of Pt/CdS/CuGa₃Se₅/(Ag,Cu)GaSe₂ photocathode and NiOOH/FeOOH/Mo:BiVO₄ photoanode in a neutral phosphate buffer solution as an electrolyte. The tandem cell displayed hydrogen and oxygen evolution with a STH conversion efficiency of 0.67% for 2 h and without degradation. Kwong *et al.* [240] demonstrated the utility of transparent FeOOH-coated WO₃ in a solar-powered, tandem water-splitting device by combining it with a double-junction Si solar cell and a Ni-Mo hydrogen evolution catalyst. This device performed at a STH conversion efficiency of 1.8% in near-neutral K₂SO₄ electrolyte. Peng *et al.* [241] have shown a combination of semi-transparent single-junction solar cell and a BiVO₄ photoanode coated with oxygen evolution catalysts can be used to achieve a STH conversion efficiency of 2.2%. Qiu *et al.* [242] deposited nanoporous Mo-doped BiVO₄ (Mo: BiVO₄) on a cone-shaped nanostructure. The nanocone/Mo:BiVO₄/Fe(Ni)OOH photoanode exhibits a high water-splitting photocurrent of 5.82 ± 0.36 mA cm⁻² at 1.23 V vs. RHE under 1-sun illumination. The PEC cell in tandem with a single perovskite solar cell exhibited STH conversion efficiency of up to 6.2%. Walzcak *et al.* [243] have shown a PEC water-splitting system which comprised of WO₃/FTO/p+n Si as photoanode and Pt/TiO₂/Ti/n+p Si as photocathode. The system shows STH efficiency of 0.24% with hydrogen production rate of 0.17 mL hr⁻¹. Xu *et al.* [244] reported a PEC tandem device consisting of BiVO₄ photoanode and Si nanoarray photocathode without using external bias. A STH efficiency of 0.57% (corresponding to photocurrent density of 0.46 mA cm⁻²) was achieved under AM1.5G illumination (100 mW cm⁻²) with two-electrode configuration. The dissolution of cobalt phosphate electrocatalyst causes a decrease in the photocurrent density of this tandem cell. Zhang *et al.* [245] designed a novel core/shell TiO₂@BiVO₄ photoanode in combination

with a $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cell for unassisted solar water splitting. Compared to pristine TiO_2 NRs, the resulting $\text{TiO}_2@\text{BiVO}_4$ film exhibits a 3.25-fold enhanced photocurrent density (1.3 mA cm^{-2}) under irradiation of 100 mW cm^{-2} . The perovskite solar cell- $\text{TiO}_2@\text{BiVO}_4$ PEC tandem device exhibited an overall STH efficiency of 1.24%, comparable to other TiO_2 -based PV/PEC systems. A detailed comparison of various tandem systems has been shown in Table 3.4.

3.5 Conclusion and Outlook

This chapter presents the fundamental aspects of PEC splitting of water together with recent developments in hydrogen production. The working principle and the current scientific challenges in realizing an efficient PEC cell have been discussed in detail. The development of stable, cheap, and efficient photoelectrode material is the key to commercialization of PEC technology for hydrogen production. To achieve unbiased water-splitting process, the band edges of the photoelectrode must straddle well with the reduction and oxidation potential of water, and target of 10% STH efficiency can be achieved provided the photoelectrodes are active under irradiation up to 600 nm. Earlier only few metal oxides were used for PEC application, but now the field has expanded and other hybrid semiconductors are being used. This chapter also describes and covers the different approaches adapted to improve the PEC performance of monocomponent metal oxides, branched structure, and complex component metal oxides systems using plasmonics, heterojunctions, biophotosensitizers, surface treatment, etc. There are other atomic combinations that are waiting to be tested so that the ideal photoelectrode material could be discovered. Tandem systems based on multistep photoexcitation liberate the semiconducting materials from thermodynamic equilibrium limitations and enable the application of a variety of materials to unbiased water-splitting process. New tandem configurations can help in achieving the target of STH efficiency greater than 10%.

In our opinion, the PEC water-splitting reaction requires many factors that should be satisfied by the photoelectrode material simultaneously such as absorption of light in the entire solar spectrum, proper charge segregation, and low recombination rate. The integration of different components into one composite material (to club all the above properties in one photoelectrode) to achieve higher efficiencies is one of the possible approaches. The natural photoreceptors present in plants utilize the complicated architectures and return a high solar to chemical energy yield because of high

Table 3.4 A comparative table of various tandem systems reported for PEC water splitting.

Device	Light intensity	Electrolyte	STH efficiency (%)	Reference
Ni-Mo/FeOOH-WO ₃ /Si-solar cell	100 mW/cm ²	0.5 M K ₂ SO ₄	1.8	[240]
BiVO ₄ -WO ₃ / Pt/ DSSC	100 mW/cm ²	0.1 M Na ₂ HPO ₄ , (pH = 6.9)	5.7	[246]
Nanocone Mo: BiVO ₄ /Fe (Ni) OOH/pervoskite solar cell	100 mW/cm ²	0.5 M KH ₂ PO ₄	6.2	[242]
Heterotype BiVO ₄ -Fe ₂ O ₃ /C-Si	100 mW/cm ²	1.0 M KCl (pH=9.2)	7.7	[238]
Single-junction CH ₃ NH ₃ PbI ₃ / BiVO ₄	100 mW/cm ²	0.5 M Na ₂ SO ₄	2.5	[234]
Pervoskite solar cell/ TiO ₂ @BiVO ₄	100 mW/cm ²	0.1 M KH ₂ PO ₄ with 0.1 M Na ₂ SO ₃	1.9	[233]
Cocatalyzed dual-doped BiVO ₄ /pervoskite tandem cell	100 mW/cm ²	0.1 M bicarbonate	4.3	[237]
Tandem semitransparent organic PV cells/ BiVO ₄	100 mW/cm ²	1.0 M KBi(pH= 9.3)	2.2	[241]
Hematite/Si	100 mW/cm ²	KH ₂ PO ₄ (pH= 11.8)	0.91	[247]
CoPi/SnOx-treated hematite/pervoskite tandem cell	100 mW/cm ²	1.0 M NaOH	3.4	[248]
Co1+P1@NiO/Ru1+L0@TiO ₂	100 mW/cm ²	KH ₂ PO ₄	0.05	[249]

(Continued)

Table 3.4 Cont.

Device	Light intensity	Electrolyte	STH efficiency (%)	Reference
MnO ₂ :TiO ₂ /triple-junction amorphous Si/stainless steel	100 mW/cm ²	2.5 M KOH	3.25	[235]
WO ₃ /FTO/p+n Si-Pt/TiO ₂ /Ti/ n+ p Si	200 mW/cm ²	1.0 M HClO ₄	0.24	[243]
n-p ⁺ Si/FTO/TiO ₂ microwire array	100 mW/cm ²	1.0 M H ₂ SO ₄	0.39	[250]
Si/TiO ₂ nanotree	150 mW/cm ²	0.5 M H ₂ SO ₄	0.12	[251]
n-Si:H/nc-Si:H/W:BiVO ₄	100 mW/cm ²	0.1 M KPi	5.2	[236]
p+n- black Si/W-doped BiVO ₄	100 mW/cm ²	0.5 M KPi	0.45	[232]
BiVO ₄ /Si nanoarray	100 mW/cm ²	0.1 M KBi	0.57	[244]
Gradient-doped BiVO ₄ /2 Jn a-Si	100 mW/cm ²	0.1 M KBi	4.9	[229]
BiVO ₄ -Cu ₂ O tandem cell	100 mW/cm ²	0.09 M KH ₂ PO ₄ , 0.01 M K ₂ HPO ₄	0.5	[231]
Si nanowire/WO ₃ core shell	100 mW/cm ²	0.5 M Na ₂ SO ₄	1.9	[233]
n-Si nanowire/hematite/Au nanoparticles	60 mW/cm ²	1.0 M NaOH	6.0	[252]

quantum coherence. So, high emphasis should be on understanding the mechanistic aspects of PEC splitting of water on the surface of the deposited material on the photoelectrode. Since the processes involved at the photoelectrode material are complex, molecular modeling of the catalyst surface can help in the investigations. The solar harvesting materials that show high lifetime of charge carriers are likely to exhibit high efficiency. With the advent of nanotechnology and advancements in ultrafast optical spectroscopy, microscopic, and electrochemical characterization, the mechanistic studies of the photocatalyst surface at the nanometer scale will further expedite and will lead to the development of an efficient PEC cell.

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References

1. Turner, J.A., Sustainable hydrogen production. *Science*, 305(5686), 972–4, 2004.
2. Sartbaeva, A., Kuznetsov, V.L., Wells, S.A., Edwards, P.P., Hydrogen nexus in a sustainable energy future. *Energy Environ. Sci.*, 1(1), 79–85, 2008.
3. [https://www.eia.gov/outlooks/ieo/pdf/0484\(2016\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf), World energy demand and economic outlook, U.S. Energy Information Administration | International Energy Outlook, 2016.
4. Lewis, N.S., Nocera, D.G., Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci.*, 103(43), 15729–35, 2006.
5. <http://www.world-nuclear.org/information-library/facts-and-figures/heat-values-of-various-fuels.aspx>, Heat Values of Various Fuels.
6. Soltani, R., Rosen, M.A., Dincer, I., Assessment of CO₂ capture options from various points in steam methane reforming for hydrogen production. *Int. J. Hydrogen Energy*, 39(35), 20266–75, 2014.
7. Nowotny, J., Sorrell, C.C., Sheppard, L.R., Bak, T., Solar-hydrogen: environmentally safe fuel for the future. *Int. J. Hydrogen Energy*, 30(5), 521–44, 2005.
8. Tollefson, J., Hydrogen vehicles: fuel of the future? *Nature News*, 464(7293), 1262–4, 2010.

9. Grätzel, M., Photoelectrochemical cells. *Nature*, 414(6861), 338–44, 2001.
10. Fujishima, A., Honda, K., Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238(5358), 37–8, 1972.
11. Khaselev, O., Turner, J.A., A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. *Science*, 280(5362), 425–7, 1998.
12. Bak, T., Nowotny, J., Rekas, M., Sorrell, C.C., Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *Int. J. Hydrogen Energy*, 27(10), 991–1022, 2002.
13. Jiang, C., Moniz, S.J., Wang, A., Zhang, T., Tang J., Photoelectrochemical devices for solar water splitting—materials and challenges. *Chem. Soc. Rev.*, 46(15), 4645–60, 2017.
14. Li, Y., Zhang, J.Z., Hydrogen generation from photoelectrochemical water splitting based on nanomaterials. *Laser Photonics Rev.*, 4(4), 517–28, 2010.
15. Hisatomi, T., Kubota, J., Domen, K., Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.*, 43(22), 7520–35, 2014.
16. Sivula, K., Van De Krol, R., Semiconducting materials for photoelectrochemical energy conversion. *Nat. Rev. Mater.*, 1(17), 15010, 2016.
17. Li, J., Wu, N., Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review. *Catal. Sci. Technol.*, 5(3), 1360–84, 2015.
18. Yang, Y., Niu, S., Han, D., Liu, T., Wang, G., Li, Y., Progress in Developing Metal Oxide Nanomaterials for Photoelectrochemical Water Splitting. *Adv. Energy Mater.*, 7(19), 1700555 (26), 2017.
19. Nichols, E.M., Gallagher, J.J., Liu, C., Su, Y., Resasco, J., Yu, Y., Sun, Y., Yang, P., Chang, M.C., Chang, C.J., Hybrid bioinorganic approach to solar-to-chemical conversion. *Proc. Natl. Acad. Sci.*, 112(37), 11461–6, 2015.
20. Passalacqua, R., Perathoner, S., Centi, G., Semiconductor, molecular and hybrid systems for photoelectrochemical solar fuel production. *J. Energy Chem.*, 26 (2), 219–240, 2017.
21. Lewis, N.S., Developing a scalable artificial photosynthesis technology through nanomaterials by design. *Nat. Nanotechnol.*, 11(12), 1010–9, 2016.
22. Zhang, K., Ma, M., Li, P., Wang, D.H., Park, J.H., Water splitting progress in tandem devices: moving photolysis beyond electrolysis. *Adv. Energy Mater.*, 6(15), 1600602(16), 2016.
23. Jia, J., Seitz, L.C., Benck, J.D., Huo, Y., Chen, Y., Ng, J.W., Bilir, T., Harris, J.S., Jaramillo, T.F., Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nat. Commun.*, 7(6), 13237, 2016.
24. Sivula, K., Solar-to-chemical energy conversion with photoelectrochemical tandem cells. *CHIMIA Int. J. Chem.*, 67(3), 155–61, 2013.
25. Jeon, H.S., Koh, J.H., Park, S.J., Jee, M.S., Ko, D.H., Hwang, Y.J., Min, B.K., A monolithic and standalone solar-fuel device having comparable efficiency to photosynthesis in nature. *J. Mater. Chem. A.*, 3(11), 5835–42, 2015.

26. Grimes, C.A., Varghese, O.K., Ranjan, S., Hydrogen generation by water splitting, in: *Light, Water, Hydrogen*, pp. 35–113, Springer US, 2008.
27. Van de Krol, R., Grätzel, M., *Photoelectrochemical hydrogen production*, Springer, New York, 2012.
28. Chen, S., Wang, L.W., Thermodynamic oxidation and reduction potentials of photocatalytic semiconductors in aqueous solution. *Chem. Mater.*, 24(18), 3659–66, 2012.
29. Chen, Z., Dinh, H.N., Miller, E. *Photoelectrochemical water splitting*, pp. 49–61, Springer Briefs in Energy, New York, 2013.
30. Luttrell, T., Halpegamage, S., Tao, J., Kramer, A., Sutter, E., Batzill, M., Why is anatase a better photocatalyst than rutile?—Model studies on epitaxial TiO_2 films. *Sci. Rep.*, 4(7), 4043, 2014.
31. Takahashi, M., Tsukigi, K., Uchino, T., Yoko, T., Enhanced photocurrent in thin film TiO_2 electrodes prepared by sol–gel method. *Thin Solid Films.*, 388(1), 231–6, 2001.
32. Salvador, P., Hole diffusion length in n- TiO_2 single crystals and sintered electrodes: Photoelectrochemical determination and comparative analysis. *J. Appl. Phys.*, 55(8), 2977–85, 1984.
33. Li, Z., Luo, W., Zhang, M., Feng, J., Zou, Z., Photoelectrochemical cells for solar hydrogen production: current state of promising photoelectrodes, methods to improve their properties, and outlook. *Energy Environ. Sci.*, 6(2), 347–70, 2013.
34. Docampo, P., Ivaturi, A., Gunning, R., Diefenbach, S., Kirkpatrick, J., Palumbiny, C.M., Sivaram, V., Geaney, H., Schmidt-Mende, L., Welland, M.E., Snaith, H.J., The influence of 1D, meso- and crystal structures on charge transport and recombination in solid-state dye-sensitized solar cells. *J. Mater. Chem. A.*, 1(39), 12088–95, 2013.
35. Kim, C.W., Yeob, S.J., Cheng, H.M., Kang, Y.S., A selectively exposed crystal facet-engineered TiO_2 thin film photoanode for the higher performance of the photoelectrochemical water splitting reaction. *Energy Environ. Sci.*, 8(12), 3646–53, 2015.
36. Wolcott, A., Smith, W.A., Kuykendall, T.R., Zhao, Y., Zhang, J.Z., Photoelectrochemical water splitting using dense and aligned TiO_2 nanorod arrays. *Small*, 5(1), 104–11, 2009.
37. Cho, I.S., Chen, Z., Forman, A.J., Kim, D.R., Rao, P.M., Jaramillo, T.F., Zheng, X., Branched TiO_2 nanorods for photoelectrochemical hydrogen production. *Nano Lett.*, 11(11), 4978–84, 2011.
38. Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K., Grimes, C.A., Enhanced photocleavage of water using titania nanotube arrays. *Nano Lett.*, 5(1), 191–5, 2005.
39. Yang, J.S., Liao, W.P., Wu, J.J., Morphology and interfacial energetics controls for hierarchical anatase/rutile TiO_2 nanostructured array for efficient photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 5(15), 7425–31, 2013.

40. Janotti, A., Van de Walle, C.G., Fundamentals of zinc oxide as a semiconductor. Reports on progress in physics. *Rep. Prog. Phys.*, 72(12), 126501 (29), 2009.
41. Faid, A.Y., Allam, N.K., Stable solar-driven water splitting by anodic ZnO nanotubular semiconducting photoanodes. *RSC Adv.*, 6(83), 80221–5, 2016.
42. Chandiran, A.K., Abdi-Jalebi, M., Nazeeruddin, M.K., Grätzel, M., Analysis of electron transfer properties of ZnO and TiO₂ photoanodes for dye-sensitized solar cells. *ACS Nano.*, 8(3), 2261–8, 2014.
43. Wang, Z.L., Zinc oxide nanostructures: growth, properties and applications. Journal of Physics: Condensed Matter. *J. Phys.: Condens. Matter.*, 16(25), R829–R858, 2004.
44. Wolcott, A., Smith, W.A., Kuykendall, T.R., Zhao, Y., Zhang, J.Z., Photoelectrochemical study of nanostructured ZnO thin films for hydrogen generation from water splitting. *Adv. Funct. Mater.*, 19(12), 1849–56, 2009.
45. Rokade, A., Rondiya, S., Sharma, V., Prasad, M., Pathan, H., Jadkar, S., Electrochemical synthesis of 1D ZnO nanoarchitectures and their role in efficient photoelectrochemical splitting of water. *J. Solid State Electrochem.*, 21(9), 2639–48, 2017.
46. Babu, E.S., Hong, S.K., Vo, T.S., Jeong, J.R., Cho, H.K., Photoelectrochemical water splitting properties of hydrothermally-grown ZnO nanorods with controlled diameters. *Electron. Mater. Lett.*, 11(1), 65–72, 2015.
47. Ren, X., Sangle, A., Zhang, S., Yuan, S., Zhao, Y., Shi, L., Hoyer, R.L., Cho, S., Li, D., MacManus-Driscoll, J.L., Photoelectrochemical water splitting strongly enhanced in fast-grown ZnO nanotree and nanocluster structures. *J. Mater. Chem. A*, 4(26), 10203–11, 2016.
48. Hassan, N.K., Hashim, M.R., Allam, N.K., ZnO nano-tetrapod photoanodes for enhanced solar-driven water splitting. *Chem. Phys. Lett.*, 549, 62–6, 2012.
49. Sun, X., Li, Q., Jiang, J., Mao, Y., Morphology-tunable synthesis of ZnO nanoforest and its photoelectrochemical performance. *Nanoscale*, 6(15), 8769–80, 2014.
50. Liu, X., Wang, F., Wang, Q., Nanostructure-based WO₃ photoanodes for photoelectrochemical water splitting. *Phys. Chem. Chem. Phys.*, 14(22), 7894–911, 2012.
51. Santato, C., Ulmann, M., Augustynski, J., Photoelectrochemical properties of nanostructured tungsten trioxide films. *J. Phys. Chem. B*, 105(5), 936–40, 2001.
52. Wang, S., Chen, H., Gao, G., Butburee, T., Lyu, M., Thaweesak, S., Yun, J.H., Du, A., Liu, G., Wang, L., Synergistic crystal facet engineering and structural control of WO₃ films exhibiting unprecedented photoelectrochemical performance. *Nano Energy*, 24, 94–102, 2016.
53. Bhatt, M.D., Lee, J.S., Recent theoretical progress in the development of photoanode materials for solar water splitting photoelectrochemical cells. *J. Mater. Chem. A*, 3(20), 10632–59, 2015.
54. Dias, P., Lopes, T., Meda, L., Andrade, L., Mendes, A., Photoelectrochemical water splitting using WO₃ photoanodes: the substrate and temperature roles. *Phys. Chem. Chem. Phys.*, 18(7), 5232–43, 2016.

55. Butler, M.A., Photoelectrolysis and physical properties of the semiconducting electrode WO_3 . *J. Appl. Phys.*, 48(5), 1914–20, 1977.
56. Ahn, K.S., Lee, S.H., Dillon, A.C., Tracy, C.E., Pitts, R., The effect of thermal annealing on photoelectrochemical responses of WO_3 thin films. *J. Appl. Phys.*, 101(9), 093524 (4), 2007.
57. Zhang, T., Su, J., Guo, L., Hierarchical architecture of WO_3 nanosheets by self-assembly of nanorods for photoelectrochemical applications. *Cryst. Eng. Comm.*, 18(5), 665–9, 2016.
58. Balberg, I., Pinch, H.L., The optical absorption of iron oxides. *Journal of Magnetism and Magnetic Materials. J. Magn. Magn. Mater.*, 7(1–4), 12–5, 1978.
59. Young, K.M., Klahr, B.M., Zandi, O., Hamann, T.W., Photocatalytic water oxidation with hematite electrodes. *Catal. Sci. Technol.*, 3(7), 1660–71, 2013.
60. Sivula, K., Le Formal, F., Grätzel, M., Solar water splitting: progress using hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoelectrodes. *Chem. Sus. Chem.*, 4(4), 432–49, 2011.
61. Katz, M.J., Riha, S.C., Jeong, N.C., Martinson, A.B., Farha, O.K., Hupp, J.T., Toward solar fuels: Water splitting with sunlight and “rust”? *Coord. Chem. Rev.*, 256(21), 2521–9, 2012.
62. Tilley, S.D., Cornuz, M., Sivula, K., Grätzel, M., Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chem.*, 122(36), 6549–52, 2010.
63. Souza, F.L., Lopes, K.P., Longo, E., Leite, E.R., The influence of the film thickness of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ on water photooxidation. *Phys. Chem. Chem. Phys.*, 11(8), 1215–9, 2009.
64. Vincent, T., Gross, M., Dotan, H., Rothschild, A., Thermally oxidized iron oxide nanoarchitectures for hydrogen production by solar-induced water splitting. *Int. J. Hydrogen Energy*, 37(9), 8102–9, 2012.
65. Tamirat, A.G., Rick, J., Dubale, A.A., Su, W.N., Hwang, B.J., Using hematite for photoelectrochemical water splitting: a review of current progress and challenges. *Nanoscale Horiz.*, 1(4), 243–67, 2016.
66. Mohapatra, S.K., John, S.E., Banerjee, S., Misra, M., Water photooxidation by smooth and ultrathin $\alpha\text{-Fe}_2\text{O}_3$ nanotube arrays. *Chem. Mater.*, 21(14), 3048–55, 2009.
67. Morrish, R., Rahman, M., MacElroy, J.M., Wolden, C.A., Activation of hematite nanorod arrays for photoelectrochemical water splitting. *ChemSusChem*, 4(4), 474–9, 2011.
68. Yang, J., Bao, C., Yu, T., Hu, Y., Luo, W., Zhu, W., Fu, G., Li, Z., Gao, H., Li, F., Zou, Z., Enhanced Performance of Photoelectrochemical Water Splitting with ITO@ $\alpha\text{-Fe}_2\text{O}_3$ Core–Shell Nanowire Array as Photoanode. *ACS Appl. Mater. Interfaces*, 7(48), 26482–90, 2015.
69. Kim, J.Y., Magesh, G., Youn, D.H., Jang, J.W., Kubota, J., Domen, K., Lee, J.S., Single-crystalline, wormlike hematite photoanodes for efficient solar water splitting. *Scientific Rep.*, 3, 2681, 2013.
70. Marelli, M., Naldoni, A., Minguzzi, A., Allieta, M., Virgili, T., Scavia, G., Recchia, S., Psaro, R., Dal Santo, V., Hierarchical hematite nanoplatelets for

- photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 6(15), 11997–2004, 2014.
71. Iordanova, N., Dupuis, M., Rosso, K.M., Charge transport in metal oxides: a theoretical study of hematite $\alpha\text{-Fe}_2\text{O}_3$. *J. Chem. Phys.*, 122(14), 144305 (10), 2005.
 72. Kim, S.J., Thomann, I., Park, J., Kang, J.H., Vasudev, A.P., Brongersma, M.L., Light trapping for solar fuel generation with Mie resonances. *Nano Lett.*, 14(3), 1446–52, 2014.
 73. Boudoire, F., Toth, R., Heier, J., Braun, A., Photonic light trapping in self-organized all-oxide microspheroids impacts photoelectrochemical water splitting. *Energy Environ. Sci.*, 7(8), 2680–8, 2014.
 74. Qiu, Y., Leung, S.F., Zhang, Q., Hua, B., Lin, Q., Wei, Z., Tsui, K.H., Zhang, Y., Yang, S., Fan, Z., Efficient photoelectrochemical water splitting with ultra-thin films of hematite on three-dimensional nanophotonic structures. *Nano Lett.*, 14(4), 2123–9, 2014.
 75. Fan, H., Jiang, T., Li, H., Wang, D., Wang, L., Zhai, J., He, D., Wang, P., Xie, T., Effect of BiVO_4 crystalline phases on the photoinduced carriers behavior and photocatalytic activity. *J. Phys. Chem. C*, 116(3), 2425–30, 2012.
 76. Pihosh, Y., Turkevych, I., Mawatari, K., Uemura, J., Kazoe, Y., Kosar, S., Makita, K., Sugaya, T., Matsui, T., Fujita, D., Tosa, M., Photocatalytic generation of hydrogen by core-shell $\text{WO}_3/\text{BiVO}_4$ nanorods with ultimate water splitting efficiency. *Scientific Rep.*, 5(10), 11141, 2015.
 77. Abdi, F.F., van de Krol, R., Nature and light dependence of bulk recombination in Co-Pi-catalyzed BiVO_4 photoanodes. *J. Phys. Chem. C*, 116(17), 9398–404, 2012.
 78. Han, L., Abdi, F.F., Rodriguez, P.P., Dam, B., van de Krol, R., Zeman, M., Smets, A.H., Optimization of amorphous silicon double junction solar cells for an efficient photoelectrochemical water splitting device based on a bismuth vanadate photoanode. *Phys. Chem. Chem. Phys.*, 16(9), 4220–9, 2014.
 79. Kudo, A., Ueda, K., Kato, H., Mikami, I., Photocatalytic O_2 evolution under visible light irradiation on BiVO_4 in aqueous AgNO_3 solution. *Catal. Lett.*, 53(3), 229–30, 1998.
 80. Luo, W., Yang, Z., Li, Z., Zhang, J., Liu, J., Zhao, Z., Wang, Z., Yan, S., Yu, T., Zou, Z., Solar hydrogen generation from seawater with a modified BiVO_4 photoanode. *Energy Environ. Sci.*, 4(10), 4046–51, 2011.
 81. Su, J., Guo, L., Yoriya, S., Grimes, C.A., Aqueous growth of pyramidal-shaped BiVO_4 nanowire arrays and structural characterization: application to photoelectrochemical water splitting. *Cryst. Growth Des.*, 10(2), 856–61, 2009.
 82. Hernández, S., Thalluri, S.M., Sacco, A., Bensaid, S., Saracco, G., Russo, N., Photo-catalytic activity of BiVO_4 thin-film electrodes for solar-driven water splitting. *Appl. Catal. A*, 504, 266–71, 2015.
 83. Hartmann, P., Lee, D.K., Smarsly, B.M., Janek, J., Mesoporous TiO_2 : comparison of classical sol–gel and nanoparticle based photoelectrodes for the water splitting reaction. *ACS Nano*, 4(6), 3147–54, 2010.

84. Hwang, Y.J., Hahn, C., Liu, B., Yang, P., Photoelectrochemical properties of TiO_2 nanowire arrays: a study of the dependence on length and atomic layer deposition coating. *ACS Nano*, 6(6), 5060–9, 2012.
85. Wang, W., Dong, J., Ye, X., Li, Y., Ma, Y., Qi, L., Heterostructured TiO_2 nanorod@ nanobowl arrays for efficient photoelectrochemical water splitting. *Small*, 12(11), 1469–78, 2016.
86. Qiu, J., Guo, M., Feng, Y., Wang, X., Electrochemical deposition of branched hierarchical ZnO nanowire arrays and its photoelectrochemical properties. *Electrochim. Acta*, 56(16), 5776–82, 2011.
87. Ahn, K.S., Yan, Y., Shet, S., Jones, K., Deutsch, T., Turner, J., Al-Jassim, M., ZnO nanocoral structures for photoelectrochemical cells. *Appl. Phys. Lett.*, 93(16), 163117 (3), 2008.
88. Li, Q., Sun, X., Lozano, K., Mao, Y., Dependence of Photoelectrochemical Properties on Geometry Factors of Interconnected “Caterpillar-like” ZnO Networks. *Electrochim. Acta*, 222, 232–45, 2016.
89. Baek, M., Kim, D., Yong, K., Simple but Effective Way To Enhance Photoelectrochemical Solar-Water-Splitting Performance of ZnO Nanorod Arrays: Charge-Trapping $\text{Zn}(\text{OH})_2$ Annihilation and Oxygen Vacancy Generation by Vacuum Annealing. *ACS Appl. Mater. Interfaces*, 9(3), 2317–25, 2017.
90. Alexander, B.D., Kulesza, P.J., Rutkowska, I., Solarska, R., Augustynski, J., Metal oxide photoanodes for solar hydrogen production. *J. Mater. Chem.*, 18(20), 2298–303, 2008.
91. Cristino, V., Caramori, S., Argazzi, R., Meda, L., Marra, G.L., Bignozzi, C.A., Efficient photoelectrochemical water splitting by anodically grown WO_3 electrodes. *Langmuir*, 27(11), 7276–84, 2011.
92. Marsen, B., Miller, E.L., Paluselli, D., Rocheleau, R.E., Progress in sputtered tungsten trioxide for photoelectrode applications. *Int. J. Hydrogen Energy*, 32(15), 3110–5, 2007.
93. De Tacconi, N.R., Chenthamarakshan, C.R., Yogeewaran, G., Watcharenwong, A., De Zoysa, R.S., Basit, N.A., Rajeshwar, K., Nanoporous TiO_2 and WO_3 films by anodization of titanium and tungsten substrates: influence of process variables on morphology and photoelectrochemical response. *J. Phys. Chem. B*, 110(50), 25347–55, 2006.
94. Hilliard, S., Baldinozzi, G., Friedrich, D., Kressman, S., Strub, H., Artero, V., Laberty-Robert, C., Mesoporous thin film WO_3 photoanode for photoelectrochemical water splitting: a sol–gel dip coating approach. *Sustainable Energy Fuels*, 1(1), 145–53, 2017.
95. Qin, D.D., Tao, C.L., Friesen, S.A., Wang, T.H., Varghese, O.K., Bao, N.Z., Yang, Z.Y., Mallouk, T.E., Grimes, C.A., Dense layers of vertically oriented WO_3 crystals as anodes for photoelectrochemical water oxidation. *Chem. Commun.*, 48(5), 729–31, 2012.
96. Jiao, Z., Wang, J., Ke, L., Sun, X.W., Demir, H.V., Morphology-tailored synthesis of tungsten trioxide (hydrate) thin films and their photocatalytic properties. *ACS Appl. Mater. Interfaces*, 3(2), 229–36, 2011.

97. Feng, X., Chen, Y., Qin, Z., Wang, M., Guo, L., Facile fabrication of sandwich structured WO_3 nanoplate arrays for efficient photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 8(28), 18089–96, 2016.
98. Cai, M., Fan, P., Long, J., Han, J., Lin, Y., Zhang, H., Zhong, M., Large-scale Tunable 3D Self-supporting WO_3 Micro-nano Architectures as Direct Photoanodes for Efficient Photoelectrochemical Water Splitting. *ACS Appl. Mater. Interfaces*, 9, 17856–17864, 2017.
99. Zheng, J.Y., Song, G., Hong, J., Van, T.K., Pawar, A.U., Kim, D.Y., Kim, C.W., Haider, Z., Kang, Y.S., Facile fabrication of WO_3 nanoplates thin films with dominant crystal facet of (002) for water splitting. *Cryst. Growth Des.*, 14(11), 6057–66, 2014.
100. Khan, S.U., Aikusa, J., Photoelectrochemical splitting of water at nanocrystalline $\text{n-Fe}_2\text{O}_3$ thin-film electrodes. *J. Phys. Chem. B*, 103(34), 7184–9, 1999.
101. Sivula, K., Zboril, R., Le Formal, F., Robert, R., Weidenkaff, A., Tucek, J., Frydrych, J., Gratzel, M., Photoelectrochemical water splitting with mesoporous hematite prepared by a solution-based colloidal approach. *J. Am. Chem. Soc.*, 132(21), 7436–44, 2010.
102. Duret, A., Grätzel, M., Visible light-induced water oxidation on mesoscopic $\alpha\text{-Fe}_2\text{O}_3$ films made by ultrasonic spray pyrolysis. *J. Phys. Chem. B*, 109(36), 17184–91, 2005.
103. Wang, C.W., Yang, S., Fang, W.Q., Liu, P., Zhao, H., Yang, H.G., Engineered hematite mesoporous single crystals drive drastic enhancement in solar water splitting. *Nano Lett.*, 16(1), 427–33, 2015.
104. Hilliard, S., Friedrich, D., Kressman, S., Strub, H., Artero, V., Laberty-Robert, C., Solar-Water-Splitting BiVO_4 Thin-Film Photoanodes Prepared By Using a Sol–Gel Dip-Coating Technique. *ChemPhotoChem*, 1(6), 273–280, 2017.
105. Iwase, A., Kudo, A., Photoelectrochemical water splitting using visible-light-responsive BiVO_4 fine particles prepared in an aqueous acetic acid solution. *J. Mater. Chem.*, 20(35), 7536–42, 2010.
106. Berglund, S.P., Flaherty, D.W., Hahn, N.T., Bard, A.J., Mullins, C.B., Photoelectrochemical oxidation of water using nanostructured BiVO_4 films. *J. Phys. Chem. C*, 115(9), 3794–802, 2011.
107. Vo, T.G., Chiu, J.M., Chiang, C.Y., Tai, Y., Solvent-engineering assisted synthesis and characterization of BiVO_4 photoanode for boosting the efficiency of photoelectrochemical water splitting. *Sol. Energy Mater. Sol. Cells*, 166:212–21, 2017.
108. Maier, S.A., *Plasmonics: fundamentals and applications*. Springer Science & Business Media, 2007.
109. Warren, S.C., Thimsen, E., Plasmonic solar water splitting. *Energy & Environmental Science. Energy Environ. Sci.*, 5(1), 5133–46, 2012.
110. Paramelle, D., Sadovoy, A., Gorelik, S., Free, P., Hobley, J., Fernig, D.G., A rapid method to estimate the concentration of citrate capped silver nanoparticles from UV-visible light spectra. *Analyst*, 139(19), 4855–61, 2014.

111. Wang, H., Brandl, D.W., Nordlander, P., Halas, N.J., Plasmonic nanostructures: artificial molecules. *Accounts of chemical research. Acc. Chem. Res.*, 40(1), 53–62, 2007.
112. Linic, S., Christopher, P., Ingram, D.B., Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat. Mater.*, 10(12), 911–921, 2011.
113. Kumar, M.K., Krishnamoorthy, S., Tan, L.K., Chiam, S.Y., Tripathy, S., Gao, H., Field effects in plasmonic photocatalyst by precise SiO_2 thickness control using atomic layer deposition. *ACS Catal.*, 1(4), 300–8, 2011.
114. Li, J., Cushing, S.K., Zheng, P., Meng, F., Chu, D., Wu, N., Plasmon-induced photonic and energy-transfer enhancement of solar water splitting by a hematite nanorod array. *Nat. Commun.*, 4, 2651(8), 2013.
115. Zhang, X., Liu, Y., Kang, Z., 3D branched ZnO nanowire arrays decorated with plasmonic Au nanoparticles for high-performance photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 6(6), 4480–9, 2014.
116. Wang, J., Pan, S., Chen, M., Dixon, D.A., Gold nanorod-enhanced light absorption and photoelectrochemical performance of $\alpha\text{-Fe}_2\text{O}_3$ thin-film electrode for solar water splitting. *J. Phys. Chem. C*, 117(42), 22060–8, 2013.
117. Patra, K.K., Gopinath, C.S., Bimetallic and Plasmonic Ag–Au on TiO_2 for Solar Water Splitting: An Active Nanocomposite for Entire Visible-Light-Region Absorption. *ChemCatChem* 8(20), 3294–311, 2016.
118. Moakhar, R.S., Kushwaha, A., Jalali, M., Goh, G.K., Dolati, A., Ghorbani, M., Enhancement in solar driven water splitting by Au–Pd nanoparticle decoration of electrochemically grown ZnO nanorods. *J. Appl. Electrochem.*, 46(8), 819–27, 2016.
119. Momeni, M.M., Ghayeb, Y., Photoinduced deposition of gold nanoparticles on $\text{TiO}_2\text{-WO}_3$ nanotube films as efficient photoanodes for solar water splitting. *Appl. Phys. A*, 122(6), 620 (10), 2016.
120. Zhou, J., Yin, L., Li, H., Liu, Z., Wang, J., Duan, K., Qu, S., Weng, J., Feng, B., Heterojunction of $\text{SrTiO}_3/\text{TiO}_2$ nanotubes with dominant (001) facets: synthesis, formation mechanism and photoelectrochemical properties. *Mater. Sci. Semicond. Process.*, 40, 107–16, 2015.
121. Zhang, J., Bang, J.H., Tang, C., Kamat, P.V., Tailored $\text{TiO}_2\text{-SrTiO}_3$ heterostructure nanotube arrays for improved photoelectrochemical performance. *ACS Nano.*, 4(1), 387–95, 2009.
122. Tuan, A.C., Kaspar, T.C., Droubay, T., Rogers, Jr. J.W., Chambers. S.A., Band offsets for the epitaxial $\text{TiO}_2/\text{SrTiO}_3/\text{Si}$ (001) system. *Appl. Phys. Lett.*, 83(18), 3734–6, 2003.
123. Wang, M., Sun, L., Lin, Z., Cai, J., Xie, K., Lin, C., p–n Heterojunction photoelectrodes composed of Cu_2O -loaded TiO_2 nanotube arrays with enhanced photoelectrochemical and photoelectrocatalytic activities. *Energy Environ. Sci.*, 6(4), 1211–20, 2013.
124. Moniz, S.J., Shevlin, S.A., Martin, D.J., Guo, Z.X., Tang, J., Visible-light driven heterojunction photocatalysts for water splitting—a critical review. *Energy Environ. Sci.*, 8(3), 731–59, 2015.

125. Wang, J., Liu, X.L., Yang, A.L., Zheng, G.L., Yang, S.Y., Wei, H.Y., Zhu, Q.S., Wang, Z.G., Measurement of wurtzite ZnO/rutile TiO₂ heterojunction band offsets by X-ray photoelectron spectroscopy. *Appl. Phys. A*, 103(4), 1099–1103, 2011.
126. Lin, Y., Xu, Y., Mayer, M.T., Simpson, Z.I., McMahon, G., Zhou, S., Wang, D., Growth of p-type hematite by atomic layer deposition and its utilization for improved solar water splitting. *J. Am. Chem. Soc.*, 134(12), 5508–11, 2012.
127. Jang, J.S., Kim, H.G., Lee, J.S., Heterojunction semiconductors: A strategy to develop efficient photocatalytic materials for visible light water splitting. *Catal. Today*, 185(1), 270–7, 2012.
128. Chen, X., Zhang, Z., Chi, L., Nair, A.K., Shangguan, W., Jiang, Z., Recent advances in visible-light-driven photoelectrochemical water splitting: Catalyst nanostructures and reaction systems. *Nano-Micro Lett.*, 8(1), 1–2, 2016.
129. Zhang, H., Zhou, W., Yang, Y., Cheng, C., 3D WO₃/BiVO₄/Cobalt Phosphate Composites Inverse Opal Photoanode for Efficient Photoelectrochemical Water Splitting. *Small*, 13(16), 1603840(8), 2017.
130. Li, Y., Zhang, L., Liu, R., Cao, Z., Sun, X., Liu, X., Luo, J., WO₃@ α -Fe₂O₃ Heterojunction Arrays with Improved Photoelectrochemical Behavior for Neutral pH Water Splitting. *ChemCatChem*, 8(17), 2765–70, 2016.
131. Wang, Y., Tian, W., Chen, L., Cao, F., Guo, J., Li, L., Three-Dimensional WO₃ Nanoplates/Bi₂S₃ Nanorods Heterojunction as Highly Efficient Photoanode for Improved Photoelectrochemical Water Splitting. *ACS Appl. Mater. Interfaces*, 9(46), 40235–40243, 2017.
132. Barreca, D., Carraro, G., Gasparotto, A., Maccato, C., Warwick, M.E., Kaunisto, K., Sada, C., Turner, S., Gönüllü, Y., Ruoko, T.P., Borgese, L., Fe₂O₃-TiO₂ Nano-heterostructure Photoanodes for Highly Efficient Solar Water Oxidation. *Adv. Mater. Interfaces*, 2, 1500313(11), 2015.
133. Hsu, Y.K., Chen, Y.C., Lin, Y.G., Novel ZnO/Fe₂O₃ core-shell nanowires for photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 7(25), 14157–62, 2015.
134. Bai, Z., Zhang, Y., CdS nanoparticles sensitized large-scale patterned ZnO nanowire arrays for enhanced solar water splitting. *J. Solid State Electrochem.*, 20(12), 3499–505, 2016.
135. Bard, A.J., Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors. *J. Photochem.*, 10(1), 59–75, 1979.
136. Maeda, K., Z-scheme water splitting using two different semiconductor photocatalysts. *ACS Catal.*, 3(7), 1486–503, 2013.
137. Li, J.M., Cheng, H.Y., Chiu, Y.H., Hsu, Y.J., ZnO-Au-SnO₂ Z-scheme photoanodes for remarkable photoelectrochemical water splitting. *Nanoscale*, 8(34), 15720–9, 2016.
138. Li, H., Sun, Y., Cai, B., Gan, S., Han, D., Niu, L., Wu, T., Hierarchically Z-scheme photocatalyst of Ag@AgCl decorated on BiVO₄ (040) with

- enhancing photoelectrochemical and photocatalytic performance. *Appl. Catal. B*, 170, 206–14, 2015.
139. Park, H.S., Lee, H.C., Leonard, K.C., Liu, G., Bard, A.J., Unbiased Photoelectrochemical Water Splitting in Z-Scheme Device Using W/Mo-Doped BiVO₄ and Zn_xCd_{1-x}Se. *ChemPhysChem*, 14(10), 2277–87, 2013.
 140. Xing, Z., Shen, S., Wang, M., Ren, F., Liu, Y., Zheng, X., Liu, Y., Xiao, X., Wu, W., Jiang, C., Efficient enhancement of solar-water-splitting by modified “Z-scheme” structural WO₃-W-Si photoelectrodes. *Appl. Phys. Lett.*, 105(14), 143902(5), 2014.
 141. Li, H., Tu, W., Zhou, Y., Zou, Z., Z-Scheme Photocatalytic Systems for Promoting Photocatalytic Performance: Recent Progress and Future Challenges. *Adv. Sci.*, 3, 1500389(12), 2016.
 142. Chen, L., He, F., Zhao, N., Guo, R., Fabrication of 3D quasi-hierarchical Z-scheme RGO-Fe₂O₃-MoS₂ nanoheterostructures for highly enhanced visible-light-driven photocatalytic degradation. *Appl. Surf. Sci.*, 420, 669–80, 2017.
 143. Kamat, P.V., Quantum dot solar cells. Semiconductor nanocrystals as light harvesters. *J. Phys. Chem. C*, 112(48), 18737–53, 2008.
 144. Ornes, S., Core Concept: Quantum dots. *Proc. Natl. Acad. Sci.*, 113(11), 2796–7, 2016.
 145. Rajaambal, S., Sivaranjani, K., Gopinath, C.S., Recent developments in solar H₂ generation from water splitting. *J. Chem. Sci.*, 127(1), 33–47, 2015.
 146. Robel, I., Subramanian, V., Kuno, M., Kamat, P.V., Quantum dot solar cells. Harvesting light energy with CdSe nanocrystals molecularly linked to mesoscopic TiO₂ films. *J. Am. Chem. Soc.*, 128(7), 2385–93, 2006.
 147. Kongkanand, A., Tvrdy, K., Takechi, K., Kuno, M., Kamat, P.V., Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture. *J. Am. Chem. Soc.*, 130(12), 4007–15, 2008.
 148. Nozik, A.J., Exciton multiplication and relaxation dynamics in quantum dots: applications to ultrahigh-efficiency solar photon conversion. *Inorg. Chem.*, 44(20), 6893–9, 2005.
 149. Liu, F., Jin, Z., Zhu, J., Xu, Y., Zhou, L., Dai, S., Modified surface loading process for achieving improved performance of the quantum dot-sensitized solar cells. *Chem. Phys. Lett.*, 653, 173–7, 2016.
 150. Zeng, M., Zeng, X., Peng, X., Zhu, Z., Liao, J., Liu, K., Wang, G., Lin, S., Improving photoelectrochemical performance on quantum dots co-sensitized TiO₂ nanotube arrays using ZnO energy barrier by atomic layer deposition. *Appl. Surf. Sci.*, 388, 352–8, 2016.
 151. Trevisan, R., Rodenas, P., Gonzalez-Pedro, V., Sima, C., Sanchez, R.S., Barea, E.M., Mora-Sero, I., Fabregat-Santiago, F., Gimenez, S., Harnessing infrared photons for photoelectrochemical hydrogen generation. A PbS quantum dot based “quasi-artificial leaf”. *J. Phys. Chem. Lett.*, 4(1), 141–6, 2012.
 152. Subramanian, A., Pan, Z., Li, H., Zhou, L., Li, W., Qiu, Y., Xu, Y., Hou, Y., Muzi, C., Zhang, Y., Synergistic Promotion of Photoelectrochemical Water

- Splitting Efficiency of TiO₂ Nanorods Using Metal-Semiconducting Nanoparticles. *Appl. Surf. Sci.*, 420, 631–637, 2017.
153. Zhang, C., Fan, W., Bai, H., Yu, X., Chen, C., Zhang, R., Shi, W., Sandwich-Nanostructured NiO-ZnO Nanowires/ α -Fe₂O₃ Film Photoanode with a Synergistic Effect and p-n Junction for Efficient Photoelectrochemical Water Splitting. *ChemElectroChem*, 1(12), 2089–97, 2014.
 154. Hensel, J., Wang, G., Li, Y., Zhang, J.Z., Synergistic effect of CdSe quantum dot sensitization and nitrogen doping of TiO₂ nanostructures for photoelectrochemical solar hydrogen generation. *Nano Lett.*, 10(2), 478–83, 2010.
 155. Kuang, P.Y., Su, Y.Z., Xiao, K., Liu, Z.Q., Li, N., Wang, H.J., Zhang, J., Double-shelled CdS-and CdSe-cosensitized ZnO porous nanotube arrays for superior photoelectrocatalytic applications. *ACS Appl. Mater. Interfaces*, 7(30), 16387–94, 2015.
 156. Liu, Y., Ren, F., Shen, S., Fu, Y., Chen, C., Liu, C., Xing, Z., Liu, D., Xiao, X., Wu, W., Zheng, X., Efficient enhancement of hydrogen production by Ag/Cu₂O/ZnO tandem triple-junction photoelectrochemical cell. *Appl. Phys. Lett.*, 106(12), 123901 (5), 2015.
 157. Primc, D., Bärtsch, M., Barreca, D., Carraro, G., Maccato, C., Sada, C., Niederberger, M., Doping of TiO₂ as a tool to optimize the water splitting efficiencies of titania-hematite photoanodes. *Sustainable Energy Fuels*, 1(1), 199–206, 2017.
 158. Hou, Y., Zuo, F., Dagg, A.P., Liu, J., Feng, P., Branched WO₃ nanosheet array with layered C₃N₄ heterojunctions and CoOx nanoparticles as a flexible photoanode for efficient photoelectrochemical water oxidation. *Adv. Mater.*, 26(29), 5043–9, 2014.
 159. Hou, Y., Zuo, F., Dagg, A., Feng, P., Visible Light-Driven α -Fe₂O₃ Nanorod/Graphene/BiV_{1-x}Mo_xO₄ Core/Shell Heterojunction Array for Efficient Photoelectrochemical Water Splitting. *Nano Lett.*, 12(12), 6464–73, 2012.
 160. Prasad, M., Sharma, V., Aher, R., Rokade, A., Ilaiyaraja, P., Sudakar, C., Jadkar, S., Synergistic effect of Ag plasmon-and reduced graphene oxide-embedded ZnO nanorod-based photoanodes for enhanced photoelectrochemical activity. *J. Mater. Sci.*, 52(23), 13572–85, 2017.
 161. Shen, S., Zhou, J., Dong, C.L., Hu, Y., Tseng, E.N., Guo, P., Guo, L., Mao, S.S., Surface engineered doping of hematite nanorod arrays for improved photoelectrochemical water splitting. *Scientific Rep.*, 4, 6627, 2014.
 162. Wang, D., Zhang, X., Sun, P., Lu, S., Wang, L., Wang, C., Liu, Y., Photoelectrochemical water splitting with rutile TiO₂ nanowires array: synergistic effect of hydrogen treatment and surface modification with anatase nanoparticles. *Electrochim. Acta*, 130, 290–5, 2014.
 163. Li, X., Bassi, P.S., Boix, P.P., Fang, Y., Wong, L.H., Revealing the role of TiO₂ surface treatment of hematite nanorods photoanodes for solar water splitting. *ACS Appl. Mater. Interfaces*, 7(31), 16960–6, 2015.
 164. Tamirat, A.G., Dubale, A.A., Su, W.N., Chen, H.M., Hwang, B.J., Sequentially surface modified hematite enables lower applied bias photoelectrochemical water splitting. *Chem. Phys.*, 19(31), 20881–90, 2017

165. Yang, J., Wang, D., Han, H., Li, C., Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Acc. Chem. Res.*, 46(8), 1900–9, 2013.
166. Hisatomi, T., Takanabe, K., Domen, K., Photocatalytic water-splitting reaction from catalytic and kinetic perspectives. *Catal. Lett.*, 145(1), 95–108, 2015.
167. Roger, I., Shipman, M.A., Symes, M.D., Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.*, 1, 0003.
168. Kudo, A., Miseki, Y., Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.*, 38(1), 253–78, 2009.
169. Osterloh, F.E., Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.*, 42(6), 2294–320, 2013.
170. Ran, J., Zhang, J., Yu, J., Jaroniec, M., Qiao, S.Z., Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. *Chem. Soc. Rev.*, 43(22), 7787–812, 2014.
171. Bai, S., Wang, L., Chen, X., Du, J., Xiong, Y., Chemically exfoliated metallic MoS_2 nanosheets: A promising supporting co-catalyst for enhancing the photocatalytic performance of TiO_2 nanocrystals. *Nano Res.*, 8(1), 175–83, 2015.
172. Shi, X., Zhang, K., Park, J.H., Understanding the positive effects of (Co-Pi) co-catalyst modification in inverse-opal structured $\alpha\text{-Fe}_2\text{O}_3$ -based photoelectrochemical cells. *Int. J. Hydrogen Energy*, 38(29), 12725–32, 2013.
173. Lu, R., Du, K., Liu, G., Yang, C., Wang, K., Preparation and Photoelectrochemical Properties of Multilayered WS_2 Coated Titanium Dioxide Nanocomposites. *ECS Trans.*, 66(14), 57–63, 2015.
174. Bledowski, M., Wang, L., Ramakrishnan, A., Bétard, A., Khavryuchenko, O.V., Beranek, R., Visible-Light Photooxidation of Water to Oxygen at Hybrid TiO_2 -Polyheptazine Photoanodes with Photodeposited Co-Pi (CoOx) Cocatalyst. *ChemPhysChem*, 13(12), 3018–24, 2012.
175. Zhang, P., Wang, T., Chang, X., Zhang, L., Gong, J., Synergistic cocatalytic effect of carbon nanodots and Co_3O_4 nanoclusters for the photoelectrochemical water oxidation on hematite. *Angew. Chem.*, 55(19), 5851–5, 2016.
176. Jiao, W., Xie, Y., Chen, R., Zhen, C., Liu, G., Ma, X., Cheng, H.M., Synthesis of mesoporous single crystal rutile TiO_2 with improved photocatalytic and photoelectrochemical activities. *Chem. Commun.*, 49(100), 11770–2, 2013.
177. Han, C., Yan, L., Zhao, W., Liu, Z., $\text{TiO}_2/\text{CeO}_2$ core/shell heterojunction nanoarrays for highly efficient photoelectrochemical water splitting. *Int. J. Hydrogen Energy*, 42(17), 12276–83, 2017.
178. Cho, I.S., Choi, J., Zhang, K., Kim, S.J., Jeong, M.J., Cai, L., Park, T., Zheng, X., Park, J.H., Highly efficient solar water splitting from transferred TiO_2 nanotube arrays. *Nano Lett.*, 15(9), 5709–15, 2015.
179. Cheng, B.Y., Yang, J.S., Cho, H.W., Wu, J.J., Fabrication of an Efficient BiVO_4 - TiO_2 Heterojunction Photoanode for Photoelectrochemical Water Oxidation. *ACS Appl. Mater. Interfaces*, 8(31), 20032–9, 2016.
180. Reyes-Gil, K.R., Robinson, D.B., WO_3 -enhanced TiO_2 nanotube photoanodes for solar water splitting with simultaneous wastewater treatment. *ACS Appl. Mater. Interfaces*, 5(23), 12400–10, 2013.

181. Peerakiatkhajohn, P., Butburee, T., Yun, J.H., Chen, H., Richards, R.M., Wang, L., A hybrid photoelectrode with plasmonic Au@TiO₂ nanoparticles for enhanced photoelectrochemical water splitting. *J. Mater. Chem. A*, 3(40), 20127–33, 2015.
182. Wei, Y., Du, H., Kong, J., Lu, X., Ke, L., Sun, X.W., Multi-walled carbon nanotubes modified ZnO nanorods: a photoanode for photoelectrochemical cell. *Electrochim. Acta*, 143, 188–95, 2014.
183. Bai, Z., Yan, X., Li, Y., Kang, Z., Cao, S., Zhang, Y., 3D-Branched ZnO/CdS Nanowire Arrays for Solar Water Splitting and the Service Safety Research. *Adv. Energy Mater.*, 6(3), 1501459(8), 2016.
184. Mali, M.G., Yoon, H., Joshi, B.N., Park, H., Al-Deyab, S.S., Lim, D.C., Ahn, S., Nervi, C., Yoon, S.S., Enhanced photoelectrochemical solar water splitting using a platinum-decorated CIGS/CdS/ZnO photocathode. *ACS Appl. Mater. Interfaces*, 7(38), 21619–25, 2015.
185. Zhang, L., Reisner, E., Baumberg, J.J., Al-doped ZnO inverse opal networks as efficient electron collectors in BiVO₄ photoanodes for solar water oxidation. *Energy Environ. Sci.*, 7(4), 1402–8, 2014.
186. Xu, Y.F., Rao, H.S., Wang, X.D., Chen, H.Y., Kuang, D.B., Su, C.Y., *In situ* formation of zinc ferrite modified Al-doped ZnO nanowire arrays for solar water splitting. *J. Mater. Chem. A*, 4(14), 5124–9, 2016.
187. Yan, L., Zhao, W., Liu, Z., 1D ZnO/BiVO₄ heterojunction photoanodes for efficient photoelectrochemical water splitting. *Dalton Trans.*, 45(28), 11346–52, 2016.
188. Deng, J., Lv, X., Gao, J., Pu, A., Li, M., Sun, X., Zhong, J., Facile synthesis of carbon-coated hematite nanostructures for solar water splitting. *Energy Environ. Sci.*, 6(6), 1965–70, 2013.
189. Dias, P., Andrade, L., Mendes, A., Hematite-based photoelectrode for solar water splitting with very high photovoltage. *Nano Energy*, 38, 218–231, 2017.
190. Liu, Y., Liu, J., Luo, W., Wen, X., Liu, X., Zou, Z., Huang, W., Ultrafine Ti₄⁺ doped α -Fe₂O₃ nanorod array photoanodes with high charge separation efficiency for solar water splitting. *J. Phys. D: Appl. Phys.*, 50(25), 255502(8), 2017.
191. Monfort, O., Raptis, D., Satrapinskyy, L., Roch, T., Plesch, G., Lianos, P., Production of hydrogen by water splitting in a photoelectrochemical cell using a BiVO₄/TiO₂ layered photoanode. *Electrochim. Acta*, 251, 244–9, 2017.
192. Tong, R., Wang, X., Zhou, X., Liu, Q., Wang, H., Peng, X., Liu, X., Zhang, Z., Wang, H., Lund, P.D., Cobalt-Phosphate modified TiO₂/BiVO₄ nanoarrays photoanode for efficient water splitting. *Int. J. Hydrogen Energy*, 42(8), 5496–504, 2017.
193. Kim, T.W., Choi, K.S., Improving stability and photoelectrochemical performance of BiVO₄ photoanodes in basic media by adding a ZnFe₂O₄ layer. *J. Phys. Chem. Lett.*, 7(3), 447–51, 2016.
194. Zhong, M., Hisatomi, T., Kuang, Y., Zhao, J., Liu, M., Iwase, A., Jia, Q., Nishiyama, H., Minegishi, T., Nakabayashi, M., Shibata, N., Surface Modification of CoOx Loaded BiVO₄ Photoanodes with Ultrathin p-Type

- NiO Layers for Improved Solar Water Oxidation. *J. Am. Chem. Soc.*, 137(15), 5053–60, 2015.
195. Ye, K.H., Chai, Z., Gu, J., Yu, X., Zhao, C., Zhang, Y., Mai, W., BiOI-BiVO₄ photoanodes with significantly improved solar water splitting capability: p-n junction to expand solar adsorption range and facilitate charge carrier dynamics. *Nano Energy*, 18, 222–31, 2015.
 196. Kalanur, S.S., Yoo, I.H., Seo, H., Fundamental investigation of Ti doped WO₃ photoanode and their influence on photoelectrochemical water splitting activity. *Electrochim. Acta*, 254, 348–57, 2017.
 197. Liu, C., Yang, Y., Li, W., Li, J., Li, Y., Chen, Q., Construction of novel Bi₂S₃ nanobelt@WO₃ nanoplate arrays on FTO glass with high photoelectrochemical activity. *Int. J. Hydrogen Energy*, 41(14), 5878–86, 2016.
 198. Liu, Y., Li, J., Li, W., Yang, Y., Li, Y., Chen, Q., Enhancement of the photoelectrochemical performance of WO₃ vertical arrays film for solar water splitting by gadolinium doping. *J. Phys. Chem. C*, 119(27), 14834–42, 2015.
 199. Yun, G., Balamurugan, M., Kim, H.S., Ahn, K.S., Kang, S.H., Role of WO₃ layers electrodeposited on SnO₂ inverse opal skeletons in photoelectrochemical water splitting. *J. Phys. Chem. C*, 120(11), 5906–15, 2016.
 200. Baek, J.H., Kim, B.J., Han, G.S., Hwang, S.W., Kim, D.R., Cho, I.S., Jung, H.S., BiVO₄/WO₃/SnO₂ Double-Heterojunction Photoanode with Enhanced Charge Separation and Visible-Transparency for Bias-Free Solar Water-Splitting with a Perovskite Solar Cell. *ACS Appl. Mater. Interfaces*, 9(2), 1479–87, 2017.
 201. Rao, P.M., Cai, L., Liu, C., Cho, I.S., Lee, C.H., Weisse, J.M., Yang, P., Zheng, X., Simultaneously efficient light absorption and charge separation in WO₃/BiVO₄ core/shell nanowire photoanode for photoelectrochemical water oxidation. *Nano Lett.*, 14(2), 1099–105, 2014.
 202. Pihosh, Y., Turkevych, I., Mawatari, K., Asai, T., Hisatomi, T., Uemura, J., Tosa, M., Shimamura, K., Kubota, J., Domen, K., Kitamori, T., Nanostructured WO₃/BiVO₄ photoanodes for efficient photoelectrochemical water splitting. *Small*, 10(18), 3692–9, 2014.
 203. Yuan, K., Cao, Q., Li, X., Chen, H.Y., Deng, Y., Wang, Y.Y., Luo, W., Lu, H.L., Zhang, D.W., Synthesis of WO₃@ZnWO₄@ZnO-ZnO hierarchical nanocactus arrays for efficient photoelectrochemical water splitting. *Nano Energy*, 41, 543–51, 2017.
 204. Ihssen, J., Braun, A., Faccio, G., Gajda-Schranz, K., Thony-Meyer, L., Light harvesting proteins for solar fuel generation in bioengineered photoelectrochemical cells. *Curr. Protein Pept. Sci.*, 15(4), 374–84, 2014.
 205. Chu, L.K., Yen, C.W., El-Sayed, M.A., Bacteriorhodopsin-based photoelectrochemical cell. *Biosens. Bioelectron.*, 26(2), 620–6, 2010.
 206. Hampp, N., Bacteriorhodopsin as a photochromic retinal protein for optical memories. *Chem. Rev.*, 100(5), 1755–76, 2000.
 207. Allam, N.K., Yen, C.W., Near, R.D., El-Sayed, M.A., Bacteriorhodopsin/TiO₂ nanotube arrays hybrid system for enhanced photoelectrochemical water splitting. *Energy Environ. Sci.*, 4(8), 2909–14, 2011.

208. Mohammadpour, R., Janfaza, S., Efficient nanostructured biophotovoltaic cell based on bacteriorhodopsin as biophotosensitizer. *ACS Sustainable Chem. Eng.*, 3(5), 809–13, 2015.
209. Balasubramanian, S., Wang, P., Schaller, R.D., Rajh, T., Rozhkova, E.A., High-performance bioassisted nanophotocatalyst for hydrogen production. *Nano Lett.*, 13(7), 3365–71, 2013.
210. Molaeirad, A., Rezaeian, N., Oriented assembly of bacteriorhodopsin on ZnO nanostructured electrode for enhanced photocurrent generation. *Biotechnol. Appl. Biochem.*, 62(4), 489–93, 2015.
211. Naseri, N., Janfaza, S., Irani, R., Visible light switchable bR/TiO₂ nanostructured photoanodes for bio-inspired solar energy conversion. *RSC Adv.*, 5(24), 18642–6, 2015.
212. Lu, Y., Yuan, M., Liu, Y., Tu, B., Xu, C., Liu, B., Zhao, D., Kong, J., Photoelectric performance of bacteria photosynthetic proteins entrapped on tailored mesoporous WO₃-TiO₂ films. *Langmuir*, 21(9), 4071–6, 2005.
213. Bora, D.K., Rozhkova, E.A., Schrantz, K., Wyss, P.P., Braun, A., Graule, T., Constable, E.C., Functionalization of Nanostructured Hematite Thin-Film Electrodes with the Light-Harvesting Membrane Protein C-Phycocyanin Yields an Enhanced Photocurrent. *Adv. Funct. Mater.*, 22(3), 490–502, 2012.
214. Wang, W., Wang, Z., Zhu, Q., Han, G., Ding, C., Chen, J., Shen, J.R., Li, C., Direct electron transfer from photosystem II to hematite in a hybrid photoelectrochemical cell. *Chem. Commun.*, 51(95), 16952–5, 2015.
215. Kay, A., Graetzel, M., Artificial photosynthesis. 1. Photosensitization of titania solar cells with chlorophyll derivatives and related natural porphyrins. *J. Phys. Chem.*, 97(23), 6272–7, 1993.
216. Schrantz, K., Wyss, P.P., Ihssen, J., Toth, R., Bora, D.K., Vitol, E.A., Rozhkova, E.A., Piesles, U., Thöny-Meyer, L., Braun, A., Hematite photoanode co-functionalized with self-assembling melanin and C-phycocyanin for solar water splitting at neutral pH. *Catal. Today*, 284, 44–51, 2017.
217. Shah, V.B., Henson, W.R., Chadha, T.S., Lakin, G., Liu, H., Blankenship, R.E., Biswas, P., Linker-free deposition and adhesion of photosystem I onto nanostructured TiO₂ for biohybrid photoelectrochemical cells. *Langmuir*, 31(5), 1675–82, 2015.
218. Yaghoubi, H., Schaefer, M., Yaghoubi, S., Jun, D., Schlaf, R., Beatty, J.T., Takshi, A., A ZnO nanowire bio-hybrid solar cell. *Nanotechnol.*, 28(5), 054006(8), 2016.
219. Prasad, M., Sharma, V., Mayabadi, A., Rokade, A., Pawbake, A., Rondiya, S., Waykar, R., Jadhavar, A., Pathan, H., Jadkar, S., Chlorophyll-a/ZnO Nanorod Based Hybrid Photoanodes for Enhanced Photoelectrochemical Splitting of Water. *ChemistrySelect*, 2(5), 1911–6, 2017.
220. Molaeirad, A., Janfaza, S., Karimi-Fard, A., Mahyad, B., Photocurrent generation by adsorption of two main pigments of *Halobacterium salinarum* on TiO₂ nanostructured electrode. *Biotechnol. Appl. Biochem.*, 62(1), 121–5, 2015.

221. Janfaza, S., Molaeirad, A., Mohamadpour, R., Khayati, M., Mehrvand, J., Efficient bio-nano hybrid solar cells via purple membrane as sensitizer. *J. Bionanosci.*, 4(1), 71–7, 2014.
222. Ding, X., Gao, Y., Zhang, L., Yu, Z., Liu, J., Sun, L., Visible light-driven water splitting in photoelectrochemical cells with supramolecular catalysts on photoanodes. *ACS Catal.*, 4(7), 2347–50, 2014.
223. Mershin, A., Matsumoto, K., Kaiser, L., Yu, D., Vaughn, M., Nazeeruddin, M.K., Bruce, B.D., Graetzel, M., Zhang, S., Self-assembled photosystem-I biophotovoltaics on nanostructured TiO₂ and ZnO. *Scientific Rep.*, 2(7), 234, 2012.
224. Amao, Y., Yamada, Y., Aoki, K., Preparation and properties of dye-sensitized solar cell using chlorophyll derivative immobilized TiO₂ film electrode. *J. Photochem. Photobiol. A*, 164(1), 47–51, 2004.
225. Delahoy, A.E., Gau, S.C., Murphy, O.J., Kapur, M., Bockris, J.M., A one-unit photovoltaic electrolysis system based on a triple stack of amorphous silicon (pin) cells. *Int. J. Hydrogen Energy*, 10(2), 113–6, 1985.
226. Lin, C.Y., Lai, Y.H., Mersch, D., Reisner, E., Cu₂O/NiOx nanocomposite as an inexpensive photocathode in photoelectrochemical water splitting. *Chem. Sci.*, 3(12), 3482–7, 2012.
227. Miller, E.L., Marsen, B., Paluselli, D., Rocheleau, R., Optimization of hybrid photoelectrodes for solar water-splitting. *Electrochem. Solid-State Lett.*, 8(5), A247–9, 2005.
228. Reece, S.Y., Hamel, J.A., Sung, K., Jarvi, T.D., Esswein, A.J., Pijpers, J.J., Nocera, D.G., Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts. *Science*, 334(6056), 645–8, 2011.
229. Abdi, F.F., Han, L., Smets, A.H., Zeman, M., Dam, B., Van De Krol, R., Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode. *Nat. commun.*, 4(7), 2195, 2013.
230. Joya, K.S., Joya, Y.F., Ocakoglu, K., van de Krol, R., Water-splitting catalysis and solar fuel devices: Artificial leaves on the move. *Angew. Chem.*, 52(40), 10426–37, 2013.
231. Bornoz, P., Abdi, F.F., Tilley, S.D., Dam, B., Van De Krol, R., Graetzel, M., Sivula, K., A bismuth vanadate-cuprous oxide tandem cell for overall solar water splitting. *J. Phys. Chem. C*, 118(30), 16959–66, 2014.
232. Chakthranont, P., Hellstern, T.R., McEnaney, J.M., Jaramillo, T.F., Design and Fabrication of a Precious Metal-Free Tandem Core-Shell p⁺n Si/W-Doped BiVO₄ Photoanode for Unassisted Water Splitting. *Adv. Energy Mater.*, 7(22), 1701515(8), 2017.
233. Chen, Z., Minghui, N., Ma, G., Meng, Q., Zhang, Y., Gao, J., Jin, M., Chen, Z., Yuan, M., Wang, X., Liu, J., Effective silicon nanowire arrays/WO₃ core/shell photoelectrode for neutral pH water splitting. *Nanotechnol.*, 28(275401), 275401(9), 2017.
234. Chen, Y.S., Manser, J.S., Kamat, P.V., All solution-processed lead halide perovskite-BiVO₄ tandem assembly for photolytic solar fuels production. *J. Am. Chem. Soc.*, 137(2), 974–81, 2015.

235. Frites, M., Ingler, Jr. W.B., Khan, S.U., A Single Chip Standalone Water Splitting Photoelectrochemical Cell. *J. Technol. Innovations Renew. Energy*, 3(1), 6–11, 2014.
236. Han, L., Abdi, F.F., van de Krol, R., Liu, R., Huang, Z., Lewerenz, H.J., Dam, B., Zeman, M., Smets, A.H., Efficient water-splitting device based on a bismuth vanadate photoanode and thin-film silicon solar cells. *ChemSusChem*, 7(10), 2832–8, 2014.
237. Kim, J.H., Jo, Y., Kim, J.H., Jang, J.W., Kang, H.J., Lee, Y.H., Kim, D.S., Jun, Y., Lee, J.S., Wireless solar water splitting device with robust cobalt-catalyzed, dual-doped BiVO_4 photoanode and perovskite solar cell in tandem: a dual absorber artificial leaf. *ACS Nano.*, 9(12), 11820–9, 2015.
238. Kim, J.H., Jang, J.W., Jo, Y.H., Abdi, F.F., Lee, Y.H., Van De Krol, R., Lee, J.S., Hetero-type dual photoanodes for unbiased solar water splitting with extended light harvesting. *Nat. Commun.*, 7(9), 13380, 2016.
239. Kim, J.H., Kaneko, H., Minegishi, T., Kubota, J., Domen, K., Lee, J.S., Overall photoelectrochemical water splitting using tandem cell under simulated sunlight. *ChemSusChem*, 9(1), 61–6, 2016.
240. Kwong, W.L., Lee, C.C., Messinger, J., Transparent Nanoparticulate FeOOH Improves the Performance of a WO_3 Photoanode in a Tandem Water-Splitting Device. *J. Phys. Chem. C*, 120(20), 10941–50, 2016.
241. Peng, Y., Govindaraju, G.V., Lee, D.K., Choi, K.S., Andrew, T.L., Integrating a Semitransparent, Fullerene-Free Organic Solar Cell in Tandem with a BiVO_4 Photoanode for Unassisted Solar Water Splitting. *ACS Appl. Mater. Interfaces*, 9(27), 22449–55.
242. Qiu, Y., Liu, W., Chen, W., Zhou, G., Hsu, P.C., Zhang, R., Liang, Z., Fan, S., Zhang, Y., Cui, Y., Efficient solar-driven water splitting by nanocone BiVO_4 -perovskite tandem cells. *Sci. Adv.*, 2(6), e1501764(8), 2016.
243. Walczak, K., Chen, Y., Karp, C., Beeman, J.W., Shaner, M., Spurgeon, J., Sharp, I.D., Amashukeli, X., West, W., Jin, J., Lewis, N.S., Modeling, Simulation, and Fabrication of a Fully Integrated, Acid-stable, Scalable Solar-Driven Water-Splitting System. *ChemSusChem*, 8(3), 544–51, 2015.
244. Xu, P., Feng, J., Fang, T., Zhao, X., Li, Z., Zou, Z., Photoelectrochemical cell for unassisted overall solar water splitting using a BiVO_4 photoanode and Si nanoarray photocathode. *RSC Adv.*, 6(12), 9905–10, 2016.
245. Zhang, X., Zhang, B., Cao, K., Brillet, J., Chen, J., Wang, M., Shen, Y., A perovskite solar cell- $\text{TiO}_2/\text{BiVO}_4$ photoelectrochemical system for direct solar water splitting. *J. Mater. Chem. A*, 3(43), 21630–6, 2015.
246. Shi, X., Zhang, K., Shin, K., Ma, M., Kwon, J., Choi, I.T., Kim, J.K., Kim, H.K., Wang, D.H., Park, J.H., Unassisted photoelectrochemical water splitting beyond 5.7% solar-to-hydrogen conversion efficiency by a wireless monolithic photoanode/dye-sensitized solar cell tandem device. *Nano Energy*, 13, 182–91, 2015.
247. Jang, J.W., Du, C., Ye, Y., Lin, Y., Yao, X., Thorne, J., Liu, E., McMahon, G., Zhu, J., Javey, A., Guo, J., Enabling unassisted solar water splitting by iron oxide and silicon. *Nature Commun.*, 6(5), 7447, 2015.

248. Gurudayal, John, R.A., Boix, P.P., Yi, C., Shi, C., Scott, M.C., Veldhuis, S.A., Minor, A.M., Zakeeruddin, S.M., Wong, L.H., Grätzel, M., Mathews, N., Atomically Altered Hematite for Highly Efficient Perovskite Tandem Water-Splitting Devices. *ChemSusChem*, 10(11), 2449–56, 2017.
249. Li, F., Fan, K., Xu, B., Gabrielsson, E., Daniel, Q., Li, L., Sun, L., Organic dye-sensitized tandem photoelectrochemical cell for light driven total water splitting. *J. Am. Chem. Soc.*, 137(28), 9153–9, 2015.
250. Shaner, M.R., McDowell, M.T., Pien, A., Atwater, H.A., Lewis, N.S., Si/TiO₂ tandem-junction microwire arrays for unassisted solar-driven water splitting. *J. Electrochem. Soc.*, 163(5), H261–4, 2016.
251. Liu, C., Tang, J., Chen, H.M., Liu, B., Yang, P., A fully integrated nanosystem of semiconductor nanowires for direct solar water splitting. *Nano Lett.*, 13(6), 2989–92.
252. Wang, X., Peng, K.Q., Hu, Y., Zhang, F.Q., Hu, B., Li, L., Wang, M., Meng, X.M., Lee, S.T., Silicon/hematite core/shell nanowire array decorated with gold nanoparticles for unbiased solar water oxidation. *Nano Lett.*, 14(1), 18–23, 2013.

Hydrogen Generation from Photoelectrochemical Water Splitting

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Abstract

In the past decades, the exploitation of sunlight for water splitting via photoelectrochemical cell (PEC) served as a fascinating but challenging path for the production of clean and renewable hydrogen energy. This chapter initiates the fundamental principle of PEC hydrogen generation and discusses recent improvement on both promising photoanode and photocathode materials. Some strategies for boosting the PEC performance of photoelectrodes are introduced, such as (a) doping elements to regulate bandgap, (b) tuning structural morphology for better light utilization, (c) modifying cocatalysts to optimize the sluggish kinetics of water splitting, and (d) constructing surface protection layer to improve the photostability of catalysts, etc. Moreover, the advances of monocomponent catalyst, functional cocatalyst and z-scheme catalyst and their performances of charge carriers transfer, light absorption, and stability in PEC hydrogen generation are summarized. Although photoelectrodes and photocatalysts with micro-/nano-scale possess the many merits for water splitting, their weaknesses still exist and cause the nonnegligible side effects. Thus, both the pros and cons of these photoelectrodes and photocatalysts are summarized. Finally, the obstructions that hinder the development of PEC water splitting and outlooks for the enhancement of photoelectrode materials are proposed.

Keywords: Photoelectrochemical cell, water splitting, photoelectrode materials, cocatalyst structural morphology, stability

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4.1 Introduction

While addressing environment issue and energy crisis by harvesting solar energy to produce hydrogen remains a significant challenge [1–3], photoelectrochemical (PEC) hydrogen generation utilizing solar energy provides a prospective chance to produce renewable fuels. Since Fujishima and Honda demonstrated the water splitting by irradiating light on titanium dioxide (TiO_2) in the early 1970s, TiO_2 , as a promising photoelectrode material with earth abundance, nontoxicity, and high stability, has been widely investigated for hydrogen generation [4, 5]. Nevertheless, TiO_2 exhibits a wide bandgap (3.0–3.2 eV) that limits to absorption only in the ultraviolet region, which is $\sim 4\%$ of the solar spectrum energy on Earth. In practical PEC water splitting system, however, the theoretical solar-to-hydrogen conversion efficiency (STH) of at least 10% is necessary [6]. In addition, some semiconductor photoelectrode materials including Si, InP, GaP, GaInP_2 , CdS were also widely explored [7–11], but most of them suffer from photocorrosion under light irradiation [11]. As a result, different approaches such as doping, surface protection layer, deposition of cocatalysts have been employed to enhance their performance [12–15]. The visible-light responsive photoelectrodes (BiVO_4 , $\alpha\text{-Fe}_2\text{O}_3$, CuGa_3Se_5 , etc.) have also been studied for many years [16–18], given that the theoretical STH values of BiVO_4 and $\alpha\text{-Fe}_2\text{O}_3$ can reach 9.1% and 12.9%, respectively [19, 20].

This chapter will focus on some recent progress of promising and important photoelectrodes for PEC hydrogen generation. The principle of PEC hydrogen generation and the related parameters, such as IPCE, APCE and STH, for evaluating photoelectrode performance will be summarized. The photoelectrode materials currently explored for PEC water splitting will also be included. In addition, the advance of PEC water splitting, together with pros and cons of photoelectrodes and photocatalysts in nanostructures, will be discussed. Finally, we will provide some future outlook of this field.

4.2 Principle of Photoelectrochemical (PEC) Hydrogen Generation

Briefly, the solar water splitting can be described as the following two-step process. Under solar light illumination, the photoelectrode absorbs photon and produces the photogenerated electrons/holes (e^-/h^+) in the first step, then in the second step, electrons/holes separate and transfer to the interface of photoelectrode/electrolyte, resulting in the production of hydrogen

and oxygen by splitting water. In such process, the valence/conduction band edges of photoelectrode material must straddle the redox potential level for water splitting without external bias. While the process of photoelectrochemical (PEC) hydrogen production seems straightforward, the internal principles are relatively complicated [3]. PEC cell generally consists of a working electrode and a counterelectrode. The space charge layer, the diffuse layer (or called the Gouy layer), and the inner or the compact layer (also called the Helmholtz or the Stern layer) form the composition of semiconductor–electrolyte junction (Figure 4.1) [21–23]. To be more specific, compact layer is about 0.3–0.5 nm in thickness (nearly constant) and is of the material's nature. For photoelectrode and electrolyte, when concentrations of the charge carriers increase, the space charge layer and the Gouy layer will decrease in thickness. For instance, the thickness of the diffuse layer varies between 10 to 100 nm in aqueous solutions with low

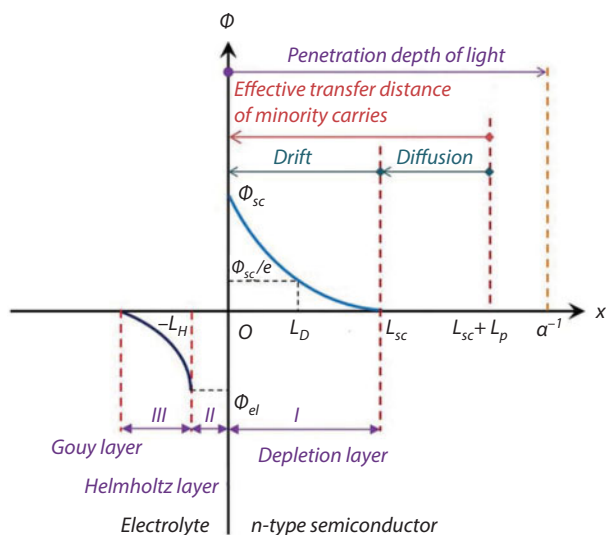


Figure 4.1 The composition of a semiconductor–electrolyte junction. The depletion layer, as a type of the space charge layer, is a common one and shows the significant importance. In the range of the depleted layer, Φ_{sc} represents the potential drop and L_D represents the Debye length, which has the connection with the characteristic length of potential attenuation (Φ_{sc}). In the range of the Gouy layer, Φ_{el} represents the potential drop; L_{sc} represents the width of the space charge layer (the depletion layer is the most common and important type of the space charge layer); L_p represents the minority carrier diffusion length, and α is the optical absorption coefficient of the photoelectrode. For the depletion layer, $L_{sc} > L_D$, while $L_{sc} < L_D$ for accumulation layer or inversion layer. The number e is about 2.71828. Reprinted with permission from [11], Copyright 2013, Royal Society of Chemistry.

ionic strength, whereas a diffuse layer with monomolecular thickness can be obtained in concentrated ionic solution (~ 1 M) [21]. Generally speaking, the thickness of the diffuse layer can be expressed by the following equation (4.1, 4.2):

$$L_{sc} = L_D \left[\frac{2q|\phi_{sc}|}{kT} \right]^{1/2} = L_D \left[\frac{2q(V - V_{fb})}{kT} \right]^{1/2} \quad (4.1)$$

$$L_D = \left[\frac{\epsilon_0 \epsilon kT}{q^2(n_0 + p_0)} \right]^{1/2} \quad (4.2)$$

where, for photoelectrode, V_{fb} , ϵ , n_0 , and p_0 represent the flat potential, the relative dielectric constant, the electron and hole concentration, respectively; L_D is determined by the concentration of charge carriers; ϵ_0 represents the dielectric constant in vacuum; k is the Boltzmann constant; T is temperature in Kelvin [24].

The energy conversion efficiency is often used to evaluate the performance of photoelectrode and thus an important factor for photoelectrochemical (PEC) cell [25]. In particular, incident photon-to-current efficiency (IPCE) of electrode is one of the key parameters in PEC hydrogen generation. The IPCE value is influenced by several factors including light absorption coefficient, the width of the space charge layer, and the minority carrier diffusion length [22]. The IPCE of a photoelectrode can be measured in either a two-electrode or three-electrode configuration. While two-electrode configurations might possibly lead to errors induced by the properties of various counterelectrodes, the three-electrode configuration provides fundamental advantage by introducing a reference counter to measure the photocurrent density, which eliminated the interferences of counterelectrode. In addition, a direct comparison with reversible hydrogen electrode (RHE) at the same potential can be made with the IPCE measured using three-electrode configurations. It is, however, critical to interpret the measurements correctly when using three-electrode configurations measurement. The IPCE at a fix wavelength can be described as the following equation (4.3):

$$IPCE(\lambda) = \frac{\text{Total energy of converted electrons}}{\text{Total energy of incident photons}} = \frac{\left(\frac{J_{photo}(\lambda)}{e} \right) \times \frac{hc}{\lambda}}{P(\lambda)} \times 100\% \quad (4.3)$$

where, in a fixed wavelength $\lambda(\text{nm})$, J_{photo} represents the photocurrent density (mA/cm^2); $P(\lambda)$ represents the incident light intensity (mW/cm^2); e , h , c are the charge of an electron, Planck's constant, and the speed of light, respectively.

It is worth noting that in the calculation of IPCE, the inevitable optical losses are actually ignored. To correct the deviation caused by this approximation, researchers often utilize the absorbed photon-to-current conversion efficiency (APCE) to identify the quantum efficiency. The APCE is defined as the number of photogenerated charge carriers contributed to the photocurrent per absorbed photon and can be calculated using the following equation (4.4):

$$APCE(\lambda) = \frac{IPCE(\lambda)}{A(\lambda)} = \frac{IPCE(\lambda)}{1 - R - T} \quad (4.4)$$

where A , R , and T represent the absorption, reflection, and transmission of light, respectively [25].

The solar-to-hydrogen conversion efficiency (STH) is another commonly used parameter to evaluate the PEC performance. It can reflect the true efficiency of hydrogen generation under sunlight irradiation (1.5G AM, $100 \text{ mW} \cdot \text{cm}^{-2}$) with the following equation (4.5):

$$\eta_{\text{STH}} = \frac{273 \text{ KJ} / \text{mol} \times r_{\text{H}_2} \text{ mole} / \text{s}}{P_{\text{sun}} \times S \text{ cm}^2} \quad (4.5)$$

where $273 \text{ KJ}/\text{mol}$ represents Gibbs free energy of the reaction for water splitting, r_{H_2} represents the rate of hydrogen production, P_{sun} represents the incident light intensity ($100 \text{ mW}/\text{cm}^2$), and S represents the illuminated area of the photoelectrode.

4.3 Photoelectrode Materials

4.3.1 Photoanode Materials

4.3.1.1 TiO_2 -Based Photoelectrode

TiO_2 -based photoelectrode materials have drawn great attention because of their advantages of low cost, nontoxic, photocorrosion resistance, and high stability in acidic or basic condition [5]. However, the wide bandgap of TiO_2 includes anatase (3.2 eV) and the rutile (3.0 eV) phase, limiting its optical absorption in ultraviolet light region of the solar spectrum and

therefore leads to low STH efficiency. Many approaches including doping with elements, tuning morphology [26–28], and modification with electrocatalysts [29, 30] have been applied to improve the performance of TiO_2 photoanode. For example, hydrogen-treated rutile TiO_2 nanowires were reported and showed a high photocurrent of $\sim 2.5 \text{ mA/cm}^2$ at $0.6 \text{ V}_{\text{Ag/AgCl}}$ and low photocurrent saturation potentials of $0.6 \text{ V}_{\text{Ag/AgCl}}$ in 1 M NaOH , indicating hydrogen treatment can promote the formation of oxygen vacancies. Oxygen vacancies are crucial in electron donors for TiO_2 [31], as PEC performance can be improved by increasing electron donors for charge transportation enhancement [26]. Zhang *et al.* reported TiO_2 nanotube (NT) arrays via a two-step anodization method. The optimal photocurrent density and photoconversion efficiency of the unique hierarchical TiO_2 NT arrays were as high as 1.59 mA/cm^2 at 1.23 V vs. RHE and 0.84% , respectively, under AM 1.5G irradiation. The enhanced PEC performance was attributed to longer electron lifetime, better charge separation, and transportation [28].

The introduction of oxygen evolution reaction (OER) cocatalysts, such as IrO_x [32], CoO_x [33], and FeOOH [34], can also enhance the PEC performance of TiO_2 by optimizing the kinetics of water oxidation. More recently, Ning *et al.* reported core-shell hierarchical $\text{TiO}_2/\text{rGO}/\text{NiFe}$ -layered double hydroxide (LDH) nanorod arrays (NAs), given that NiFe-LDH materials often possess high OER performance [30]. A photocurrent density of 1.74 mA/cm^2 at $0.6 \text{ V}_{\text{RHE}}$ under 100 mW/cm^2 and a maximum IPCE of 5.12% at 400 nm were observed from $\text{TiO}_2/\text{rGO}/\text{NiFe-LDH}$, which were nearly twice as much as those of pristine TiO_2 (0.92 mA/cm^2 at $0.6 \text{ V}_{\text{RHE}}$ and 2.77% at 400 nm , respectively). In addition, the $\text{TiO}_2/\text{rGO}/\text{NiFe-LDH}$ exhibits an impressive stability with no decay of oxygen production in 5 cycles (Figure 4.2). This enhanced performance can be attributed to the simultaneously improved charge separation and water oxidation efficiency of photoanode by the synergistic effect between rGO and NiFe-LDH.

4.3.1.2 BiVO_4 -Based Photoelectrode

BiVO_4 is a promising photoelectrode material because of its 2.4 eV direct bandgap and earth abundance. In 1998, Kudo *et al.* firstly reported BiVO_4 as a photocatalyst for water oxidation with sacrificial reagents [35]. Since BiVO_4 exhibits theoretical high photocurrent (7.4 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$) and STH (9.1%) values [36], significant effort has been dedicated to obtain BiVO_4 for practical application. However, there are several major limitations on BiVO_4 efficiency, including (a) fast recombination of charge carrier,

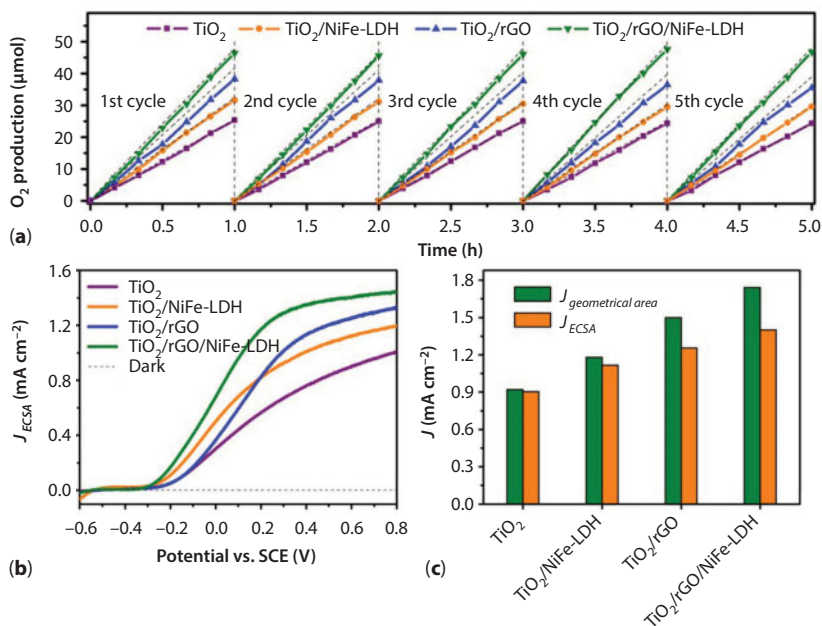


Figure 4.2 (a) O₂ production of different samples in five cycles and the dash lines represent the theoretic O₂ production, (b) photocurrent density vs. voltage curves normalized by ECSA, (c) the photocurrent density at 0.6 V of different samples normalized by the geometrical area and the ECSA for comparing. Reprinted with permission from [30], Copyright 2016, Royal Society of Chemistry.

(b) a sluggish hole transfer kinetics for water oxidation, and (c) poor conductivity [37].

In general, the poor charge carrier recombination and slow transfer kinetics for water oxidation can be optimized by modifying with oxygen evolution catalysts (OEC) such as FeOOH [38], Co-Pi [39]. For example, by incorporating both FeOOH and NiOOH OEC layers on BiVO₄, the charge carrier recombination on the interface and transfer kinetics were significantly improved. At a potential as low as 0.6 V_{RHE}, a high photocurrent density of 2.80±0.2 mA/cm² and a maximum IPCE and APCE of 60% and 72% at 420 nm were observed from nanoporous BiVO₄/FeOOH/NiOOH [38]. More recently, Zhang *et al.* reported a Co-Pi modified WO₃/BiVO₄ heterojunction with a maximum IPCE of 70% at ~450 nm and a photocurrent density of 4.5 mA/cm² at 1.4 V_{Ag/AgCl}, respectively [39]. On the other hand, the poor conductivity of BiVO₄ can be improved by introducing impurity such as Mo, W [40, 41]. For instance, Xie *et al.* reported a 3D-ordered Mo:BiVO₄ macromesoporous architecture with 2.0 mA/cm² photocurrent

density and $\sim 40\%$ IPCEs at $1.0\text{ V}_{\text{Ag/AgCl}}$ (Figure 4.3). In such design, the conductivity of BiVO_4 is improved by introducing Mo^{6+} , because Mo^{6+} has one more valence electron than that of V^{5+} host atom. As a result, Mo^{6+} can substitute into the V^{5+} host lattice as electron donors, resulting in enhanced charge transfer in comparison to pure BiVO_4 [42]. In addition, Luo *et al.* demonstrated that the surface pretreatment of BiVO_4 by electrochemical cyclic voltammetry before doping can enhance the PEC performance of Mo-doped BiVO_4 [43]. Qiu *et al.* reported nanocone BiVO_4 -perovskite tandem cells with excellent water oxidation performance. A high photocurrent of $5.82 \pm 0.36\text{ mA/cm}^2$ at 1.23 V vs. RHE under 1-sun illumination was observed. The applied-bias photon-to-current efficiency (ABPE) of $\text{Mo:BiVO}_4/\text{Fe(Ni)OOH}$ photoanode ranges between 1.75% and 1.92% , and the PEC cell in tandem with a single perovskite solar cell (PSC) showed a high STH efficiency up to 6.2% [44].

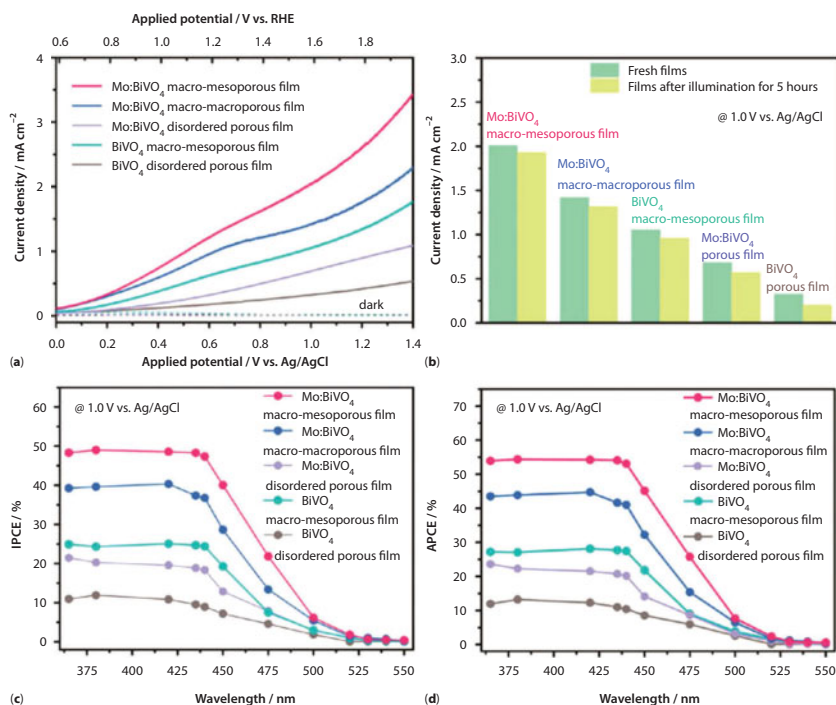


Figure 4.3 (a) Solid line represents photocurrent density potential curves and dashed line represents dark-current density potential curves of various films at the scan rate of 10 mV/s . (b) Photocurrent density stability of various films at $1.0\text{ V}_{\text{Ag/AgCl}}$. The films for measurement are fresh and after illumination for 5 h , respectively. (c, d) IPCEs and APCEs of various films as a function of the wavelength at $1.0\text{ V}_{\text{Ag/AgCl}}$. Reprinted with permission from [42], Copyright 2014, American Chemical Society.

4.3.1.3 α -Fe₂O₃-Based Photoelectrode

α -Fe₂O₃, or hematite, is an important n-type semiconductor with a bandgap between 1.9 and 2.32 eV, and a theoretical STH efficiency of 16.8%, while α -Fe₂O₃ has the advantages of nontoxicity, low cost, visible-light response, relatively good stability and earth abundance, its shorter diffusion length of holes than those of TiO₂ and WO₃ severely hampered its applications [45–49]. To overcome this disadvantage of α -Fe₂O₃ as photoelectrode material, multiple methods have been developed in recent years. First of all, doping different elements such as Sn, Zr, and Si into α -Fe₂O₃ has been proven to be effective for decreasing charge transfer resistance and can lead to performance enhancement [20]. For instance, Sn-doped α -Fe₂O₃ nanowires and nanocorals exhibited photocurrent density of 1.24 mA/cm² and 1.86 mA/cm² at 1.23 V_{RHE}, respectively, in which the enhancement can be attributed to a better electrical conductivity and large surface area [50]. In addition, Wheeler *et al* stated that synthesize nanostructured hematite (branched nanorods, core–shells, etc.) is another effective method to improve charge carrier dynamics through inhibiting the recombination of e^-/h^+ [51]. Recent progress on the PEC performance of α -Fe₂O₃-based materials is summarized in Table 4.1.

4.3.2 Photocathode Materials

4.3.2.1 Copper-Based Chalcogenides-Based Photoelectrode

Copper-based chalcopyrite materials such as Cu(In, Ga)Se₂ (CIGS), Cu₂ZnSnS₄ (CZTS), CuGaSe₂, and CuGa₃Se₅ have been extensively

Table 4.1 Recent progress on PEC performance of α -Fe₂O₃-based materials.

Photoelectrode	Cocatalyst	Electrolyte and illustration	Onset potential	Photocurrent
Co/ α -Fe ₂ O ₃ nano-flakes [52]	Co	1 M NaOH, AM 1.5G	0.61 V _{RHE}	6.8 mA/cm ² at 1.55 V _{RHE}
C/Co ₃ O ₄ / α -Fe ₂ O ₃ [53]	Carbon, Co ₃ O ₄	1 M NaOH, AM 1.5G	0.85 V _{RHE}	1.48 mA/cm ² at 1.23 V _{RHE}
Ag/Co-Pi/ α -Fe ₂ O ₃ [54]	Ag, Co-Pi	1 M NaOH, AM 1.5G	-	4.68 mA/cm ² at 1.23 V _{Ag} /AgCl
Sn, Zr codoped /NiOOH/ α -Fe ₂ O ₃ [55]	NiOOH	1 M NaOH, AM 1.5G	0.58 V _{RHE}	1.64 mA/cm ² at 1.23 V _{RHE}
Zr doped α -Fe ₂ O ₃ [56]	-	1 M NaOH, 150 mW/cm ²	-	2.1 mA/cm ² at 1.64 V _{RHE}

reported as photocathode materials [18, 57–59]. Numerous investigations on photovoltaic applications suggested that CIGS are promising materials with high conversion efficiency as photocathode. For example, Cu(In, Ga)Se₂ modified with Pt and TiO₂ showed a high photocurrent density up to 15 mA/cm² at 0 V_{RHE} and a STH efficiency of 18%, respectively. Pt implemented for simultaneous optimization of conductivity, electrocatalytic activity, and light guidance toward the material is responsible for this enhanced performance [60]. Chae *et al.* reported a Cu(In, Ga)(Se, S)₂ photocathode modified with ZnS layer, resulting in a significant high photocurrent density of ~24 mA/cm² at -0.3 V_{RHE}. At the same time, an average Faradaic efficiency of ~94% was observed, suggesting most of electrons involved can be used to split water [61]. In addition, Cu(In, Ga)S₂ deposited with CdS layer and Pt can exhibit a relatively high onset potential of 0.89 V_{RHE} [58]. However, the poor stability of CdS layer rendered a rapid decay of the Pt-CdS/CIGS photocurrent in the first 10 minutes, potentially limiting its practical applications [62]. Kanko *et al.* reported Pt/Mo/Ti/CdS/(ZnSe)_{0.85}(CIGS)_{0.15} photocathode with a high photocurrent of 7.1 mA/cm² at 0 V_{RHE} and an onset potential of 0.89 V_{RHE}, respectively. By connecting Pt/Mo/Ti/CdS/(ZnSe)_{0.85}(CIGS)_{0.15} with a NiFeO_x-Bi/BiVO₄ photoanode, a maximum STH efficiency of 0.91% with a faradaic efficiency of ~100% can be obtained from this two-electrode system [63].

Cu₂ZnSnS₄ (CZTS), CuInS₂ (CIS), CuGaSe₂, and CuGa₃Se₅ were also widely investigated recently [62, 64]. Similar to those for CIGS, ZnS and CdS are widely deposited to PEC photocathode to form p-n junction for charge separation enhancement. For instance, Kim *et al.* reported a photocurrent density of 8.03 mA/cm² from CuGa₃Se₅ composite deposited with ZnS and Pt, compared to that of 3.04 mA/cm² without the ZnS layer [18]. Moriya *et al.* reported CdS-modified CuGaSe₂ with a significantly increased photocurrent and stability under hydrogen evolution reaction conditions for over 10 day. One main reason for such enhancement is that the thin CdS layer is completely covered by the depletion layer, resulting in cathodic polarization, in which the diffusion of holes to the interface of semiconductor/electrolyte is obstructed (Figure 4.4) [59].

4.3.2.2 Silicon-Based Photoelectrode

Silicon is widely utilized in many research fields, including PV-PEC tandem cells for water splitting [25]. However, two major fundamental drawbacks still limit its practical application in hydrogen evolution. First of all, silicon, as a photocathode material, suffers from photocorrosion in a PEC cell under illumination because of its redox potential level, making

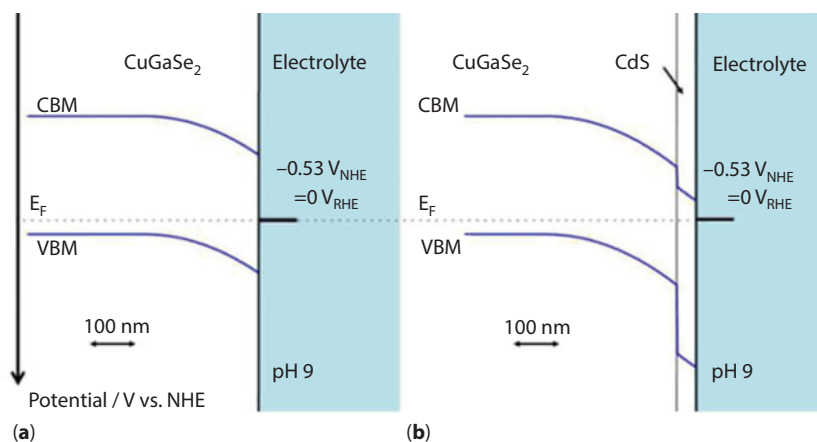


Figure 4.4 Band alignment of (a) CGSe and (b) CGSe/CdS electrodes by calculating at the solid electrolyte interfaces. Reprinted with permission from [59], Copyright 2014, American Chemical Society.

it necessary to deposit surface protective layers on silicon-based materials. For example, Ji *et al.* reported a Si-based photocathode protected by SrTiO_3 layer with high stability. In this work, a high photocurrent density of 35 mA/cm^2 and an onset potential shift of 450 mV were observed from SrTiO_3/Si photocathode for water reduction. In addition, an ABPE of 4.9% in 0.5 M H_2SO_4 was yielded by tuning the spacing and size of structured metal catalyst [65]. Secondly, the high reflectance of water–Si interface can severely hinder the STH value of Si. Therefore, further investigations to decrease the reflectance of Si surface mean a lot for its practical usage. For instance, Oh *et al.* reported nanoporous black Si photocathode, which increased H_2 -producing photocurrent density by $\sim 20\%$. The enhanced H_2 generation performance was attributed to the unique nanostructured black Si surface [66]. In addition, silicon-based (p/n Si-PEC) tandem PEC water splitting devices seem to be quite promising because it could operate water splitting without bias under light irradiation. The photocurrents of amorphous Si tandem cell in a single or double junction could reach 3 or 4 mA/cm^2 , respectively. The double-junction amorphous Si tandem cell can also exhibit a STH efficiency of 4.9% [67].

4.3.2.3 Cu_2O -Based Photoelectrode

Cuprous oxide, as an important p-type semiconductor, owns a high theoretical STH efficiency of 18% [68]. Due to its suitable band edge

and bandgap (1.9 to 2.2 eV) [14, 69], Cu_2O is a promising material for water splitting under sun illumination [25]. However, the fast electron–hole recombination and the poor stability of Cu_2O severely hinder the application of Cu_2O in PEC water splitting [70]. Up to date, there are several approaches that can be used to stabilize and improve the efficiency of Cu_2O as photoelectrode, including (1) utilizing a suitable n-type semiconductor to combine with Cu_2O , given that the formation of p-n junction is favorable for inhibiting the fast recombination of e^-/h^+ and (2) depositing carbon or metal oxides as surface protective layers/catalyst to hinder self-redox. In addition to stabilize Cu_2O -based PEC electrode, there exists some problems to be solved: (1) the p-n junction is required for the property of contiguity and uniformity; (2) the surface protective layer is required for the characteristic of conformity and no pinholes; and (3) cocatalysts is required for the quality of high activity and uniform deposition [25]. For example, by using the abovementioned approaches, a $\text{Cu}_2\text{O}/\text{Al}:\text{ZnO}/\text{TiO}_2/\text{Pt}$ composite can achieve a photocurrent of $-7.6 \text{ mA}/\text{cm}^2$ at $0V_{\text{RHE}}$ and a faradaic efficiency of $\sim 100\%$, respectively (Figure 4.5) [69]. With the introduction of MoS_{2+x} and Ni-Mo as catalysts, $\text{MoS}_{2+x}/\text{Ni-Mo}/\text{Cu}_2\text{O}$ photocathode exhibited photocurrents of $-6.3 \text{ mA}/\text{cm}^2$ at $0V_{\text{RHE}}$ and a STH efficiency of 7.7% [71]. Li *et al.* reported Cu_2S -coated Cu_2O nanowires (NWs) on a three-dimensional porous copper foam, in which Cu_2S served as sensitizer, electron trapper, electrocatalyst, and protector. The photocurrent density of $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$ nanowire reached $-5.05 \text{ mA}/\text{cm}^2$ and can stay stable for 5 h at $0 V_{\text{RHE}}$ in the absence of Pt electrocatalysts [72]. It can be envisioned that this noble metal-free HER catalyst process might provide a new strategy for PEC water splitting [71].

4.3.2.4 III-V Group Materials

Some III-V group materials with relatively narrow bandgap, such as binary compounds GaP [10], InP [73], and ternary compounds GaInP [74], [In, Ga]N [75], have exhibited high solar-spectrum response [14].

Though GaP is suitable for photovoltage application, its major drawbacks include high cost and weak charge collection of its large planar structure [14]. Liu *et al.* reported a Zn-doped GaP nanowire photocathode with a quite low loading amount (about $60 \mu\text{g}/\text{cm}^2$), a loading amount that is only 1/3000 compared with the amount of material used in a planar wafer electrode ($0.2 \text{ g}/\text{cm}^2$). This as-prepared photoelectrode exhibited a photocurrent density of $\sim 0.1 \text{ mA}/\text{cm}^2$ at $0 V_{\text{RHE}}$ under AM 1.5G [13]. Assisted by noble-metal-free MoS_3 electrocatalysts, Gao *et al.* fabricated InP nanowire arrays in vertical alignment, which achieved an overall STH of 6.4% under

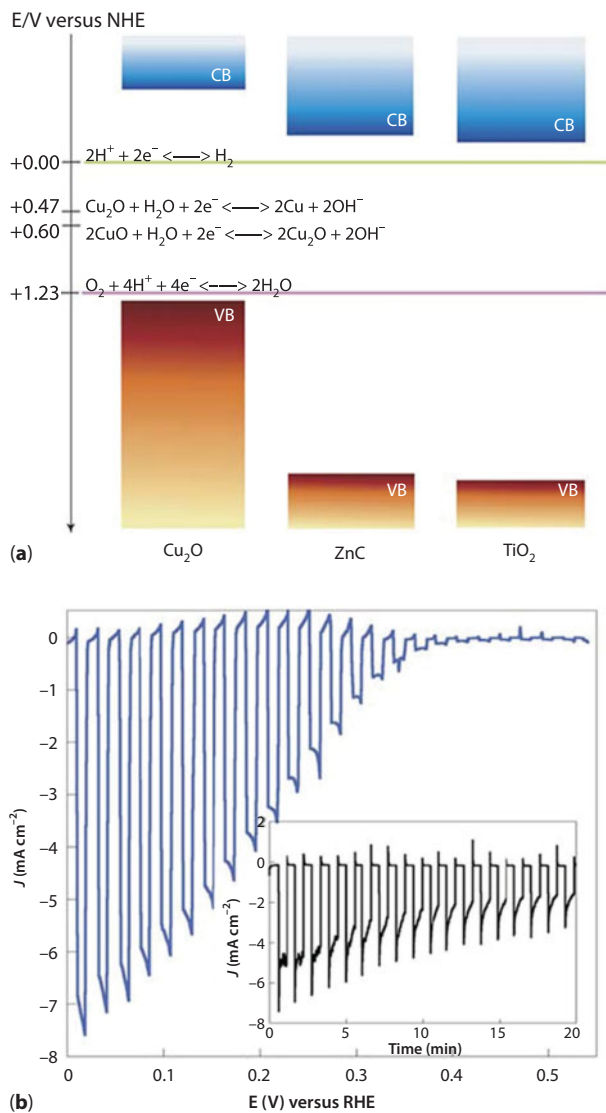


Figure 4.5 (a) Energy band positions of the semiconductors utilized in the multilayered photocathode and the relative redox levels of the involved chemical reactions. (b) Current–potential characteristics of $\text{Cu}_2\text{O}/\text{Al}:\text{ZnO}/\text{TiO}_2/\text{Pt}$ in 1M Na_2SO_4 solution, under chopped AM 1.5G. The inset shows the photocurrent transients for the electrodes held at 0V vs. RHE in chopped light illumination with N_2 purging. Reprinted from [69], Copyright 2011, Macmillan Publishers Limited.

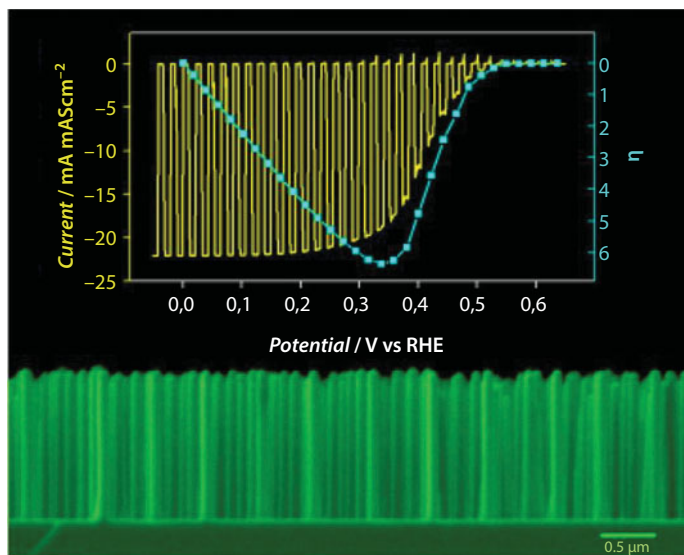


Figure 4.6 Yellow solid line represents current–potential curves and blue squares represent energy conversion efficiencies of the as-grown InP nanowire arrays photocathode modified with MoS_3 in 1 M HClO_4 under AM 1.5G illumination. Reprinted with permission from [73], Copyright 2014, American Chemical Society.

AM 1.5G (Figure 4.6) [73]. However, severe photocorrosion limited the PEC performance of InP-based photoelectrodes.

For GaInP_2 , Khaselev *et al.* reported a p-n GaAs/p-n tunnel junction/ GaInP_2 /Pt tandem cell with a high energy conversion efficiency of 12.4%, which inspired great interests from researchers all over the world [76]. In this configuration, a visible-light responsive GaInP_2 top cell is combined with a near-infrared responsive GaAs bottom cell via a interconnect tunnel. A voltage-biased PEC device and an integrated PV device are also included in the setup. Sun light drives electrons and holes separately to the surface and the ohmic contact, respectively. Jia *et al.* designed a photovoltaic (PV)-electrolysis system with a significantly high 48-hour average STH value of 30%. In this device, two polymer electrolyte membrane electrolyzers are tandem with a triple-junction $\text{InGaP/GaAs/GaInNAsSb}$ cell [74].

4.3.2.5 CdS-Based Photoelectrode

CdS, with a direct bandgap (2.4 eV) and appropriate band edges, can be utilized as a photoelectrode to split water without bias [1, 77]. Unfortunately, the n-type CdS intrinsically suffered from photocorrosion because of its

self-oxidation reactions induced by hole generation [14]. Other semiconductors utilized as photocathode, such as CdTe and CdSe, also experience similar problem and thus require stabilization or protection from photocorrosion. Li *et al.* reported gold nanoparticles (AuNPs) and TiO₂-modified CdS nanorod array with a ~2.8% energy conversion efficiency at $-0.56 \text{ V}_{\text{Ag/AgCl}}$. The photocurrent of the as-prepared electrode can be as high as 4.07 mA/cm^2 at $0 \text{ V}_{\text{Ag/AgCl}}$, which is resulted by the CdS-generated charge carriers that transferred to TiO₂ via AuNPs at wavelengths below 525 nm. The enhancement of IPCE and IPCE factors at wavelengths corresponding to the localized surface plasmon resonance (LSPR) was attributed to the deposition of AuNPs [15]. Zheng *et al.* reported a 3D CdS networks photoelectrode decorated with Nafion. The observed photocurrent density of Nafion-coated CdS photoelectrode is 5.68 mA/cm^2 . In addition, a 75% IPCE is obtained at 0 V_{RHE} at 350–500 nm. DFT calculations demonstrated that the coupling effect of Nafion and CdS is favored for charge separation and the transfer kinetics of hydrogen generation [78].

Due to the bandgap of 1.44 eV, CdTe is a suitable material for the application of thin film solar cell and has various preparation methods. For instance, by modifying CdTe/FTO photocathode with a CdS layer and Pt, the as-prepared photocathode exhibited improved performance with a 6.0 mA/cm^2 at $0.1 \text{ V}_{\text{RHE}}$ cathodic photocurrent and a $0.6 \text{ V}_{\text{RHE}}$ onset potential, respectively [79].

4.4 Advances in Photoelectrochemical (PEC) Hydrogen Generation

4.4.1 Monocomponent Catalyst

Photocatalytic processes require active semiconductor photocatalyst. As we mentioned above, a perfect photocatalyst should have narrow bandgap, strong light absorption, fast photocarrier transmission, low recombination rate, and good photocorrosion stability, which provide low energy loss and highly efficient photocatalytic performance under solar light. Semiconductor photocatalyst research began in 1972. Since then, many semiconductor photocatalysts like TiO₂ [80], ZnO [81], SnO₂ [82], Co₃O₄ [83], BiVO₄ [84], CuO [85], CdS [86–88] have been successfully developed. They are so-called photosensitizers. Photosensitizers are essential for hydrogen production—as we discussed in the principle part, electronic transitions of photoactive materials that generate electron–hole pairs are key to the entire PEC system. For example, TiO₂ and g-C₃N₄

are one-component photocatalysts that are nontoxic and possess decent photocatalytic properties. TiO_2 , with a bandgap of ~ 3.2 eV, is the earliest monocomponent material that can be found in photocatalytic and photoelectrochemical hydrogen production. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) also exhibits excellent activity in PEC hydrogen production, with its lower bandgap (2.7 eV) and special electronic structure. $\text{g-C}_3\text{N}_4$ has received widespread interests in the field of visible light responsive semiconductor materials with its characteristics of metal-free, good stability, easy preparation, and so on [89–92]. Since carbon (C) and nitrogen (N) elements may have weaker affinity to O–O bonds than those of metallic ones, they ensure a natural, media-free regeneration process and gradually decompose water in a cyclically stable manner [93]. In recent studies, some new semiconductor photocatalysts like BiOI , BiVO_4 , Bi_2WO_6 [94–96], and SrTiO_3 [97–102] have attracted the attention of many scientific researchers. For example, while SrTiO_3 is often used for photoelectrochemical decomposition of z-scheme, it is also a single-component photocatalyst, in which SrTiO_3 is used as a photocatalyst electrode where mainly hydrogen evolves. Some combination systems with SrTiO_3 such as Rh-doped SrTiO_3 (SrTiO_3 : Rh) photocatalyst electrode can further strengthen this process. For instance, Iwashina *et al.* found the cathodic photocurrent can be generated under visible light irradiation ($\lambda > 420$ nm) by coating SrTiO_3 : Rh powder on a transparent indium tin oxide electrode. With the doping amount increase up to 7 atom%, the cathodic photocurrent also experiences a gradual increase under visible light irradiation up to 540 nm [97]. Wang *et al.* proposed a sheet system with SrTiO_3 : La, Rh, as H_2 evolution photocatalyst, BiVO_4 : Mo as O_2 evolution photocatalyst, and C as electron mediator. The solar energy conversion efficiency (STH) can achieve a significant 1.2% at pH 6.8, 331 K, and 10 kPa, while also maintaining 80% of this efficiency at 91 kPa.

Under the pure water decomposition through z-scheme at ambient pressure, the highest attainable STH value is $\sim 1.0\%$, and the reverse reactions of H_2 and O_2 are well suppressed in such case. The proposed carbon-based photocatalyst sheet is a vital alternative to those similar photochemical and electrochemical systems [102–105]. However, the monocomponent catalysts have some common disadvantages, especially low light quantum efficiency, easy deactivation, and insufficient solar energy utilization. Take pure TiO_2 semiconductor photocatalyst as an example; it has a bandgap of about 3.2 eV, which corresponds to a light absorption band edge wavelength of 387 nm, resulting in a very limited absorption of solar energy. Similarly, $\text{g-C}_3\text{N}_4$ also has the following disadvantages: (1) $\text{g-C}_3\text{N}_4$ only absorbs blue light at 450 nm and is inefficient for other regions of visible

light; (2) Low efficiency induced by recombination of photogenerated electrons and holes; (3) $g\text{-C}_3\text{N}_4$ is easily decomposed by the self-generated holes, leading to poor cycle stability. All these limitations make the practical photoelectrochemical application of semiconductors greatly reduced. This is why Iwashina *et al.* and Wang *et al.* conducted surface modification of SrTiO_3 or developed different system combinations instead of using pure SrTiO_3 . In order to improve the catalytic performance of monocomponent photocatalysts, the most common approaches include doping of anions and cations, coupling with other semiconductors, and reduction of the semiconductor particle size. In short, surface modification is a simple and practical method for improving the performance of semiconductor photocatalysts.

4.4.2 Functional Cocatalyst

In the past decade, numerous reports have been published in regard to approaches to photocatalytic water splitting with monocomponent or heterostructured photocatalysts. Taking TiO_2 as an example, researchers have utilized different approaches to modify TiO_2 for its catalytic activity improvement, such as nonmetal doping (N [106], C [107], S [108]), the deposition of noble metal (Pt [109], Au [110], Ag [111]), compositing with semiconductor materials AgBr [112], RuO_2 [113], WO_3 [114], CdS [115], etc. These materials can sensitize quasi-titanium dioxide-like semiconductors to achieve catalyst modification. Functional cocatalyst plays an increasingly important role in this field [116]. Generally speaking, photoelectrochemical water decomposition hydrogen production with a PEC cell or a z-scheme photocatalytic system suffers from low energy conversion efficiency and is still far from practical application. The main reason is that while the three key steps of the photocatalytic water decomposition are sunlight collection, charge separation, and transport, the involved catalytic reduction and oxidation reactions are typically either ineffective or not taking place simultaneously [12]. In addition, the process of water splitting requires multiple electron transfers, making it one of the most difficult chemical reactions to achieve in practical use. Therefore, cocatalysts are becoming indispensable to allow breakthroughs in the photocatalytic process.

In PEC hydrogen production reactions, cocatalysts facilitate the charge separation and transfer and thus lead to the enhancement of photocatalysis activity. The addition of proper cocatalysts to semiconductors (as photosensitizers) can significantly promote water oxidation and reduction process, and at the same time, inhibiting charge recombination and

reverse reactions. As we presented above, a PEC system consists of cathode and anode where water oxidation and reduction take place, respectively. Photocatalytic H_2 generation includes two basic surface reactions, followed by semiconductor bandgap excitation and charge transfers to the surface: one is protons reduction by photogenerated electrons and the other is electron donor oxidation by h^+ . Cocatalysts loaded on the semiconductor materials mainly act as electron transfer promoting media, similar to that of natural photosynthesis. In other words, the presence of cocatalyst allows Fermi energy level readaptation, which promotes photogenerated charge transfer and reduces the recombination of electron–hole pairs, thus enhancing the photocatalytic process. In addition, it is vital importantly to control the shape and size of cocatalysts, as well as their interaction with semiconductors, which can remarkably affect the catalytic performance. For example, Iwase *et al.* reported that Au/NaTaO₃: La [117] exhibited improved activity and stability in water splitting through an impregnation method that can achieve the smaller perimeter of Au/NaTaO₃: La interface. In addition, the catalytic water decomposition can be enhanced by tuning the shape and size of the AuNPs. While the whole system resulted in a lower activation energy, the AuNPs cocatalysts fulfilled the purpose of protecting the semiconductor by continuously consuming photogenerated electrons, especially holes, so the photostability is improved.

Photoelectrochemical catalysis efficiency generally could not reach the theoretical value mainly due to the facile recombination of electron–hole pairs before completing the entire reaction. This is because the slow kinetics of surface reaction resulted in low charge consumption efficiency. To solve this problem, metals, particularly noble metals, gained extensive attention from the research society. For example, TiO₂ is the earliest photosensitizer for hydrogen production [80, 118–123] due to its photocatalytic stability and relatively nontoxicity. Daskalaki *et al.* have found that the presence of Pt could improve the photocatalytic performance of TiO₂ significantly. The effect is even more pronounced when the suspension contains organic compounds [124]. Liu *et al.* have demonstrated that the performance increased by ~66 times after loading a 5-nm-thick gold layer on TiO₂, possibly due to the strengthening of TiO₂ electric field by the SPR effect [125]. The whole system also uses plasma near-field coupling to improve the of TiO₂ photocatalytic wavelength range. Bai *et al.* produced Pd@Pt quasi-core–shell cocatalysts in combination with total atomically controlled TiO₂. The combination of Schottky junction and interface charge polarization improves charge separation, averting the recombination of charge and hole and thus boosting the catalysis performance [126]. Ning *et al.* applied artificial gill in the TiO₂/CdS system to remove the newly formed O₂ from catalyst surface,

so that the reverse reaction to water can be suppressed, as well as prevent the photocorrosion of CdS [127]. There are also other photosensitizers, in addition to TiO_2 , such as ZnO, CdS, and CdSe. CdS and CdSe are fluorescent materials with extensive explorations in recent years [128]. Holmes *et al.* found high efficiency of CdSe nanocrystals in hydrogen production due to their degree of quantum confinement [129]. The Zhang *et al.* reported three-component ZnO/Ag/CdS nanocomposite photoanode for photocatalytic water splitting, in which CdS and Ag act as narrow band-gap sensitizer and cocatalyst, respectively [130]. This ZnO/Ag/CdS system improves photocatalytic water decomposition performance because of its localized surface plasmon resonance (LSPR) similar to that of Au/ TiO_2 , which was further confirmed by the difference of electric field intensity obtained from FDTD simulation. Another major function of cocatalyst attachment is to enhance photostability. However, sulfur-containing semiconductors like CdS and nitride semiconductors are often keen to degrade under solar light [12]. To address this issue, the most common strategy is to add a protective layer on the surface of CdS. For example, while Pt/ CuInS_2 shows a stable cathodic photocurrent, the modification with CdS rendered a significant increase of cathode photocurrent to greater than 8 mA/cm^2 . However, the photocurrent decays rapidly because of the poor stability of CdS. After a protective layer of TiO_2 film is added on the surface of CdS, the cathodic photocurrent has been steadily increased to about 13 mA/cm^2 , and no obvious decay is observed [62].

4.4.3 Z-Scheme Catalyst

Two-photon system (z-scheme) is a promising strategy on hydrogen production. Z-scheme photocatalytic reaction system is named because its charge transportation mechanism is similar to the photosynthesis of green plants [131]. The z-scheme consists of a H_2 -evolving photocatalyst, an O_2 -evolving photocatalyst, and an electron mediator. With the assistance of the two-photon excitation process, the oxidation reaction and the reduction reaction are individually performed on different photocatalysts, which effectively promotes the separation and migration of photogenerated charges [132]. In addition, the photocatalytic reduction site and the oxidation site are on two separate photocatalytic semiconductors, which can effectively suppress the reverse reaction. To date, many reports have been published about photocatalysts containing electron mediator and sacrificial reagents in z-scheme with visible-light-driven hydrogen production activities, including WO_3 [133], Rh-doped SrTiO_3 (SrTiO_3 : Rh) [97], La-doped SrTiO_3 (SrTiO_3 : La), BiVO_4 [101], GaN: ZnO [134], $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ /

GaN: ZnO [135], Ta_3N_5 [136], and GaN [137]. While these catalysts almost have no activity in the absence of sacrificial reagents, water splitting could carry on smoothly if a suitable electron mediator is applied in the system. Table 4.2 summarizes some popular z-scheme photocatalyst systems for hydrogen production.

Taking the system of SrTiO_3 and BiVO_4 for example, Wang *et al.* reported that the SrTiO_3 : La, Rh/Au/ BiVO_4 : Mo system with Au serving as a solid electron mediator exhibited an AQY of 33% (419 nm) and an STH of 1.1% in overall water splitting at pH 6.8 [102]. While it demonstrated that a proper electron mediator is needed in the z-scheme, it is also worth noting that this system only works when SrTiO_3 is used as a hydrogen-producing photocatalyst.

Photocatalytic performance of water-splitting hydrogen production using z-scheme systems is strongly influenced by pH, cocatalysts, and electron mediators [132]. pH plays a significant role in these systems, given that the electron transfer process is often dependent on pH, and changes in pH could then directly affect the reactivity of the system and the nature of electron mediators [149, 150].

Table 4.2 Z-scheme Photocatalytic Water Decomposition Systems under Visible Light Irradiation.

H_2 -evolving photocatalyst	O_2 -evolving photocatalyst	Electron mediator
Fe^{2+}	RuO_2/WO_3	$\text{Fe}^{2+}/\text{Fe}^{3+}$ [138]
Pt/SrTiO_3	BiVO_4	$\text{Fe}^{2+}/\text{Fe}^{3+}$ [139]
SrTiO_3 : Rh	BiVO_4	$\text{Fe}^{2+}/\text{Fe}^{3+}$ [140]
Pt/TiO_2 (anatase phase)	TiO_2 (rutile phase)	I/IO_3 [141]
Pt/TaON	Pt/WO_3	I/IO_3 [142]
m- ZrO_2/TaON	Pt/WO_3	I/IO_3 [143]
Pt/SrTiO_3 : Cr, Ta	Pt/WO_3	I/IO_3 [144]
SrTiO_3 : La, Rh	BiVO_4 : Mo	Au [102]
CdS	ZnO	Cd [145]
CdS	TiO_2	Au [146]
Pt/CdS	TiO_2	Au [147]
Ru/SrTiO_3 : Rh	BiVO_4	RGO [148]
Metal sulfide	RGO- TiO_2	RGO [118]

Besides the pH effect, functional cocatalysts also have been influenced by providing a shortcut to produce H_2 on the surface of a photocatalyst. To be more specific, the presence of cocatalysts could profoundly affect the morphology of semiconductor photocatalysts. Changing the structure of the photocatalytic material is likely to change the mechanism of the photocatalytic reaction, resulting in significant changes in performance. In general, doping elements can lead to extrinsic defects in semiconductor materials. The formation of defects has two fundamental roles: (1) Formation of defect levels: A defect level is formed between the valence band and the conduction band to provide a "springboard" for the electronic transition; (2) To change the band gap width: The valence band and the conduction band are brought closer by the formation of defects, facilitating electrons to transfer under lower light energy [151]. For example, in the $SrTiO_3$: La, Rh/Au/ $BiVO_4$: Mo photocatalyst sheet system, Au, as a solid electron mediator, has strong influences on both ends of the photoelectrodes. As we have discussed above, Au cocatalyst has a positive effect on H_2 generation because of its unique surface plasmon resonance (SPR). This surface modification, defined as the rational use of the cocatalyst, could effectively inhibit the progress of the reverse reaction and enhance z-scheme catalysis. In addition, with Au on semiconductors, the photogenerated electron-hole pairs are consumed during photocatalytic water decomposition due to the readaptation of Fermi energy levels, which further suppressed the reverse reaction. In short, suppressing the reverse reaction of H_2 and O_2 is the key step in the process of overall water splitting for H_2 production.

When it comes to z-scheme system of water splitting, the abovementioned three major factors are indispensable. However, commonly used ionic electron mediators can also have a negative impact on the system. For example, when exposed to visible light, colored electron mediator can absorb part of the solar energy, making it necessary to use specific electronic transfer media. In this regard, solid-state electron mediators or z-scheme photocatalytic systems that do not use electron mediator gradually attract the attention of researchers in recent years.

Exploration of photoelectrochemical hydrogen generation has progressed a lot, with large numbers of attempts in using different materials. Z-scheme photocatalytic materials can possess narrow bandgaps, where the conduction band bottom of photosemiconductor I (PSI) is more negative than the reduction potential of H^+ , and the valence band top of photosemiconductor II (PSII) is more positive than the oxidation potential of H_2O . Such setup can ensure both full utilization of light and strong redox ability (Figure 4.7), providing the system foundations for overall water splitting. The catalytic materials have also been developed a lot with

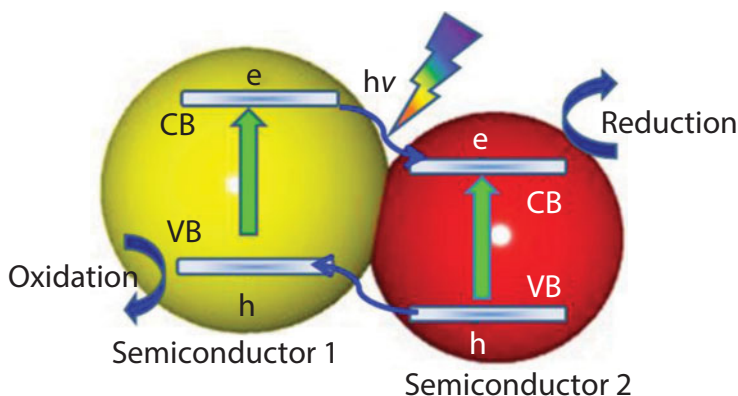


Figure 4.7 Z-scheme photocatalytic water-splitting system. Reprinted from [152], Copyright 2015, John Wiley and Sons.

excellent candidates found. It is undoubted that the simplest and most practical method is to use powdered photocatalysts for solar water splitting. Given it is highly desired to effectively utilize sun light for H_2 and O_2 evolution, z-scheme photocatalytic system is the promising way in future research. By utilizing narrow bandgap stable semiconductor materials, the efficiency of converting light energy into hydrogen energy could be significantly improved. At the same time, the reverse reaction is effectively suppressed. Therefore, the z-scheme system, different from one-component system, provides us a unique opportunity in photocatalytic and photoelectrochemical water splitting for potential breakthrough in this field. At present, ionic electron transmission media were mainly used in this system, but they have two major drawbacks: (1) It is mainly used for liquid phase reactions, probably causes some reverse reactions, and (2) colored ion electronic media may also absorb some incident light. As a result, the development of solid-state electron mediator z-scheme system to improve light trapping, stability, redox capability, and separation efficiency of photogenerated electron–hole pairs will be the main research direction in the future.

4.5 Pros and Cons of Photoelectrodes and Photocatalysts

The discovery and explorations of photoelectrode and photocatalyst have a profound and far-reaching significance for the use of clean energy sources, including: (1) Shortened carrier collection pathways. Depending on the material, the type of carrier, and the intensity of incoming light, the

photogenerated charge carriers have a limited mobility and lifetime. To drive the water redox reaction forward, though, these carriers would need to reach the surface of the electrolyte material. Through doping and modification, the carrier concentration, lifetime, and diffusion length could be all changed significantly; (2) Improve the use efficiency of light energy, that is, improve the distribution of light. The degree of horizontal distribution by light scattering could be increased by micro- or nanoscaled surface structuring. While light would be reflected directly from the flat surface and disappear, particle suspension can help light scattering because the presence of particles increases the contact area with incoming light, thus improving the light efficiency; (3) Quantum size limitations. The quantum size effect and “support effect” depend on the material and the morphology of nanocrystals. These effects will likely be commonly used in advanced solar water separators; (4) Surface-enhanced electron transfer. As earlier mentioned, sensitization of single-component photocatalysts can effectively enhance charge transfer through a series of modifications. For example, the larger surface area of nanosemiconductor materials facilitates the charge transfer at the interface of the connecting material, resulting in the water redox reaction to occur at low current densities and low overpotentials. In short, an increment in surface area could indirectly promote the decomposition of water to produce hydrogen; (5) Multiple excitons. Since changes in the electronic structure of large-sized nanocrystals can cause multiple excitons, the intersection of band gap and photon energy is the key to achieve efficient solar energy conversion.

While nanostructures can improve light collection, charge transfer, kinetics, and energy parameters of optoelectronic synthesizers, they also exhibit severe drawbacks of reduced energy conversion efficiency and low device lifetime. (1) Increased surface recombination. The dominate cause of loss in solar cells and photocatalysts is electron-hole recombination. The photogenerated charge carriers are recombined at the semiconductor surface defects through either radiation or nonradiative processes. These processes reduce the steady-state concentration of available charge carriers, significantly decreasing energy conversion efficiency; (2) Lower absorbed photon flux; (3) Slower charge transportation between particles. In nanocrystalline films, charge carriers transfer diffuse inefficiently [23, 152, 153]. As a result, the charge transportation is much slower than those in the body, increasing the chance of recombination and reverse reactions. Since nanostructured films can have a thickness of about a few hundred nanometers, the charge transportation resistance is an important factor for low energy conversion outcome [154]. Certainly, there are still many similar disadvantages, but in order to solve the abovementioned problems, we can start from the following aspects: (1) Decrease bulk phase

recombination: photogenerated electrons or holes are easily recombined in the bulk phase during the transport process, resulting in a lower concentration of holes (electrons) transferred to the reaction interface layer, which greatly reduces the catalytic performance of the electrode; (2) Reduce surface recombination: the formation of carrier recombination centers due to the presence of surface states, segregation phases, impurity atoms, etc, has negative influences for improving photoelectrode performance; (3) Inhibit back reaction: back reaction is the reaction between photoelectrons and oxidation products. The inhibition of back reaction can reduce the starting potential of the electrode, so as to achieve the purpose of improving the performance of the electrode.

4.6 Conclusion and Outlook

In conclusion, great efforts have been made to find appropriate photoelectrodes for solar hydrogen generation in the past decade; however, no photoelectrode is identified as a perfect candidate for large-scale solar water splitting to date. The application of photoelectrode materials is mainly limited as no photoelectrode can simultaneously fulfill the four major requirements of broad-spectrum response, high stability, appropriate bandgap, and low cost.

The energy conversion efficiency is no doubt a vital parameter for the performance of photoelectrode. Since the theoretical upper limit of energy conversion efficiency is determined by spectrum response, broad spectrum response in the visible light and/or near-infrared regions is necessary for photoelectrodes. While the energy conversion efficiency is often restricted by the light absorption efficiency, significant progress is made to enhance light absorption. It is also of fundamental importance to choose appropriate bandgap to generate enough energy for water splitting and overcome the overpotential for redox reactions. Moreover, nanostructures can improve light absorption of photoelectrode materials via light scattering, so that the thickness of necessary light-absorbing layer can be minimized because the plasmonic and photonic effects could confine light energy to the near-surface region of the photoelectrode. While current studies on plasmonic effect for solar water splitting were focused on Au, Pt, or Ag nanoparticles-loaded photoanodes [155, 156], further studies on plasmonic effect of photocathodes are needed for deeper understanding with more consideration of noble metal cost in practical usage.

In addition, the large specific surface area of nanostructures can promote the e^-/h^+ transfer, which is favorable for the slow kinetics of water

splitting. Although nanostructure has been proved to play a positive role in light absorption and e^-/h^+ separation, nanostructures also brought some significant disadvantages, for example, charge carriers recombination at defects on the surface. More understanding on the effect of defects in nanostructures should be attained [14]. While depositing suitable cocatalysts is widely employed [12], more methods to avoid or alleviate the disadvantages brought by nanostructures should be further considered.

Stability is a critical factor for the overall cost of PEC water splitting. Photocathodes may suffer from photocorrosion when they have more positive reduction potential level in NHE than that of the water reduction potential. As a result, surface protection layers are necessary to stabilize the photocathode materials. From this perspective, the surface protection layers should allow e^-/h^+ to transfer and stay stable in electrolyte under light illumination. While early investigation found that metal oxides can be often utilized as surface protection layers to efficiently protect the photocathode material from corrosion, the efficiency of charge transfer is significantly decreased when the thick surface protection layers increased [14, 157]. To tackle this problem, the addition of thin surface protection layers is developed by techniques such as atomic layer deposition (ALD). Ultimately, surface protection layers with good conductivity, high crystalline, and nice band alignment should be continuously explored in further investigations to fine-tune the balance between charge transfer efficiency and corrosion resistance [158–161].

Taken together, though researchers have achieved a huge number of breakthroughs in the last decades, much more efforts are still needed to make large-scale PEC hydrogen generation possible.

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References

1. Grätzel, M. Photoelectrochemical cells. *Nature*, 414, 338–344, 2001.
2. Lewis, N.S., Nocera, D.G. Powering the planet: chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci.*, 103, 15729–15735, 2006.

3. Zhang, J.Z. Metal oxide nanomaterials for solar hydrogen generation from photoelectrochemical water splitting. *MRS Bull.*, 36, 48–55, 2011.
4. Fujishima, A., Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, 37, 1972.
5. Xu, H., Ouyang, S., Liu, L., Reunchan, P., Umezawa, N., Ye, J. Recent advances in TiO_2 -based photocatalysis. *J. Mater. Chem. A*, 2, 12642–12661, 2014.
6. Bard, A.J., Fox, M.A. Artificial photosynthesis: solar splitting of water to hydrogen and oxygen. *Acc. Chem. Res.*, 28, 141–145, 1995.
7. Dominey, R.N., Lewis, N.S., Bruce, J.A., Bookbinder, D.C., Wrighton, M.S. Improvement of photoelectrochemical hydrogen generation by surface modification of p-type silicon semiconductor photocathodes. *J. Am. Chem. Soc.*, 104, 467–482, 1982.
8. Heller, A., Vadimsky, R.G. Efficient solar to chemical conversion: 12% efficient photoassisted electrolysis in the (p-type $\text{InP}(\text{Ru})$)/ $\text{HCl-KCl/Pt}(\text{Rh})$ cell. *Phys. Rev. Lett.*, 46, 1153, 1981.
9. Khaselev, O., Turner, J.A. Electrochemical stability of p- GaInP_2 in aqueous electrolytes toward photoelectrochemical water splitting. *J. Electrochem. Soc.*, 145, 3335–3339, 1998.
10. Sun, J., Liu, C., Yang, P. Surfactant-free, large-scale, solution–liquid–solid growth of gallium phosphide nanowires and their use for visible-light-driven hydrogen production from water reduction. *J. Am. Chem. Soc.*, 133, 19306–19309, 2011.
11. Li, Z., Luo, W., Zhang, M., Feng, J., Zou, Z. Photoelectrochemical cells for solar hydrogen production: current state of promising photoelectrodes, methods to improve their properties, and outlook. *Energy Environ. Sci.*, 6, 347–370, 2013.
12. Yang, J., Wang, D., Han, H., Li, C. Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Acc. Chem. Res.*, 46, 1900–1909, 2013.
13. Liu, C., Sun, J., Tang, J., Yang, P. Zn-doped p-type gallium phosphide nanowire photocathodes from a surfactant-free solution synthesis. *Nano Lett.*, 12, 5407–5411, 2012.
14. Huang, Q., Ye, Z., Xiao, X. Recent progress in photocathodes for hydrogen evolution. *J. Mater. Chem. A*, 3, 15824–15837, 2015.
15. Li, J., Cushing, S.K., Zheng, P., Senty, T., Meng, F., Bristow, A.D., Manivannan, A., Wu, N. Solar hydrogen generation by a CdS-Au-TiO_2 sandwich nanorod array enhanced with Au nanoparticle as electron relay and plasmonic photosensitizer. *J. Am. Chem. Soc.*, 136, 8438–8449, 2014.
16. Lin, Y., Yuan, G., Sheehan, S., Zhou, S., Wang, D. Hematite-based solar water splitting: challenges and opportunities. *Energy Environ. Sci.*, 4, 4862–4869, 2011.
17. Tilley, S.D., Cornuz, M., Sivula, K., Grätzel, M. Light-induced water splitting with hematite: improved nanostructure and iridium oxide catalysis. *Angew. Chem.*, 122, 6549–6552, 2010.

18. Kim, J., Minegishi, T., Kobota, J., Domen, K. Enhanced photoelectrochemical properties of CuGa_3Se_5 thin films for water splitting by the hydrogen mediated co-evaporation method. *Energy Environ. Sci.*, 5, 6368–6374, 2012.
19. Murphy, A.B., Barnes, P.R.F., Randeniya, L.K., Plumb, I.C., Grey, I.E., Horne, M.D., Glasscock, J.A. Efficiency of solar water splitting using semiconductor electrodes. *Int. J. Hydrogen Energy*, 31, 1999–2017, 2006.
20. Sivula, K., Le Formal, F., Grätzel, M. Solar water splitting: Progress using hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoelectrodes. *ChemSusChem*, 4, 432–449, 2011.
21. Sato, N. *Electrochemistry at metal and semiconductor electrodes*, Elsevier, 1998.
22. Salvador, P. Hole diffusion length in n- TiO_2 single crystals and sintered electrodes: photoelectrochemical determination and comparative analysis. *J. Appl. Phys.*, 55, 2977–2985, 1984.
23. Hagfeldt, A., Graetzel, M. Light-induced redox reactions in nanocrystalline systems. *Chem. Rev.*, 95, 49–68, 1995.
24. Bicelli, L.P. A review of photoelectrochemical methods for the utilization of solar energy. *Surf. Technol.*, 20, 357–381, 1983.
25. Jiang, C., Moniz, S.J., Wang, A., Zhang, T., Tang, J. Photoelectrochemical devices for solar water splitting – materials and challenges. *Chem. Soc. Rev.*, 46, 4645–4660, 2017.
26. Wang, G., Wang, H., Ling, Y., Tang, Y., Yang, X., Fitzmorris, R.C., Wang, C., Zhang, J.Z., Li, Y. Hydrogen-treated TiO_2 nanowire arrays for photoelectrochemical water splitting. *Nano Lett.*, 11, 3026–3033, 2011.
27. Yang, W., Yu, Y., Starr, M.B., Yin, X., Li, Z., Kvit, A., Wang, S., Zhao, P., Wang, X. Ferroelectric polarization-enhanced photoelectrochemical water splitting in TiO_2 – BaTiO_3 core-shell nanowire photoanodes. *Nano Lett.*, 15, 7574–7580, 2015.
28. Zhang, Z., Wang, P. Optimization of photoelectrochemical water splitting performance on hierarchical TiO_2 nanotube arrays. *Energy Environ. Sci.*, 5, 6506–6512, 2012.
29. Zhang, R., Shao, M., Xu, S., Ning, F., Zhou, L., Wei, M. Photo-assisted synthesis of zinc-iron layered double hydroxides/ TiO_2 nanoarrays toward highly-efficient photoelectrochemical water splitting. *Nano Energy*, 33, 21–28, 2017.
30. Ning, F., Shao, M., Xu, S., Fu, Y., Zhang, R., Wei, M., Evans, D.G., Duan, X. TiO_2 /graphene/NiFe-layered double hydroxide nanorod array photoanodes for efficient photoelectrochemical water splitting. *Energy Environ. Sci.* 9, 2633–2643, 2016.
31. Janotti, A., Varley, J.B., Rinke, P., Umezawa, N., Kresse, G., Van de Walle, C.G. Hybrid functional studies of the oxygen vacancy in TiO_2 . *Phys. Rev. B*, 81, 085212, 2010.
32. Li, W., Sheehan Stafford, W., He, D., He, Y., Yao, X., Grimm Ronald, L., Brudvig Gary, W., Wang, D. Hematite-based solar water splitting: challenges and opportunities. *Angew. Chem. Int. Ed.*, 54, 11428–11432, 2015.

33. Dincă, M., Surendranath, Y., Nocera, D.G. Nickel-borate oxygen-evolving catalyst that functions under benign conditions. *Proc. Natl. Acad. Sci.*, 107, 10337, 2010.
34. Chemelewski, W.D., Lee, H.C., Lin, J.F., Bard, A.J., Mullins, C.B. Amorphous FeOOH oxygen evolution reaction catalyst for photoelectrochemical water splitting. *J. Am. Chem. Soc.*, 136, 2843–2850, 2014.
35. Kudo, A., Ueda, K., Kato, H., Mikami, I. Photocatalytic O₂ evolution under visible light irradiation on BiVO₄ in aqueous AgNO₃ solution. *Catal. Lett.*, 53, 229–230, 1998.
36. Hodes, G. Photoelectrochemical cell measurements: getting the basics right. *J. Phys. Chem. Lett.*, 3, 1208–1213, 2012.
37. Park, Y., McDonald, K.J., Choi, K.S. Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chem. Soc. Rev.*, 42, 2321–2337, 2013.
38. Kim, T.W., Choi, K.W. Nanoporous BiVO₄ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. *Science*, 343, 990–994, 2014.
39. Zhang, H., Zhou, W., Yang, Y., Cheng, C. 3D WO₃/BiVO₄/cobalt phosphate composites inverse opal photoanode for efficient photoelectrochemical water splitting. *Small*, 13, 1603840, 2017.
40. Park, H.S., Kweon, K.E., Ye, H., Paek, E., Hwang, G.S., Bard, A.J. Factors in the metal doping of BiVO₄ for improved photoelectrocatalytic activity as studied by scanning electrochemical microscopy and first-principles density-functional calculation. *J. Phys. Chem. C*, 115, 17870–17879, 2011.
41. Berglund, S.P., Rettie, A.J., Hoang, S., Mullins, C.B. Incorporation of Mo and W into nanostructured BiVO₄ films for efficient photoelectrochemical water oxidation. *Phys. Chem. Chem. Phys.*, 14, 7065–7075, 2012.
42. Zhou, M., Bao, J., Xu, Y., Zhang, J., Xie, J., Guan, M., Wang, C., Wen, L., Lei, Y., Xie, Y. Photoelectrodes based upon Mo:BiVO₄ inverse opals for photoelectrochemical water splitting. *ACS Nano*, 8, 7088–7098, 2014.
43. Luo, W., Li, Z., Yu, T., Zou, Z. Effects of surface electrochemical pretreatment on the photoelectrochemical performance of Mo-doped BiVO₄. *J. Phys. Chem. C*, 116, 5076–5081, 2012.
44. Qiu, Y., Liu, W., Chen, W., Chen, W., Zhou, G., Hsu, P.C., Zhang, R., Liang, Z., Fan, S., Zhang, Y., Cui, Y. Efficient solar-driven water splitting by nanocone BiVO₄-perovskite tandem cells. *Sci. Adv.*, 2, 2016.
45. Cherepy, N.J., Liston, D.B., Lovejoy, J.A., Deng, H., Zhang, J.H. Ultrafast studies of photoexcited electron dynamics in γ- and α-Fe₂O₃ semiconductor nanoparticles. *J. Phys. Chem. B*, 102, 770–776, 1998.
46. Kennedy, J.H., Frese, K.W. Photooxidation of water at α-Fe₂O₃ electrodes. *J. Electrochem. Soc.*, 125, 709–714, 1978.
47. Bosman, A., Van Daal, H. Small-polaron versus band conduction in some transition-metal oxides. *Adv. Phys.*, 19, 1–117, 1970.
48. Maruska, H.P., Ghosh, A.K. Photocatalytic decomposition of water at semiconductor electrodes. *Solar Energy*, 20, 443–458, 1978.

49. Butler, M. Photoelectrolysis and physical properties of the semiconducting electrode WO_2 . *J. Appl. Phys.*, 48, 1914–1920, 1977.
50. Ling, Y., Wang, G., Wheeler, D.A., Zhang, J.Z., Li, Y. Sn-doped hematite nanostructures for photoelectrochemical water splitting. *Nano Lett.*, 11, 2119–2125, 2011.
51. Wheeler, D.A., Wang, G., Ling, Y., Li, Y., Zhang, J.Z. Nanostructured hematite: synthesis, characterization, charge carrier dynamics, and photoelectrochemical properties *Energy Environ. Sci.*, 5, 6682–6702, 2012.
52. Kang, J.S., Noh, Y., Kim, J., Choi, H., Jeon, T.H., Ahn, D., Kim, J. Y., Yu, S.H., Park, H., Yum, J.H., Choi, W., Dunand, D.C., Choe, H., Sung, Y.E. Iron oxide photoelectrode with multidimensional architecture for highly efficient photoelectrochemical water splitting. *Angew. Chem.*, 129, 6683–6688, 2017.
53. Zhang, P., Wang, T., Chang, X., Zhang, L., Gong, J. Synergistic cocatalytic effect of carbon nanodots and Co_3O_4 nanoclusters for the photoelectrochemical water oxidation on hematite. *Angew. Chem. Int. Ed.*, 55, 5851–5855, 2016.
54. Peerakiatkhajohn, P., Yun, J.H., Chen, H., Lyu, M., Butburee, T., Wang, L. Stable hematite nanosheet photoanodes for enhanced photoelectrochemical water splitting. *Adv. Mater.*, 28, 6405–6410, 2016.
55. Tamirat, A.G., Su, W.N., Dubale, A.A., Chen, H.M., Hwang, B.J. Photoelectrochemical water splitting at low applied potential using a NiOOH coated codoped (Sn, Zr) $\alpha\text{-Fe}_2\text{O}_3$ photoanode. *J. Mater. Chem. A*, 3, 5949–5961, 2015.
56. Kumar, P., Sharma, P., Shrivastav, R., Dass, S., Satsangi, V.R. Electrodeposited zirconium-doped $\alpha\text{-Fe}_2\text{O}_3$ thin film for photoelectrochemical water splitting. *Int. J. Hydrogen Energy*, 36, 2777–2784, 2011.
57. Guijarro, N., Prévot, M.S., Yu, X., Jeanbourquin, X.A., Bornoz, P., Bourée, W., Johnson, M., Le Formal, F., Sivula, K. A bottom-up approach toward all-solution-processed high-efficiency Cu(In,Ga)S_2 photocathodes for solar water splitting. *Adv. Energy Mater.*, 6, 1501949, 2016.
58. Septina, W., Gunawan, Ikeda, S., Harada, T., Higashi, M., Abe, R., Matsumura, M. Photosplitting of water from wide-gap Cu(In,Ga)S_2 thin films modified with a CdS layer and Pt nanoparticles for a high-onset-potential photocathode. *J. Phys. Chem. C*, 119, 8576–8583, 2015.
59. Moriya, M., Minegishi, T., Kumagai, H., Katayama, M., Kubota, J., Domen, K. Stable hydrogen evolution from CdS -modified CuGaSe_2 photoelectrode under visible-light irradiation. *J. Am. Chem. Soc.*, 135, 3733–3735, 2013.
60. Azarpira, A., Lublow, M., Steigert, A., Bogdanoff, P., Greiner, D., Kaufmann, C.A., Krüger, M., Gernert, U., van de Krol, R., Fischer, A., Schedel-Niedrig, T. Efficient and stable $\text{TiO}_2\text{:Pt-Cu(In,Ga)Se}_2$ composite photoelectrodes for visible light driven hydrogen evolution. *Adv. Energy Mater.*, 5, 1402148, 2015.
61. Chae, S.Y., Park, S.J., Han, S.G., Jung, H., Kim, C.W., Jeong, C., Joo, O.S., Min, B.K., Hwang, Y.J. Enhanced photocurrents with ZnS passivated Cu(In,Ga)(Se,S)_2 photocathodes synthesized using a nonvacuum process for solar water splitting. *J. Am. Chem. Soc.*, 138, 15673–15681, 2016.

62. Zhao, J., Minegishi, T., Zhang, L., Zhong, M., Nakabayashi, M., Ma, G., Hisatomi, T., Katayama, M., Ikeda, S., Shibata, N. Enhancement of solar hydrogen evolution from water by surface modification with CdS and TiO₂ on porous CuInS₂ photocathodes prepared by an electrodeposition–sulfurization method. *Angew. Chem. Int. Ed.*, 53, 11808–11812, 2014.
63. Kaneko, H., Minegishi, T., Nakabayashi, M., Shibata, N., Domen, K. Enhanced hydrogen evolution under simulated sunlight from neutral electrolytes on (ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se₂)_{0.15} photocathodes prepared by a bilayer method. *Angew. Chem. Int. Ed.*, 55, 15329–15333, 2016.
64. Yu, X., Shavel, A., An, X., Luo, Z., Ibáñez, M., Cabot, A. Cu₂ZnSnS₄-Pt and Cu₂ZnSnS₄-Au heterostructured nanoparticles for photocatalytic water splitting and pollutant degradation. *J. Am. Chem. Soc.*, 136, 9236–9239, 2014.
65. Ji, L., McDaniel, M.D., Wang, S., Posadas, A.B., Li, X., Huang, H., Lee, J. C., Demkov, A.A., Bard, A.J., Ekerdt, J.G., Yu, E.T. A silicon-based photocathode for water reduction with an epitaxial SrTiO₃ protection layer and a nanostructured catalyst. *Nat. Nanotechnol.*, 10, 84, 2014.
66. Oh, J., Deutsch, T.G., Yuan, H.C., Branz, H.M. Nanoporous black silicon photocathode for H₂ production by photoelectrochemical water splitting. *Energy Environ. Sci.*, 4, 1690–1694, 2011.
67. Abdi, F.F., Han, L., Smets, A.H.M., Zeman, M., Dam, B., van de Krol, R. Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode. *Nat. Commun.*, 4, 2195, 2013.
68. Moniz, S.J.A., Shevlin, S.A., Martin, D.J., Guo, Z.X., Tang, J. Visible-light driven heterojunction photocatalysts for water splitting – a critical review. *Energy Environ. Sci.*, 8, 731–759, 2015.
69. Paracchino, A., Laporte, V., Sivula, K., Grätzel, M., Thimsen, E. Highly active oxide photocathode for photoelectrochemical water reduction. *Nat. Mater.*, 10, 456, 2011.
70. Paracchino, A., Mathews, N., Hisatomi, T., Stefik, M., Tilley, S.D., Gratzel, M. Ultrathin films on copper(I) oxide water splitting photocathodes: a study on performance and stability. *Energy Environ. Sci.*, 5, 8673–8681, 2012.
71. Morales-Guio, C.G., Liardet, L., Mayer, M.T., Tilley, S.D., Grätzel, M., Hu, X. Photoelectrochemical hydrogen production in alkaline solutions using Cu₂O coated with earth-abundant hydrogen evolution catalysts. *Angew. Chem. Int. Ed.*, 54, 664–667, 2015.
72. Li, Z., Zhang, Z. Tetrafunctional Cu₂S thin layers on Cu₂O nanowires for efficient photoelectrochemical water splitting. *Nano Res.*, 11, 1530–1540, 2018.
73. Gao, L., Cui, Y., Wang, J., Cavalli, A., Standing, A., Vu, T.T.T., Verheijen, M.A., Haverkort, J.E.M., Bakkers, E.P.A.M., Notten, P.H.L. Photoelectrochemical hydrogen production on InP nanowire arrays with molybdenum sulfide electrocatalysts. *Nano Lett.*, 14, 3715–3719, 2014.
74. Jia, J., Seitz, L.C., Benck, J.D., Huo, Y., Chen, Y., Ng, J.W.D., Bilir, T., Harris, J.S., Jaramillo, T.F. Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nat. Commun.*, 7, 13237, 2016.

75. Kamimura, J., Bogdanoff, P., Lähnemann, J., Hauswald, C., Geelhaar, L., Fiechter, S., Riechert, H. Photoelectrochemical properties of (In,Ga)N nanowires for water splitting investigated by *in situ* electrochemical mass spectroscopy. *J. Am. Chem. Soc.*, 135, 10242–10245, 2013.
76. Khaselev, O., Turner, J.A. A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. *Science*, 280, 425, 1998.
77. Walter, M.G., Warren, E.L., McKone, J.R., Boettcher, S.W., Mi, Q., Santori, E.A., Lewis, N.S. Solar water splitting cells. *Chem. Rev.*, 110, 6446–6473, 2010.
78. Zheng, X.L., Song, J.P., Ling, T., Hu, Z.P., Yin, P.F., Davey, K., Du, X. W., Qiao, S.Z. Strongly coupled nafion molecules and ordered porous CdS networks for enhanced visible-light photoelectrochemical hydrogen evolution. *Adv. Mater.*, 28, 4935–4942, 2016.
79. Su, J., Minegishi, T., Katayama, M., Domen, K. Photoelectrochemical hydrogen evolution from water on a surface modified CdTe thin film electrode under simulated sunlight. *J. Mater. Chem. A*, 5, 4486–4492, 2017.
80. Liu, S.H., Syu, H.R. One-step fabrication of N-doped mesoporous TiO₂ nanoparticles by self-assembly for photocatalytic water splitting under visible light. *Appl. Energy*, 100, 148–154, 2012.
81. Jang, E.S., Won, J.H., Hwang, S.J., Choy, J.H. Fine tuning of the face orientation of ZnO crystals to optimize their photocatalytic activity. *Adv. Mater.*, 18, 3309–3312, 2006.
82. Mazloom, J., Ghodsi, F.E., Golmojdeh, H. Synthesis and characterization of vanadium doped SnO₂ diluted magnetic semiconductor nanoparticles with enhanced photocatalytic activities. *J. Alloys Compounds*, 639, 393–399, 2015.
83. Dong, Y., He, K., Yin, L., Zhang, A. A facile route to controlled synthesis of Co₃O₄ nanoparticles and their environmental catalytic properties. *Nanotechnology*, 18, 435602, 2007.
84. Wu, Q., Han, R., Chen, P., Qi, X., Yao, W. Novel synthesis and photocatalytic performance of BiVO₄ with tunable morphologies and macroscopic structures. *Mater. Sci. Semicond. Process.*, 38, 271–277.
85. Li, J., Sun, F., Gu, K., Wu, T., Zhai, W., Li, W., Huang, S. Preparation of spindly CuO micro-particles for photodegradation of dye pollutants under a halogen tungsten lamp. *Appl. Catal. A: Gen.*, 406, 51–58, 2011.
86. Bao, N., Shen, L., Takata, T., Domen, K. Self-templated synthesis of nanoporous CdS nanostructures for highly efficient photocatalytic hydrogen production under visible light. *Chem. Mater.*, 20, 110–117, 2007.
87. Qiu, B., Zhu, Q., Du, M., Fan, L., Xing, M., Zhang, J. Efficient solar light harvesting CdS/Co₉S₈ hollow cubes for z-scheme photocatalytic water splitting. *Angew. Chem.*, 129, 2728–2732, 2017.
88. Ma, D., Shi, J.W., Zou, Y., Fan, Z., Ji, X., Niu, C. Highly efficient photocatalyst based on a CdS quantum dots/ZnO nanosheets 0D/2D heterojunction for hydrogen evolution from water splitting. *ACS Appl. Mater. Inter.*, 9, 25377–25386, 2017.

89. Liu, J., Liu, Y., Liu, N., Han, Y., Zhang, X., Huang, H., Lifshitz, Y., Lee, S.T., Zhong, J., Kang, Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science*, 347, 970–974, 2015.
90. Ji, C., Yin, S.N., Sun, S., Yang, S. An *in situ* mediator-free route to fabricate $\text{Cu}_2\text{O/g-C}_3\text{N}_4$ type-II heterojunctions for enhanced visible-light photocatalytic H_2 generation. *Appl. Surf. Sci.*, 434, 1224–1231, 2018.
91. Liu, Y., Yang, S., Yin, S.N., Feng, L., Zang, Y., Xue, H. *In situ* construction of fibrous AgNPs/g- C_3N_4 aerogel toward light-driven CO_x -free methanol dehydrogenation at room temperature. *Chem. Eng. J.*, 334, 2401–2407, 2018.
92. Zhang, Q., Yang, S., Yin, S.N., Xue, H. Over two-orders of magnitude enhancement of the photocatalytic hydrogen evolution activity of carbon nitride via mediator-free decoration with gold-organic microspheres. *Chem. Commun.*, 53, 11814–11817, 2017.
93. Liu, J., Zhang, Y., Lu, L., Wu, G., Chen, W. Self-regenerated solar-driven photocatalytic water-splitting by urea derived graphitic carbon nitride with platinum nanoparticles. *Chem. Commun.*, 48, 8826–8828, 2012.
94. Rodriguez, M.M., Peng, X., Liu, L., Li, Y., Andino, J.M. A density functional theory and experimental study of CO_2 interaction with brookite TiO_2 . *J. Phys. Chem. C*, 116, 19755–19764, 2012.
95. Pan, Y.X., Liu, C.J., Mei, D., Ge, Q. Effects of hydration and oxygen vacancy on CO_2 adsorption and activation on $\beta\text{-Ga}_2\text{O}_3(100)$. *Langmuir*, 26, 5551–5558, 2010.
96. Dutta, D., Wood, B.C., Bhide, S.Y., Ayappa, K.G., Narasimhan, S. Enhanced gas adsorption on graphitic substrates via defects and local curvature: A density functional theory study. *J. Phys. Chem. C*, 118, 7741–7750, 2014.
97. Iwashina, K., Kudo, A. Rh-doped SrTiO_3 photocatalyst electrode showing cathodic photocurrent for water splitting under visible-light irradiation. *J. Am. Chem. Soc.*, 133, 13272–13275, 2011.
98. Townsend, T.K., Browning, N.D., Osterloh, F.E. Overall photocatalytic water splitting with $\text{NiO}_x\text{-SrTiO}_3$ – a revised mechanism. *Energy Environ. Sci.*, 5, 9543–9550, 2012.
99. Asai, R., Nemoto, H., Jia, Q., Saito, K., Iwase, A., Kudo, A. A visible light responsive rhodium and antimony-codoped SrTiO_3 powdered photocatalyst loaded with an IrO_2 cocatalyst for solar water splitting. *Chem. Commun.*, 50, 2543–2546, 2014.
100. Mu, L., Zhao, Y., Li, A., Wang, S., Wang, Z., Yang, J., Wang, Y., Liu, T., Chen, R., Zhu, J. Enhancing charge separation on high symmetry SrTiO_3 exposed with anisotropic facets for photocatalytic water splitting. *Energy Environ. Sci.*, 9, 2463–2469, 2016.
101. Wang, Q., Hisatomi, T., Suzuki, T., Pan, Z., Seo, J., Katayama, M., Minegishi, T., Nishiyama, H., Takata, T., Seki, K. Particulate photocatalyst sheets based on carbon conductor layer for efficient z-scheme pure-water splitting at ambient pressure. *J. Am. Chem. Soc.*, 139, 1675–1683, 2017.

102. Wang, Q., Hisatomi, T., Jia, Q., Tokudome, H., Zhong, M., Wang, V., Pan, Z., Takata, T., Nakabayashi, M., Shibata, N. Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nat. Mater.*, 15, 611, 2016.
103. Zhang, G., Lan, Z.A., Lin, L., Lin, S., Wang, X. Overall water splitting by Pt/g-C₃N₄ photocatalysts without using sacrificial agents. *Chem. Sci.*, 7, 3062–3066, 2016.
104. Pan, Z., Zheng, Y., Guo, F., Niu, P., Wang, X. Decorating CoP and Pt nanoparticles on graphitic carbon nitride nanosheets to promote overall water splitting by conjugated polymers. *ChemSusChem*, 10, 87–90, 2017.
105. Liu, W., Cao, L., Cheng, W., Cao, Y., Liu, X., Zhang, W., Mou, X., Jin, L., Zheng, X., Che, W. Single-site active cobalt-based photocatalyst with long carriers lifetime for spontaneous overall water splitting. *Angew. Chem. Int. Ed.*, 129, 9440–9445, 2017.
106. Vaiano, V., Sacco, O., Sannino, D., Ciambelli, P. Nanostructured N-doped TiO₂ coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation. *Appl. Catal. B: Environ.*, 170–171, 153–161, 2015.
107. Zhang, Y., Zhao, Z., Chen, J., Cheng, L., Chang, J., Sheng, W., Hu, C., Cao, S. C-doped hollow TiO₂ spheres: *in situ* synthesis, controlled shell thickness, and superior visible-light photocatalytic activity. *Appl. Catal. B: Environ.*, 165, 715–722, 2015.
108. Ohno, T., Akiyoshi, M., Umebayashi, T., Asai, K., Mitsui, T., Matsumura, M. Preparation of S-doped TiO₂ photocatalysts and their photocatalytic activities under visible light. *Appl. Catal. A: Gen.*, 265, 115–121, 2004.
109. An, H., Zhou, J., Li, J., Zhu, B., Wang, S., Zhang, S., Wu, S., Huang, W. Deposition of Pt on the stable nanotubular TiO₂ and its photocatalytic performance. *Catal. Commun.*, 11, 175–179, 2009.
110. Zheng, Z., Huang, B., Qin, X., Zhang, X., Dai, Y., Whangbo, M.H. Facile *in situ* synthesis of visible-light plasmonic photocatalysts M@TiO₂ (M = Au, Pt, Ag) and evaluation of their photocatalytic oxidation of benzene to phenol. *J. Mater. Chem.*, 21, 9079, 2011.
111. Li, C., Hsieh, Y., Chiu, W., Liu, C., Kao, C. Study on preparation and photocatalytic performance of Ag/TiO₂ and Pt/TiO₂ photocatalysts. *Sep. Purif. Technol.*, 58, 148–151, 2007.
112. Wang, D., Duan, Y., Luo, Q., Li, X., An, J., Bao, L., Shi, L. Novel preparation method for a new visible light photocatalyst: mesoporous TiO₂ supported Ag/AgBr. *J. Mater. Chem.*, 22, 4847, 2012.
113. Ibhaddon, A.O., Greenway, G.M., Yue, Y. Photocatalytic activity of surface modified TiO₂/RuO₂/SiO₂ nanoparticles for azo-dye degradation. *Catal. Commun.*, 9, 153–157, 2008.
114. Ke, D., Liu, H., Peng, T., Liu, X., Dai, K. Preparation and photocatalytic activity of WO₃/TiO₂ nanocomposite particles. *Mater. Lett.*, 62, 447–450, 2008.

115. Bessekhoud, Y., Robert, D., Weber, J.V. $\text{Bi}_2\text{S}_3/\text{TiO}_2$ and CdS/TiO_2 heterojunctions as an available configuration for photocatalytic degradation of organic pollutant. *J. Photoch. Photobio. A*, 163, 569–580, 2004.
116. Ni, M., Leung, M.K.H., Leung, D.Y.C., Sumathy, K. A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. *Renew. Sust. Energy Rev.*, 11, 401–425, 2007.
117. Iwase, A., Kato, H., Kudo, A. The effect of Au cocatalyst loaded on La-doped NaTaO_3 on photocatalytic water splitting and O_2 photoreduction. *Appl. Catal. B: Environ.*, 136, 89–93, 2013.
118. Iwashina, K., Iwase, A., Ng, Y.H., Amal, R., Kudo, A. Z-schematic water splitting into H_2 and O_2 using metal sulfide as a hydrogen-evolving photocatalyst and reduced graphene oxide as a solid-state electron mediator. *J. Am. Chem. Soc.*, 137, 604–607, 2015.
119. He, Z., Fu, J., Cheng, B., Yu, J., Cao, S. $\text{Cu}_2(\text{OH})_2\text{CO}_3$ clusters: novel noble-metal-free cocatalysts for efficient photocatalytic hydrogen production from water splitting. *Appl. Catal. B: Environ.*, 205, 104–111, 2017.
120. Preethi, L., Mathews, T., Nand, M., Jha, S., Gopinath, C.S., Dash, S. Band alignment and charge transfer pathway in three phase anatase-rutile-brookite TiO_2 nanotubes: an efficient photocatalyst for water splitting. *Appl. Catal. B: Environ.*, 218, 9–19, 2017.
121. Tanaka, A., Teramura, K., Hosokawa, S., Kominami, H., Tanaka, T. Visible light-induced water splitting in an aqueous suspension of a plasmonic Au/TiO_2 photocatalyst with metal co-catalysts. *Chem. Sci.*, 8, 2574–2580, 2017.
122. Wang, P., Zhan, S., Xia, Y., Ma, S., Zhou, Q., Li, Y. The fundamental role and mechanism of reduced graphene oxide in $\text{rGO}/\text{Pt-TiO}_2$ nanocomposite for high-performance photocatalytic water splitting. *Appl. Catal. B: Environ.*, 207, 335–346, 2017.
123. Yang, Y., Gao, P., Wang, Y., Sha, L., Ren, X., Zhang, J., Chen, Y., Wu, T., Yang, P., Li, X. A direct charger transfer from interface to surface for the highly efficient spatial separation of electrons and holes: the construction of Ti–C bonded interfaces in TiO_2 -C composite as a touchstone for photocatalytic water splitting. *Nano Energy*, 33, 29–36, 2017.
124. Daskalaki, V.M., Panagiotopoulou, P., Kondarides, D.I. Production of peroxide species in Pt/TiO_2 suspensions under conditions of photocatalytic water splitting and glycerol photoreforming. *Chem. Eng. J.*, 170, 433–439, 2011.
125. Liu, Z., Hou, W., Pavaskar, P., Aykol, M., Cronin, S.B. Plasmon resonant enhancement of photocatalytic water splitting under visible illumination. *Nano Lett.*, 11, 1111–1116, 2011.
126. Bai, S., Yang, L., Wang, C., Lin, Y., Lu, J., Jiang, J., Xiong, Y. Boosting photocatalytic water splitting: interfacial charge polarization in atomically controlled core-shell cocatalysts. *Angew. Chem. Int. Ed.*, 54, 14810–14814, 2015.
127. Ning, X., Li, J., Yang, B., Zhen, W., Li, Z., Tian, B., Lu, G. Inhibition of photo-corrosion of CdS via assembling with thin film TiO_2 and removing formed

- oxygen by artificial gill for visible light overall water splitting. *Appl. Catal. B: Environ.*, 212, 129–139, 2017.
128. Liu, Y., Yin, S.N., Yang, S. Glutathione as both ligand and sulfur source for the synthesis of full-color luminescent water-soluble CdS nanocrystals. *Mater. Lett.*, 196, 260–263, 2017.
 129. Holmes, M.A., Townsend, T.K., Osterloh, F.E. Quantum confinement controlled photocatalytic water splitting by suspended CdSe nanocrystals. *Chem. Commun.*, 48, 371–373, 2012.
 130. Zhang, X., Li, Y., Zhao, J., Wang, S., Li, Y., Dai, H., Sun, X. Advanced three-component ZnO/Ag/CdS nanocomposite photoanode for photocatalytic water splitting. *J. Power Sources*, 269, 466–472, 2014.
 131. Yürüm, Y., Taralp, A., Veziroglu, T.N. Storage of hydrogen in nanostructured carbon materials. *Int. J. Hydrogen Energy*, 34, 3784–3798, 2009.
 132. Kudo, A., Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.*, 38, 253–278, 2009.
 133. Wang, F., Di Valentin, C., Pacchioni, G. Doping of WO_3 for photocatalytic water splitting: hints from density functional theory. *J. Phys. Chem. C*, 116, 8901–8909, 2012.
 134. Ohno, T., Bai, L., Hisatomi, T., Maeda, K., Domen, K. Photocatalytic water splitting using modified GaN:ZnO solid solution under visible light: long-time operation and regeneration of activity. *J. Am. Chem. Soc.*, 134, 8254–8259, 2012.
 135. Dionigi, F., Vesborg, P.C., Pedersen, T., Hansen, O., Dahl, S., Xiong, A., Maeda, K., Domen, K., Chorkendorff, I. Gas phase photocatalytic water splitting with $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3/\text{GaN:ZnO}$ in μ -reactors. *Energy Environ. Sci.*, 4, 2937–2942, 2011.
 136. Qi, Y., Chen, S., Li, M., Ding, Q., Li, Z., Cui, J., Dong, B., Zhang, F., Li, C. Achievement of visible-light-driven z-scheme overall water splitting using barium-modified Ta_3N_5 as a H_2 -evolving photocatalyst. *Chem. Sci.*, 8, 437–443, 2017.
 137. Wang, D., Pierre, A., Kibria, M.G., Cui, K., Han, X., Bevan, K.H., Guo, H., Paradis, S., Hakima, A.R., Mi, Z. Wafer-level photocatalytic water splitting on GaN nanowire arrays grown by molecular beam epitaxy. *Nano Lett.*, 11, 2353–2357, 2011.
 138. Sayama, K., Yoshida, R., Kusama, H., Okabe, K., Abe, Y., Arakawa, H. Photocatalytic decomposition of water into H_2 and O_2 by a two-step photo-excitation reaction using a WO_3 suspension catalyst and an $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system. *Chem. Phys. Lett.*, 277, 387–391, 1997.
 139. Sasaki, Y., Nemoto, H., Saito, K., Kudo, A. Solar water splitting using powdered photocatalysts driven by z-schematic interparticle electron transfer without an electron mediator. *J. Phys. Chem. C*, 113, 17536–17542, 2009.
 140. Kato, H., Sasaki, Y., Shirakura, N., Kudo, A. Synthesis of highly active rhodium-doped SrTiO_3 powders in z-scheme systems for visible-light-driven

- photocatalytic overall water splitting. *J. Mater. Chem. A*, 1, 12327–12333, 2013.
141. Abe, R., Sayama, K., Domen, K., Arakawa, H. A new type of water splitting system composed of two different TiO_2 photocatalysts (anatase, rutile) and a IO_3^-/I^- shuttle redox mediator. *Chem. Phys. Lett.*, 344, 339–344, 2001.
 142. Abe, R., Takata, T., Sugihara, H., Domen, K. Photocatalytic overall water splitting under visible light by TaON and WO_3 with an IO_3^-/I^- shuttle redox mediator. *Chem. Commun.*, 0, 3829–3831, 2005.
 143. Maeda, K., Terashima, H., Kase, K., Higashi, M., Tabata, M., Domen, K. Surface modification of TaON with monoclinic ZrO_2 to produce a composite photocatalyst with enhanced hydrogen evolution activity under visible light. *Bull. Chem. Soc. Japan*, 81, 927–937, 2008.
 144. Sayama, K., Mukasa, K., Abe, R., Abe, Y., Arakawa, H. Stoichiometric water splitting into H_2 and O_2 using a mixture of two different photocatalysts and an IO_3^-/I^- shuttle redox mediator under visible light irradiation. *Chem. Commun.*, 2416–2417, 2001.
 145. Wang, X., Liu, G., Wang, L., Chen, Z.G., Lu, G.Q.M., Cheng, H.M. ZnO–CdS@ Cd heterostructure for effective photocatalytic hydrogen generation. *Adv. Energy Mater.*, 2, 42–46, 2012.
 146. Ding, L., Zhou, H., Lou, S., Ding, J., Zhang, D., Zhu, H., Fan, T. Butterfly wing architecture assisted CdS/Au/ TiO_2 z-scheme type photocatalytic water splitting. *Int. J. Hydrogen Energy*, 38, 8244–8253, 2013.
 147. Tada, H., Mitsui, T., Kiyonaga, T., Akita, T., Tanaka, K. All-solid-state z-scheme in CdS–Au– TiO_2 three-component nanojunction system. *Nat. Mater.*, 5, 782, 2006.
 148. Iwase, A., Ng, Y.H., Ishiguro, Y., Kudo, A., Amal, R. Reduced graphene oxide as a solid-state electron mediator in z-scheme photocatalytic water splitting under visible light. *J. Am. Chem. Soc.*, 133, 11054–11057, 2011.
 149. Ma S.S.K., Maeda K., Hisatomi T., Tabata M., Kudo A., Domen K. A redox-mediator-free solar-driven z-scheme water-splitting system consisting of modified Ta_3N_5 as an oxygen-evolution photocatalyst. *Chem.-Eur. J.*, 19, 7480–7486, 2013.
 150. Kato, H., Sasaki, Y., Iwase, A., Kudo, A. Role of iron ion electron mediator on photocatalytic overall water splitting under visible light irradiation using z-scheme systems. *Bull. Chem. Soc. Japan*, 80, 2457–2464, 2007.
 151. Modak, B., Ghosh, S.K. Exploring the role of La codoping beyond charge compensation for enhanced hydrogen evolution by Rh– SrTiO_3 . *J. Phys. Chem. B*, 119, 11089–11098, 2015.
 152. Soedergrén, S., Hagfeldt, A., Olsson, J., Lindquist, S.E. Theoretical models for the action spectrum and the current-voltage characteristics of microporous semiconductor films in photoelectrochemical cells. *J. Phys. Chem.*, 98, 5552–5556, 1994.
 153. Hagfeldt, A., Björkstén, U., Lindquist, S.E. Photoelectrochemical studies of colloidal TiO_2 -films: the charge separation process studied by means of

- action spectra in the UV region. *Solar Energy Mater. Solar Cells*, 27, 293–304, 1992.
154. Osterloh, F.E. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.*, 42, 2294–2320, 2013.
 155. Chen, H.M., Chen, C.K., Liu, R.S., Zhang, L., Zhang, J., Wilkinson, D.P. Nano-architecture and material designs for water splitting photoelectrodes. *Chem. Soc. Rev.*, 41, 5654–5671.
 156. Warren, S.C., Thimsen, E. Plasmonic solar water splitting. *Energy Environ. Sci.*, 5, 5133–5146, 2012.
 157. Kohl, P.A., Frank, S.N., Bard, A.J. Semiconductor electrodes XI. behavior of n- and p-type single crystal semiconductors covered with thin n-TiO₂ films. *J. Electrochem. Soc.*, 124, 225–229, 1977.
 158. Huang, S., Zhang, H., Wu, Z., Kong, D., Lin, D., Fan, Y., Yang, X., Zhong, Z., Huang, S., Jiang, Z. Large-area ordered p-type Si nanowire arrays as photocathode for highly efficient photoelectrochemical hydrogen generation. *ACS Appl. Mater. Inter.*, 6, 12111–12118, 2014.
 159. Guo, L., Hung, D., Wang, W., Shen, W., Zhu, L., Chien, C.L., Searson, P.C. Tunnel barrier photoelectrodes for solar water splitting. *Appl. Phys. Lett.*, 97, 063111, 2010.
 160. Yoon, K.H., Shin, C.W., Kang, D.H. Photoelectrochemical conversion in a WO₃ coated p-Si photoelectrode: effect of annealing temperature. *J. Appl. Phys.*, 81, 7024–7029, 1997.
 161. Zhang, Z., Dua, R., Zhang, L., Zhu, H., Zhang, H., Wang, P. Carbon-layer-protected cuprous oxide nanowire arrays for efficient water reduction. *ACS Nano*, 7, 1709–1717, 2013.

Part II

PHOTOACTIVE MATERIALS FOR SOLAR HYDROGEN GENERATION

Hematite Materials for Solar-Driven Photoelectrochemical Cells

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Abstract

This chapter presents the recent endeavors in developing hematite as a photoanode candidate for solar-driven photoelectrochemical cells. Hematite stands out from other photoanodes due to its favorable optical bandgap (~ 2.2 eV), high theoretical solar-to-hydrogen conversion efficiency (14–17%) and economic viability. The chapter covers discussions on the physical properties (crystal structure, optical and electrical characteristics) of hematite, recent developed synthesis strategies of high-performance hematite photoanodes, and mechanistic understandings of the photoelectrochemical processes pertaining to light absorption, charge carrier separation and surface kinetics of water oxidation. Challenges and opportunities to further improve the photocurrent density of hematite-based photoanodes are discussed at last. Each section is exemplified with relevant highly cited papers.

Keywords: Hematite, photoelectrochemical cells, photoanodes, water splitting, mechanistic understandings, synthesis strategies

5.1 Introduction

Since the seminal research on hydrogen generation by photoelectrochemical (PEC) water splitting at a titanium dioxide (TiO_2) semiconductor surface [1], the pursuit for low-cost photoelectrode materials to realize cost-effective hydrogen production has progressed. Particularly, hematite ($\alpha\text{-Fe}_2\text{O}_3$) has sparked interest in recent decades as a photoanode due to

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its narrow bandgap (~ 2.2 eV), high thermodynamic stability, and its most economically significant factor: natural abundance.

Although hydrogen generation does not take place directly on a photoanode surface, the photoanode is indispensable for sustaining such a process. As shown in Figure 5.1, upon illumination with solar light, the photoanode generates pairs of electrons and holes (together termed excitons). These holes diffuse to the surface of the photoanode and oxidize water to oxygen, while the electrons are directed via an outer electric circuit to a semiconductor photocathode (e.g., silicon) or a metallic cathode (e.g., platinum). The electrons then migrate to the surface of the photocathode where they reduce water to evolve hydrogen gas. However, if holes cannot be successfully directed to interact with water molecules, they will recombine with the generated electrons and perish. As a result, fewer electrons can reduce water and the yield of hydrogen gas will decrease. The electron–hole recombination is a notable limiting factor of the PEC performance of a wide range of photoanodes.

Hematite stands out as a promising photoanode material because it is able to harvest solar energy spanning both visible and ultraviolet light, a much wider range compared to other photoanodes with larger bandgaps,

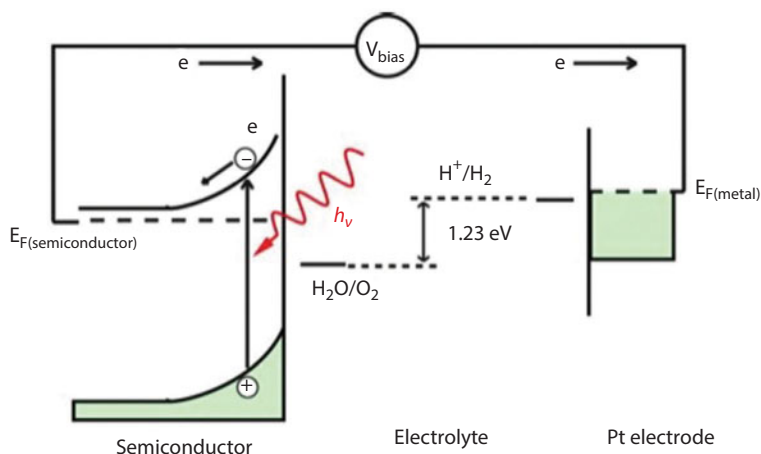


Figure 5.1 A schematic illustration of the working mechanism of a PEC cell. Upon illumination, the semiconductor (left, a photoanode) generates electrons and holes that are used for hydrogen generation and oxygen evolution, respectively. The Pt electrode (right, a cathode) functions as an electron reservoir that accepts electrons from the photoanode and reduces water to hydrogen gas on its surface. The flow of electrons is driven by an external bias (V_{bias}).

such as TiO_2 (3.2 eV) and WO_3 (2.6–2.8 eV). In addition, with a band-gap around 2.2 eV, hematite exhibits a high theoretical solar-to-hydrogen (STH) efficiency of 14–17% and a theoretical photocurrent density of 12 mA/cm² under standard air mass 1.5G illumination (100 mW/cm²). Although this is well above the benchmark STH efficiency of 10%, which is generally required for commercial applications, hematite as a photoanode has yet to reach its theoretical limit. Factors limiting the STH efficiency of hematite are the material's low photon absorption coefficient, electron–hole recombination, short hole diffusion length (2–4 nm), poor electronic properties, and sluggish water oxidation kinetics (see Section 5.2.5).

In this chapter, we will concentrate on the promises and challenges of using hematite as a photoanode material for PEC hydrogen generation. We begin by presenting the physical properties of hematite, including crystal structure, optical properties, and electronic properties that are associated with PEC applications, as well as challenges rooted in the intrinsic physical properties of hematite for achieving excellent PEC performance (Section 5.2). Section 5.3 will review the developed strategies that address the aforementioned intrinsic challenges and exemplify them with state-of-the-art experimental works. Section 5.4 will summarize recent advancement in fundamental understandings on the mechanisms of the developed strategies introduced in Section 5.3.

5.2 Physical Properties of Hematite

5.2.1 Crystal Structure

Hematite is the most common naturally occurring and thermodynamically stable polymorph of iron oxide. It is dense (5.26 g/cm³), hard (6.5 on Mohs scale), and decomposes at a very high temperature (91566 °C) [2]. It is isostructural with corundum ($\alpha\text{-Al}_2\text{O}_3$). Hematite crystallizes in a rhombohedral lattice system belonging to the space group $R\bar{3}c$ with lattice parameters of $a = 5.0356 \text{ \AA}$, $c = 13.7489 \text{ \AA}$. [3]

The structure of the unit cell of hematite is shown in Figure 5.2a. The O^{2-} anions are arranged in a hexagonal closed-packed lattice along the [001] c -axis direction; the Fe^{3+} cations occupy two-thirds of the octahedra consisting of the (001) basal planes, forming Fe_2O_9 dimers and iron bilayers. Each adjacent pair of Fe_2O_9 dimers shares its faces and configures a trigonal distortion, where iron atoms are repelled and the O—O distance in shared faces is shorter than in unshared faces.

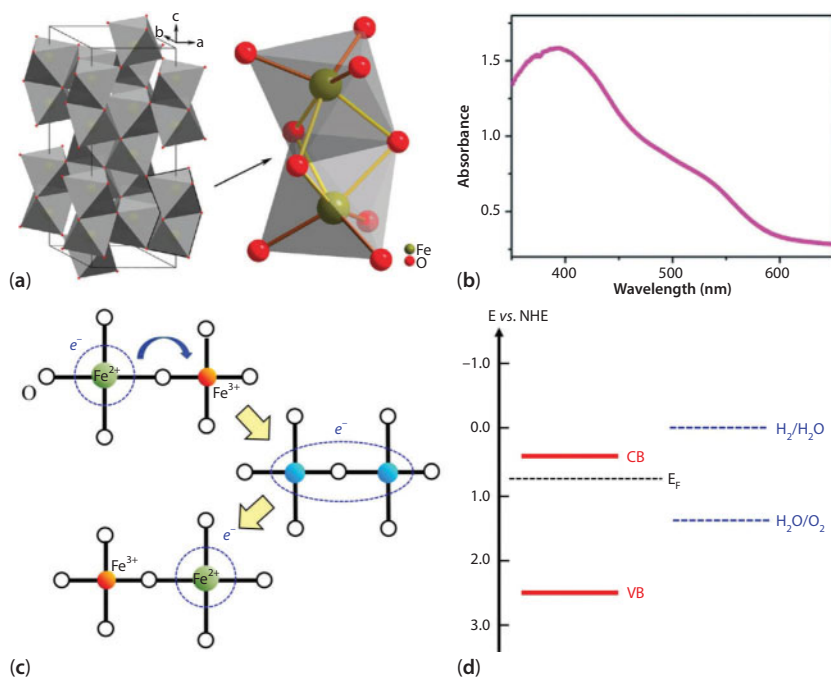


Figure 5.2 Physical properties of hematite. (a) Crystal structure; (b) light absorption profile; (c) an illustration depicting the “polaron hopping” mechanism: a $\text{Fe}^{2+/3+}$ valence alternation during the electron hopping between adjacent iron atoms in hematite. Longer Fe-O bonds are associated with the larger Fe^{2+} cation; (d) the band structure of hematite showing the location of VB, CB, E_F with the potentials for OER ($\text{H}_2\text{O}/\text{O}_2$) and HER ($\text{H}_2/\text{H}_2\text{O}$) added for comparison. Figures reproduced with permission from (a) Ref. [15], Copyright 2010, American Chemical Society and (b) Ref. [16], Copyright 2014, Royal Society of Chemistry.

5.2.2 Optical Properties

Hematite has a high refractive index of 3.15 and transmits orange to infrared light. The characteristic red color results from the indirect bandgap of hematite with typical values between 1.9 eV and 2.2 eV (corresponding to wavelength between 625 nm and 564 nm). The variation in bandgap correlates with different fabrication techniques that yield hematite with different degrees of crystallinity and concentration of defects. Generally, high crystallinity degrees and few defects reduce the bandgap [4].

In addition, the light-harvesting efficiency (LHE) of hematite, measuring the percentage of photons absorbed, is determined by the following equation:

$$\text{LHE} = 1 - e^{-\alpha l} \quad (5.1)$$

where α is the absorption coefficient of hematite (wavelength-dependent) and l is its length. In order to absorb 95% of incident light at a given wavelength, hematite must be $3/\alpha$ thick. Given $\alpha = 84700 \text{ cm}^{-1}$ at 550 nm (the wavelength corresponding to hematite's bandgap), the thickness of a hematite film required to capture 95% of incident photons is ~ 350 nm. However, the 550 nm light can only penetrate 118 nm (penetration depth is defined as α^{-1} at a certain wavelength, representing the length over which 63.2% of the incident photons are absorbed) [5]. This discrepancy indicates that proper morphological engineering is needed for hematite to maximize its light-harvesting efficiency.

Figure 5.3b presents an absorption spectrum collected from a hematite thin film deposited on F-doped tin oxide substrate (FTO, a transparent and conductive substrate commonly used for hematite growth). The strong absorption peak centered at ~ 400 nm is ascribed to indirect charge transitions from the O 2p nonbonding orbitals to the Fe 3d orbitals, and pair excitations of two adjacent Fe^{3+} cations [6]. A weak and broad absorption around 575 nm is assigned to spin-forbidden d-d ligand field transitions.

5.2.3 Electronic Properties

The carrier mobility of hematite is extremely low. For example, at room temperature, its electron mobility is on the order of $0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (compared to $1350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for silicon). This is because in hematite, extremely strong electron-phonon interactions cause trapping of the free electrons or holes by local lattice distortion. The trapped charge carriers and the distorted local lattice together are termed “small polarons.” Smart *et al.* claimed that small polarons in pristine hematite evolve naturally at Fe sites [7]. Small polarons migrate through the lattice of hematite by hopping between adjacent iron atoms to transport charge carriers (“polaron hopping”), with the hopping energy provided by thermal excitation [7]. A schematic illustration of the hopping process is shown in Figure 5.2c. Due to the increased effective mass of the charge carrier induced by small polarons, the mobility of charge carriers in hematite is exceedingly sluggish and the electrical conductivity of hematite is poor [8]. Pure sintered polycrystalline hematite showed low electrical conductivities around $10^{-14} \Omega^{-1}\text{cm}^{-1}$ [3].

In addition to low mobility and electrical conductivity, hematite has a number of disadvantages as a photoanode. The first limitation is the short-lived lifetime (3–10 ps) of excitons and ultrashort hole diffusion length (2–4 nm). Durrant and coworkers reported that within the first 6 picoseconds (ps) after light irradiation, half of excitons are recombined in the

bulk [9]. As a consequence, excitons induced by photon absorption will transiently recombine and vanish. The recombination is particularly frequent for holes (minority charge carriers) generated in the bulk of hematite, since in the bulk of *n*-type semiconductors, electrons (majority carriers) are abundant (*a.k.a.* high density of trap states). The second hurdle is the sluggish OER kinetics. While mainly associated with the high activation energy of certain intermediate steps toward OER (discussed in detail in Section 5.4.4.1), the sluggish OER kinetics also correlate with the strong interaction between holes and electrons, hole trapping by mid-bandgap electronic states, internal defect-induced trap states, and to a lesser extent, surface defects [6]. The accumulation of holes at the semiconductor's surface causes a sluggish OER rate constant of $0.1\text{--}10\text{ s}^{-1}$ [10].

Despite the overall limited electrical conductivity, its magnitude is anisotropic. The electrical conductivity is four times higher in basal planes than that along the [001] direction, due to the hopping mechanism related to $\text{Fe}^{2+}/\text{Fe}^{3+}$ valence state alternation within the iron bilayers [11]. A study by Patra *et al.* showed that the photocatalytic activity of bitruncated-dodecahedron nanocrystals with exposed (104), (100), and (001) was higher than bitruncated-octahedral nanocrystals with exposed (101) and (001), and still higher than nanorods with exposed (001) and (110). The nanocuboids with (012) showed the lowest photocatalytic activity [12].

5.2.4 Band Structure

Hematite is an indirect bandgap semiconductor. As shown in Figure 5.1d, its valence band (VB) maximum and conduction band (CB) minimum lie at 2.4–2.7 V (*vs.* reversible hydrogen electrode, RHE) and 0.3–0.6 V (*vs.* RHE), respectively. The VB is strongly hybridized by O^{2-} 2p orbitals and Fe^{2+} 3d orbitals (intrinsic defects), but due to limited concentration of Fe^{2+} , the VB is reported to be mostly O^{2-} 2p in nature [13]. A recent study demonstrates that the degree of such hybridization can be tuned by using different synthesis methods which result in modified PEC performance [14]. The CB is primarily composed of Fe^{3+} 3d orbitals. As an *n*-type semiconductor, hematite's fermi level (E_F) is located close to the CB. Change in charge carrier concentration by introducing defects and/or dopants can shift the E_F position.

Due to its band structure, hematite can be combined with a cathode (such as a Pt cathode) to sustain simultaneous generation of hydrogen gas and oxygen gas. However, by itself, hematite cannot drive such the simultaneous generation. Its VB sits below the oxygen evolution reaction (OER) potential which allows holes generated by hematite to oxidize water into

oxygen without any external energy input. However, its CB sits below the potential needed for the hydrogen evolution reaction (HER). This configuration requires an average external bias of 0.4 V (the theoretical overpotential) to elevate the CB to above 0 V vs. RHE in order to initiate water oxidation. In experiments, overpotential is even higher than the theoretical value due to sluggish OER kinetics. The high overpotential demands a large amount of energy input for hydrogen production.

5.2.5 Overview of Hematite Bottlenecks and Corresponding Strategies

The limitations of hematite hampering its PEC performance include (1) poor light absorption efficiency due to its indirect bandgap, (2) short photohole lifetime and hole diffusion length, as well as (3) sluggish surface OER kinetics. The key to successfully utilizing hematite as a feasible photoanode lies in tackling the aforementioned limitations of the material. The ultimate goal of hematite modifications is to improve the saturated photocurrent density with little applied external bias or with low onset potential (Figure 5.3a).

There are five critical steps for a typical PEC process (Figure 5.3b): (1) Hematite absorbs incident photons with energy larger than its bandgap [“light absorption,” (1)]. (2) Electrons are excited from the VB to CB [“charge separation,” (2)]. (3) The excitation and separation are followed by electron–hole recombination in the bulk within the first several picoseconds. (4) Only the holes which evolve near the surface and manage to reach the hematite–water interface can potentially participate in subsequent water oxidation reactions (3). Due to the sluggish OER kinetics of hematite, a portion of the surface holes will be scavenged by electrons via surface charge recombination and cannot oxidize water [“surface charge recombination,” (4)]. (5) The surviving holes will transfer to water molecules [“charge injection,” (5)] and contribute to a photocurrent.

Equation 5.1 shows the correlation of experimentally observed photocurrent density (J_{exp}) with theoretical photocurrent density (J_{theo}). Three efficiencies associated with three different steps play key roles in dictating the magnitude of observed photocurrent density. The three efficiency terms, η_{abs} , η_{sep} , η_{inj} represent the efficiency of the aforementioned “light absorption,” “charge separation,” and “charge injection,” respectively.

$$J_{\text{exp}} = J_{\text{theo}} \times \eta_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{inj}} \quad (5.2)$$

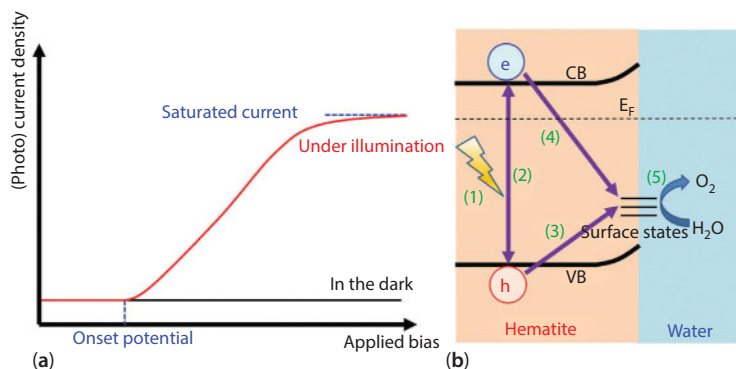


Figure 5.3 (a) A schematic illustration showing a typical linear scan voltammogram (LSV) profile for a semiconductor-based photoelectrode. When placed in the dark, the current density produced by the electrode is negligible due to a lack of electron excitation. Upon illumination with sufficient energy, electrons are excited to the CB and correspondingly leave identical amount of holes at the VB. At the onset potential, the photoinduced electrons can be extracted from hematite and a current becomes discernible. Current increases with increasing applied bias (more electrons are extracted) until reaching a plateau, *i.e.*, the saturated photocurrent. Further increasing bias will decompose water and raise the current again. (b) A schematic illustration showing the key steps of hematite-assisted water splitting (the dotted line represents the location of E_F): (1) light absorption; (2) charge separation; (3) hole transport to surface; (4) surface electron–hole recombination; and (5) hole injection. Please refer to the second paragraph of Section 5.2.5 for the definitions of these processes.

The J_{theo} of hematite is $\sim 12 \text{ mA/cm}^2$, but experimental values typically fall below 5 mA/cm^2 . This discrepancy is due to the fact that three efficiency terms are far less than unity. Therefore, worldwide researchers have demonstrated and continue exploring ways to enhance one or more of the efficiencies. The following section will present a brief overview of demonstrated methods which target the shortcoming(s) of hematite. Representative and state-of-the-art examples of each method will be elaborated in Section 5.3, and the progress of fundamental understandings on mechanisms will follow as Section 5.4.

5.2.5.1 Addressing Poor Light Absorption Efficiency

Hematite is superior to other *n*-type semiconductors in its ability to absorb light of wavelengths up to 600 nm (which includes part of the visible spectrum). Unfortunately, its indirect bandgap requires the aid of phonons for electron excitation. The involvement of phonons makes the excitation process less likely to happen than in direct bandgap semiconductors.

Although the indirect bandgap nature can hardly be altered, coupling of species which aid the light absorption of hematite helps to improve η_{abs} . These species can be noble metals (e.g., Au) with surface plasmons that boost light absorption [17, 18], as well as semiconductors that upconvert infrared light to visible light that is able to be absorbed by hematite [19].

5.2.5.2 Addressing Fast Charge Carrier Recombination

One of the main limitations in using hematite as a photoanode is the high rate of recombination between photogenerated excitons. With a light penetration depth of 118 nm at 550 nm and a hole diffusion length of only 2–4 nm, charge transport is inefficient and holes generated very near the electrode's surface become the only holes available for OER. “Rescuing” as many surface holes as possible is indispensable for achieving excellent PEC performance, particularly for semiconductors with short-lived charge carriers, such as hematite. One frequently proposed solution is to deposit ultrathin hematite films on electrically conductive substrates. However, these ultrathin films exhibit low photon absorption.

Engineering hematite into nanostructures with reduced thickness and increased surface area boosts the number of holes harnessed because of the reduced hole diffusion distance to the material's surface as well as an increase in the surface area in contact with water. Formation of heterojunctions with a second semiconductor has multifaceted effects on improving the PEC performance of hematite, but in general improves PEC performance via facilitating charge separation.

5.2.5.3 Addressing Sluggish Water Oxidation Kinetics

The last critical step of PEC is transferring holes at the surface to water molecules. Unfortunately, this process is retarded by hematite's sluggish OER kinetics. Severe hole–electron recombination at the hematite/electrolyte interface is widely accepted as the cause of the large OER overpotential [20]. Strategies to offset this limitation are to decorate the hematite surface with OER catalysts and/or surface passivation layers. OER catalysts allow for routes with lower activation energies, resulting in facilitated hole transfer and reduction in onset potential. Surface passivation removes the excessive surface states (energy states close to the surface or associated with the surface defects) and mitigates surface electron–hole recombination.

In addition, fundamental research focusing on the water oxidation mechanism of hematite is a critical add of making the necessary modifications for hematite to become a cost-effective photoanode.

5.3 Experimental Strategies to Enhance the Photoactivity of Hematite

5.3.1 Nanostructuring

Engineering hematite into various nanostructures is an effective strategy to remedy the discrepancy between light absorption depth and hole diffusion length. As discussed in Section 5.2.2, in order for hematite to absorb 95% of the incident photons ($\lambda = 550$ nm), the thickness of hematite must be no less than ~ 350 nm. However, the maximal diffusion length for photoinduced holes in hematite is ~ 10 nm. A thickness of roughly double this diffusion length, *i.e.*, 20 nm is required to allow all holes to diffuse to the surface, assuming holes move straight to the surface along the shortest available pathways. In practice, the critical thickness can be slightly larger than 20 nm, due to applied external bias that assists hole diffusion, but typically should still be restricted to no more than 50 nm [21]. This value is still much smaller than the length required for 95% photon capture and the maximal light penetration depth (118 nm).

One strategy to address the short hole diffusion length of hematite is to construct nanostructures with ultrafine features that have relatively low thickness along the vectoral diffusion directions. Currently, there is insufficient understanding of the role of nanostructures (the available mechanistic insights will be discussed in Section 5.4.2). In this section, we will focus on the strategies developed to prepare nanostructured hematite photoanodes for water splitting.

5.3.1.1 Direct Synthesis

Growing hematite nanostructures on conductive substrates (*e.g.*, FTO) is most commonly used to prepare nanostructured hematite photoanodes.

Utilizing hydrothermal methods to grow near-vertically aligned nanorod or nanowire arrays on top of FTO is a prevalent way to obtain hematite nanostructures. The hydrothermal reactions rely on the hydrolysis of Fe^{3+} in water. The key steps are illustrated in Figure 5.4. Under mild heating conditions (~ 90 °C) and at the presence of alkaline species (Equation 5.3), the hydrolysis of Fe^{3+} to akaganeite ($\beta\text{-FeOOH}$) is promoted (Equation 5.4). In acidic solution, the hydrolysis of Fe^{3+} proceeds according to Equation 5.5. This process introduces akaganeite nuclei onto FTO substrates. Guided by capping agents such as urea and driven by reduced surface energy, akaganeite grows epitaxially from the loaded seeds and eventually yields akaganeite nanorod or nanowire arrays. This

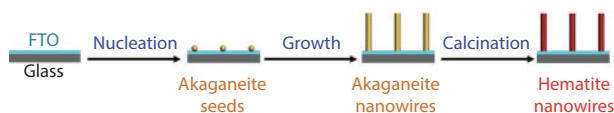


Figure 5.4 Schematic illustration showing the hydrothermal growth process of the hematite nanowire array on a piece of FTO glass substrate.

process typically requires hours. The nanorod and nanowire arrays grow in predominantly the (001) direction, exposing the most densely packed [001] facets [22]. Subsequent annealing of akaganeite in air at temperatures higher than 500 °C readily dehydrates akaganeite and yields hematite ($\alpha\text{-Fe}_2\text{O}_3$) as described by Equation 5.6.

Hydrolysis of urea releases ammonium hydroxide:



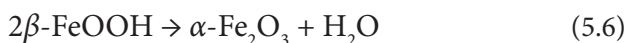
Hydrolysis of Fe^{3+} and yield of akaganeite:



In acidic environments, Equations 3.1 and 3.2 are replaced by Equation 3.3:



Production of hematite via dehydration of akaganeite:



The hydrothermal synthesis route is versatile because the concentration of iron and other salts, pH value, duration of reaction, *etc.* can have a significant effect on the synthesized hematite nanostructures. For example, Ling *et al.* demonstrated that adding Sn^{4+} and ethanol into the hydrothermal reaction system produced nanocoral-shaped akaganeite clusters (Figure 5.7a) [23]. These nanocorals exhibited twice as much photocurrent density compared to the hematite nanowires from a Sn^{4+} - and ethanol-free synthesis. Liu *et al.* discovered that Ge^{4+} -induced formation of hematite nanosheets (Figure 5.7b) [24]. While the exact mechanism of how the guest ions alter the product morphology was not evident, it is generally ascribed to surface energy alteration caused by guest ion adsorption that alters the growth pattern.

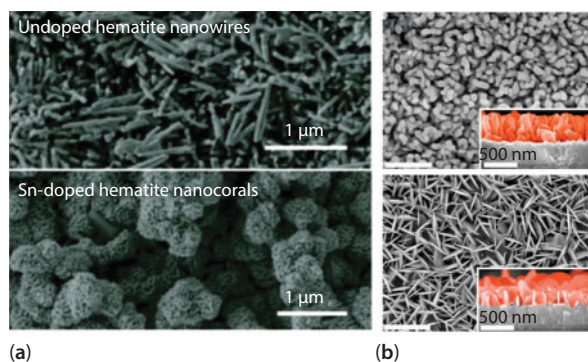


Figure 5.5 (a) SEM images of unmodified hematite nanowires (top) and hematite nanocorals prepared by adding SnCl_4 (bottom). Figure reproduced from Ref. [23], Copyright 2011, American Chemical Society. (b) SEM images of unmodified hematite nanorods (top) and Ge-doped ultrathin hematite nanosheets (bottom). Figure reproduced from Ref. [24], Copyright 2014, Elsevier.

Utilizing templates (either hard templates such as anodic aluminum oxide [25] or soft templates such as surfactants [26]) enables the synthesis of sophisticated nanostructures in addition to those epitaxially grown on FTO. Typical examples of advanced designs include inverse opals [27], nanonets, nanoporous films, and nanotubes. More recently, manually assembled hematite nanocubes were constructed to expose crystal facets with high photocatalytic activity [28].

It should be noted here that creating hematite nanostructures with ultrahigh surface area might counteract any efforts made to enhance the PEC performance. High surface area tends to introduce a large number of surface states that could adversely increase the onset potential. In this case, coupling OER catalysts with nanostructured hematite electrodes is necessary for lowering the onset potential (see Section 5.4.4.2 for more mechanistic insights).

5.3.1.2 *In Situ Structural Transformation*

The aforementioned hematite nanorods synthesized from the hydrothermal reaction can serve as precursors to other nanostructures. Liu *et al.* observed a morphological transition from hematite nanorods to nanosheets induced by applying a potential of -1.2 V vs. Ag/AgCl (Figure 5.6) [29]. The *in situ* transformation was initiated by dissolution of hematite followed by recrystallization of akaganeite. Because no capping agent was present, the recrystallization process extended along the [001] direction, exposing the most densely packed (001) facets of hematite. This resulted in a

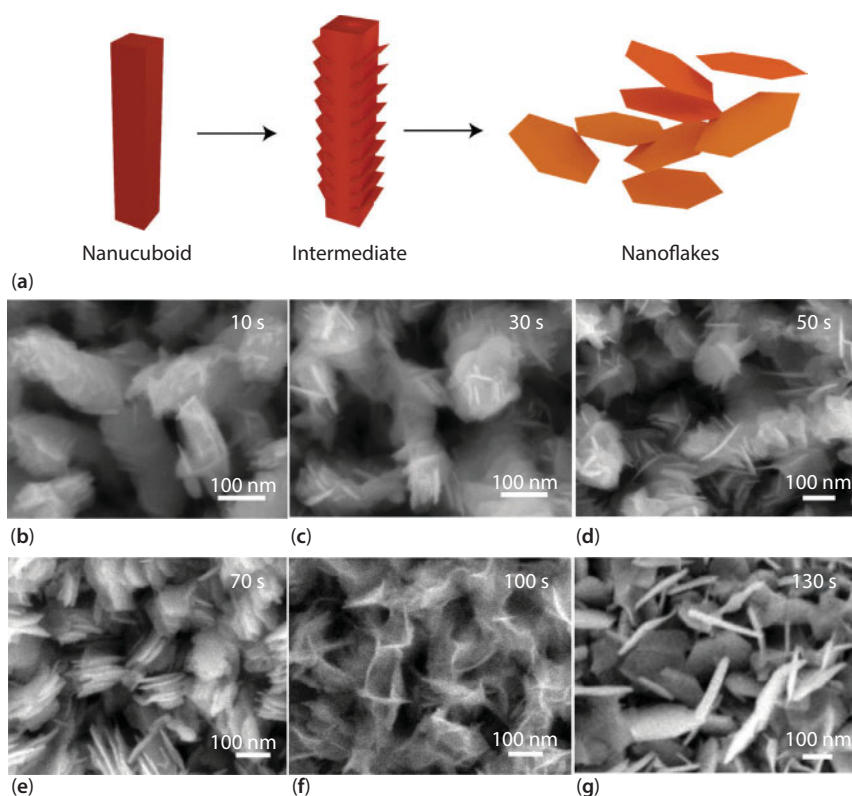


Figure 5.6 (a) Schematic illustration of the *in situ* transformation of hematite induced by applying a negative potential of -1.2 V vs. Ag/AgCl. (b–g) SEM images collected at different moments displaying the morphological transformation process. Figures reproduced from Ref. [29], Copyright 2014, Elsevier.

nanosheet morphology with (001) facets exposed. Cibrev *et al.* subjected hematite nanorods to a reductive treatment with a potential of -1.3 V for 10 s [30] and observed that the reductive treatment induced the separation of nanowires that were previously bundled together as nanorods.

5.3.1.3 “Locking” Nanostructures

Thermal annealing to convert akaganeite to hematite is commonly adopted to obtain hematite photoanodes. While such a conversion can readily take place at 550°C , more elevated temperatures such as 800°C are widely adopted for postannealing. This favors the diffusion of Sn^{4+} from the FTO substrates to *n*-dope and activate hematite [31]. However, the high-temperature annealing causes distortion and coalescence of hematite

nanostructures driven by a reduction in surface energy. This sintering of nanostructures reduces surface area and shortens their length (particularly for nanorods or nanowires), leading to compromised light absorption and charge separation efficiencies [32].

To date, a few publications have offered three main solutions to “lock” the hematite nanostructures during high-temperature annealing: (1) to modify the annealing conditions, (2) to encapsulate nanostructures with structural confinement materials, and (3) to engineer the hematite/substrate interfaces.

A typical example belonging to the first approach was performed by Kim *et al.* The authors showed that microwave heating could successfully convert akaganeite to hematite with decent PEC performance, maintaining the original nanorod morphology. The preservation of morphology was enabled by the rapid heating from microwaves which reduces the heating duration to no more than 15 minutes [33]. Alternatively, Ling *et al.* developed a low-temperature activation method to prepare hematite photoanodes with pronounced photoactivity [31]. They first annealed akaganeite at 350°C in N₂ to form magnetite (Fe₃O₄), followed by partial oxidation at 350°C in air to convert magnetite to hematite. Owing to some oxygen defects introduced during the first annealing step, the recovered hematite photoanode exhibited nearly 20 times higher photocurrent density at identical applied biases.

A second strategy capable of preserving the morphology of hematite at elevated temperatures involves applying structure-confinement coatings or scaffolds. Silica [34], zirconia [35], and alumina [36] have been developed as confinement materials because of their high melting points and thermal stability. These coatings or scaffolds can withstand high temperatures without deformation and hence the resultant hematite maintains the morphology of akaganeite (Figure 5.9). Afterward, the coatings or scaffolds are etched to reveal the stabilized hematite nanostructures.

A third method is to engineer the hematite/substrate interfaces. For example, Wang *et al.* initially deposited FTO glass substrates with antimony-doped tin oxide nanoparticles [32]. These nanoparticles served as nucleation sites for the growth of hematite nanorods with high crystallinity and few intrinsic defects. The resulting improved quality of hematite boosted its lattice energy and strengthened its thermal stability, contributing to the material's ability to conserve morphology at temperatures as high as 800 °C.

5.3.2 Doping

Strategies of doping hematite with oxygen deficiencies, metal elements, and nonmetal elements improve the PEC performance of hematite by

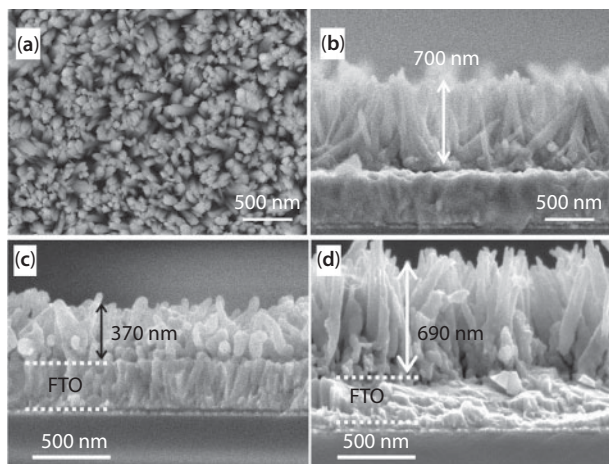
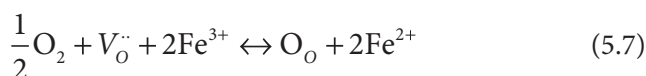


Figure 5.7 Morphology evolution and preservation at 800 °C. (a) A top-view SEM image of the as-prepared akaganeite nanorods. (b–d) Side-view SEM image of (b) the as-prepared akaganeite nanorods, (c) the coalesced hematite nanorods, and (d) the structure-maintained hematite nanorods by silica encapsulation. Coalescence leads to reduced nanorod length and subsequently light absorption efficiency. Figures reproduced with permission from Ref. [34], Copyright 2017, American Chemical Society.

directly modifying its intrinsic optical and/or electrical properties. Based on how the dopants are introduced, doping strategies can be divided into two classes: intrinsic doping by creating oxygen deficiencies and extrinsic doping by introducing foreign dopant elements.

5.3.2.1 Oxygen Vacancies

Introduction of oxygen vacancies can substantially improve the performance of the hematite photoanode for water oxidation, suggested by the cathodic shift in onset potential and pronounced photocurrent generation (Figure 5.10) [37, 38]. Creating oxygen-deficient hematite electrodes is often performed by annealing hematite in an oxygen-deficient atmosphere [37], though plasma treatment is also viable [39]. The presence of oxygen is detrimental to the creation of oxygen deficiencies ($V_{\text{O}}^{\cdot\cdot}$) because it oxidizes $V_{\text{O}}^{\cdot\cdot}$ back to an oxygen atom (O_{O}):



Quantitatively, the degree of doping by oxygen deficiencies (n) follows a power rule of oxygen partial pressure (P_{O_2}): $n \propto (P_{O_2})^{1/6}$ [40].

Based on Equation 5.7, it is intuitive to assume annealing hematite in an oxygen-free environment should give rise to the maximal oxygen deficiency concentration that contributes to the highest performance. However, this is not the case. First, creating excessive amounts of deficiencies could degrade the photoactivity as deficiencies located deep inside the bulk trigger severe electron-hole recombination and reduce carrier mobility. Second, compounds with lower valence states and limited photoactivity such as magnetite and iron(0) can evolve as reduction products from hematite if no oxygen is present [31]. Therefore, the annealing atmosphere is nontrivial and deserves delicate design. Ling *et al.* blended nitrogen gas mixture with 0.43 vol% O_2 to avoid the formation of magnetite [31]. Compared to air-annealed hematite, the oxygen-deficient hematite exhibited pronounced enhancement in photocurrent density at potentials beyond the onset potential (Figure 5.8a). It also showed much higher charge carrier density than the pristine counterpart (Figure 5.8b). Zhou *et al.* used ammonia borane (NH_3BH_3)-blended air to introduce hydrogen gas since NH_3BH_3 decomposes and slowly releases hydrogen gas at 800 °C, reducing Fe^{3+} to Fe^{2+} and contributing oxygen deficiencies (the reverse reaction of Equation 5.7).

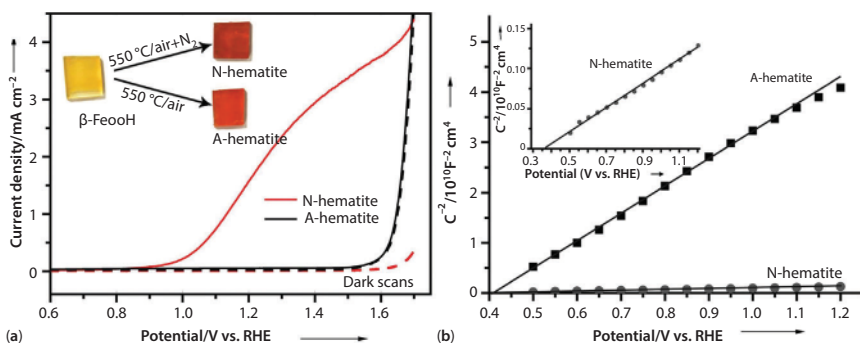


Figure 5.8 (a) Linear sweep voltammograms collected for pristine (“A-hematite”) and oxygen-deficient (“N-hematite”) samples, in 1 M NaOH electrolyte (pH=13.6) under illumination of simulated solar light of 100 mW/cm² and in the dark. (b) Mott–Schottky plots of A-hematite and N-hematite collected with a scan rate of 10 mV/s in the dark at a frequency of 10 kHz. Inset: Mott–Schottky plots of N-hematite collected at the same conditions. The reduced slope of N-hematite indicates its enhanced charge carrier density. Figures reproduced with permission from Ref. [37], Copyright 2012, Wiley.

5.3.2.2 Foreign Ion Doping

Doping hematite with foreign ions belongs to the extrinsic doping class and also presents a family of efficient strategies to enhance the photoactivity of hematite. Foreign ion doping can directly tune the optical, electrical, and surface chemical kinetic properties of hematite. Based on the relationship between the valence state of the extrinsic ion dopants and that of hematite, the dopants can be grouped into three types:

- (i) *n*-type dopants (dopant's valence state $> +3$): Sn^{4+} , Ti^{4+} , Si^{4+} , Mo^{6+} , *etc.*
- (ii) *p*-type dopants (dopant's valence state $< +3$): Mg^{2+} , Zn^{2+} , Ag^+ , *etc.*
- (iii) Isovalent dopants (dopant's valence state $= +3$): Al^{3+} , B^{3+} , *etc.*

Different dopants vary in their influence on the PEC performance of hematite, as discussed below.

1. *n*-type dopants

The effect of *n*-type dopants on the enhancement of photoactivity of hematite is largely ascribed to augmentation of electron density which increases electrical conductivity. It is based on the rationale that when an *n*-type dopant substitutes one Fe^{3+} site in the hematite lattice, one electron will be created by each dopant. The presence of the extra electrons improves the charge carrier density, and hence the electrical conductivity, assuming the carrier mobility remains unchanged. Studies associated with the advanced and fundamental understandings elucidating the roles of the *n*-type dopants will be thoroughly discussed in Section 5.4.3.2.

Intentional doping is a common way to introduce *n*-type dopants. For the hydrothermal synthesis of hematite, adding salts containing the dopant cations along with iron salts, *i.e.*, in-growth doping, is a typical example. TiCl_4 and SnCl_4 are two examples of salts for the introduction of Ti^{4+} and Sn^{4+} dopants, respectively. Ling *et al.* introduced SnCl_4 into the hydrothermal reaction system and successfully prepared Sn^{4+} -doped hematite. They observed that the Sn-doped hematite annealed at 800 °C exhibited a pronounced photocurrent density of 1.24 mA/cm² at 1.23 V *vs.* RHE, while the as-prepared hematite annealed at 550 °C only yielded a limited photocurrent of 0.035 mA/cm² at the same potential. The authors attributed the enlarged photocurrent density to Sn doping and the doping-induced morphological transformation which exposed enhanced surface area in contact with water molecules.

Unintentional (or, more appropriately called “indirect” hereafter) doping introduces a particular n -type dopant, Sn^{4+} , into hematite from the Sn^{4+} reservoir—FTO substrates. At temperatures elevated above 550 °C, Sn^{4+} doped in FTO will diffuse upward, across the FTO/hematite interface, and enter into hematite. The thermal diffusion of Sn^{4+} from FTO to hematite was first observed by Sivula *et al.* in 2010 [15] and was further studied by Ling *et al.* in 2012 [23].

The indirect Sn doping, though beneficial to enhance the performance of hematite, is not ideal. Li *et al.* utilized secondary ion mass spectrometry to map the Sn content along the longitudinal axis of a single indirectly Sn-doped hematite nanowire [34]. The authors revealed that the Sn distribution followed a gradient profile, with Sn^{4+} concentrated near the hematite/FTO interface, and relatively diluted at the tip (Figure 5.9a, the blue line). This nonuniform doping pattern impaired the overall performance of the Sn-doped hematite. To resolve this problem, the authors coupled the “intentional doping” and “unintentional doping” strategies. Specifically, SnCl_4 solution was first dropped onto the top of the nanowires and then the SnCl_4 -wetted nanowires were subjected to annealing at 800 °C. During thermal annealing, Sn^{4+} diffused bidirectionally from the FTO substrates and the SnCl_4 -coated tips. This strategy managed to prepare hematite nanowires with a relatively uniform Sn doping of ~3 atom% along the longitudinal axis of nanowires (Figure 5.9a, the red line). The uniformly doped hematite displayed a photocurrent of 2.2 mA/cm² at 1.23 V *vs.* RHE, which is more than two times higher than hematite nanowires merely doped by Sn^{4+} from FTO (Figure 5.9b). Consistently, the positive effect of uniform doping was also confirmed by Wang *et al.* They utilized atomic layer deposition of a Ti-containing oxide layer onto hematite surface followed by thermal annealing at 500 °C for 1 h. Ti^{4+} dopants diffused from the coated overlayer directly to hematite nanorods. The doped electrode achieved an impressive photocurrent density of 2.28 mA/cm² at 1.23 V *vs.* RHE, a value among the state-of-the-art performance of Ti-doped hematite photoanodes [41].

In recent years, nonmetal n -type dopants with high valence states, including Si^{4+} , [42] S^{4+} [43], S^{6+} [44], and P^{5+} [45] have also been identified to improve the photoactivity of hematite. Compared to metal ion dopants, nonmetal ion dopants tend to form dopant-O bonds with reduced ionicity, avoiding the formation of deep electron trapping states and resulting in small onset potentials. For example, Luo *et al.* prepared a type of phosphorus-doped hematite using a facile dipping-annealing method [45]. The onset potential was only ~0.7 V *vs.* RHE with a photocurrent density of 1.48 mA/cm² achieved at a bias of 1.23 V.

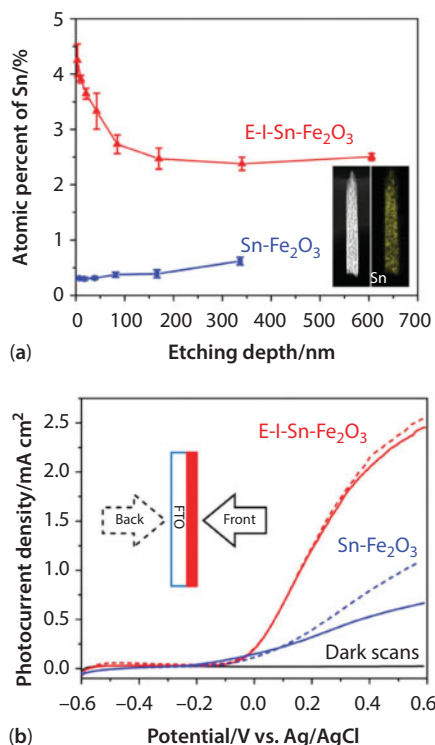


Figure 5.9 (a) Secondary ion mass spectrometry depth profile of the bidirectionally (from a FTO substrate and SnCl₄-coated nanowire tips) Sn-doped hematite (red), and the single directionally (merely from a FTO substrate) Sn-doped hematite nanowire (blue). The inset shows the relative uniform Sn doping across a single nanowire. The particular high Sn concentration at tips is possibly due to the uneven deposition of SnCl₄ atop densely packed hematite nanowires. (b) Linear sweep voltammograms collected for the bidirectionally Sn-doped hematite nanowires (red) and the indirectly Sn-doped hematite nanowires (blue). The marginal photocurrent density difference between back and front illumination indicates charge carrier transport in bidirectionally Sn-doped hematite nanowires is rapid. Figures reproduced with permission from Ref. [34], Copyright 2017, American Chemical Society.

(2) *p*-type dopants

Ions with valence state lower than 3 are also effective in promoting the photoactivity of hematite. A wide selection of these *p*-type dopants, including Mg²⁺ [46], Zn²⁺ [47], and Ag⁺ [48], have already been demonstrated as efficient dopants to improve the performance of hematite. Lin *et al.* deposited Mg-doped *p*-type hematite atop a pristine *n*-type hematite thin layer using atomic layer deposition [46]. The onset potential of the heterostructure shifted 200 mV cathodically. Shen *et al.* sonicated the as-prepared

β -FeOOH nanorods in silver acetate aqueous solution followed by annealing and successfully prepared Ag-doped hematite. The Ag^+ substitutional doping resulted in 340% enhancement in photocurrent density compared to untreated hematite nanorods [48].

Using p -type dopants to improve the PEC performance of hematite seems counterintuitive, because doping n -type hematite with p -type dopants will deplete the charge carrier density. In Section 5.4.3.3, we will discuss the mechanism for the p -type dopant-induced performance enhancement.

(3) Isovalent dopants

Though isovalent dopants do not exhibit a pronounced effect on changing the charge carrier density of hematite, they can affect the electronic properties by altering the crystal structure. Kleiman-Shwarsstein *et al.* observed that hematite films electrodeposited at the presence of Al^{3+} yielded defective hematite films with Fe^{3+} substituted by Al^{3+} [49]. The photocurrent density of hematite with different Al^{3+} doping concentrations was compared. A twofold improvement in photocurrent density was seen for samples of up to 1.47% of Al^{3+} . Further increasing the doping concentration to 10% resulted in alumina coating layers on the surface, which deteriorates the PEC performance by blocking hole transfer at the electrode/electrolyte interface.

It is worth mentioning here that by combining these strategies, namely performing codoping, better performance can be achieved due to synergistic effects the dopants provide [50]. We will elaborate the “synergistic effect” in Section 5.4.3.5.

5.3.3 Construction of Heterojunctions

Creating hematite-based heterojunctions is another diverse group of hematite modification for PEC applications. These strategies can be carried out by coupling hematite with an additional semiconductor to promote charge separation, a light sensitizer to improve light absorption, a water oxidation catalyst to accelerate OER, and/or a modified current collector to impede back electron–hole recombination. In most cases, these strategies are combined to significantly advance the PEC performance of hematite-based water splitting.

5.3.3.1 Semiconducting Overlayers

Researchers have investigated a wide range of semiconductors (n -type and p -type) that successfully enhance the photocurrent density of hematite.

Recently, Ahmed *et al.* deposited a *p*-type CaFe_2O_4 layer on top of hematite via a hydrothermal reaction [51]. The heterojunction achieved a photocurrent density of 0.53 mA/cm^2 at 1.23 V vs. RHE , 100% higher than a bare hematite electrode. An ultrathin overlayer of TiO_2 grown on hematite using atomic layer deposition was also shown to reduce the onset potential by 100 mV (compared to untreated hematite), with enhanced photocurrent density reaching 2.0 mA/cm^2 at 1.23 V vs. RHE [52].

The effects of semiconductor coating include forming heterojunctions and passivating surface states which both reduces the possibility of surface electron–hole recombination and increases the photocurrent density. A more detailed discussion will be presented in Section 5.4.5.

It should be noted here that when designing heterojunctions, the selection of the coated semiconductors needs to be evaluated based on the VB and CB positions of the semiconductors. A type-II band alignment forming a staggered gap is preferred to maximize the number of holes and electrons available for water splitting.

5.3.3.2 Sensitization and Tandem Cells

To promote the PEC performance of hematite, employing sensitizers amplifies the material's light absorption intensity or supplements the wavelength of light absorbed. Huang *et al.* utilized nitrogen-doped carbon quantum dots as the light sensitizers for hematite and achieved a 3.4 times increase in photocurrent density (0.41 mA/cm^2) with a 280 mV cathodic shift of onset potential [19]. Due to a multiphoton active process, the nitrogen-doped carbon quantum dots are able to upconvert light with wavelength between 580 nm and 800 nm to light with shorter wavelength (400–600 nm). Such light conversion ability enables the absorption of infrared energy by hematite. Besides the aforementioned quantum dots, noble metals (e.g., Au) with inherent surface plasmons are also implemented as sensitizers [17, 18]. Since the small bandgap of hematite already allows hematite to absorb a large portion of visible light, incorporation of light sensitizers with hematite is not as prevalent as other semiconductors with wider bandgaps such as TiO_2 .

Creating hematite-based tandem architectures is another method to improve light utilization. Instead of depositing light absorbers onto hematite, a tandem cell uses a photocathode with a light absorption profile complementary to hematite to extract light energy in a broad range of wavelengths. For example, Mayer *et al.* coupled *n*-type silicon with hematite via deposition of hematite thin layers onto silicon nanowires [53]. The silicon nanowires are able to capture photons that are transparent to

hematite (between 600 nm and 1100 nm in wavelength). Gurudaya *et al.* also demonstrated a tandem cell with $\text{CH}_3\text{NH}_3\text{PbI}_3$ (a halide perovskite) to serve as the photocathode that absorbs light with wavelength up to 800 nm [54]. One of the outstanding features of this tandem cell is its ability to generate a high potential of 1.87 V that realizes spontaneous hydrogen production through water splitting.

5.3.3.3 OER Catalysts

Coupling water oxidation catalysts with hematite improves photocurrent density by directly addressing the water oxidation kinetic bottleneck of pristine hematite. A variety of catalysts have been adopted as OER catalysts for hematite. They can be grouped into five categories based on their chemical compositions:

1. Metal oxides: IrO_2 [55], RuO_2 [56], Co_3O_4 [57], NiFeO_x [58], AgFeO_x [48], *etc.*
2. Metal hydroxides: FeOOH [59], Ni(OH)_2 [60], Co(OH)_2 [61], FeNiOOH [62], NiFe-layered double hydroxide [63], ZnCo-layered double hydroxide [64], *etc.*
3. Metals: Pt [65], Ni-Bi [66], *etc.*
4. Metal salts: metal complexes [67], CoF_3 [68], cobalt phosphate (Co-Pi) [69], MoS_x [70] *etc.*
5. Complex metal ion clusters: polyoxometalates [71], *etc.*

Co-Pi is an OER catalyst that has received a lot of attention due to its ease of fabrication (via electrodeposition or photodeposition) and high catalytic efficiency. One widely accepted molecular structure of Co-Pi is a network consisting of edge-sharing cobalt–oxygen octahedra (Figure 5.10e). For each octahedron, the central cobalt atom is surrounded by six oxygen atoms with a Co-O bond length of ~ 1.9 Å. Gamelin and coworkers electrodeposited sparsely distributed Co-Pi microdots on the surface of mesoporous hematite films [72]. Compared to bare hematite, a fivefold enhancement in photocurrent density and ~ 200 mV cathodic shift of onset potential were observed after Co-Pi catalyst decoration (Figure 5.10f). The Co-Pi catalyst is chemically stable in both alkaline and neutral electrolytes, making it durable in various working conditions.

It is worth mentioning that beyond the abiotic species mentioned above, some electrogenic bacteria, such as *Shewanella oneidensis* strain MR-1, are effective in promoting the PEC performance of hematite. Qian *et al.* inoculated *Shewanella oneidensis* MR-1 cells onto hematite nanorods and

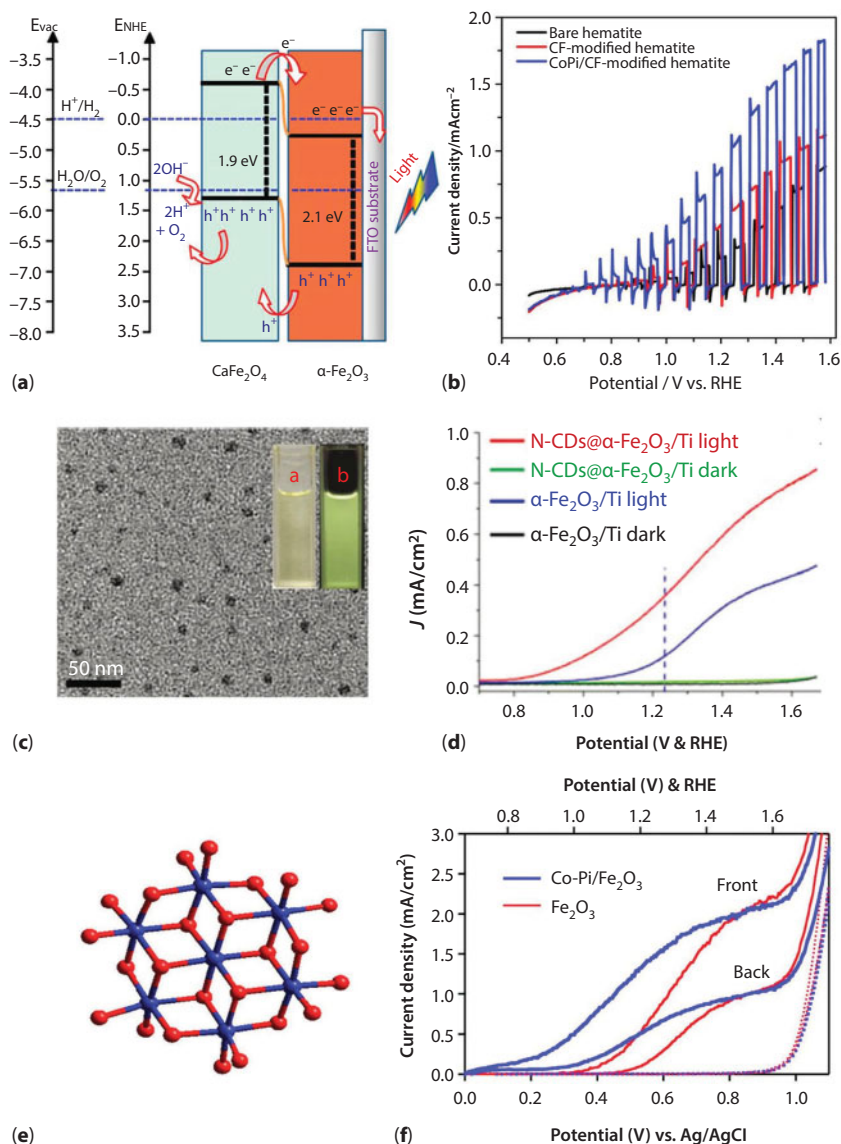
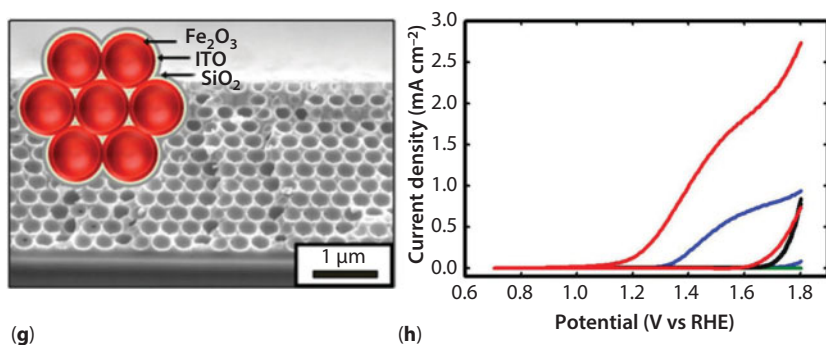


Figure 5.10 (a) The band structure of the $p\text{-CaFe}_2\text{O}_4/n\text{-Fe}_2\text{O}_3$ heterojunction. (b) Linear sweep voltammograms of bare $p\text{-CaFe}_2\text{O}_4/n\text{-Fe}_2\text{O}_3$ photoanode and Co-Pi-catalyzed $p\text{-CaFe}_2\text{O}_4/n\text{-Fe}_2\text{O}_3$ photoanode, collected under chopped simulated solar light (air mass 1.5G, 100 mW cm^{-2}). (c) A TEM image of the N-doped carbon quantum dots. The inset shows the digital picture of a solution containing the N-doped carbon quantum dots illuminated with sunlight (left) and 365 nm UV light (right). (d) LSVs of hematite electrodes with and without the N-doped carbon quantum dots. (e) The molecular structure of the Co-Pi catalyst. Red spheres and blue spheres represent oxygen and cobalt atoms, respectively. (f) LSVs of hematite electrodes with and without the Co-Pi

(Continued)



catalyst. (g) A SEM image showing the inverse opal morphology of the hematite-coated ITO network. The schematic illustration presents the cross-sectional structure of the nanostructured hematite electrode. (h) Photocurrent density vs. applied potential for FTO/aITO (atomic layer deposited ITO)/hematite (blue), FTO/IO (inverse opal)/aITO/hematite (red), FTO/IO/hematite (black), and FTO/IO/aITO (green). Figures reproduced with permission from (a, b) Ref. [51], Copyright 2015, Royal Society of Chemistry; (c, d) Ref. [19], Copyright 2017, Royal Society of Chemistry; (e) Ref. [79], Copyright 2012, American Chemical Society; (f) Ref. [72], Copyright 2010, American Chemical Society; (g, h) Ref. [27], Copyright 2013, American Chemical Society.

observed a 150% augmentation in photocurrent compared to identical hematite nanorods with no bacteria [73]. The authors attributed the performance improvement to redox species released by MR-1 cells that serve as hole scavengers with faster kinetics than water molecules.

5.3.3.4 Engineering of Current Collectors

Current collectors play an important role in determining the PEC performance of photoanodes, because they are responsible for collecting the photoinduced electrons to generate photocurrent and mitigate electron–hole recombination. The predominant current collector used to fabricate photoanodes for PEC applications is FTO (or indium-doped tin oxide, ITO) glass, a flat glass base with a thin layer of electrically conductive FTO coated on surface. However, the smooth surface of FTO glass exposes limited surface area for light absorption as well as charge transfer, which limits the PEC performance. Particularly for semiconductors with short-lived holes such as hematite, the thickness must remain low enough to allow for the diffusion of holes from the depletion layers (subsurface regions where bands bend) to the surface for water oxidation. The flat FTO glass can only support a small amount of hematite, which hinders hydrogen production.

To address the aforementioned challenge, researchers have mainly developed two approaches. The first one is to engineer hematite into various nanostructures to be grown on the conventional flat substrate (discussed in Section 5.3.1). The second approach is to build nanotextured conductive current collectors to support a confocal layer of hematite. These nanotextured substrates include ITO nanowires [74], ITO inverse opal networks [27], nanocarbon materials (*e.g.*, carbon nanotubes [75], graphene oxide [76], reduced graphene oxide [77]), and TiSi_2 nanonets [78]). Coating the conventional flat conductive substrates with a second semiconductor to form heterojunctions at the current collector/hematite interface has proven to be effective in enhancing the PEC performance of hematite.

Riha *et al.* utilized atomic layer deposition to fabricate an ITO inverse opal-shaped conductive network (Figure 5.10g) [27]. Hematite was subsequently deposited on the surface of this network, and a hematite photoanode supported on a large-surface area current collector was fabricated. This uniquely structured network enabled a large amount of hematite deposited with a thickness that falls within the limit of the hole diffusion length. In addition, the porous structure could reflect light internally and improve light absorption. The nanoengineered hematite photoanode showed a photocurrent density of 1.60 mA/cm^2 at 1.53 V vs. RHE , while the hematite electrode with a flat ITO substrate only exhibited a photocurrent density of 0.55 mA/cm^2 at 1.53 V vs. RHE (Figure 5.10h).

Table 5.1 summarizes some selected representative PEC performances (onset potential and photocurrent density) of modified hematite photoanodes based on the modification methods.

5.4 Fundamental Characteristics of the PEC Behaviors of Hematite

Based on the most current research, this section presents a summary of the fundamentals of hematite-based PEC systems. Efficient methodologies are proposed to guide future experimental works.

5.4.1 Transient Absorption Spectroscopy

Transient absorption (TA) spectroscopy remains active at the forefront of studying the charge carrier dynamics of hematite and is a major tool to elucidate how hematite functions under different conditions. It allows probing chemical kinetics within a wide timeframe ranging from femtoseconds to seconds. This time scale correlates well with the exciton dynamics in

Table 5.1 The photocatalytic performance of selected hematite photoanodes for PEC water splitting cells.

Photoanodes	Onset potential (V vs. RHE)	Photocurrent density in mA/cm ² (@ Potential vs. RHE)*	Comment(s)	Ref.
Nanostructuring				
Negative potential-treated hematite	0.47	0.3 (@1.23)	The negative potential treatment brings in several factors: (1) increasing electrical conductivity; (2) reducing film compactness to expose additional surface area; (3) introducing new electron acceptor states with energy close to VB.	[30]
Hybrid microwave-annealed hematite nanowires	0.7	1.58 (@1.23)	Microwave annealing prevents coalescence of hematite nanowires.	[33]
FeF ₃ -derived porous hematite nanowire film	0.9	0.36 (@1.23)	Pores increases surface area in contact with water molecules.	[80]
Hematite thin films	~1.0	0.94 (@1.45)	Stable performance over 1000 h.	[81]
Hematite film modified with polyvinylpyrrolidone	0.9	~0.7 (@1.23)	The use of polyvinylpyrrolidone forms small crystal grain size.	[26]
TiSi ₂ nanonet-supported hematite films	1.0	1.6 (@1.23)	The synthesized TiSi ₂ nanonets are highly conductive and possess large surface area. Hematite coating thickness: ~25 nm	[82]

Hematite nanotube arrays	0.90	2.2 (@1.43)	Nanotubes possess a hollow structure that can expose more surface area than solid nanorods or nanowires.	[83]
Hematite-coated ITO nanowires	~0.97	1.1 (@1.23)	The ITO nanowires were grown by chemical vapor deposition on quartz substrates.	[74]
(0 1 2) plane-oriented hematite film	0.85	0.8 (@1.23)	(012) possesses the highest photoactivity as the authors claimed.	[28]
Ultrathin hematite nanoflakes	~0.9	~0.40 (@1.23)	The ultrathin nanoflakes are derived from hematite nanorods by electrochemical reduction.	[29]
Doping				
Oxygen-deficient hematite nanowires	~1.0	1.82 (@1.23)	Annealing hematite in vacuum or zero-oxygen environment yields photoinactive magnetite.	[37]
Plasma-treated hematite ultrathin nanoflakes	~0.75	2.03 (@1.23)**	Plasma treatment introduces oxygen deficiency.	[39]
Gradient P-doped hematite film	~0.7	1.48 (@1.23)	Gradient doping retards surface charge recombination.	[45]
Sn-doped low temperature-activated hematite nanowires	~1.05	0.10 (@1.4 V)	Annealing temperature as low as 350 °C.	[31]

(Continued)

Table 5.1 Cont.

Photoanodes	Onset potential (V vs. RHE)	Photocurrent density in mA/cm ² (@ Potential vs. RHE)*	Comment(s)	Ref.
S-doped hematite nanocorals	0.8	~0.16 (@1.4 V)	Cation S ⁴⁺ substitution is more possible than anion S ²⁻ substitution, as the authors claimed.	[43]
S-doped hematite nanorod arrays	~0.8	1.42 (@1.23)	The identified effective dopants are S ⁶⁺ ions.	[44]
Zr-doped hematite nanotubes	~0.8	1.5 (@1.23)	The formation of nanotubes is ascribed to Kirkendall effect.	[35]
Hematite thin films with diffusive back-contact layers	~1.0	0.49 (@1.23)	The existence of the diffusive back-contact layer reduces charge recombination at the hematite/FTO interface.	[84]
Mo-doped hematite nanorods	~0.7	~0.8 (@1.23)	The dual role of the Mo dopants improves electrical conductivity and passivates surface states.	[85]
Ti-doped amorphous SiO _x coated	0.95	2.44 (@1.23) 3.70 (@1.50)	SiO _x is a surface passivation layer.	[86]
Hematite-coated ITO inverse opal framework	~1.15	0.55 (@1.53)	The engineered substrate improves light absorption and reduces charge collection distance	[27]

Boron-doped hematite nanowires	~0.85	1.12 (@1.23)	Gradient doping retards surface charge recombination.	[87]
Hydrogenated hematite film	0.8	2.12 (@1.23)	Hydrogenation is realized by annealing FeOOH in the atmosphere of NH_3BH_3 ; NH_3BH_3 releases hydrogen gas at elevated temperatures.	[88]
Mg-doped hematite films	~0.8	~0.55 (@1.23)	Mg doping results in a $p\text{-Fe}_2\text{O}_3$ overlayer, forming a $p\text{-}n$ heterojunction.	[46]
Zn^{2+} and Ti^{4+} codoped hematite nanoparticles	~0.9	1.5 (@1.23)	The role of Zn^{2+} and Ti^{4+} : enhancing electrical conductivity and facilitating charge transfer in bulk and on surface. Zn^{2+} also functions as an OER catalyst.	[89]
KOH-treated and Ti^{4+} -doped hematite film	0.8	2.1 (@1.5)	The KOH treatment introduces hydroxyl groups on surface that passivate surface states	[90]
Co-Pi Zr-doped hematite nanotubes	0.65	1.87 (@1.23)	Co-Pi is an OER catalyst.	[35]
Sn-doped hematite nanorods	0.8	1.86 (@1.23)	Adding SnCl_4 during the hydrothermal reaction yielded akaganeite nanorods.	[23]
Sn/Be codoped hematite nanorods	~0.95	1.7 (@1.23)	The effect of Be^{2+} : removing localized recombination sites, reducing microstrain and increasing Fe-O bond ordering.	[50]

(Continued)

Table 5.1 Cont.

Photoanodes	Onset potential (V vs. RHE)	Photocurrent density in mA/cm ² (@ Potential vs. RHE)*	Comment(s)	Ref.
Al-doped hematite films	0.7	~1 (@1.23)	0.46% doping and 10% doping results in the highest photocurrent density and smallest onset potential, respectively.	[49]
Bi-directional Sn-doped hematite nanowires	~0.9	1.36 (@1.23)	Silica encapsulation retains the nanowire morphology during the high-temperature thermal annealing and promotes uniform Sn doping.	[34]
P-doped hematite nanorods	~0.8	2.7 (@1.23)	Phosphor doping enhances electron mobility.	[91]
Heterostructuring				
Phosphate-bonded hematite nanowires	0.8	1.3 (@1.7)	PO ₄ ³⁻ diminishes the population of electron-hole recombination sites.	[92]
Acid-treated hematite nanowires	~0.9	~1.3 (@1.23)	Acid treatment enhances the electron detrapping rate possibly by surface modification.	[93]
Atomic layer-deposited Sn-doped hematite nanowires	0.8	3.12 (@1.23)	Atomic layer deposition enables conformal coating of Sn precursors onto FeOOH.	[94]

Iridium-based complex monolayer-coated hematite particles	0.6	~0.9 (@1.23)	The monolayer with small amount of iridium compounds reduces fabrication cost; acidic environment tolerate.	[67]
p -LaFeO ₃ / n -Fe ₂ O ₃ heterojunction	~1.00	0.58 (@1.23)	Formation of p - n junctions	[95]
Cobalt oxide-decorated p -LaFeO ₃ / n -Fe ₂ O ₃	~0.95	1.12 (@1.23)	Cobalt oxide is an OER catalyst.	[95]
N-doped carbon dot-decorated hematite nanowires	0.79	0.41 (@1.23)	The upconversion ability of the N-doped carbon dots augments the light absorption of hematite in the wavelength ranging from 400 to 600 nm.	[19]
Hematite thin films derived from low-temperature atomic layer deposition [Ni(OH) ₂ catalyzed]	~0.8	0.3 (@1.23)	Growth temperature is 230 °C and no need for postannealing	[96]
TiO ₂ -coated hematite thin film	~0.75	1.2 (@1.23)	The TiO ₂ coating passivates surface states but not serves as an OER catalyst.	[97]
Co-Pi decorated plasma-treated hematite ultrathin nanoflakes	~0.6	3.02 (@1.23)**	Plasma treatment induces formation of oxygen deficiencies.	[39]
Ga ₂ O ₃ -coated hematite thin layer	0.91	0.25 (@1.02)	The role of Ga ₂ O ₃ coating includes (1) to release lattice strain and (2) to passivate surface states	[98]

(Continued)

Table 5.1 Cont.

Photoanodes	Onset potential (V vs. RHE)	Photocurrent density in mA/cm ² (@ Potential vs. RHE)*	Comment(s)	Ref.
IrO ₂ /RuO ₂ cocatalyzed hematite thin films	0.48	1.52 (@1.23)	IrO ₂ and RuO ₂ are OER catalysts.	[99]
Cobalt-doped hematite/MgFe ₂ O ₄ heterostructured nanoarrays	~0.3	3.34 (@1.4)	The current collector Ti mesh renders excellent flexibility of the electrode.	[100]
Co-Pi Ti-doped amorphous SiO _x -coated hematite "worms"	0.80	3.19 (@1.23)	Co-Pi is an OER catalyst.	[86]
FeOOH-coated hematite thin film	0.65	1.21 (@1.23)	FeOOH behaves as a cocatalyst for water oxidation.	[59]
Dendritic hematite nanoarrays with TiO ₂ underlayers	~0.95	2.5 (@1.23)	The TiO ₂ underlayer is a Ti ⁴⁺ dopant source and a passivation layer which reduces interfacial charge recombination	[101]
FeOOH-catalyzed dendritic hematite nanoarray with a TiO ₂ underlayer	~0.73	3.1 (@1.23)	FeOOH is an OER catalyst.	[101]
Spray-pyrolyzed hematite@hydrothermally grown-hematite core@shell nanorods	~1.0	1.2 (@1.23)	The sprayed hematite shell passivates the surface.	[102]

Cobalt-catalyzed FeF_3 -derived porous hematite nanowire film	0.77	0.54 (@1.23)V	Cobalt is an OER catalyst.	[80]
FeNiO_x and P-doped hematite film	0.62	2.67 (@1.23)	FeNiO_x is an OER catalyst.	[88]
Pt nanoparticle-decorated hematite nanorod arrays	~0.75	10 (@0.5)	The Pt nanoparticles reduce the electrical resistance of hematite as well as serve as photoelectron reservoirs to trap surface holes and minimize surface electron-hole recombination.	[25]
Co-Pi-decorated and Pt NP-incorporated hematite wormlike nanorod arrays	~0.7	4.32 (@1.23)	Pt improves charge transfer and Co-Pi serves as an OER catalyst.	[103]
Structure-preserved hematite nanorods	~0.8	2.12 (@1.23)	Interface engineering preserves the nanorod structure during thermal annealing	[32]
Ge-doped hematite ultrathin nanosheets	~0.95	1.4 (@1.23)	Adding Ge colloidal solution during the hydrothermal reaction yielded akaganeite nanocorals.	[24]
Uniformly Ti-doped hematite nanorods	~1.0	2.28 (@1.23)	The uniform Ti doping is realized by atomic layer deposition.	[41]

(Continued)

Table 5.1 Cont.

Photoanodes	Onset potential (V vs. RHE)	Photocurrent density in mA/cm ² (@ Potential vs. RHE)*	Comment(s)	Ref.
$p\text{-CaFe}_2\text{O}_4/n\text{-Fe}_2\text{O}_3$ heterojunction	~0.8	0.53 (@1.23)	The $p\text{-CaFe}_2\text{O}_4/n\text{-Fe}_2\text{O}_3$ forms a $p\text{-}n$ junction that facilitates electron-hole separation.	[51]
$\text{ZnFe}_{2-x}\text{Al}_x\text{O}_4$ - or $\text{Fe}_{2-x}\text{Al}_x\text{O}_3$ - coated hematite porous films	~0.85	~0.4 (@1.4)	Al^{3+} passivates surface states.	[104]
$\text{Fe}_x\text{Sn}_{1-x}\text{O}_4$ - coated hematite NRs	0.62	2.25 (@1.23)	$\text{Fe}_x\text{Sn}_{1-x}\text{O}_4$ forms a heterojunction with hematite and as a surface passivation layer.	[105]
Cobalt iron oxide-catalyzed Ti-doped hematite nanorods	0.78	2.49 (@1.23)	Cobalt iron oxide role includes an OER catalyst; forming a $p\text{-}n$ junction; passivating surface states.	[106]
Nb_2O_5 back-contacted hematite ultrathin layers	1.1	0.42 (@1.43)	The Nb_2O_5 layer suppresses electron back injection from FTO to hematite.	[21]

Hematite/NiOOheterostructured photoanode	0.62	0.625 (@1.23)	NiOOH as an OER catalyst by offering a redox cycle ($\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+} \leftrightarrow \text{Ni}^{4+}$) that facilitates hole injection.	[107]
Hematite nanorods incorporated into gold nanohole arrays	~0.9	~0.95 (@1.23)	Gold nanohole arrays sustain surface plasmon polaritons and localized surface plasmon resonance, which enhance light absorption in the wavelength range of 300–500 nm and 550–750 nm, respectively.	[17]
Gold nanopillar-supported hematite thin films	~1.15	~0.48 (@1.5)	Thickness of hematite film: 140 nm. The performance enhancement is ascribed to increased light absorption originating from (1) surface plasmon resonances and light trapping by the nanostructured gold substrate.	[18]

Note:

* All photocurrent density data are collected under standard air mass 1.5G illumination (100 mW/cm²), unless otherwise stated.

** Illumination conditions: 500 W Xe lamp, 285 mW/cm².

hematite: excitons generate within femtoseconds, in-bulk electron–hole pairs recombine in picoseconds, holes near the surface have a lifetime of microseconds to milliseconds, and water is oxidized by surface holes within a time period between milliseconds and seconds [20]. The ability of gauging the transient processes is of critical importance to provide insightful and fundamental understandings of hematite.

The fundamental mechanism of TA spectroscopy involves two beams of light pulse. The first pulse (the “pump”) strikes the tested material and induces excitons. The second pulse (the “probe”), coming after the pump with a short delay, interacts with the excitons and generates a spectrum. By changing the delay time of the probe, a series of time-resolved spectra can be collected. These spectra contain critical information on the charge carrier dynamics of the tested materials.

TA spectroscopy is a versatile probing technique that is under rapid upgrading. For example, a heterodyne transient grating technique [108] is a recently developed probing technique spinoff from conventional TA spectroscopy which studies photoexcited carrier dynamics in hematite. By coupling with PEC setups, TA spectroscopy allows for *in situ* and *in operando* characterization of the charge carrier behaviors in an electrode. An extensive discussion on the mechanisms of these techniques is beyond the scope of this chapter, but interested readers can refer to some pertinent review articles [8, 109, 110].

The most significant discovery achieved by TA spectroscopy is the elucidation of the correlation between photoinduced holes and photocurrent. Figure 5.11a depicts the TA signals of hematite collected with different external biases. A striking feature of these spectra is that at 100 milliseconds, their peak intensity increases with increasing applied bias. Figure 5.11b displays that the peak intensity at 100 milliseconds changes in accordance with the intensity of photocurrent density. Through systematic experimental investigations, the origin of the peak at 100 milliseconds has been assigned to the absorption from the holes trapped at the hematite surface [111–113]. This observation unequivocally illustrates that it is the holes on the surface that participate in water oxidation and generation of photocurrent. Therefore, to increase the yield of surface holes becomes the “holy grail” to construct high-performance hematite photoanodes.

5.4.2 Effects of Morphology

Creating nanostructures with shortened hole diffusion length is an effective way to circumvent the consequences of short-lived holes. Without any treatment, the thickness of hematite film is restricted to less than 50 nm to

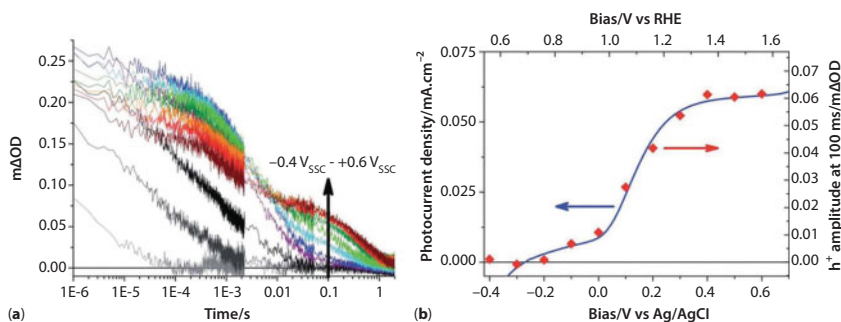


Figure 5.11 (a) The TA signal collected at different applied biases. The arrow indicates the position of the peak associated with surface holes. When increasing the external bias, the peak intensity increases as the number of surface holes increases. (b) The correlation between the intensity of the transient absorption signal associated with surface state-trapped holes (red dots) and experimentally measured photocurrent density (blue). Figure reproduced with permission from Ref. [111], Copyright 2012, Royal Society of Chemistry.

minimize recombination loss in the bulk of the material [21]. With ultra-fine features, nanostructures offer holes a remarkably shorter diffusion length compared to films without textures (Figure 5.12). When nanorod arrays are illuminated, the resultant holes are able to easily access the surface, if the diameter of the nanorod is comparable with that of the hole diffusion length. As a result, more holes can oxidize water in nanorods than in films. Pu *et al.* demonstrated that a hematite nanorod film can be as thick as ~ 350 nm and maintain satisfactory PEC performance [114]. Another advantage of nanostructuring is that incident light is reflected from within the voids or space between nanorods, nanowires, or the hollow space of nanotubes. This boosts light absorption efficiency.

To date, there is still need for more investigation into the interplay between nanostructuring morphology and the corresponding photoactivity. Performance differences between architectures are often attributed to change of surface area. For example, upon comparing the photoactivity of hematite nanorod arrays and nanotube arrays, Mao *et al.* observed that nanotubes achieved $\sim 200\%$ more photocurrent density than nanorods at an identical applied bias [83]. The open-ended tubes provided additional surface area (compared to solid nanowires), which boosted the photocatalytic performance.

Another effective method for nanostructuring hematite is facet engineering. Due to the anisotropic electrical conductivity of hematite, researchers have sought ways to synthesize hematite nanostructures with the highly conductive facets, *e.g.*, the (001) facets, exposed. Additionally, facets such as (012) are highly packed with iron atoms. The dangling bonds

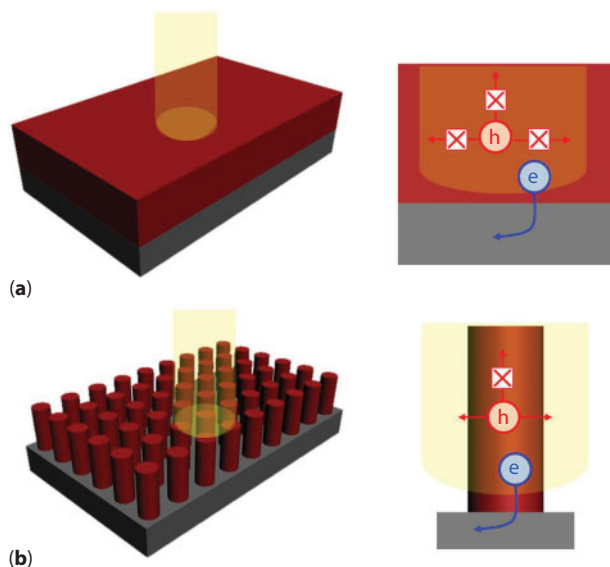


Figure 5.12 Schematic illustration of the different diffusion patterns of photoinduced charge carriers between (a) a plain hematite film photoanode and (b) a hematite nanowire array photoanode. Holes trapped in films can hardly diffuse to film surface due to their limited diffusion length. Holes generated in a nanowire manage to move to the surface by diffusing horizontally across a small length.

of the surface atoms are likely the active sites for OER; as such, exposing these facets is beneficial to achieving outstanding PEC performance [28]. Recently, Warren *et al.* claimed that removal of the high-angle grain boundaries is another issue that merits consideration when designing hematite nanostructures [115]. The group employed a novel characterization method involving dark-field transmission electron microscopy and atomic force microscopy to investigate the electrical resistance across different facets. They observed that current obtained along the path crossing the highest angle grain boundaries was the smallest. Therefore, to reduce the overall resistance of hematite, it is necessary to (1) increase the crystallinity and (2) of even greater importance, assemble hematite nanocrystals in a pattern that diminishes high-angle grain boundaries.

5.4.3 Effect of Doping

5.4.3.1 Oxygen (O) Vacancies

The exact role of oxygen vacancies in hematite is controversial. Some researchers claim that O vacancies serve as shallow donors in hematite

with relatively low formation energies [116]. These vacancies enhance the donor density of hematite and, in return, increase the electrical conductivity and the band bending at the hematite surface that facilitates the separation of photoinduced holes. However, Ping and coworkers studied the influence of O vacancies by first-principle calculations and arrived at different conclusions. Based on their calculations, the O vacancies are deep impurities and only behave as defect bands without modifying the band structure [7]. This discrepancy could potentially be resolved by revising the simulations to include the interaction between small polarons, defects, and water molecules at the hematite/water interface. Experiments employing the TA technique (discussed in Section 5.4.1) proved the main role of O vacancy is blocking the surface electron-hole recombination pathway [117] and improving electron collection [118] which is helpful in harvesting more surface-trapped holes.

During the thermal treatment, two Fe^{2+} ions will be created per O vacancy formed (charge balance). Thermal annealing is the commonly applied method to realize the conversion, though more complicated methods, such as plasma treatment [39], are also viable. The presence of mixed-valence metal centers in hematite can improve charge transport [37].

The presence of O vacancies has little influence on the optical characteristics of hematite. Zhao *et al.* compared the light absorption profiles of pristine hematite and oxygen-deficient hematite and observed no appreciable changes [119]. This observation aligns with simulations which suggest that the incorporation of O vacancies in hematite does not change its band edge positions and band dispersion [7]. The quantitative understandings of the roles of O vacancies in hematite remain scant, due mainly to the challenges of creating O deficiencies with well-controlled concentrations, location, and distribution.

5.4.3.2 *n*-type Dopants

The effect of *n*-type dopants on PEC performance of hematite is generally ascribed to enhance the charge carrier density. Following are two specific examples of the most commonly adopted *n*-types dopants, Ti^{4+} and Sn^{4+} ; most other *n*-type dopants behave similarly to either of the dopants discussed below.

(1) Ti^{4+}

Ti^{4+} dopants exert multifaceted effects on the electronic and surface properties of hematite. Ti^{4+} dopes hematite through substituting Fe^{3+} . The presence of Ti^{4+} shortens the intraplane Fe-Fe bond length and increases the

probability of polaron hopping, hence making hematite more electrically conductive [120]. Another factor accounting for the enhancement in electrical conductivity is the reduction of effective mass of electrons in hematite, triggered by hybridization of Ti *d* and *s* orbitals in the CB minimum. The reduced effective mass of electrons improves electron mobility which in turn reduces the electrical resistance of hematite.

With the help of transient absorption spectroscopy, Morin observed no significant change in the signal across a time frame of 0 to 1000 ps, indicating Ti doping has negligible influence on the lifetime of the photoinduced holes or electron–hole recombination probability [121].

Ti doping also changes the surface nature of hematite. For example, Fe^{III}-OH groups can be induced by Ti doping [122]. The introduced hydroxyl groups improve OER efficiency. Mollor-Satoca *et al.* further elaborated on this point by studying the interplay between Ti doping concentration and PEC performance [123]. The optimal doping concentration was determined to be 10%. While lower doping concentrations had limited improvement in PEC performance, higher doping concentrations gave birth to TiO₂ surface coating. The surface coating alters the band diagram that favors introduction of electrons to surface states, which severely degrade the PEC performance of Ti-doped hematite.

(2) Sn⁴⁺

Sn⁴⁺ serves as an *n*-type dopant and its major effect is to increase the charge carrier density that makes hematite more electrically conductive. Sn⁴⁺ dopes hematite by substituting Fe³⁺ (yielding Fe²⁺ as a result of charge balance). The Fe²⁺-Sn⁴⁺ pairs reportedly serve as electron donors that enhance electrical conductivity of hematite [38]. The increment in charge carrier density upshifts the fermi level of hematite and increases the band bending at the hematite/electrolyte interface, which in turn facilitates charge separation near surface regions and hole injection into water molecules. The increased conductive nature also reduces energy loss at the hematite/substrate interface.

In addition, Sn doping can alter the surface composition of hematite. Xi *et al.* demonstrated that Sn doping resulted in surfaces coated with a tin dioxide layer above a thin surface layer of Fe_xSn_{1-x}O₄ [105]. The Fe_xSn_{1-x}O₄ passivation contributed to a reduced electron–hole recombination rate at the hematite/electrolyte interface.

In addition to effects on electrical properties, Sn doping is capable of modifying the band structure of hematite. Doping a high concentration of Sn into hematite reduces its band gap and broadens the absorption range in visible light. The slight distortion in structure induced by the large size

of Sn^{4+} can increase the light absorption coefficient of hematite by a factor of 2. In both cases the increased number of photons absorbed is expected to result in enhanced photocurrent.

5.4.3.3 *p-type Dopants*

(1) Formation of *p-n* junctions

Engineering the distribution of dopants can form *p-n* junctions on the hematite surface. The resulting *p*-type hematite surface layer builds a *p-n* junction with the pristine *n*-type hematite bulk. The *p-n* junction builds an internal electric field at the junction that drives holes to the surface and repels electrons to the bulk, facilitating charge separation (more details will be discussed in Section 5.4.5.1). The enhanced charge separation has been experimentally verified by interfacial hole transfer kinetics studies and electrochemical impedance spectroscopy [46].

(2) Surface redox activity

Some *p*-type dopants are redox active and can directly interact with water molecules on behalf of hematite. One typical example is Ag^+ . Shen *et al.* claimed that the doped Ag^+ can accept holes passed from hematite (while forming Ag^{2+}) and subsequently transfer them to oxidize water molecules [48]. The Ag-assisted hole transfer exhibits much faster kinetics and contributes to more than three times augmented photocurrent density compared to its undoped counterpart.

5.4.3.4 *Isovalent Dopants*

Isovalent dopants such as Al^{3+} can affect the crystal structure of hematite, though they can only impose marginal effects on modifying hematite's bandgap and band positions. However, because Al^{3+} is smaller than Fe^{3+} , the presence of Al^{3+} shrinks the volume of the unit cell and decreases Fe-Fe separation distance. This is favorable in facilitating polaron hopping and improving electrical conductivity [49].

5.4.3.5 *Multiple Dopants*

Recently, codoping hematite with two or more dopants has been reported to be more efficient in activating hematite than monodoping strategies. The performance difference is at the root of crystal structural alteration. Considering most commonly adopted dopants, *e.g.*, Sn^{4+} , have different sizes from Fe^{3+} , substituting Fe^{3+} with these guest ions will likely distort

the crystal structure of hematite. The lattice deformation introduces lattice strain and can retard polaron hopping. More detrimentally, irreversible structural damage could take place if hematite is overdoped. Both factors lead to reduction in electrical conductivity despite any enhanced charge carrier concentration.

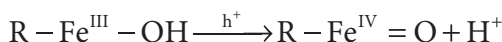
Codoping with more than one type of ion has proven to be effective in remedying the negative impacts of lattice distortion. Properly choosing a second dopant with suitable size can counteract the negative influence exerted by the first dopant toward maintaining the pristine crystal structure of hematite. A typical example was demonstrated by Annamalai *et al.* where they observed an enhancement in photocurrent density of Sn- and Be-codoped hematite (compared to Sn-doped hematite) [50]. It should be noted that the introduction of a second dopant can affect a number of properties beyond structure, including optical and electronic properties. Therefore, it is preferable to prescreen feasible dopant combinations with molecular simulations before proceeding to experimental investigations.

5.4.4 Effect of Water Oxidation Catalysts

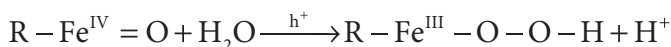
5.4.4.1 Mechanism of Uncatalyzed Water Oxidation

Although the precise mechanism pertaining to water oxidation reactions on the hematite surface is still under active investigation, some encouraging preliminary results have been obtained by *in situ* probing techniques, such as *in operando* infrared spectroscopy [124] and photoinduced absorption spectroscopy [10]. One of the identified intermediate species of OER on the hematite surface is high-valent iron-oxo ($\text{Fe}^{\text{IV}}=\text{O}$). Based on this finding, the mechanism of water oxidation on hematite surface is proposed as follows.

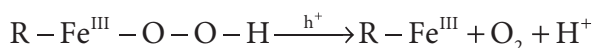
1. The hydroxyl groups from hydration of hematite are oxidized by photoinduced holes into iron-oxo groups (R represents the bulk of hematite):



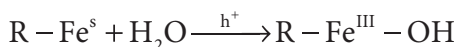
2. The iron-oxo groups are further oxidized by holes to peroxide groups at the presence of water:



3. Oxygen is evolved via decomposition of the peroxide groups:



4. Rehydration of hematite and closing the reactions loop:



The second step, involving formation of the peroxide bonds, is defining the rate-determining steps [10]. TA spectroscopy confirmed that water oxidation occurs over a range of seconds [10], while the lifetime of surface-trapped holes can only stretch to milliseconds. Such a discrepancy in duration leads to poor hole injection efficiency and unsatisfactory PEC performance.

5.4.4.2 Mechanism of Catalyzed Water Oxidation

Decorating hematite with OER catalysts is efficient in changing the OER pathway and facilitates hole transfer to water molecules (Figure 5.13a and b). A number of OER catalysts have been coupled with hematite and successfully improved the PEC performance. Among them, Co-Pi is a significantly promising OER catalyst.

Co-Pi is a phosphate-mediated cobalt oxide catalyst that was first adopted by Gamelin [72] and Nocera [125]. While the mechanism for the catalytic activity of Co-Pi is not agreed upon, one of the Co-Pi-assisted water oxidation pathways based on experimental evidence and proposed by the Nocera's group is illustrated in Figure 5.13c [126]. At low applied potentials, Co-Pi is able to store holes without triggering oxidation of water molecules. The stored holes oxidize $\text{Co}^{\text{II}}\text{-OH}$ groups to $\text{Co}^{\text{IV}}\text{=O}$ groups via a proton-coupled electron transfer (PCET). At a sufficiently high concentration of stored holes such that two $\text{Co}^{\text{IV}}\text{=O}$ groups are in close proximity with each other, water oxidation begins and oxygen gas evolves. This mechanism is based on the assumption that holes oxidizing water are from Co-Pi, not from hematite. The experimental results collected by Klahr *et al.* corroborate with this argument [127]. They observed that by increasing the thickness of the Co-Pi layer, the onset potential is shifted cathodically. The authors attributed this phenomenon to the existence of holes in the Co-Pi layer which are brought farther from the hematite surface when increasing the thickness, and are thus unlikely to recombine with electrons.

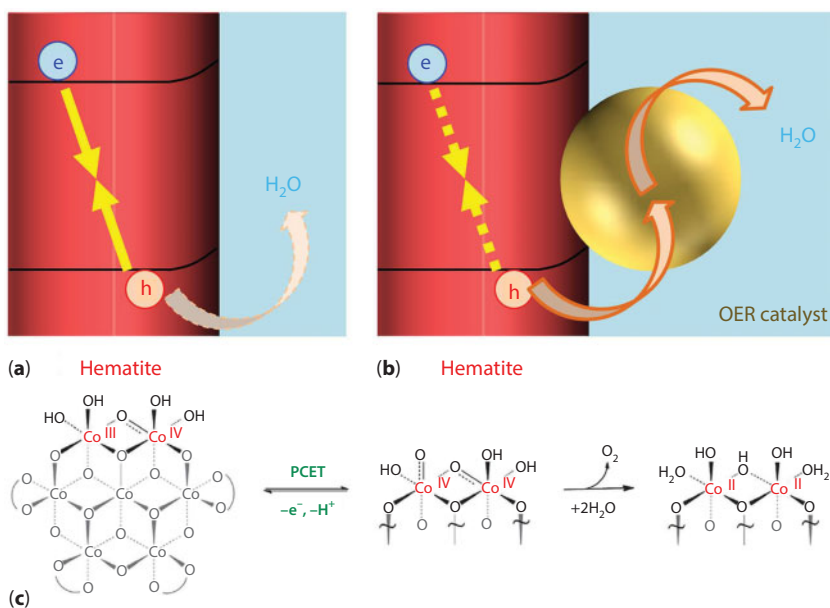


Figure 5.13 A schematic illustration depicting the charge carrier dynamics of (a) pristine hematite and (b) OER catalyst-decorated hematite. For simplicity, the surface states where holes need to fill in before transferring to water molecules are omitted. OER catalysts facilitate hole injection and reduce electron–hole recombination near the hematite surface. (c) The OER mechanism of Co-Pi. Figure c reproduced with permission from Ref. [126], Copyright 2010, American Chemical Society.

The onset potential can generally be cathodically shifted by 100–240 mV by incorporation of the Co-Pi catalyst.

5.4.5 Effect of Heterojunctions

5.4.5.1 Facilitating Charge Separation and Transfer

Engineering hematite and a second semiconductor to form a heterojunction is beneficial for charge separation and subsequently improving the concentration of surface holes. The two major mechanisms correlating with the performance enhancement are forming *p-n* junctions and Z-schemes.

The *p-n* junction is formed by infusing an *n*-type semiconductor with a *p*-type semiconductor (Figure 5.14a). Because the *n*-type semiconductor lacks holes, the major charge carrier of the *p*-type semiconductor, *i.e.*, holes will diffuse to the *n*-type semiconductor side driven by a concentration difference. Electrons in the *n*-type semiconductor flow opposite to the holes.

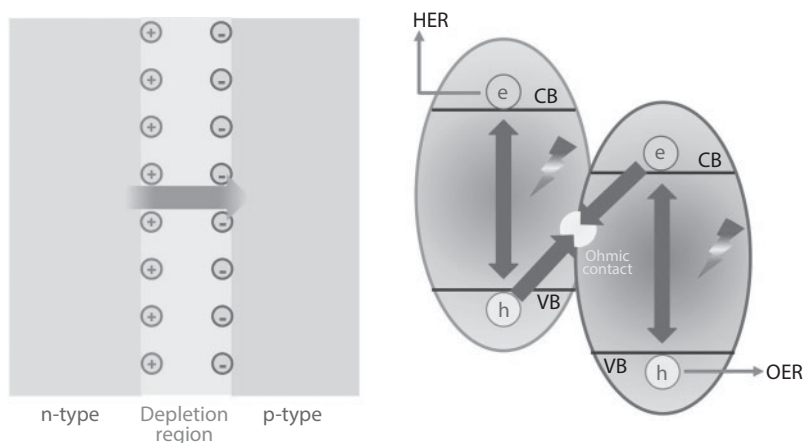


Figure 5.14 Two heterojunction configurations that facilitate charge separation. (a) A *p-n* junction. The electric force (represented by the orange arrow) in the depletion region shoots holes from the *n*-type side to the *p*-type side while preventing electrons from going the same way. (b) A “Z-scheme” formed by two coupled semiconductors. The Z-shaped purple arrows indicate the flow of charge carriers.

As a result, a depletion layer with holes and electrons accumulated at both ends forms between the two semiconductors. This charge distribution pattern induces an electric field whose direction points from the *n*-type semiconductor to the *p*-type. The minor charge carriers, *e.g.*, holes in *n*-hematite, once formed near the contact region, will be driven by the electric field and discharged to the *p*-type semiconductor. The electrons in the *n*-type semiconductor experience a counterforce exerted by the electric field and are repelled from entering the depletion region. This unique property of *p-n* junctions eases the charge separation and augments photocurrent.

The second type of junction is a Z-scheme. This design is analogous to the configuration of photosynthesis clusters existing in plants where two light-harvesting units are coupled by a series of redox shuttles. Absorbed photons excite electrons in both units, creating one exciton in each component per photon absorbed (Figure 5.14b). After excitation, one electron–hole pair is recombined at the interface between the two contacted semiconductors (*i.e.*, the ohmic contact). This leaves another exciton with the electron and hole remotely separated, which reduces the probability of recombination. The long-lived holes and electrons then contribute to high photocurrent density due to improved charge separation. Depending on the configuration, the ohmic contact can be the interface between two semiconductors (direct Z-scheme) or solid electron mediators such as Au, Ag, and graphene (electron-mediated Z-scheme) [128].

Because for both cases, a second semiconductor is used and a new semiconductor/semiconductor interface is introduced, it is crucial to ensure the seamless contact that brings in little contact resistance without undermining the overall PEC performance.

5.4.5.2 Surface Passivation

Surface states are a double-sided sword for PEC water splitting. Specifically for photoanodes such as hematite, successful water oxidation relies on the surface states to hold photoinduced holes near the hematite surface for charge injection. However, if the surface states function as hole traps that prevent holes from moving out, these trapped holes will be eventually scavenged through recombination with electrons located at excited energy states. In addition, a large number of surface states introduces additional electrical resistance and pins the fermi level, which further reduces the exciton lifetime and impedes efficient electron–hole separation, respectively. Therefore, the surface nature of hematite is regarded as a crucial factor determining the onset potential of hematite.

The chemical nature of surface states is still under debate. Some researchers believe surface states are iron-based intermediates that directly participate in OER [127]. Others claim surface states are electronic states that do not participate in the water oxidation reaction, *e.g.*, from inactive adsorbates [129]. In 2014, Klahr *et al.* performed *in situ* UV-vis absorption spectroscopy to probe the evolution of surface functionalities at different applied biases [127]. By increasing the bias, an absorption peak centered at 572 nm became visible. The authors tentatively ascribed this absorption feature to the oxidation of surface iron-aqua ($\text{Fe}-\text{H}_2\text{O}$) or iron hydroxyl ($\text{Fe}-\text{OH}$) groups to iron-oxo ($\text{Fe}=\text{O}$) groups. Coating an ultrathin layer of Al_2O_3 suppressed the absorption peak at identical bias, suggesting that the surface states of hematite were related to the oxo-terminated iron atoms. Research dedicated to elucidating the surface state nature is still in progress.

As surface states belong to surface functionalities, dissolution and recrystallization are proven to reconstruct hematite surfaces with reduced concentration of surface states. Jang *et al.* used an acidic solution to convert the surface region of hematite nanorods to FeOOH [130]. Heating the $\text{FeOOH}/\text{Fe}_2\text{O}_3$ core/shell structure converted the oxyhydroxide shell to hematite. The authors observed in the onset potential of the regrown hematite a nearly 400 mV cathodic shift. Such an effect was claimed as a result of surface passivation due to the regrowing process. Yang *et al.* dipped hematite nanowire films in glacial acetic acid solution and further annealed the sample in air at 450 °C for 30 min [93]. Though the onset

potential did not change appreciably after the acid treatment, the photocurrent showed substantial increase from $\sim 0.2 \text{ mA/cm}^2$ to $\sim 1.3 \text{ mA/cm}^2$ at 1.23 V vs. RHE. TA spectroscopic studies suggested that the electron detrapping rate was greatly enhanced by the acid treatment, which the authors ascribed to potential passivation of surface states.

Besides engineering the hematite surface itself, coating a thin passivation layer using a second material with better crystallinity than the hematite is essential to passivate surface states as well. Choi and coworkers claimed that the surface states of hematite are Fe^{3+} ions exposed on the surface which have imperfect coordination environments [104]. They discovered that by treating the surface with Al^{3+} to form $\text{ZnFe}_{2-x}\text{Al}_x\text{O}_4$ or $\text{Fe}_{2-x}\text{Al}_x\text{O}_3$ surface layers, the photocurrent density of hematite experienced more than two times enhancement at potentials higher than the onset potential. Xi *et al.* applied a surface coating of $\text{Fe}_x\text{Sn}_{1-x}\text{O}_4$ and observed more than two times higher oxygen gas generation compared to untreated samples. This observation was linked to a reduction of recombination events, partly contributed by surface passivation [105].

5.4.5.3 Back-Contact Engineering

Beside the hematite/water interface, there is another interface that receives relatively less attention, *i.e.*, the hematite/conductive substrate interface known as back contact. The quality of back contact dictates the ability to rapidly discharge photoinduced electrons from hematite and hence elongates the lifetime of holes. Formal *et al.* utilized transient photocurrent spectroscopy and impedance spectroscopy to thoroughly investigate the back electron flow from FTO to hematite. They claimed that such a back flow accounts for the large onset potential of hematite and should be suppressed to reduce the external bias needed to observe appreciable photocurrent [131]. Decorating FTO substrates using properly selected semiconductors with ultrathin thickness is a typical way to engineer the back contact.

The back-contact layer exerts three positive influences on the PEC performance of hematite, depending on the type of semiconductor layer deposited. The first function is to suppress electron back injection from FTO to hematite or directly to water molecules. This function is realized by the band alignment where the VB maximum of the deposited semiconductor must be more positive than that of hematite. Such the band alignment only allows electrons to flow one way from hematite to FTO but not in reverse. Ultrathin Nb_2O_5 and TiO_2 layers deposited by atomic layer deposition are two examples that enhance the photocurrent density

and cathodically shift onset potential of hematite based on the rationale discussed above [21].

The second beneficial role of back-contact layers is to increase the conformity and crystallinity of hematite grown atop. The crystal structure of hematite does not match perfectly with that of FTO. The lattice mismatch usually leads to perceptible contact resistance that impedes electron transfer. The trapped electrons have to recombine with holes, reducing the overall photocurrent density. Decorating FTO with a buffer layer that shows reduced lattice mismatch of hematite alters the nucleation and growth mode of hematite films, thus leading to a conformal coating. In this case, electron transfer from hematite to FTO experiences small interface resistance. As a result, few electrons are recombined with holes at the interface. The increased number of electrons discharged from hematite contributes to enhanced photocurrent density. Ga_2O_3 is the commonly utilized underlayer with little lattice mismatch with hematite [21].

The third positive effect is doping. For example, Nb_2O_5 and TiO_2 underlayers can serve as p -type dopant Nb^{5+} and Ti^{4+} reservoirs, respectively. Thermal conversion of FeOOH to hematite triggers these dopants to diffuse upward into hematite. However, some researchers experimentally observed the existence of back-contact doping [132], while others found that the diffusion is insignificant [21]. The reason for this discrepancy has not yet been resolved (but might relate to the different thermal treatment conditions).

It should be noted here that the thickness of the underlayer must be meticulously adjusted to achieve optimal performance. Ultrathin coating might not form a conformal coating, leading to nonuniform modifications with compromised performance. Ultrathick coatings could significantly decelerate electron flow from hematite to beneath the conductive substrates, as the coated layers are usually semiconductors with limited electrical conductivities. Thus a set of controlled experiments with different coating thickness may be needed to identify the optimal layer thicknesses, particularly for novel materials with no available preliminary results.

5.5 Summary

This chapter introduces hematite as a photoanode material for solar-assisted hydrogen generation. Its role in PEC applications, properties associated with PEC performance (e.g., optical, electrical, and surface properties), challenges impeding high PEC performance, strategies for obtaining efficient electrode materials, and fundamental understandings of different modification strategies have been thoroughly introduced

with state-of-the-art examples. Although the current PEC performance of hematite is still far below its theoretical performance, researchers are optimistic about the future of hematite. A number of encouraging results have been achieved. And, more in-depth fundamental understandings are rapidly becoming available with the development of *in situ* simulations and *in operando* measuring techniques. Hematite, along with other promising semiconductors, will continue to be a promising source of research in the development of PEC cells for cost-effective and environmentally friendly solar hydrogen generation.

References

1. Fujishima, A., Honda, K., Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, 37–38, 1972.
2. Sivula, K., Nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, in: Krol, R.V.D., Grätzel, M. (Eds.), *Photoelectrochemical Hydrogen Production*, pp. 121–156, Springer, New York, 2012.
3. Sivula, K., Formal, F.L., Grätzel, M., Solar water splitting: Progress using hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoelectrodes. *ChemSusChem*, 4, 432–449, 2011.
4. Dghoughi, L., Elidrissi, B., Bernède, C., Addou, M., Lamrani, M.A., Regragui, M., Erguig, H., Physico-chemical, optical and electrochemical properties of iron oxide thin films prepared by spray pyrolysis. *Appl. Surf. Sci.*, 253, 1823–1829, 2006.
5. Cesar, I., Sivula, K., Kay, A., Zboril, R., Grätzel, M., Influence of feature size, film thickness, and silicon doping on the performance of nanostructured hematite photoanodes for solar water splitting. *J. Phys. Chem. C*, 113, 772–782, 2009.
6. Tamirat, A.G., Rick, J., Dubale, A.A., Su, W.-N., Hwang, B.-J., Using hematite for photoelectrochemical water splitting: a review of current progress and challenges. *Nanoscale Horiz.*, 1, 243–267, 2016.
7. Smart, T.J., Ping, Y., Effect of defects on the small polaron formation and transport properties of hematite from first-principles calculations. *J. Phys. Condens. Matter*, 29, 394006, 2017.
8. Shen, S., Lindley, S.A., Chen, X., Zhang, J.Z., Hematite heterostructures for photoelectrochemical water splitting rational materials design and charge carrier dynamics. *Energy Environ. Sci.*, 9, 2744–2775, 2016.
9. Pendlebury, S.R., Wang, X., Le Formal, F., Cornuz, M., Kafizas, A., Tilley, S.D., Grätzel, M., Durrant, J.R., Ultrafast charge carrier recombination and trapping in hematite photoanodes under applied bias. *J. Am. Chem. Soc.*, 136, 9854–9857, 2014.
10. Le Formal, F., Pastor, E., Tilley, S.D., Mesa, C.A., Pendlebury, S.R., Grätzel, M., Durrant, J.R., Rate law analysis of water oxidation on a hematite surface. *J. Am. Chem. Soc.*, 137, 6629–6637, 2015.

11. Iordanova, N., Dupuis, M., Rosso, K.M., Charge transport in metal oxides: A theoretical study of hematite $\alpha\text{-Fe}_2\text{O}_3$. *J. Chem. Phys.*, 122, 144305, 2005.
12. Patra, A.K., Kundu, S.K., Bhaumik, A., Kim, D., Morphology evolution of single-crystalline hematite nanocrystals: Magnetically recoverable nanocatalysts for enhanced facet-driven photoredox activity. *Nanoscale*, 8, 365–377, 2016.
13. Catti, M., Valerio, G., Dovesi, R., Theoretical study of electronic, magnetic, and structural properties of $\alpha\text{-Fe}_2\text{O}_3$ (hematite). *Phys. Rev. B*, 51, 7441–7450, 1995.
14. Ye, Y., Thorne, J.E., Wu, C.H., Liu, Y.-S., Du, C., Jang, J.-W., Liu, E., Wang, D., Guo, J., Strong O 2p–Fe 3d hybridization observed in solution-grown hematite films by soft X-ray spectroscopies. *J. Phys. Chem. B*, 122(2), 2017.
15. Sivula, K., Zboril, R., Formal, F.L., Robert, R., Weidenkaff, A., Tucek, J., Frydrych, J., Grätzel, M., Photoelectrochemical water splitting with mesoporous hematite prepared by a solution-based colloidal approach. *J. Am. Chem. Soc.*, 132, 7436–7444, 2010.
16. Jia, L., Harbauer, K., Bogdanoff, P., Herrmann-Geppert, I., Ramírez, A., Krol, R.V.D., Fiechter, S., $\alpha\text{-Fe}_2\text{O}_3$ films for photoelectrochemical water oxidation – insights of key performance parameters. *J. Mater. Chem. A*, 2, 20196–20202, 2014.
17. Li, J., Cushing, S.K., Zheng, P., Meng, F., Chu, D., Wu, N., Plasmon-induced photonic and energy-transfer enhancement of solar water splitting by a hematite nanorod array. *Nat. Commun.*, 4, 2651, 2013.
18. Gao, G., Liu, C., Jeong, H.E., Yang, P., Plasmon-enhanced photocatalytic activity of iron oxide on gold nanopillars. *ACS Nano*, 6, 234–240, 2012.
19. Huang, X., Yang, L., Hao, S., Zheng, B., Yan, L., Qu, F., Asiri, A.M., Sun, X., N-doped carbon dots: A metal-free co-catalyst on hematite nanorod arrays toward efficient photoelectrochemical water oxidation. *Inorg. Chem. Front.*, 4, 537–540, 2017.
20. Ruoko, T.-P., Kaunisto, K., Bärtsch, M., Pohjola, J., Hiltunen, A., Niederberger, M., Tkachenko, N.V., Lemmetyinen, H., Subpicosecond to second time-scale charge carrier kinetics in hematite–titania nanocomposite photoanodes. *J. Phys. Chem. Lett.*, 6, 2859–2864, 2015.
21. Hisatomi, T., Dotan, H., Stefić, M., Sivula, K., Rothschild, A., Grätzel, M., Mathews, N., Enhancement in the performance of ultrathin hematite photoanode for water splitting by an oxide underlayer. *Adv. Mater.*, 24, 2699–2702, 2012.
22. Lu, J., Peng, Q., Wang, Z., Nan, C., Li, L., Li, Y., Hematite nanodiscs exposing (001) facets: synthesis, formation mechanism and application for Li-ion batteries. *J. Mater. Chem. A*, 1, 5232–5237, 2013.
23. Ling, Y., Wang, G., Wheeler, D.A., Zhang, J.Z., Li, Y., Sn-doped hematite nanostructures for photoelectrochemical water splitting. *Nano Lett.*, 11, 2119–2125, 2011.

24. Liu, J., Cai, Y.Y., Tian, Z.F., Ruan, G.S., Ye, Y.X., Liang, C.H., Shao, G.S., Highly oriented Ge-doped hematite nanosheet arrays for photoelectrochemical water oxidation. *Nano Energy*, 9, 282–290, 2014.
25. Mao, A., Park, N.-G., Han, G.Y., Park, J.H., Controlled growth of vertically oriented hematite/Pt composite nanorod arrays: use for photoelectrochemical water splitting. *Nanotechnology*, 22, 175703, 2011.
26. Ishaq, S., Sikora, A., Scheidler, N., Hambleton, C., Katz, J.E., Enhancement of water oxidation photocurrent for hematite thin films electrodeposited with polyvinylpyrrolidone. *J. Electrochem. Soc.*, 163, F1330–F1336, 2016.
27. Riha, S.C., DeVries Vermeer, M.J., Pellin, M.J., Hupp, J.T., Martinson, A.B. F., Hematite-based photo-oxidation of water using transparent distributed current collectors. *ACS Appl. Mater. Interfaces*, 5, 360–367, 2013.
28. Cha, H.G., Kang, M.J., Hwang, I.C., Kim, H., Yoon, K.B., Kang, Y.S., Manual assembly of nanocrystals for enhanced photoelectrochemical efficiency of hematite film. *Chem. Commun.*, 51, 6407–6410, 2015.
29. Liu, T., Ling, Y., Yang, Y., Finn, L., Collazo, E., Zhai, T., Tong, Y., Li, Y., Investigation of hematite nanorod–nanoflake morphological transformation and the application of ultrathin nanoflakes for electrochemical devices. *Nano Energy*, 12, 169–177, 2015.
30. Cibrev, D., Tallarida, M., Das, C., Lana-Villarreal, T., Schmeisser, D., Gómez, R., New insights into water photooxidation on reductively pretreated hematite photoanodes. *Phys. Chem. Chem. Phys.*, 19, 21807–21817, 2017.
31. Ling, Y., Wang, G., Wang, H., Yang, Y., Li, Y., Low-temperature activation of hematite nanowires for photoelectrochemical water oxidation. *ChemSusChem*, 7, 848–853, 2014.
32. Wang, D., Zhang, Y., Peng, C., Wang, J., Huang, Q., Su, S., Wang, L., Huang, W., Fan, C., Crystallinity engineering of hematite nanorods for high-efficiency photoelectrochemical water splitting. *Adv. Sci.*, 2, 1500005, 2015.
33. Kim, J.Y., Youn, D.H., Kim, J.H., Kim, H.G., Lee, J.S., Nanostructure-preserved hematite thin film for efficient solar water splitting. *ACS Appl. Mater. Interfaces*, 7, 14123–14129, 2015.
34. Li, M., Yang, Y., Ling, Y., Qiu, W., Wang, F., Liu, T., Song, Y., Liu, X., Fang, P., Tong, Y., Li, Y., Morphology and doping engineering of Sn-doped hematite nanowire photoanodes. *Nano Lett.*, 17, 2490–2495, 2017.
35. Li, C., Li, A., Luo, Z., Zhang, J., Chang, X., Huang, Z., Wang, T., Gong, J., Surviving high-temperature calcination: ZrO₂-induced hematite nanotubes for photoelectrochemical water oxidation. *Angew. Chem.*, 129, 4214–4219, 2017.
36. Bachmann, J., Jing, J., Knez, M., Barth, S., Shen, H., Mathur, S., Gösele, U., Nielsch, K., Ordered iron oxide nanotube arrays of controlled geometry and tunable magnetism by atomic layer deposition. *J. Am. Chem. Soc.*, 129, 9554–9555, 2007.
37. Ling, Y., Wang, G., Reddy, J., Wang, C., Zhang, J.Z., Li, Y., The influence of oxygen content on the thermal activation of hematite nanowires. *Angew. Chem.*, 124, 4150–4155, 2012.

38. Ling, Y., Li, Y., Review of Sn-doped hematite nanostructures for photoelectrochemical water splitting. *Part. Part. Syst. Charact.*, 31, 1113–1121, 2014.
39. Zhu, C., Li, C., Zheng, M., Delaunay, J.-J., Plasma-induced oxygen vacancies in ultrathin hematite nanoflakes promoting photoelectrochemical water oxidation. *ACS Appl. Mater. Interfaces*, 7, 22355–22363, 2015.
40. Steier, L., Herraiz-Cardona, I., Gimenez, S., Fabregat-Santiago, F., Bisquert, J., Tilley, S.D., Grätzel, M., Understanding the role of underlayers and overlayers in thin film hematite photoanodes. *Adv. Funct. Mater.*, 24, 7681–7688, 2014.
41. Wang, D., Chen, H., Chang, G., Lin, X., Zhang, Y., Aldalbahi, A., Peng, C., Wang, J., Fan, C., Uniform doping of titanium in hematite nanorods for efficient photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 7, 14072–14078, 2015.
42. Chemelewski, W.D., Hahn, N.T., Mullins, C.B., Effect of Si doping and porosity on hematite's ($\alpha\text{-Fe}_2\text{O}_3$) photoelectrochemical water oxidation performance. *J. Phys. Chem. C*, 116, 5255–5261, 2012.
43. Bemana, H., Rashid-Nadimi, S., Effect of sulfur doping on photoelectrochemical performance of hematite. *Electrochim. Acta*, 229, 396–403, 2017.
44. Zhang, R., Fang, Y., Chen, T., Qu, F., Liu, Z., Du, G., Asiri, A.M., Gao, T., Sun, X., Enhanced photoelectrochemical water oxidation performance of Fe_2O_3 nanorods array by S doping. *ACS Sustainable Chem. Eng.*, 5, 7502–7506, 2017.
45. Luo, Z., Li, C., Liu, S., Wang, T., Gong, J., Gradient doping of phosphorus in Fe_2O_3 nanoarray photoanodes for enhanced charge separation. *Chem. Sci.*, 8, 91–100, 2017.
46. Lin, Y., Xu, Y., Mayer, M.T., Simpson, Z.I., McMahon, G., Zhou, S., Wang, D., Growth of p-Type hematite by atomic layer deposition and its utilization for improved solar water splitting. *J. Am. Chem. Soc.*, 134, 5508–5511, 2012.
47. Qi, X., She, G., Wang, M., Mu, L., Shi, W., Electrochemical synthesis of p-type Zn-doped $\alpha\text{-Fe}_2\text{O}_3$ nanotube arrays for photoelectrochemical water splitting. *Chem. Commun.*, 49, 5742–5744, 2013.
48. Shen, S., Zhou, J., Dong, C.-L., Hu, Y., Tseng, E.N., Guo, P., Guo, L., Mao, S. S., Surface engineered doping of hematite anorod arrays for improved photoelectrochemical water splitting. *Sci. Rep.*, 4, 6627, 2014.
49. Kleiman-Shwarsstein, A., Huda, M.N., Walsh, A., Yan, Y., Stucky, G.D., Hu, Y.-S., Al-Jassim, M.M., McFarland, E.W., Electrodeposited aluminum-doped $\alpha\text{-Fe}_2\text{O}_3$ photoelectrodes: Experiment and theory. *Chem. Mater.*, 22, 510–517, 2010.
50. Annamalai, A., Lee, H.H., Choi, S.H., Lee, S.Y., Gracia-Espino, E., Subramanian, A., Park, J., Kong, K.-J., Jang, J.S., Sn/Be sequentially co-doped hematite photoanodes for enhanced photoelectrochemical water oxidation: Effect of Be^{2+} as co-dopant. *Sci. Rep.*, 6, 2016.
51. Ahmed, M.G., Kandiel, T.A., Ahmed, A.Y., Kretschmer, I., Rashwan, F., Bahnemann, D., Enhanced photoelectrochemical water oxidation on

- nanostructured hematite photoanodes via p-CaFe₂O₄/n-Fe₂O₃ heterojunction formation. *J. Phys. Chem. C*, 119, 5864–5871, 2015.
52. Yang, X., Liu, R., Du, C., Dai, P., Zheng, Z., Wang, D., Improving hematite-based photoelectrochemical water splitting with ultrathin TiO₂ by atomic layer deposition. *ACS Appl. Mater. Interfaces*, 6, 12005–12011, 2014.
 53. Mayer, M.T., Du, C., Wang, D., Hematite/Si nanowire dual-absorber system for photoelectrochemical water splitting at low applied potentials. *J. Am. Chem. Soc.*, 134, 12406–12409, 2012.
 54. Gurudayal, Sabba, D., Kumar, M.H., Wong, L.H., Barber, J., Grätzel, M., Mathews, N., Perovskite–hematite tandem cells for efficient overall solar driven water splitting. *Nano Lett.*, 15, 3833–3839, 2015.
 55. Tilley, S.D., Cornuz, M., Sivula, K., Grätzel, M., Light-induced water splitting with hematite: improved nanostructure and iridium oxide catalysis. *Angew. Chem. Int. Ed.*, 49, 6405–6408, 2010.
 56. Majumder, S.A., Khan, S.U.M., Photoelectrolysis of water at bare and electrocatalyst covered thin film iron oxide electrode. *Int. J. Hydrog. Energy*, 19, 881–887, 1994.
 57. Xi, L., Tran, P.D., Chiam, S.Y., Bassi, P.S., Mak, W.F., Mulmudi, H.K., Batabyal, S.K., Barber, J., Loo, J.S.C., Wong, L.H., Co₃O₄-decorated hematite nanorods as an effective photoanode for solar water oxidation. *J. Phys. Chem. C*, 116, 13884–13889, 2012.
 58. Kleiman-Shwarsstein, A., Hu, Y.-S., Stucky, G.D., McFarland, E.W., NiFe-oxide electrocatalysts for the oxygen evolution reaction on Ti doped hematite photoelectrodes. *Electrochem. Commun.*, 11, 1150–1153, 2009.
 59. Kim, J.Y., Youn, D.H., Kang, K., Lee, J.S., Highly conformal deposition of an ultrathin FeOOH layer on a hematite nanostructure for efficient solar water splitting. *Angew. Chem. Int. Ed.*, 55, 10854–10858, 2016.
 60. Wang, G., Ling, Y., Lu, X., Zhai, T., Qian, F., Tong, Y., Li, Y., A mechanistic study into the catalytic effect of Ni(OH)₂ on hematite for photoelectrochemical water oxidation. *Nanoscale*, 5, 4129–4133, 2013.
 61. Riha, S.C., Klahr, B.M., Tyo, E.C., Seifert, S., Vajda, S., Pellin, M.J., Hamann, T.W., Martinson, A.B.F., Atomic layer deposition of a submonolayer catalyst for the enhanced photoelectrochemical performance of water oxidation with hematite. *ACS Nano*, 7, 2396–2405, 2013.
 62. Deng, J., Lv, X., Zhang, H., Zhao, B., Sun, X., Zhong, J., Loading the FeNiOOH cocatalyst on Pt-modified hematite nanostructures for efficient solar water oxidation. *Phys. Chem. Chem. Phys.*, 18, 10453–10458, 2016.
 63. Youn, D.H., Park, Y.B., Kim, J.Y., Magesh, G., Jang, Y.J., Lee, J.S., One-pot synthesis of NiFe layered double hydroxide/reduced graphene oxide composite as an efficient electrocatalyst for electrochemical and photoelectrochemical water oxidation. *J. Power Sources*, 294, 437–443, 2015.
 64. Xu, D., Rui, Y., Li, Y., Zhang, Q., Wang, H., Zn-Co layered double hydroxide modified hematite photoanode for enhanced photoelectrochemical water splitting. *Appl. Surf. Sci.*, 358, 436–442, 2015.

65. Warwick, M.E.A., Barreca, D., Bontempi, E., Carraro, G., Gasparotto, A., Maccato, C., Kaunisto, K., Ruoko, T.-P., Lemmetyinen, H., Sada, C., Gönüllüf, Y., Mathurf, S., Pt-functionalized Fe_2O_3 photoanodes for solar water splitting: The role of hematite nano-organization and the platinum redox state. *Phys. Chem. Chem. Phys.*, 17, 12899–12907, 2015.
66. Hong, Y.-R., Liu, Z., Al-Bukhari, S.F.B.S.A., Lee, C.J.J., Yung, D.L., Chi, D., Hor, T.S.A., Effect of oxygen evolution catalysts on hematite nanorods for solar water oxidation. *Chem. Commun.*, 47, 10653–10655, 2011.
67. Li, W., Sheehan, S.W., He, D., He, Y., Yao, X., Grimm, R.L., Brudvig, G.W., Wang, D., Hematite-based solar water splitting in acidic solutions: functionalization by mono- and multilayers of iridium oxygen-evolution catalysts. *Angew. Chem. Int. Ed.* 54, 11428–11432, 2015.
68. Hu, Y.-S., Kleiman-Shwarsstein, A., Stucky, G.D., McFarland, E.W., Improved photoelectrochemical performance of Ti-doped $\alpha\text{-Fe}_2\text{O}_3$ thin films by surface modification with fluoride. *Chem. Commun.*, 0, 2652–2654, 2009.
69. Shi, X., Zhang, K., Park, J.H., Understanding the positive effects of (Co-Pi) co-catalyst modification in inverse-opal structured $\alpha\text{-Fe}_2\text{O}_3$ -based photoelectrochemical Cells. *Int. J. Hydrog. Energy*, 38, 12725–12732, 2013.
70. Ahn, H.-J., Yoon, K.-Y., Kwak, M.-J., Lee, J.-S., Thiyagarajan, P., Jang, J.-H., MoS_x supported hematite with enhanced photoelectrochemical performance. *J. Mater. Chem. A*, 3, 21444–21450, 2015.
71. Lauinger, S.M., Piercy, B.D., Li, W., Yin, Q., Collins-Wildman, D.L., Glass, E. N., Losego, M.D., Wang, D., Geletii, Y.V., Hill, C.L., Stabilization of polyoxometalate water oxidation catalysts on hematite by atomic layer deposition. *ACS Appl. Mater. Interfaces*, 9, 35048–35056, 2017.
72. Zhong, D.K., Gamelin, D.R., Photoelectrochemical water oxidation by cobalt catalyst (“Co-Pi”)/ $\alpha\text{-Fe}_2\text{O}_3$ composite photoanodes: Oxygen evolution and resolution of a kinetic bottleneck. *J. Am. Chem. Soc.*, 132, 4202–4207, 2010.
73. Qian, F., Wang, G., Li, Y., Solar-driven microbial photoelectrochemical cells with a nanowire photocathode. *Nano Lett.*, 10, 4686–4691, 2010.
74. Yang, J., Bao, C., Yu, T., Hu, Y., Luo, W., Zhu, W., Fu, G., Li, Z., Gao, H., Li, F., Zou, Z., Enhanced performance of photoelectrochemical water splitting with ITO@ $\alpha\text{-Fe}_2\text{O}_3$ core-shell nanowire array as photoanode. *ACS Appl. Mater. Interfaces*, 7, 26482–26490, 2015.
75. Liu, Y., Wang, D.-P., Yu, Y.-X., Zhang, W.-D., Preparation and photoelectrochemical properties of functional carbon nanotubes and Ti co-doped Fe_2O_3 thin films. *Int. J. Hydrog. Energy*, 37, 9566–9575, 2012.
76. Zhang, H., Zhu, C., Chen, Y., Yang, M., Yang, P., Wu, X., Qi, L., Meng, F., Enhanced photocatalytic Activities of Net-like Hematite Nanoparticle/Graphene Oxide Composite. *J. Mater. Chem. A*, 3, 1421–1426, 2015.
77. Tamirat, A.G., Su, W.-N., Dubale, A.A., Pan, C.-J., Chen, H.-M., Ayele, D.W., Lee, J.-F., Hwang, B.-J., Efficient photoelectrochemical water splitting using three dimensional urchin-like hematite nanostructure modified with reduced graphene oxide. *J. Power Sources*, 287, 119–128, 2015.

78. Lin, Y., Zhou, S., Sheehan, S.W., Wang, D., Nanonet-based hematite heteronanostructures for efficient solar water splitting. *J. Am. Chem. Soc.*, 133, 2398–2401, 2011.
79. Khnayzer, R.S., Mara, M.W., Huang, J., Shelby, M.L., Chen, L.X., Castellano, F.N., Structure and activity of photochemically deposited “CoPi” oxygen evolving catalyst on titania. *ACS Catal.*, 2, 2150–2160, 2012.
80. Li, L., Yu, Y., Meng, F., Tan, Y., Hamers, R. J., Jin, S., Facile solution synthesis of α - $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nanowires and their conversion to α - Fe_2O_3 nanowires for photoelectrochemical application. *Nano Lett.*, 12, 724–731, 2012.
81. Dias, P., Vilanova, A., Lopes, T., Andrade, L., Mendes, A., Extremely stable bare hematite photoanode for solar water splitting. *Nano Energy*, 23, 70–79, 2016.
82. Lin, Y., Zhou, S., Sheehan, S.W., Wang, D., Nanonet-based hematite heteronanostructures for efficient solar water splitting. *J. Am. Chem. Soc.*, 133, 2398–2401, 2011.
83. Mao, A., Shin, K., Kim, J.K., Wang, D.H., Han, G.Y., Park, J.H., Controlled synthesis of vertically aligned hematite on conducting substrate for photoelectrochemical cells: Nanorods versus nanotubes. *ACS Appl. Mater. Interfaces*, 3, 1852–1858, 2011.
84. Yang, X., Liu, R., Lei, Y., Li, P., Wang, K., Zheng, Z., Wang, D., Dual influence of reduction annealing on diffused hematite/FTO junction for enhanced photoelectrochemical water oxidation. *ACS Appl. Mater. Interfaces*, 8, 16476–16485, 2016.
85. Cots, A., Cibrev, D., Bonete, P., Gómez, R., Hematite nanorod electrodes modified with molybdenum: Photoelectrochemical studies. *ChemElectroChem*, 4, 585–593, 2017.
86. Ahn, H.-J., Yoon, K.-Y., Kwak, M.-J., Jang, J.-H., A titanium-doped SiO_x passivation layer for greatly enhanced performance of a hematite-based photoelectrochemical system. *Angew. Chem. Int. Ed.*, 55, 9922–9926, 2016.
87. Liu, A., Zhang, Y., Ma, W., Song, W., Chen, C., Zhao, J., Facial boron incorporation in hematite photoanode for enhanced photoelectrochemical water oxidation. *J. Photochem. Photobiol.*, 2017.
88. Zhou, L., Lv, X., Nie, Y., Deng, J., Zhang, H., Sun, X., Zhong, J., Hydrogenated hematite nanostructures for highefficiency solar water oxidation. *RSC Adv.*, 6, 92206–92212, 2016.
89. Mirbagheri, N., Wang, D., Peng, C., Wang, J., Huang, Q., Fan, C., Ferapontova, E.E., Visible light driven photoelectrochemical water oxidation by Zn- and Ti-doped hematite nanostructures. *ACS Catal.*, 4, 2006–2015, 2014.
90. Zheng, D., He, X., Xu, W., Lu, X., Self-surface-passivation of titanium doped hematite photoanode for efficient solar water and formaldehyde oxidation. *Mater. Res. Bull.*, 2017.
91. Zhang, Y., Jiang, S., Song, W., Zhou, P., Ji, H., Ma, W., Hao, W., Chen, C., Zhao, J., Nonmetal P-doped hematite photoanode with enhanced electron mobility and high water oxidation activity. *Energy Environ. Sci.*, 8, 1231–1236, 2015.

92. Hu, Z., Shen, Z., Yu, J. C., Covalent fixation of surface oxygen atoms on hematite photoanode for enhanced water oxidation. *Chem. Mater.*, 28, 564–572, 2016.
93. Yang, Y., Forster, M., Ling, Y., Wang, G., Zhai, T., Tong, Y., Cowan, A.J., Li, Y., Acid treatment enables suppression of electron-hole recombination in hematite for photoelectrochemical water splitting. *Angew. Chem. Int. Ed.*, 55, 3403–3407, 2016.
94. Gurudayal, John, R.A., Boix, P.P., Yi, C., Shi, C., Scott, M.C., Veldhuis, S.A., Minor, A.M., Zakeeruddin, S.M., Wong, L.H., Grätzel, M., Mathews, N., Atomically altered hematite for highly efficient perovskite tandem water-splitting devices. *ChemSusChem*, 10, 2449–2456, 2017.
95. Peng, Q., Wang, J., Feng, Z., Du, C., Wen, Y., Shan, B., Chen, R., Enhanced photoelectrochemical water oxidation by fabrication of p-LaFeO₃/n-Fe₂O₃ heterojunction on hematite nanorods. *J. Phys. Chem. C*, 121, 12991–12998, 2017.
96. Steier, L., Luo, J., Schreier, M., Mayer, M.T., Sajavaara, T., Grätzel, M., Low-temperature atomic layer deposition of crystalline and photoactive ultrathin hematite films for solar water splitting. *ACS Nano*, 9, 11775–11783, 2015.
97. Ahmed, M.G., Kretschmer, I.E., Kandiel, T.A., Ahmed, A.Y., Rashwan, F.A., Bahnemann, D.W., A facile surface passivation of hematite photoanodes with TiO₂ overlayers for efficient solar water splitting. *ACS Appl. Mater. Interfaces*, 7, 24053–24062, 2015.
98. Hisatomi, T., Le Formal, F., Cornuz, M., Brillet, J., Tétreault, N., Sivula, K., Grätzel, M., Cathodic shift in onset potential of solar oxygen evolution on hematite by 13-group oxide overlayers. *Energy Environ. Sci.*, 4, 2512, 2011.
99. Dias, P., Andrade, L., Mendes, A., Hematite-based photoelectrode for solar water splitting with very high photovoltage. *Nano Energy*, 38, 218–231, 2017.
100. Hou, Y., Zuo, F., Dagg, A., Feng, P., A three-dimensional branched cobalt-doped α -Fe₂O₃ nanorod/MgFe₂O₄ heterojunction array as a flexible photoanode for efficient photoelectrochemical water oxidation. *Angew. Chem.*, 125, 1286–1290, 2013.
101. Luo, Z., Wang, T., Zhang, J., Li, C., Li, H., Gong, J., Dendritic hematite nano-array photoanode modified with a conformal titanium dioxide interlayer for effective charge collection. *Angew. Chem. Int. Ed.*, 56, 12878–12882, 2017.
102. Gurudayal, Chee, P.M., Boix, P.P., Ge, H., Yanan, F., Barber, J., Wong, L.H., Core-shell hematite nanorods: A simple method to improve the charge transfer in the photoanode for photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces*, 7, 6852–6859, 2015.
103. Kim, J.Y., Magesh, G., Youn, D.H., Jang, J.-W., Kubota, J., Domen, K., Lee, J.S., Single-crystalline, wormlike hematite photoanodes for efficient solar water splitting. *Sci. Rep.*, 3, 2013.
104. McDonald, K.J., Choi, K.-S., Synthesis and photoelectrochemical properties of Fe₂O₃/ZnFe₂O₄ composite photoanodes for use in solar water oxidation. *Chem. Mater.*, 23, 4863–4869, 2011.

105. Xi, L., Chiam, S.Y., Mak, W.F., Tran, P.D., Barber, J., Loo, S.C.J., Wong, L.H., A novel strategy for surface treatment on hematite photoanode for efficient water oxidation. *Chem. Sci.*, 4, 164–169, 2013.
106. Xu, Y.-F., Wang, X.-D., Chen, H.-Y., Kuang, D.-B., Su, C.-Y., Toward high performance photoelectrochemical water oxidation: Combined effects of ultra-fine cobalt iron oxide nanoparticle. *Adv. Funct. Mater.*, 26, 4414–4421, 2016.
107. Malara, F., Minguzzi, A., Marelli, M., Morandi, S., Psaro, R., Dal Santo, V., Naldoni, A., α -Fe₂O₃/NiOOH: An effective heterostructure for photoelectrochemical water oxidation. *ACS Catal.*, 5, 5292–5300, 2015.
108. Sohn, W.Y., Kuwahara, S., Thorne, J.E., Wang, D., Katayama, K., Investigation of photoexcited carrier dynamics in hematite and the effect of surface modifications by an advanced transient grating technique. *ACS Omega*, 2, 1031–1035, 2017.
109. Berera, R., Grondelle, R.V., Kennis, J.T.M., Ultrafast transient absorption spectroscopy: Principles and application to photosynthetic systems. *Photosynth. Res.*, 101, 105–118, 2009.
110. Ruckebusch, C., Sliwa, M., Pernot, P., Juan, A.D., Taulerd, R., Comprehensive data analysis of femtosecond transient absorption spectra: A review. *J. Photochem. Photobiol. C*, 13, 1–27, 2012.
111. Pendlebury, S.R., Cowan, A.J., Barroso, M., Sivula, K., Ye, J., Grätzel, M., Klug, D.R., Tang, J., Durrant, J.R., Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes. *Energy Environ. Sci.*, 5, 6304–6312, 2012.
112. Huang, Z., Lin, Y., Xiang, X., Rodríguez-Córdoba, W., McDonald, K.J., Hagen, K.S., Choi, K.-S., Brunschwig, B.S., Musaev, D.G., Hill, C.L., Wang, D., Lian, T., *In-situ* probe of photocarrier dynamics in water-splitting hematite (α -Fe₂O₃) electrodes. *Energy Environ. Sci.*, 5, 8923, 2012.
113. Barroso, M., Mesa, C.A., Pendlebury, S.R., Cowan, A.J., Hisatomi, T., Sivula, K., Grätzel, M., Klug, D.R., Durrant, J.R., Dynamics of photogenerated holes in surface modified α -Fe₂O₃ photoanodes for solar water splitting. *Proc. Natl. Acad. Sci. U.S.A.*, 109, 15640–15645, 2012.
114. Pu, A., Deng, J., Hao, Y., Sun, X., Zhong, J., Thickness effect of hematite nanostructures prepared by hydrothermal method for solar water splitting. *Appl. Surf. Sci.*, 320, 213–217, 2014.
115. Warren, S., Voitchovsky, K., Dotan, H., Leroy, C.M., Cornuz, M., Stellacci, F., Hébert, C., Rothschild, A., Grätzel, M., Identifying champion nanostructures for solar water splitting. *Nat. Mater.*, 12, 842–849, 2013.
116. Rioult, M., Stanescu, D., Fonda, E., Barbier, A., Magnan, H., Oxygen vacancies engineering of iron oxides films for solar water splitting. *J. Phys. Chem. C*, 120, 7482–7490, 2016.
117. Forster, M., Potter, R.J., Ling, Y., Yang, Y., Klug, D.R., Li, Y., Cowan, A.J., Oxygen deficient α -Fe₂O₃ photoelectrodes: A balance between enhanced electrical properties and trap-mediated losses. *Chem. Sci.*, 6, 4009–4016, 2015.

118. Moir, J., Soheilnia, N., Liao, K., O'Brien, P., Tian, Y., Burch, K.S., Ozin, G.A., Activation of ultrathin films of hematite for photoelectrochemical water splitting via H_2 treatment. *ChemSusChem*, 8, 1557–1567, 2015.
119. Zhao, X., Feng, J., Chen, S., Huang, Y., Sum, T.C., Chen, Z., New insight into the roles of oxygen vacancies in hematite for solar water splitting. *Phys. Chem. Chem. Phys.*, 19, 1074–1082, 2017.
120. Huda, M.N., Walsh, A., Yan, Y., Wei, S.-H., Al-Jassim, M.M., Electronic, structural, and magnetic effects of 3d transition metals in hematite. *J. Appl. Phys.*, 107, 123712, 2010.
121. Morin, F.J., Electrical properties of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ containing titanium. *Phys. Rev.*, 83, 1005, 1951.
122. Zandi, O., Klahr, B.M., Hamann, T.W., Highly photoactive Ti-doped $\alpha\text{-Fe}_2\text{O}_3$ thin film electrodes: Resurrection of the dead layer. *Energy Environ. Sci.*, 6, 634–642, 2013.
123. Monllor-Satoca, D., Bärtsch, M., Fàbrega, C., Genç, A., Reinhard, S., Andreu, T., Arbiol, J., Niederberger, M., Morante, J.R., What do you do, titanium? Insight into the role of titanium oxide as a water oxidation promoter in hematite-based photoanodes. *Energy Environ. Sci.*, 8, 3242–3254, 2015.
124. Zandi, O., Hamann, T.W., Determination of photoelectrochemical water oxidation intermediates on hematite electrode surface using operando infrared spectroscopy. *Nat. Chem.*, 8, 778–783, 2016.
125. Kanan, M.W., Nocera, D.G., *In Situ* formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+} . *Science*, 321, 1072–1075, 2008.
126. McAlpin, J.G., Surendranath, Y., Dincă, M., Stich, T.A., Stoian, S.A., Casey, W.H., Nocera, D.G., Britt, R.D., EPR evidence for Co(IV) species produced during water oxidation at neutral pH. *J. Am. Chem. Soc.*, 132, 6882–6883, 2010.
127. Klahr, B., Hamann, T., Water oxidation on hematite photoelectrodes: Insight into the nature of surface states through *in situ* spectroelectrochemistry. *J. Phys. Chem. C*, 118, 10393–10399, 2014.
128. Li, H., Tu, W., Zhou, Y., Zou, Z., Z-scheme photocatalytic systems for promoting photocatalytic performance: Recent progress and future challenges. *Adv. Sci.*, 3, 1500389, 2016.
129. Du, C., Zhang, M., Jang, J.-W., Liu, Y., Liu, G.-Y., Wang, D., Observation and alteration of surface states of hematite photoelectrodes. *J. Phys. Chem. C*, 118, 17054–17059, 2014.
130. Jang, J.-W., Du, C., Ye, Y., Lin, Y., Yao, X., Thorne, J., Liu, E., McMahon, G., Zhu, J., Javey, A., Guo, J., Wang, D., Enabling unassisted solar water splitting by iron oxide and silicon. *Nat. Commun.*, 6, 7447, 2015.
131. Lin, Y., Yuan, G., Sheehan, S., Zhou, S., Wang, D., Hematite-based solar water splitting: Challenges and opportunities. *Energy Environ. Sci.*, 4, 4862–4869, 2011.
132. Sivula, K., Metal oxide photoelectrodes for solar fuel production, surface traps, and catalysis. *J. Phys. Chem. Lett.*, 2013, 1624–1633, 2013.

Design of Bismuth Vanadate-Based Materials: New Advanced Photoanodes for Solar Hydrogen Generation

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Abstract

While the world is facing an energy crisis based on environmental issues, photo-electrochemical (PEC) cells using solar energy are gaining stronger interest in the photochemistry community. Indeed, such PEC cells can generate hydrogen which is considered as the best green fuel and thus a viable alternative to fossil energy. In this respect, new insights in bismuth vanadate (BiVO_4) materials as advanced photoanodes for PEC solar water splitting are presented here. Although the main drawback of BiVO_4 lies in its electrophotocatalytic efficiency, this semiconductor oxide is a solar responsive material. Therefore, the design of BiVO_4 -based photoanode and PEC cell is a crucial step to reach efficient solar hydrogen generation. A key factor in the elaboration of an efficient photoanode is to evaluate the impact of cell configuration, electrolyte nature, electric bias value, and photoanode preparation on the H_2 production rate. In the present work, a comparative study between pioneered works on BiVO_4 -based photoanodes and new advanced photoanodes composed of transition metal-modified BiVO_4 films and $\text{TiO}_2/\text{BiVO}_4$ layered composites is detailed and discussed. The discussion relies not only on H_2 production rate but also on other characteristics such as the electrochemical properties and the material configuration and composition.

Keywords: BiVO_4 , composite, hydrogen, PEC, photoanode, transition metal, water splitting

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6.1 Introduction

Hydrogen is righteously considered as the future source of energy on our planet since it would certainly replace fossil fuel. Hydrogen as a solar fuel does not produce any greenhouse gases neither micropollutants in the atmosphere, i.e., hydrogen is a clean fuel. Indeed, the combustion of H_2 releases only water as a by-product. In addition, hydrogen has the advantage to have a great energy yield ($122 \text{ kJ}\cdot\text{g}^{-1}$) compared to fossil fuels ($40 \text{ kJ}\cdot\text{g}^{-1}$). However, the production of hydrogen is not economically viable since H_2 is often produced by electrochemical splitting of H_2O that requires a lot of energy. Therefore to reduce production cost and to generate hydrogen by a friendly environmental process, water can be split using photoelectrochemical (PEC) process also called electrochemically assisted photocatalysis or electrophotocatalysis. In such a process, solar energy is the main source of energy for water splitting, eventually supported by a limited quantity of electrical energy. This additional electrical energy can be derived from renewable resources, such as photovoltaic, so that hydrogen production may be entirely renewable.

The efficiency of PEC processes for solar hydrogen generation is related to the efficiency of the photoelectrode which should be able to absorb sunlight without loss of energy. The photoelectrode is most often the anode because hydrogen is generally produced at the cathode, which may be a noble metal, such as Pt. The cathode could be modified in order to reduce the amount of noble metal without loss of efficiency. On the other hand, an ideal photoanode is still a matter of intense research in order to make PEC solar H_2 generation a clean and economically viable alternative to fossil fuels, i. e. a potential “green” technology to be commercialized on the market one day. Therefore, this chapter is devoted to the design of efficient photoanodes by optimizing the way of synthesis, by tuning the PEC parameters, and also by modifying the chemical and physical structure of the photoanode. Bismuth vanadate ($BiVO_4$) appears to be an excellent candidate since this material is chemically stable and photoactive under solar irradiation.

6.2 Photoanodes in Photoelectrochemical Processes

A PEC cell is composed of an anode and a cathode in contact with an electrolyte. Two main types of PEC cells exist with electrodes either in the same compartment or separated by an ion-transfer membrane as illustrated in Figure 6.1. An external electric bias (ΔV) may be applied for both cell configurations, while chemical bias (ΔpH) may be only applied in a two-compartment PEC cell [1-3].

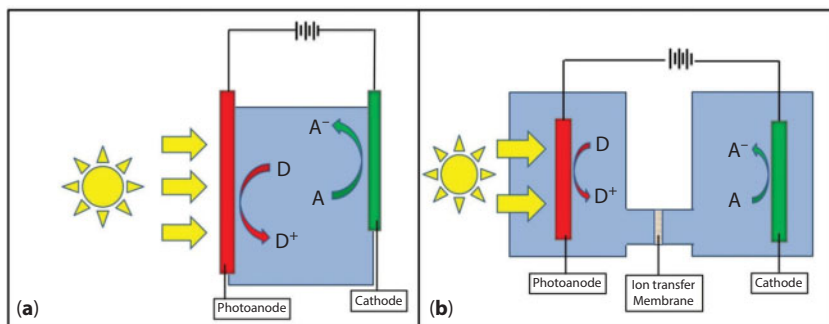


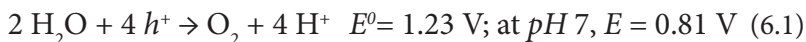
Figure 6.1 PEC cells in (a) one-compartment and (b) two-compartment configuration. Donor species D are oxidized by h^+ at the anode, while acceptor species A are reduced at the cathode by e^- .

In the case of the photoanode (anode which is irradiated for the activation of the PEC process), n -type semiconductors are often the constituting material of such photoelectrode (and p -type semiconductors in the case of photocathode). Indeed, semiconductors can generate e^-/h^+ pairs under suitable irradiation that are then involved in photoreactions [4]. Therefore, the operation of a PEC cell using a photoanode can be divided into four steps: (1) generation of e^-/h^+ pair under irradiation at the photoanode, (2) oxidation reactions at the photoanode, (3) transfer of e^- through external circuit toward the cathode, and (4) reduction reactions at the cathode [2, 3]. The main rule governing the feasibility of a photoreaction in PEC system is the necessity for the redox potential of reactants to lay within the energy bandgap (E_g) of the semiconductor material composing the photoanode [4].

Photoanodes in PEC processes can be used in the degradation of organic pollutants and the splitting of water molecules [1, 3]. For the abatement of pollutants, the most advantageous PEC cell is the one composed of one compartment (Figure 6.1A) in order to involve reactive oxygen species (ROS) produced from reactions with electrons (at the cathode) and holes (at the photoanode) [5]. Compared to non-assisted photocatalysis, PEC systems exhibited higher efficiency in mineralization of organic pollutants. Indeed, the e^-/h^+ recombination in the photoanode is limited due to vectorial charge transport along the electrochemical potential gradient and thus it provides sufficient energy to overcome activation barriers for the mineralization of pollutants [1, 5]. On the other hand, for photosplitting of water, two-compartment PEC cell (Figure 6.1B) is the most advantageous system for one main reason: O_2 and H_2 evolve simultaneously and separately, thus avoiding potentially explosive mixture and back reaction into H_2O [2].

Water photosplitting is considered as the “Holy Grail” in photochemistry. Indeed, using only solar energy to break the water molecule and

produce hydrogen is environmentally and economically the most viable alternative to fossil fuels [1, 6, 7]. As a result, most of the PEC applications are actually devoted to solar generation of H_2 by water splitting using photoanodes. The mechanism of PEC water splitting involves photogenerated electrons and holes that reduce and oxidize water, respectively, according to the reactions (6.1–6.4) [6, 8].



The overall reaction (6.4) is not thermodynamically favorable since the corresponding Gibbs energy is positive ($\Delta G^0 = 237.2 \text{ kJ}\cdot\text{mol}^{-1}$), and thus energy should be supplied for the breaking of H_2O molecule into molecular oxygen and hydrogen [1, 3, 8, 9]. In PEC processes, electric bias and/or chemical bias can supply enough energy to trigger H_2O splitting. In addition, the thermodynamic requirement for the feasibility of PEC water splitting using a particular photoanode (the redox potentials for water oxidation and reduction should lay within the energy bandgap of the semiconductor material composing the anode as in Figure 6.2) [2, 3, 6–9]. In theory, under standard conditions, the energy bandgap (E_g) of the photoanode should be at least 1.23 eV which is the minimum energy of the irradiation to photoactivate H_2O splitting [1, 3, 7–9]. In reality, this value should be much larger (about 2 eV) due to inevitable losses.

The first photoelectrochemical water splitting was reported in 1972 by *Fujishima and Honda* whom used rutile TiO_2 as photoanode under UV irradiation [10]. Since this discovery, the research on new semiconductor materials able to photolyze water under solar light has been a matter of strong interest [1, 11]. One of the main requirements for the photoanode is to have a suitable E_g and a good charge mobility through the semiconductor material in order to reach interfacial regions [1, 3]. However, visible light-driven photoanodes such as Fe_2O_3 , WO_3 , and CdS are inappropriate for PEC water splitting due to CB more positive than $E^0(H^+/H_2)$, instability under light, or high charge recombination rate (poor charge mobility) [1, 3].

Concerning the evaluation of the photocatalytic efficiency for water splitting, the apparent quantum yield in relation (6.5) can be used instead

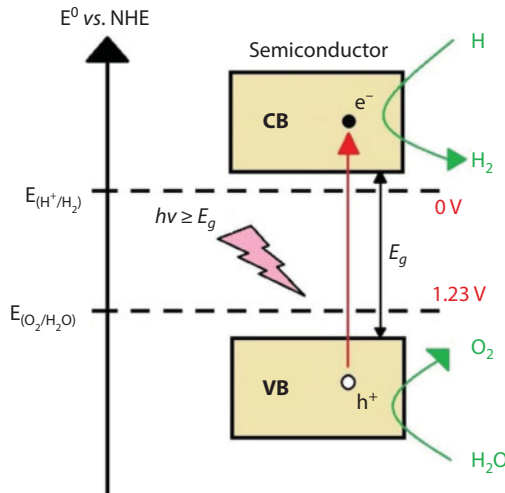


Figure 6.2 Scheme of water splitting for H_2 and O_2 production at $\text{pH} = 0$ using a semiconductor photoanode.

the real quantum yield in relation (6.6) since it is complex to state the real number of absorbed photon [9, 11]:

$$\begin{aligned} \text{Apparent Quantum Yield} &= \frac{\text{number of reacted } e^-}{\text{number of incident photons}} \\ &= 2 \times \frac{\text{number of evolved } \text{H}_2}{\text{number of incident photons}} \end{aligned} \quad (6.5)$$

$$\text{Real Quantum yield} = \frac{\text{number of reacted } e^-}{\text{number of absorbed photons}} \quad (6.6)$$

On the other hand, The efficiency in H_2 production can be expressed by the STH (solar-to-hydrogen) conversion efficiency [2]:

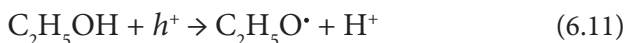
$$\text{STH} = \frac{J \left(\frac{\text{mA}}{\text{cm}^2} \right) \times \Delta E^\circ \text{ water split. (V)} \times \eta_F}{P_{\text{tot}} \left(\frac{\text{mW}}{\text{cm}^2} \right)} \quad (6.7)$$

where P_{tot} is the power density of incident radiation, J is the photocurrent density produced at zero bias, and η_F is the faradaic efficiency.

Finally, a variant of a PEC cell called photofuel cell (PFC) also known as photocatalytic fuel cell or photoactivated fuel cell is a PEC system using organic compounds as sacrificial agents. As a result, instead of the oxidation of water and the production of O_2 , organic matter is oxidized resulting in the production of CO_2 . Organics are good h^+ scavengers (e^- donors), and therefore the use of such sacrificial agents yields to an increase in e^-/h^+ pair separation. Consequently, a PFC can be used in both organic pollutant degradation and production of hydrogen by water splitting; thus such a technology is of high interest for environmental remediation [3, 5, 6, 11, 12, 54]. The following chemical reactions correspond to the operation in a PFC in the presence of ethanol as fuel [12, 54]:



in PFC system, the cathode compartment is usually sealed and purged with inert gas before starting H_2 generation. In addition, intermediate reaction steps can involve the formation of organic radicals during PFC operation as seen in reaction (6.11). Such radicals have the particularity to inject an electron to the CB of the photocatalytic material, thus leading to an increase of photocurrent in the PEC system. This effect is called current doubling effect and it is highly beneficial for achieving higher rate in H_2 production [5, 12, 54].



It should be noticed that in aerated environment, protons are not reduced at the cathode by photogenerated e^- but oxidized into water according to the reaction (6.12).



6.3 Bismuth Vanadate ($BiVO_4$)

An ideal semiconductor photoanode should fulfill many requirements to satisfy economical, chemical, physical, and biological parameters [4]. Among them, the photoresponse under solar irradiation is one of the most

crucial requirements since the main goal of PEC solar H_2 generation is to be a renewable technology using sunlight. Therefore, bismuth vanadate-based materials seem to be good candidates. Indeed, many visible light-responsive photocatalysts are heterometallic oxides (like $BiVO_4$), since it was observed that metal impurities in homometallic oxide can tune the energy bandgap by the overlapping of outer s- and d-orbitals of the p- and d-block metals ions, respectively. [11]. Therefore p- and d-block metals could be also used to design single-phase heterometallic semiconductor oxide photoanode with narrow E_g [11]. Bismuth vanadate ($BiVO_4$) is particularly a promising candidate for these reasons.

6.3.1 Structure and Properties of $BiVO_4$

Bismuth vanadate is a nontoxic yellow material. It is used as substitute to toxic pigments containing Pb or Cd and it is also resistant to chemical corrosion [13, 14]. $BiVO_4$ is a n-type semiconductor that exists in three polymorphs: monoclinic scheelite-like, tetragonal scheelite-like, and tetragonal zircon-like structures with E_g of 2.40, 2.34, and 2.90 eV, respectively [13–16]. The crystal structures are composed of $[VO_4]$ tetrahedra and $[BiO_8]$ polyhedra where V(V) and Bi(III) are in the center of the units. In the scheelite phases, each $[BiO_8]$ is surrounded by eight $[VO_4]$, whereas in zircon structure, Bi units are surrounded by only six $[VO_4]$ [16]. On the other hand, the difference between monoclinic and tetragonal scheelite structures is based on the local environment of Bi and V: the units are more distorted in the monoclinic structure [16]. In addition, the tetragonal structure is a high temperature phase, and a reversible transition between monoclinic and tetragonal scheelite occurs at 255 °C [14, 16]. Moreover, irreversible transition between tetragonal zircon and tetragonal scheelite happens at about 400–500 °C [14, 16]. Of the two $BiVO_4$ polymorphs stable at room temperature, monoclinic scheelite-like structure exhibits the best photoactivity due to better photon absorption and charge carrier transport resulted from smaller E_g and distorted V and Bi units, respectively [14–16].

Despite the advantages of $BiVO_4$, several drawbacks are responsible of the low efficiency of $BiVO_4$ photoanode [13, 14]. Bismuth vanadate suffers of poor electron mobility and high e^-/h^+ recombination [13, 14]. These main disadvantages are due to the structure where $[VO_4]$ tetrahedra are not connected to each other and also to the strong localization of V 3d orbitals that constitute the CB [14]. In addition, $BiVO_4$ has a short hole diffusion length (70–100 nm) that compromises the optimization of film thickness and light harvesting according to the optical penetration depth principle [14].

Deposited as a photoanode, BiVO_4 has a theoretical maximum photocurrent density of 7.5 mA/cm^2 assuming that all the photons from solar light with energy above 2.4 eV are absorbed [14]. Following the same assumption, the maximum STH efficiency is 9.1 % [13, 14, 17]. However, problems arise in such a semiconductor photoanode due to the necessity of using high electric potential to reach high IPCE (incident photon-to-current efficiency) under visible light [13]. This low photon-to-electron conversion limits efficient water photosplitting. Moreover, the photocurrent of BiVO_4 is not stable and strongly decreases against time (25% of initial photocurrent after 30 min illumination) because of dissolution of vanadium (V) into the electrolyte solution [13].

6.3.2 Synthesis of BiVO_4

Several methods can be employed to synthesize BiVO_4 . Bismuth vanadate was first synthesized by solid state and melting reactions in 1963 [14]. To date, the most commonly used synthesis methods for the preparation of BiVO_4 in the form of film and powder are metal organic decomposition (MOD), precipitation, and hydrothermal methods [15, 16].

In MOD, metal-organic species containing Bi(III) and V(III, IV, or V) are dissolved in organic solvent [16]. Bismuth and vanadium precursors are typically Bi(III) ethyl-hexanoate and V(IV) oxy-acetylacetonate or V(III) acetylacetonate [16]. The precursor solution is then deposited onto substrate in the form of film, and subsequent heat treatment in air at temperatures 350–500 °C is necessary to decompose organic precursors into crystalline BiVO_4 [16]. The advantages of the MOD method are the possibility to add dopants and surfactants (such as structure directing agents) into the precursor solution in order to tune the chemical composition and to control the morphology of BiVO_4 material, respectively [16]. The chemical reactions taking place in MOD process are complex and involve the formation of a heterometallic single-source molecular precursor (SSMP) which is then decomposed into BiVO_4 [18].

The precipitation method involves in most of cases ammonium meta-vanadate (NH_4VO_3) and bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$) in aqueous solution [16]. Direct coprecipitation of these two components can be performed in water to form a precursor powder. Another possibility is first to dissolve NH_4VO_3 and $\text{Bi}(\text{NO}_3)_3$ in NH_4OH and HNO_3 , respectively, (in order to add surfactant) and then to precipitate into precursor powder after mixing the solutions. After filtering, washing, and drying, the precursor powder is calcinated at 350–500 °C. Films can also be prepared by casting viscous precipitated slurries as paste onto substrates followed by calcination [19]. However, films deposited by this way are usually of bad quality.

Solvothermal and more particularly hydrothermal methods are widely used for the preparation of BiVO_4 . The precursors are basically the same as those used in the precipitation method, i.e., $\text{Bi}(\text{NO}_3)_3$ and NH_4VO_3 that are dissolved in NH_4OH and HNO_3 , respectively. After mixing the two solutions, the resulting suspension is, instead of being filtered and calcinated as in the precipitation method, transferred into an autoclave for treatment at 150–200 °C [15]. Hydrothermal method is a convenient and practical process since BiVO_4 material can be prepared with controllable morphology and crystallite size, high crystallinity, and purity [15].

Other synthesis methods such as electrochemical and sol–gel processes can be also employed to prepare BiVO_4 material. For the sol–gel method, several synthetic routes, e.g., alkoxide and aqueous sol–gel, can be used to prepare BiVO_4 [20]. On the other hand, electrochemical deposition usually involves a solution of $\text{Bi}(\text{NO}_3)_3$ and VOSO_4 where V(IV) is oxidized into V(V) under electric bias which reacts further with Bi(III) to form amorphous material that is converted thermally into BiVO_4 [16].

6.3.3 Applications of BiVO_4 Materials

Metal oxides and especially n-type semiconductors are the most used materials in photooxidative process including mineralization of organic pollutants and oxidation of water into O_2 [14, 16]. The case of BiVO_4 does not infringe this observation. Indeed the VBM, position of BiVO_4 provides sufficient energy to holes for oxidation [14, 16]. Therefore, numerous studies had been devoted to the photooxidative degradation of organic compounds such as organic dyes and phenolic compounds [20–23]. Among these works devoted to photodegradation of pollutants, differences between the removal efficiencies could appear mainly due to the type of irradiation, the synthesis parameters and methods, the pH of the photocatalytic system, and the value of electric bias (if any).

Pure BiVO_4 has been also studied for water oxidation i.e., production of O_2 [19, 24, 25]. However, sacrificial agents are necessary for efficient O_2 evolution [19] since O_2 necessitates the uptake of four photogenerated h^+ (in the case of H_2 production, only 2 electrons are required). This shows that oxygen formation is a much more complicated process which involves many intermediate reactions, thus limiting the production rate in water splitting [7]. Therefore, AgNO_3 is usually used to scavenge photogenerated e^- for improving e^-/h^+ pair separation [19]. Using such system, more than 100 $\mu\text{mol/h}$ of O_2 can be produced under visible light [19] while without electron scavenger, around 5 $\mu\text{mol/h}$ of O_2 can be evolved in a PEC system using BiVO_4 as photoanode [24].

By comparison with the most popular and commercially available TiO_2 under similar experimental conditions, the above results should be taken with precaution since the superiority of bismuth vanadate over titania is often based on a narrow selection of test reactions or even on a single organic substrate. This is problematic since many factors cannot be validated in a single test assay [4, 5].

Pure BiVO_4 has been also studied for antimicrobial applications, gas sensors, Li batteries, and degradation of inorganic pollutants [26, 27].

6.4 BiVO_4 as Photoanode for Solar Hydrogen Generation

Bismuth vanadate is already a material widely studied for photooxidative processes (Section 6.3.3). However BiVO_4 semiconductor materials are not yet used in reductive process such as solar generation of hydrogen by water splitting. Hereafter are summarized crucial points that make BiVO_4 photoanodes promising for PEC solar H_2 production.

6.4.1 Optimization of the Photoanode

6.4.1.1 Photoanode Preparation

Among the parameters to be taken into account for obtaining efficient photoanode, the way of preparation is maybe the first one to be considered in order to synthesize good quality materials. Indeed, many scientists have the tendency to skip this important step although their findings have high novelty. This could be satisfying in the point of view of fundamental science, but optimization is a mandatory step for applied science. Thus, in the case of BiVO_4 photoanodes, some crucial parameters should be investigated in order to optimize the material and wet chemical methods appear the appropriate tool for this aim. Indeed, through wet chemical methods, it is possible to tune the chemical and physical properties of an electrophotocatalytic material by modifying the nature of precursors, changing the annealing process and varying the amount of structure-directing agent.

Concerning the precursors for the synthesis of BiVO_4 , the source of Bi contained generally trivalent bismuth as in $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. However, vanadium precursor can be either V(III) or V(IV) compounds such as V(IV) oxy-acetylacetonate and V(III) acetylacetonate. The use of these

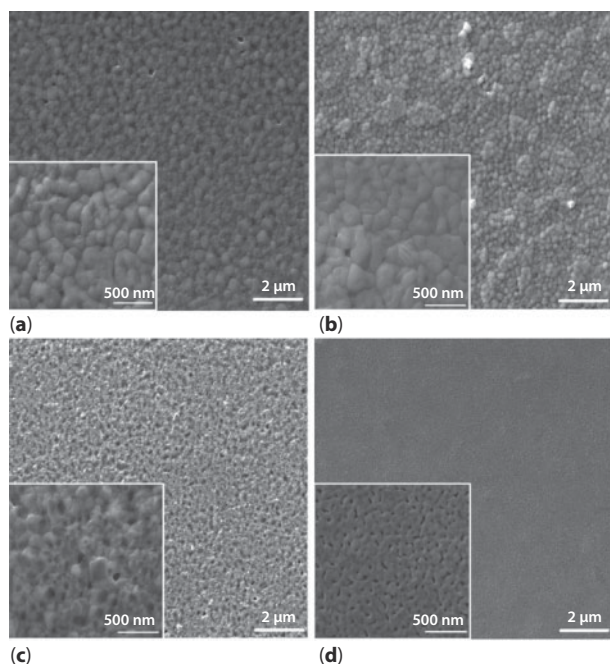


Figure 6.3 SEM of surface of films deposited on Si/SiO₂ using BiVO₄ precursor solution with V^{III}(acac)₃ (a and b) and V^{IV}O(acac)₂ (c and d). Films were annealed at 500 °C for 1 h (a and c) and 5 min (b and d). The figure insets are SEM performed at higher magnification.

different precursors affects the quality of BiVO₄ film (Figure 6.3). In the same way, the use of different annealing times on freshly deposited BiVO₄ photoanodes dramatically changes the granulometry of bismuth vanadate photoanode (Figure 6.3) and thus the exposed active surface area and the porosity of the material change also.

Based on the SEM in Figure 6.3, an optimal photoanode (with fine texture and nanoparticulated structure) can be obtained obtained using vanadium(III) precursors followed by 5 min annealing of as-deposited BiVO₄ material. The annealing temperature can be selected based on *in situ* XRD of as-deposited BiVO₄ that monitors the crystallization process (Figure 6.4). The optimal temperature seems to be around 480 °C where most of monoclinic scheelite BiVO₄ diffractions have reached maximum intensity. The annealing temperature should not be too high and the heating ramp not too slow to promote the formation of small crystallites. It is worth to notice that both vanadium and bismuth precursor solutions are mixed in stoichiometric ratio in order to obtain stoichiometric BiVO₄ [16, 18].

On the other hand, the quantity of surfactant (structure directing agent), more particularly the amount of Triton X-100™, is also crucial in the preparation of efficient BiVO_4 electrophotocatalysts since it controls the surface area of film [28]. At any concentrations of Triton in the precursor solution, all the photoanodes are composed of monoclinic scheelite bismuth vanadate [28]. Increasing the amount Triton X-100™ gives rise to a decrease in crystallite size and an increase of surface area, i.e. it improves the porosity of the material [28]. However at critical concentration, additional phase appears which is identified as nonstoichiometric bismuth vanadate $\text{Bi}_4\text{V}_2\text{O}_{11}$, and the porosity of the material is negatively affected. Therefore, the optimal concentration in Triton X-100™ was set at $0.10 \text{ g}\cdot\text{mL}^{-1}$ [28].

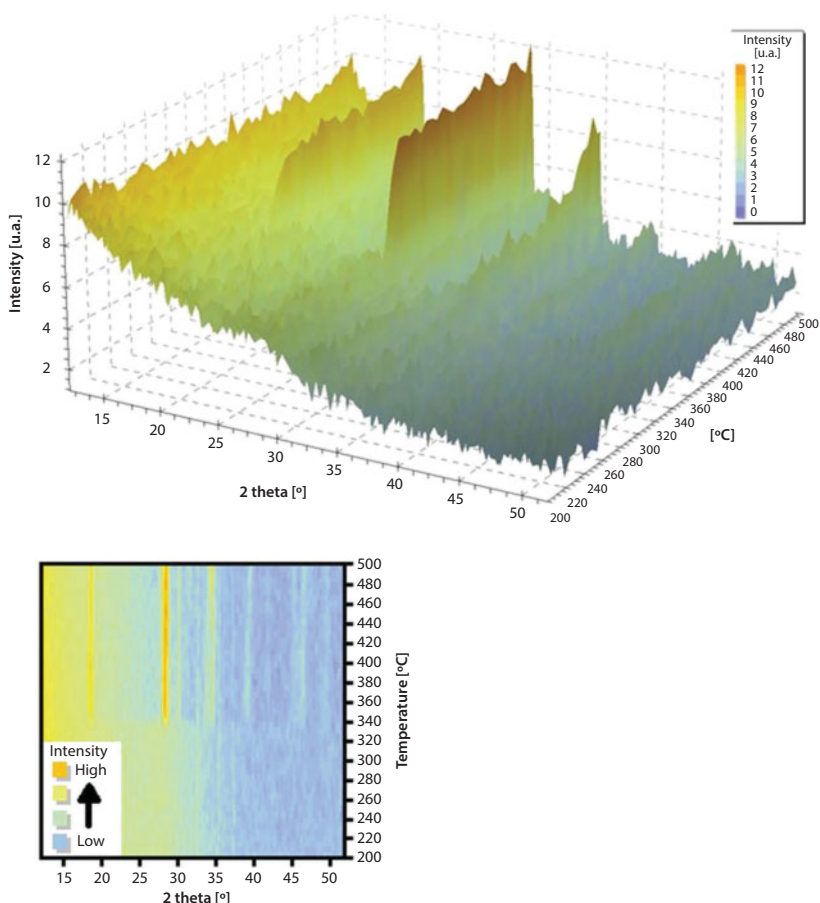


Figure 6.4 Temperature-dependent XRD of pure BiVO_4 film deposited on Si/SiO_2 .

6.4.1.2 Choice of the Electrolyte

Once the photoanode is optimized and prior to devote to PEC solar hydrogen generation, the right electrolyte should be chosen in order to reach the best photoelectrochemical properties. Therefore, the study of the effect of different electrolytes on the efficiency of BiVO_4 photoanode in the production of photocurrent should be performed. Indeed, high and stable photocurrent is synonym of available e^- for the reduction of protons into hydrogen. First the stability of photocurrent (that reflects the stability of photoanode) should be investigated. Chronoamperometry using different sodium-based electrolytes (NaOH , Na_2SO_4 , and NaHCO_3 with pH at 13, 7.4, and 8.2, respectively) is a good strategy to address this aim. Sodium salts are chosen due to their attractive cost and also because of smaller injection of counteranions into the porous photoanode compared to lithium salts that can negatively affect the electric signal [29, 30]. The measured transient photocurrents under chopped solar irradiation at 0.5 V vs. Ag/AgCl are plotted in Figure 6.5. Obviously, BiVO_4 anode is photoresponsive since a current appears under irradiation while no current is measured in the dark. However, by observing the general current density profile for each electrolyte (Figure 6.5), the photocurrent produced by BiVO_4 photoanode decreases against time and reaches a plateau after 400 s (especially in the case of Na_2SO_4 and NaHCO_3 electrolytes). The photocurrent decay reaches 87, 50, and 40 % for NaOH , NaHCO_3 , and Na_2SO_4 respectively.

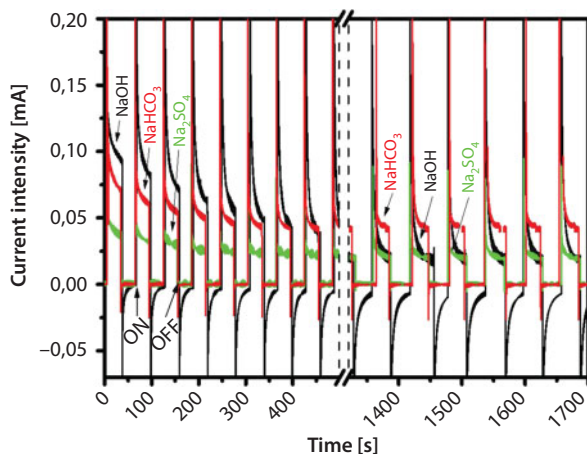


Figure 6.5 Chronoamperographs of BiVO_4 photoanode and Pt-foil cathode under chopped Xe lamp illumination measured in 0.5 M NaOH , NaHCO_3 , and Na_2SO_4 electrolytes at 0.5 V vs. Ag/AgCl .

This photocurrent profile (decay followed by stabilization) was already observed by *da Silva et al.* where they explained the stabilization of the photocurrent profile by preserved crystalline structure (vanadium was not dissolved entirely in the electrolyte; thus BiVO_4 was not degraded) [31]. This is actually the case in Na_2SO_4 and NaHCO_3 but not for NaOH . Indeed, although the photocurrent is higher in NaOH electrolyte, the steady state is never reached: the photocurrent is constantly decreasing and consequently its stability is the worst with a loss of 87 % in photocurrent (Figure 6.5). In NaOH electrolyte, the bad BiVO_4 photoperformance can be mainly attributed to alteration of BiVO_4 crystalline structure since the originally yellow material turned into a brownish color after its use (in the other electrolytes, the color remained yellow). On the other hand, the best photocurrent stability is achieved in Na_2SO_4 (with only 40 % decay), but the optimal electrolyte seems to be NaHCO_3 since it has the highest steady-state photocurrent.

In addition, during the ON/OFF cycles (Figure 6.5), a sharp spike appears every time after switching on the light followed by an exponential decay until a steady state is reached (Figure 6.5). This phenomenon is explained by e^-/h^+ pair recombination that is predominant in pure BiVO_4 and that reflects the global photocurrent decay observed in the photocurrent profile [31]. After turning OFF the light, an overshoot is also observed and then the current goes back to zero [31].

To corroborate the excellent photocurrent stability achieved in NaHCO_3 electrolyte, photocurrent should be also measured by linear sweep voltammetry (LSV) to obtain I-V curves. Among the different tested electrolytes, the photocurrent density produced by BiVO_4 photoanode in NaHCO_3 electrolyte reaches almost $1 \text{ mA}\cdot\text{cm}^{-2}$ at 1.4 V vs. Ag/AgCl [28]. Under such experimental conditions, water electrolysis occurs at electric bias higher than 1.4 V vs. Ag/AgCl in 0.5 M NaHCO_3 [28]. This is crucial information for the production of hydrogen by water photosplitting where the I-V curves are a necessary and precious knowledge. The beneficial role of NaHCO_3 electrolyte was already observed by *Saito et al.* where the effects of carbonate, sulfate, phosphate, and hydroxide electrolytes on the production of photocurrent by BiVO_4 photoanode were compared [32]. The photocurrent depends usually on the electrolyte conductivity, i.e. the concentration and the type of anion of the electrolyte [32]. However in the case of carbonate, a direct relationship between the produced photocurrent and the electrolyte conductivity does not exist [32]. The excellent photoelectrochemical properties of BiVO_4 in NaHCO_3 are due to the combination of two main processes: (1) the carbonate adsorption on BiVO_4 surface is higher than on the surface of many other semiconductor electrophotocatalysts and (2) carbonate is easily oxidized than most of other electrolytes

[31, 32]. The oxidized species like carbonate radicals and peroxocarbonate are formed by reactions with the photogenerated holes and improved charge transfer at the interface photocatalyst/electrolyte; thus the photocurrent was enhanced [31, 32]. The reactions occurring at $\text{BiVO}_4/\text{NaHCO}_3$ interface are detailed in the next section (6.4.2 about hydrogen generation) since carbonate electrolyte also affected the water photosplitting [3, 6, 32].

6.4.2 Solar Hydrogen Generation by Water Splitting

Since the position of the BiVO_4 energy bandgap (E_g) is not thermodynamically suitable for overall water splitting (CBM and VBM at 0 and 2.4 V) and the Gibbs energy is positive for this process (Section 6.2), an electric bias should be applied to enable the PEC generation of hydrogen using BiVO_4 photoanode.

A First attempt performed in one-compartment PEC cell using NaOH, NaHCO_3 , or Na_2SO_4 electrolytes, Pt/elcocarb cathode and the pure BiVO_4 photoanode is shown in Figure 6.6. Figure 6.6 exhibits the H_2 production rate as well as the cumulative hydrogen production at 1.0 V vs. Ag/AgCl under simulated sunlight irradiation. The hydrogen production follows the previous observation (section 6.4.1.2), i.e., NaHCO_3 is the optimal electrolyte for PEC H_2 generation. However, whatever the electrolyte used, after approximately 30 min of irradiation, the hydrogen production rate dramatically decreases and cumulative H_2 production rate tends to stagnate (Figure 6.6B). One plausible explanation is, in the case of NaOH electrolyte, that the BiVO_4 photoanode is degraded and subsequently deactivated, causing the dramatic decrease until zero in H_2 production rate

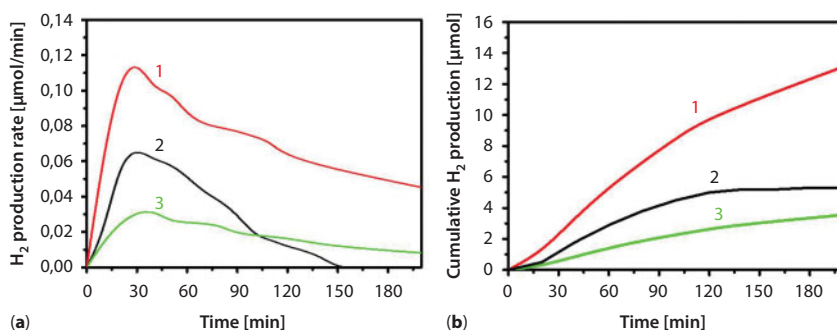


Figure 6.6 Hydrogen production rate (a) and cumulative H_2 production (b) using pure BiVO_4 photoanode and Pt/elcocarb cathode under simulated solar light in one-compartment PEC cell using 0.5 M of (1) NaHCO_3 , (2) NaOH , and (3) Na_2SO_4 at 1.0 V vs. Ag/AgCl.

(Figure 6.6A). Concerning the other electrolytes, the observed decrease in Figure 6.6A is probably caused by water recombination. Indeed, O_2 and H_2 evolve in the same compartment; thus reaction back to water formation is favored. From Figure 6.6, it is clear that $NaHCO_3$ limits water recombination. Once $NaHCO_3$ is adsorbed on the photoanode surface, it reacts readily with holes generated by $BiVO_4$ [6, 32]. Therefore, according to the reactions (6.13) and (6.14), CO_2 and proton are formed (CO_2 dissolves in water by releasing proton as by-products) and then, the protons are reduced at the cathode into H_2 , giving rise to higher production rate in hydrogen [6, 32].



In addition, e^-/h^+ pair recombination rate in $BiVO_4$ is also reduced because of the scavenging of photogenerated holes by bicarbonate and intermediates such as radicals and peroxocarbonate, thus less O_2 , which is susceptible to recombine with H_2 , is produced and more photogenerated electrons are available at the cathode to reduce protons into hydrogen [6, 32].

Another strategy to prevent water recombination is the use of two-compartment PEC cell. In such PEC system, the H_2 production rate is higher and reaches a plateau compared to one-compartment cell and thus the cumulative amount of produced hydrogen is continuously increasing [28]. This is due to the fact that O_2 and H_2 evolve from separated compartments and back reaction into H_2O does not occur. In addition, using two-compartment PEC cell, a chemical bias can be applied by replacing the electrolyte in the cathode compartment by a mineral acid. For instance, by using H_2SO_4 in the cathode compartment (instead of $NaHCO_3$), the production rate in H_2 measured at 1.4 V vs. Ag/AgCl under simulated sunlight reaches $2.5 \mu\text{mol}\cdot\text{min}^{-1}$, while using $NaHCO_3$ in both compartment or in one-compartment system, the maximal production rate is 1.6 and $0.23 \mu\text{mol}\cdot\text{min}^{-1}$, respectively [28]. The presence of a Bronsted acid in the cathode compartment increases the number of protons (due to small pH) that are then used for the reduction into H_2 by electrons.

It is worth to notify again that 1.4 V bias (vs. Ag/AgCl) gives rise to a pure photoresponse since the photoanode does not produced any hydrogen at such bias without irradiation. The use of smaller electric bias has an impact on the solar H_2 generation, resulting in smaller production rate. This can be answered by monitoring the incident photon-to-current efficiency (IPCE) that evaluates the conversion rate of photo into electricity.

It is logical that at higher bias, the photogenerated e^-/h^+ pair is more efficiently separated since higher electromotive force drives more electrons to the cathode than the use of smaller bias [17, 33]. Indeed, it was reported that IPCE reached 60% at 400 nm for 1.4 V bias (*vs.* Ag/AgCl), while only 15% and 7% were measured at 0.7 V and without bias, respectively [28].

To corroborate IPCE measurements, it is interesting to calculate the solar-to-hydrogen (STH) efficiency already defined in Section 6.2. However, the relation (6.7) should be slightly modified into relation (6.15) since an external bias is applied to the PEC system [34]:

$$STH = \frac{J \left(\frac{mA}{cm^2} \right) \times (\Delta E^\circ \text{ water split.} - E_{app})(V) \times \eta_F}{P_{tot} \left(\frac{mW}{cm^2} \right)} \quad (6.15)$$

with $E_{app} = E_{bias} - E_{OC}$ and where E_{app} is the real applied bias, E_{bias} is the applied external bias, and E_{OC} is the bias at open circuit in the same electrolyte and under the same irradiation as E_{bias} . Therefore, the maximum apparent STH efficiency for pure $BiVO_4$ photoanode was calculated at 0.68 % at 0.52 V (*vs.* Ag/AgCl) in $NaHCO_3$ electrolyte (Figure 6.7). To calculate the real STH efficiency, the photocurrent value should be directly taken from the experimental parameters of the solar PEC hydrogen generation. Based on the experimental conditions of *Monfort et al.*, the photocurrent measured in a two-compartment cell using a 12 cm^2 $BiVO_4$ photoanode at 1.4 V *vs.* Ag/AgCl with and without chemical bias is 6.27 and 3.36 mA, respectively. The faradaic efficiency should be also calculated based on the equations (6.16) and (6.17) [28]. The faradaic efficiency is the efficiency of H_2 production for a given current flowing across the PEC cell:

$$\eta_F = \frac{\text{observed current flowing across the cell}}{\text{theoretical current across the cell for 100\% conversion}} \quad (6.16)$$

And for the production of $1 \mu\text{mol}$ of hydrogen, the maximum theoretical photocurrent is:

$$\frac{1 \times 10^{-6} (\text{mol}) \times 6.022 \times 10^{23} (\text{mol}^{-1}) \times 2 \times 1.602 \times 10^{-19} (\text{C})}{60(\text{s})} = 3.21 \text{ mA} \quad (6.17)$$

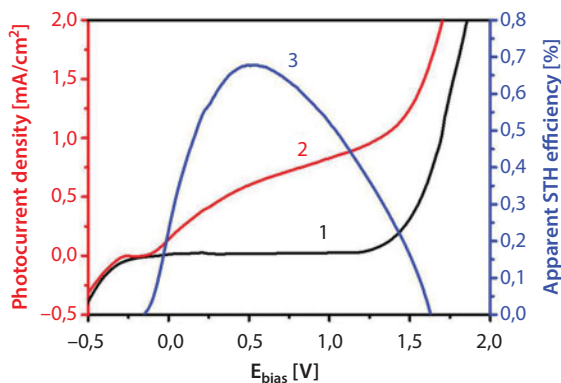


Figure 6.7 I-V curves measured using pure BiVO_4 photoanode and Pt-foil cathode in 0.5 M NaHCO_3 electrolyte (1) in the dark, (2) under simulated solar irradiation, and (3) the corresponding apparent STH efficiency.

Therefore, the corresponding faradaic efficiency for solar H_2 generation at 1.4 V vs. Ag/AgCl is 78 and 65 % with and without chemical bias, respectively; thus their corresponding real STH efficiency is 0.09 and 0.04 %. The experimental values seem to be very low compared to the maximum theoretical value (Section 6.3.1), but these real STH efficiencies are much higher than in other works where, for example, *Jia et al.* found photoconversion efficiency of 0.005 % at 1 V vs. Ag/AgCl for pure BiVO_4 in K_2SO_4 electrolyte [33]. In the case of Monfort et al., Pt-modified carbon paste is used as a cathode, thus higher value could be reached using pure Pt cathode. However modified cathode is a viable economical alternative to expensive platinum.

It is also interesting to observe that performing H_2 production at bias near the maximum apparent STH efficiency (0.68 % at 0.52 V vs. Ag/AgCl, Figure 6.7) does not improve the production rate [28]. This was an interesting fact because H_2 production does not evolve as the same manner as STH efficiency. Indeed, the solar H_2 generation in a PEC cell under electric bias increases with the faradaic efficiency due to higher applied bias, thus higher photocurrent.

6.5 Modified BiVO_4 Photoanodes

Usually, pristine semiconductor electrophotocatalysts produce low rate of H_2 mainly due to high recombination rate of e^-/h^+ pair [1, 2, 7, 8]. This is also right for bismuth vanadate which exhibits rather low electrophotocatalytic

efficiency; therefore, modifications should be performed to improve its properties particularly in PEC solar hydrogen generation.

The improvement of BiVO_4 includes the increase of active surface area, number of photocatalytic sites, absorbed photons, charge carrier separation, and also the decrease in energy bandgap [4]. The E_g position of BiVO_4 is almost ideal for overall water splitting and hydrogen evolution catalyst (HEC) can be used for improving the production of H_2 . Noble metals such as Pt and Au are often used as HEC because they trap electrons and thus they reduce efficiently proton into hydrogen [35]. Another strategy to beneficially modify BiVO_4 is to introduce defects in the structure in order to both reduce E_g and improve charge transfer within the electrophotocatalytic material [36]. For this the elaboration of doped BiVO_4 materials and composites with bismuth vanadate are ones of the most used strategies [1], which are detailed in the following sections.

6.5.1 Transition Metal-Modified BiVO_4

6.5.1.1 Generalities

Metal and nonmetal doping into BiVO_4 crystalline structure is a common method for modifying the electrophotocatalytic properties of bismuth vanadate [37]. The beneficial effects that are usually observed in a doped semiconductor material are (1) reduction of E_g , (2) enhancement of electrical conductivity, (3) increase of e^-/h^+ pair separation, and (4) improvement in surface adsorption of the target molecule [37]. However, the doping technique using conventional wet chemical methods is not trivial since the dopants should be concentrated at the surface of the material to observe a real improvement in the electronic properties while the presence of a dopant deep within the bulk favors charge recombination.

In the case of BiVO_4 , tungsten(VI) and molybdenum(VI) have been found to be the most promising dopants among numerous transition and rare earth metals [16, 37–40]. Mo(VI) and W(VI) improve the electronic properties of BiVO_4 , while other dopants such as Cu, Yb, Er, Nd, and Sm ions are beneficial to the morphology of BiVO_4 , but also its surface area and energy bandgap (decrease of E_g) [41–43]. In many works [41–43], relatively high amount of dopants is used; therefore, the metal impurity is not inserted in the BiVO_4 lattice but should be present in the form of oxide. Few works are devoted to BiVO_4 as material for solar H_2 generation by PEC water splitting, and most of the articles are focused on the production of oxygen due to its well-known photooxidative properties [28, 38, 44]. Therefore, BiVO_4 exhibits high potential to be studied in H_2 production

since bismuth vanadate has almost an ideal energy bandgap for overall water splitting (Section 6.4.2). A good candidate for PEC solar H_2 generation is the elaboration of transition metal-modified $BiVO_4$ photoanode.

6.5.1.2 Nb-Modified $BiVO_4$

To modify $BiVO_4$, it could be interesting to try transition metals that are near vanadium in the periodic table of the elements (Ti^{IV} , Zr^{IV} , and Nb^V) or that are cheap (Fe^{III} and Zn^{II}), despite many studies are focused on Mo- and W-modified $BiVO_4$. To evaluate their PEC properties, the photocurrent of M -modified $BiVO_4$ photoanodes (with $M = Ti, Zr, Nb, Fe$, and Zn) should be measured (Figure 6.8). Although some contradictions arise with some works [16, 37, 138], Nb-, Ti-, and Zr-modified bismuth vanadate exhibit substantially higher photocurrent compared to pure $BiVO_4$ photoanode, while other transition metals (Zn and Fe) have detrimental effect on the photoresponse of $BiVO_4$. The positive effect on the performance of modified $BiVO_4$ photoanode is ascribed to an increase in e^-/h^+ pair separation and charge carrier transport. However, due to high nominal amount in transition metal element in the photoanode ranging from 5 at% for Zr and Ti to 10 at% for Nb (Figure 6.8A), it cannot be assumed that M element ($M = Ti, Zr$ and Nb) is inserted within the crystal structure, but it is obvious that these metals induce changes in the morphology and the nano/micro-structure of the material composing the photoanode [43].

Since Nb-modified exhibits, so far, the best photocurrent, further studies performed on the optimal 10 at% Nb(V)- $BiVO_4$ (Figure 6.8B) show that optical properties and crystalline structure of the photoanode remain unchanged compared to pure $BiVO_4$, i.e., monoclinic scheelite $BiVO_4$ is the only identified phase assuming that Nb is present in the form of oxide either amorphous or at nanosized scale [44]. In addition, strong morphological changes are induced the addition of niobium in Nb- $BiVO_4$, giving rise to a hierarchical structure with a high degree of porosity [44]. These results are similar to other works using also relatively high amount of transition metals to beneficially modify $BiVO_4$ [43]. Moreover, the IPCE measured at 400 nm under 1.4 V bias (vs. Ag/AgCl) in $NaHCO_3$ is improved of +20% compared to pristine $BiVO_4$, thus reaching 80% in photon-to-electron conversion efficiency [44]. Therefore, it can be stated that Nb does not change the position of E_g , but it increases active surface area, promotes e^-/h^+ pair separation, and improves charge carrier transport

The PEC solar H_2 generation is also affected by the beneficial changes mentioned just above. Indeed, the production of hydrogen by water splitting is strongly enhanced using Nb-modified $BiVO_4$ [44]. The stabilized

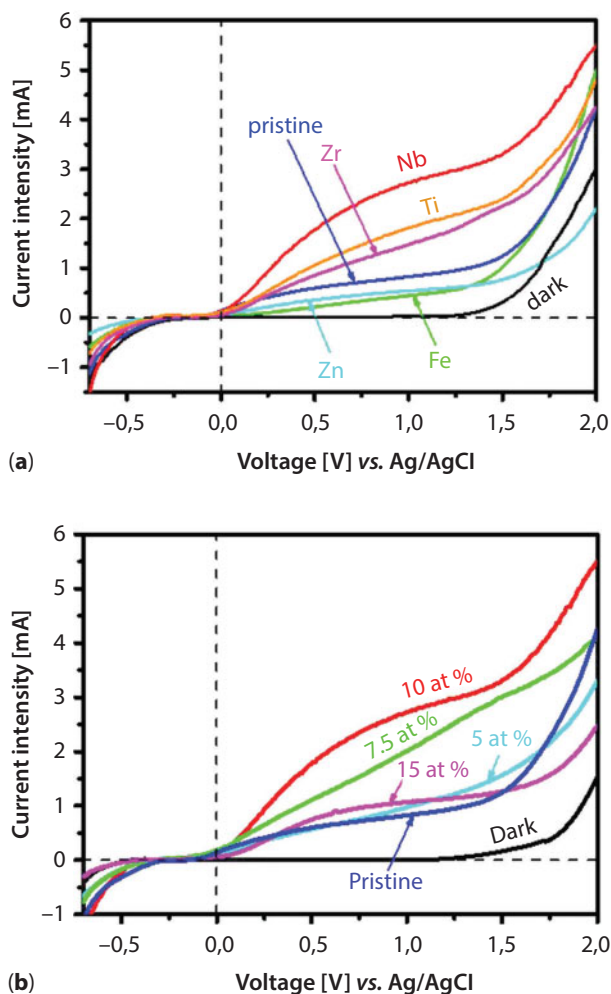


Figure 6.8 I-V curves measured in NaHCO₃ electrolyte by LSV using Pt-foil cathode and modified BiVO₄ photoanode containing (a) optimal content of the tested transition metal and (b) different quantities of Nb(V).

and maximal production rate at 1.4 V vs. Ag/AgCl in NaHCO₃ electrolyte increases from 1.6 to 3.0 $\mu\text{mol}\cdot\text{min}^{-1}$ (compared to pristine BiVO₄) and under chemical bias it even increases from 2.5 to 4.4 $\mu\text{mol}\cdot\text{min}^{-1}$ [44]. Concerning the STH efficiency (Figure 6.9), the maximum apparent efficiency is higher in the case of Nb-modified BiVO₄ photoanode than pristine film by +1.4 %, i.e., it reaches 2.11 % at 0.65 V vs. Ag/AgCl. However, similar to the case of pristine BiVO₄, the real STH efficiency should be calculated by taking into account the actual parameters used during the PEC

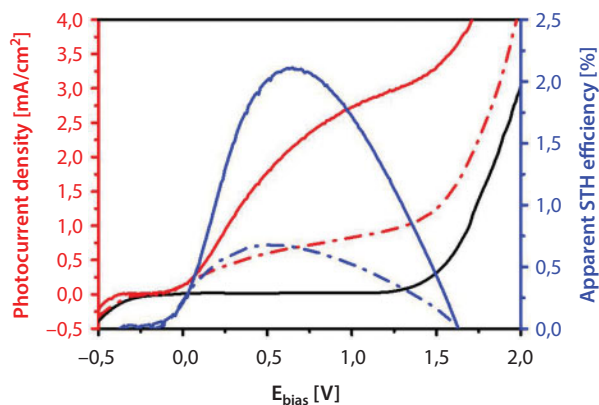


Figure 6.9 I-V curves (red) measured by LSV using pristine (dashed line) and Nb-modified (continuous line) BiVO_4 photoanodes and Pt-foil cathode under Xe lamp illumination in 0.5 M NaHCO_3 electrolyte and the corresponding apparent STH efficiency (blue).

solar H_2 generation such as photocurrent, active surface of photoanode, and faradaic efficiency. Therefore, the real STH efficiency reaches 0.16 and 0.27 % without and with chemical bias, respectively, at 1.4 V vs. Ag/AgCl in NaHCO_3 under simulated solar light. These values are higher than those obtained for pristine photoanode. Table 6.1 summarizes, by comparison with other works, different PEC parameters measured during hydrogen production using various transition metal-modified BiVO_4 photoanodes. The comparison between these works is relevant since few studies are devoted to both photoanode characterization and water splitting experiment using modified BiVO_4 [17, 38, 44]. It is important to point out that the photoanode exhibiting the best H_2 production rate (Nb- BiVO_4) is used in two-compartment PEC cell configuration, in NaHCO_3 electrolyte, and it also exhibits the highest IPCE and STH efficiency values. It is also worth to observe that between Mo- and Ag-modified BiVO_4 , the hydrogen production does not necessarily increase with the produced photocurrent because (1) seawater is a complex electrolyte where other reactions could compete with H_2 production in a PEC system and (2) applied electrical bias is different and thus could influence the faradaic efficiency that affects the real STH efficiency.

6.5.2 BiVO_4 Composites

6.5.2.1 Generalities

The elaboration of composite is also an efficient way to improve the electro-photocatalytic properties of BiVO_4 [9]. Usually, a semiconductor material

Table 6.1 Characteristics measured under solar radiation of BiVO₄ photoanode modified by different transition metals.

Photoanode	PEC cell	Electrolyte	Photocurrent	IPCE (at 400 nm)	Apparent STH efficiency	H ₂ production (after 2 h)
Nb-BiVO ₄	Two-compartment	NaHCO ₃	3 mA·cm ⁻² at 1.4 V vs. Ag/AgCl	80 %	2.11 % at 0.65 V vs. Ag/AgCl	275 μmol at 1.4 V (vs. Ag/AgCl)
Mo-BiVO ₄	One-compartment	Seawater	3 mA·cm ⁻² at 1.0 V vs. Ag/AgCl	42 %	0.6 % at 0.88 V vs. Ag/AgCl	12.5 μmol at 1.2 V
Ag-BiVO ₄	One-compartment	Na ₂ SO ₄	5.5 mA·cm ⁻² at 1.0 V vs. Ag/AgCl	44 %	0.2 % at 0.3 V vs. Ag/AgCl	120 μmol at 1.6 V

like bismuth vanadate can be either assembled with another semiconductor (to form a semiconductor heterojunction) or coupled with metals and carbon materials (such as carbon nanotube and graphene oxide) [9, 16, 37, 45]. Here, we focus on semiconductor heterojunctions which are of three types: I, II, and III [9, 37, 45]. Type I and III heterojunctions are not treated in this chapter since in type I charge carrier transfer between the components does not benefit to electrochemical properties (increase of recombination rate), while in type III an electron mediator is needed to obtain efficient Z-scheme composite [9]. On the other hand, type II heterojunction promotes efficient charge transfer between the components and increases the lifetime of photogenerated e^-/h^+ pair due to accumulation of electrons in the CB of one semiconductor while holes are amassed in the VB of the other one [9, 16, 37, 45].

There are numerous possibilities to form type II BiVO_4 composite. Among them, the use of WO_3 , which is one of the most efficient components to be associated with bismuth vanadate ($E_g = 2.6$ eV) [16, 37, 45]. Indeed, as photoanode, $\text{BiVO}_4/\text{WO}_3$ exhibits a strong increase in photocurrent, IPCE, and STH efficiency compared to pristine BiVO_4 . In addition, a buffer layer can be introduced between the two components in order to limit e^-/h^+ pair recombination, i.e. to increase the efficiency of the photoanode [13, 16]. Another interesting composite system is $\text{BiVO}_4/\text{TiO}_2$ which forms also a heterojunction of type II. Even if E_g of TiO_2 encompasses the energy bandgap of bismuth vanadate (as in type I heterojunction), the formation of type II semiconductor composite is favored due to homogenization of the Fermi levels as illustrated in Figure 6.10 [46].

These composites just introduced above are suitable for hydrogen generation by water splitting due to CB more negative than $E^\circ(\text{H}^+/\text{H}_2)$. Moreover, since such composites are type II heterojunction, e^-/h^+ pair separation is promoted and photoperformance in oxygen production as well as in H_2 generation from H_2O splitting is improved [47, 48]. However the efficiency of these type II composites is also governed by the value of electric bias, the type and concentration of electrolyte and the configuration of the PEC cell [47, 48].

6.5.2.2 $\text{BiVO}_4/\text{TiO}_2$ Composite

The case of $\text{BiVO}_4/\text{TiO}_2$ is attracting since titanium is cheap and already widely used in environmental technologies. Indeed, some studies on this system and particularly on the layer configuration of the composite photoanode were already performed [49, 50]. On the other hand, many other works are only focused on PEC cell parameters such as the type

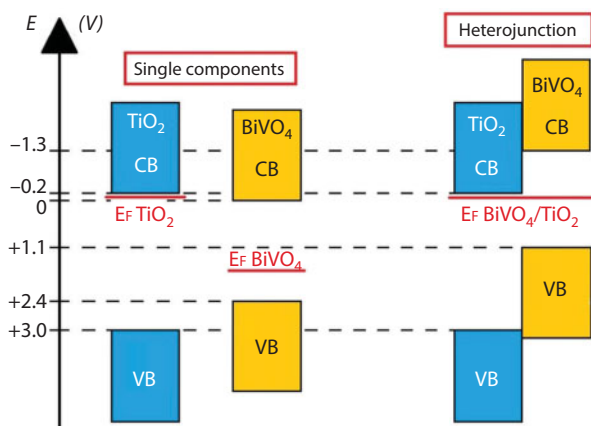


Figure 6.10 Electronic band structure at $pH = 0$ of BiVO_4 and TiO_2 as single components and in a semiconductor heterojunction. E_F refers to Fermi level.

of electrolyte and value of electric bias, but without taking into account another important parameter: the optimization of photoanode characteristics in PEC solar H_2 generation.

By varying the photoanode layer configuration, e.g., inverting BiVO_4 and TiO_2 top and bottom layers and also alternating successively BiVO_4 and TiO_2 layers, no impact on the crystalline composition is observed (only bismuth vanadate and titania crystalline phases are present). Therefore, it is assumed that no other phase is formed during the formation of the heterojunction [49, 50]. In addition, the most photoactive phase of BiVO_4 and TiO_2 is identified, i.e., monoclinic scheelite BiVO_4 and TiO_2 anatase, the latter at nanosize scale while BiVO_4 is more porous [49, 50]. The average thickness of the film is about $1\ \mu\text{m}$ and in each case BiVO_4 is thinner than TiO_2 layer [49, 50]. Concerning the optical properties of $\text{BiVO}_4/\text{TiO}_2$ -layered composites, the E_g is about 2.50 eV which is slightly higher in energy than the E_g of pure BiVO_4 (2.35 eV) but much lower than that of pure TiO_2 (3.20 eV). This indicates that the main absorbing material is BiVO_4 and the resulting blue shift in the energy bandgap of the composite is due to the presence of TiO_2 [49, 50].

The PEC properties and particularly the photocurrents of the different $\text{BiVO}_4/\text{TiO}_2$ -layered composites show very interesting consequences of the effect of layer configuration. Indeed, compared to photocurrents produced by pure BiVO_4 and TiO_2 , top-coated TiO_2 photoanodes exhibit higher photocurrents, while the other composite photoanodes exhibiting top-coated BiVO_4 are inactive under solar irradiation [50]. This result could be expected since the CB of TiO_2 is slightly more negative (about $-0.2\ \text{V}$ vs.

NHE) than that of BiVO_4 (about 0.0 V vs. NHE), thus the photogenerated e^- preferentially flow from TiO_2 to BiVO_4 , i.e., to the opposite direction from FTO substrate (opposite to the applied electric bias) in the case of top-coated BiVO_4 photoanodes as seen in Figure 6.11. Therefore, under electric bias, it was assumed that thermodynamical equilibrium does not occur in $\text{BiVO}_4/\text{TiO}_2$ composite, i.e., type II heterojunction is not formed (Figure 6.11).

The photocurrent produced by top-coated TiO_2 composite which is considered as the optimal photoanode was almost 5.5 times larger at 1.4 V vs. Ag/AgCl than that produced by pure BiVO_4 [50]. In addition, pure BiVO_4 photoanode has an onset for photoanodic current at about 0.1 V (vs. Ag/AgCl), while top-coated TiO_2 photoanode exhibits onset photocurrent at -0.2 V (vs. Ag/AgCl). Therefore, the use of titania in $\text{BiVO}_4/\text{TiO}_2$ -layered composite shifts cathodically the photocurrent onset and improved the photoresponse. This cathodic shift was also observed in several works on $\text{BiVO}_4/\text{TiO}_2$ composites [52, 53]. However, compared to these works [52, 53], the produced photocurrent by the optimized $\text{BiVO}_4/\text{TiO}_2$ photoanode presented just above was much higher mainly due to the careful design of the photoanode layered configuration.

The PEC solar hydrogen generation rate measured at 1.4 V vs. Ag/AgCl in NaHCO_3 electrolyte using the optimized $\text{BiVO}_4/\text{TiO}_2$ photoanode reaches a maximum at $1.0 \mu\text{mol}\cdot\text{min}^{-1}$ [50]. This production rate is smaller than that of pure BiVO_4 but higher than that of TiO_2 due to the fact that under electric bias, the $\text{BiVO}_4/\text{TiO}_2$ composite is not considered

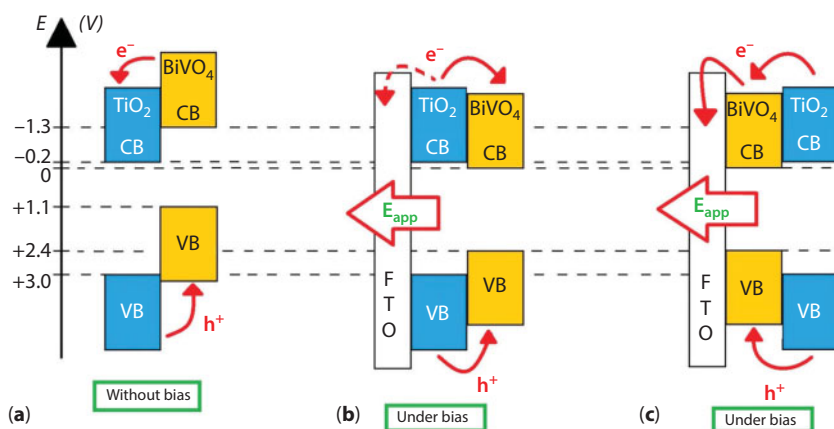


Figure 6.11 Electronic band structure at $\text{pH} = 0$ of (a) $\text{BiVO}_4/\text{TiO}_2$ heterojunction without electric bias, (b) BiVO_4 -coated TiO_2 photoanode under electric bias E_{app} and (c) TiO_2 -coated BiVO_4 photoanode under electric bias E_{app} .

as heterojunction but as a combined electrophotocatalyst where synergistic effects are lost [50]. In addition, under simulated solar irradiation, $\text{BiVO}_4/\text{TiO}_2$ photoanode is better than pure TiO_2 which is only photoactive under UV light [50]. However, the H_2 production using the optimized $\text{BiVO}_4/\text{TiO}_2$ photoanode designed by Monfort *et. al* is higher than other reported $\text{BiVO}_4/\text{TiO}_2$ systems, especially in the work of Xie *et. al* which is, to the best of our knowledge, the only reference dealing with a similar system for hydrogen production [48]. Indeed, they obtained only 4 μmol of hydrogen after 2 hours irradiation, while in our published works, we ascribe the better efficiency to the use of a two-compartment cell and the optimization of the photoactive material supported on an electrode [48, 50].

6.6 Conclusion

The design of a photoanode is a crucial step for reaching substantial PEC efficiency. Indeed, BiVO_4 , as photoactive material supported on anode, requires careful optimization of synthesis parameters in order to obtain a photoanode with improved micro- and nanostructure such as increased active surface area and porosity. In addition, the design of the PEC cell is also crucial for the purpose of producing hydrogen. Indeed, water recombination should be avoided to efficiently generate H_2 . Moreover, PEC parameters such as the choice of the electrolyte should be meticulously studied in order to obtain improved photocurrent, IPCE, and STH efficiency.

In the case of bismuth vanadate, the PEC solar H_2 generation can be enhanced by doping with niobium(V) which significantly raises the hydrogen generation compared to pristine BiVO_4 . Concerning $\text{BiVO}_4/\text{TiO}_2$ photoanode, the configuration of the layered composite plays an important role in the feasibility of hydrogen generation. Even if composite systems may be efficient for O_2 generation, it is found in the case of $\text{BiVO}_4/\text{TiO}_2$ that the efficiency for solar H_2 production is not better than pure BiVO_4 ; thus the choice of another candidate than TiO_2 appears necessary.

Finally, the efficiency of PEC system using BiVO_4 -based photoanode for the production of H_2 by water splitting is still too weak for claiming a potential use in pilot scale. However, the use of BiVO_4 -based photoanode for solar H_2 generation is not well documented; thus there are still many aspects to be explored for improving such PEC system and making new advanced BiVO_4 -based photoanodes efficient and suitable for environmental applications.

6.7 Acknowledgments

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References

1. Arnaut, L.G., Barroso, M., Serpa, C., Solar energy conversion, in: *Applied Photochemistry*, B. Giacomo and S. Serena (Eds.), pp. 267–304, Springer, Dordrecht, 2013.
2. Liao, C.-H., Huang, C.-W., Wu, J.C.C., Hydrogen production from semiconductor-based photocatalysis via water splitting. *Catalysts*, 2, 490, 2012.
3. Chiarello, G.L., Selli, E., Photocatalytic hydrogen production. *Recent Pat. Eng.*, 4, 155, 2010.
4. Ibhaddon, A.O., Fitzpatrick, P., Heterogeneous photocatalysis: Recent advances and applications. *Catalysts*, 3, 189, 2013.
5. Teoh, W.Y., Scott, J.A., Amal, R., Progress in heterogeneous photocatalysis: From classical radical chemistry to engineering nanomaterials and solar reactors. *J. Phys. Chem. Lett.*, 3, 629, 2012.
6. Ni, M., Leung, M.K.H., Leung, D.Y.C., Sumathy, K., A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. *Renew. Sust. Energ. Rev.*, 11, 401, 2007.
7. Kisch, H., *Semiconductor photocatalysis*, pp. 85–210, Wiley-VCH, 2015.
8. Ismail, A.A., Bahnemann, D.W., Photochemical splitting of water for hydrogen production by photocatalysis: A review. *Sol. Energ. Mat. Sol. C.*, 128, 85, 2014.
9. Gholipour, M.R., Dinh, C.-T., Beland, F., Do, T.-O., Nanocomposite heterojunctions as sunlight-driven photocatalysts for hydrogen production from water splitting. *Nanoscale*, 7, 8187, 2015.
10. Fujishima, A., Honda, K., Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, 37, 1972.
11. Chen, X., Shen, S., Guo, L., Mao, S.S., Semiconductor based photocatalytic hydrogen generation. *Chem. Rev.*, 110, 6503, 2010.
12. Sfaelou, S., Lianos, P., Photoactivated fuel cells (PhotoFuelCells). An alternative source of renewable energy with environmental benefits. *AIMS Mater. Sci.*, 3, 270, 2016.
13. Gan, J., Lu, X., Tong, Y., Towards highly efficient photoanodes: boosting sunlight-driven semiconductor nanomaterials for water oxidation. *Nanoscale*, 6, 7142, 2014.

14. Tolod, K.R., Hernandez, S., Russo, N., Recent advances in the BiVO_4 photocatalyst for sun-driven water oxidation: Top-performing photoanodes and scale-up challenges. *Catalysts*, 7, 13, 2017.
15. Xu, Y.-H., Liu, C.-J., Chen, M.-J., Liu, Y.-Q., A review in visible-light-driven BiVO_4 photocatalysts. *Int. J. Nanopart.*, 4, 268, 2011.
16. Park, Y., McDonald, K.J., Choi, K.-S., Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chem. Soc. Rev.*, 42, 2321, 2013.
17. Sayama, K., Nomura, A., Arai, T., Sugita, T., Abe, R., Yanagida, M., Oi, T., Iwasaki, Y., Abe, Y., Sugihara, H., Photoelectrochemical decomposition of water into H_2 and O_2 on porous BiVO_4 thin-film electrodes under visible light and significant effect of Ag ion treatment. *J. Phys. Chem. B*, 110, 11352, 2006.
18. Hubert-Pfalzgraf, L.G., Some trends in the design of homo- and heterometallic molecular precursors of high-tech oxides. *Inorg. Chem. Commun.*, 6, 102, 2003.
19. Ke, D., Peng, T., Ma, L., Cai, P., Jiang, P., Photocatalytic water splitting for O_2 production under visible-light irradiation on BiVO_4 nanoparticles in different sacrificial reagent solutions. *Appl. Catal. A-Gen.*, 350, 111, 2008.
20. Wang, X., Shen, Y., Zuo, G., Li, F., Meng, Y., Influence of heat treatment on photocatalytic performance of BiVO_4 synthesised by sol-gel method. *Mater. Technol.*, 31, 176, 2016.
21. Li, F., Kang, Y., Chen, M., Liu, G., Lv, W., Yao, K., Chen, P., Huang, H., Photocatalytic degradation and removal mechanism of ibuprofen via monoclinic BiVO_4 under simulated solar light. *Chemosphere*, 150, 139, 2016.
22. Ran, R., McEvoy, J. G., Zhang, Z., Synthesis and optimization of visible light active BiVO_4 photocatalysts for the degradation of RhB. *Int. J. Photoenergy*, 2015, 1, 2015.
23. Zhang, X., Chen, S., Quan, X., Zhao, H., Preparation and characterization of BiVO_4 film electrode and investigation of its photoelectrocatalytic (PEC) ability under visible light. *Sep. Purif. Technol.*, 64, 309, 2009.
24. Trzesniewski, B.J., Smith, W.A., Photocharged BiVO_4 photoanodes for improved solar water splitting. *J. Mater. Chem. A*, 4, 2919, 2016.
25. Sun, S., Wang, W., Li, D., Zhang, L., Jiang, D., Solar light driven pure water splitting on quantum sized BiVO_4 without any cocatalyst. *ACS Catal.*, 4, 3498, 2014.
26. Wang, W., Yu, Y., An, T., Li, G., Yip, H.Y., Yu, J.C., Wong, P.K., Visible-light-driven photocatalytic inactivation of *E. coli* K-12 by Bismuth vanadate nanotubes: Bactericidal performance and mechanism. *Environ. Sci. Technol.*, 46, 4599, 2012.
27. Zhao, Y., Xie, Y., Zhu, X., Yan, S., Wang, S., Surfactant-free synthesis of hyperbranched monoclinic Bismuth vanadate and its applications in photocatalysis, gas sensing, and lithium-ion batteries. *Chem. Eur. J.*, 14, 1601, 2008.
28. Monfort, O., Pop, L.-C., Sfaelou, S., Plecenik, T., Roch, T., Dracopoulos, V., Stathatos, E., Plesch, G., Lianos, P., Photoelectrocatalytic hydrogen production by water splitting using BiVO_4 photoanodes. *Chem. Eng. J.*, 286, 91, 2016.

29. Sfaelou, S., Pop, L.-C., Monfort, O., Dracopoulos, V., Lianos, P., Mesoporous WO_3 photoanodes for hydrogen production by water splitting and PhotoFuelCell operation. *Int. J. Hydrogen Energ.*, 41, 5902, 2016.
30. Pop, L.-C., Sfaelou, S., Lianos, P., Cation adsorption by mesoporous titania photoanodes and its effect on the current-voltage characteristics of photoelectrochemical cells. *Electrochim. Acta*, 156, 223, 2015.
31. da Silva, M.R., Lucilha, A.C., Afonso, R., Dall'Antonia, L.H., de Andrade Scalvi, L.V., Photoelectrochemical properties of FTO/m- BiVO_4 electrode in different electrolytes solutions under visible light irradiation. *Ionics*, 20, 105, 2014.
32. Saito, R., Miseki, Y., Sayama, K., Photoanode characteristics of multi-layer composite BiVO_4 thin film in a concentrated carbonate electrolyte solution for water splitting. *J. Photoch. Photobio. A*, 258, 51, 2013.
33. Jia, Q., Iwashina, K., Kudo, A., Facile fabrication of an efficient BiVO_4 thin film electrode for water splitting under visible light irradiation. *PNAS*, 109, 11564, 2012.
34. Lin, C.J., Liao, S.-J., Kao, L.-C., Liou, S.Y.H., Photoelectrocatalytic activity of a hydrothermally grown branched ZnO nanorod-array electrode for paracetamol degradation. *J. Hazard. Mater.*, 291, 9, 2015.
35. Long, M., Jiang, J., Li, Y., Cao, R., Zhang, L., Cai, W., Effect of gold nanoparticles on the photocatalytic and photoelectrochemical performance of Au modified BiVO_4 . *Nano-Micro Lett.*, 3, 171, 2011.
36. Singh, A.P., Kodan, N., Dey, A., Krishnamurthy, S., Mehta, B.R., Improvement in the structural, optical, electronic and photoelectrochemical properties of hydrogen treated bismuth vanadate thin films. *Int. J. Hydrogen Energ.*, 40, 4311, 2015.
37. Huang, Z.-F., Pan, L., Zou, J.-J., Zhang, X., Wang, L., Nanostructured Bismuth vanadate-based materials for solar-energy-driven water oxidation: A review on recent progress. *Nanoscale*, 6, 14044, 2014.
38. Luo, W., Yang, Z., Li, Z., Zhang, J., Liu, J., Zhao, Z., Wang, Z., Yan, S., Yu, T., Zou, Z., Solar hydrogen generation from seawater with a modified BiVO_4 photoanode. *Energ. Environ. Sci.*, 4, 4046, 2011.
39. Gong, H., Freudenberg, N., Nie, M., van de Krol, R., Ellmer, K., BiVO_4 photoanodes for water splitting with high injection efficiency, deposited by reactive magnetron co-sputtering. *AIP Adv.*, 6, 045108, 2016.
40. Rohloff, M., Anke, B., Zhang, S., Gernet, U., Scheu, C., Lerch, M., Fischer, A., Mo-doped BiVO_4 thin films – high photoelectrochemical water splitting performance achieved by a tailored structure and morphology. *Sust. Energ. Fuels*, 1, 1830, 2017.
41. Luo, Y., Tan, G., Dong, G., Zhang, L., Huang, J., Yang, W., Zhao, C., Ren, H., Structural transformation of Sm^{3+} doped BiVO_4 with high photocatalytic activity under simulated sun-light. *Appl. Surf. Sci.*, 324, 505, 2015.
42. Luo, Y., Tan, G., Dong, G., Ren, H., Xia, A., Effects of structure, morphology, and up- conversion on Nd-doped BiVO_4 system with high photocatalytic activity. *Ceram. Int.*, 41, 3259, 2015.

43. Huang, J., Tan, G., Zhang, L., Ren, H., Xia, A., Zhao, C., Enhanced photocatalytic activity of tetragonal BiVO_4 : Influenced by rare earth ion Yb^{3+} . *Mater. Lett.*, 133, 20, 2014.
44. Monfort, O., Sfaelou, S., Satrapinskyy, L., Plecenik, T., Roch, T., Plesch, G., Lianos, P., Comparative study between pristine and Nb-modified BiVO_4 films employed for photoelectrocatalytic production of H_2 by water splitting and for photocatalytic degradation of organic pollutants under simulated solar light. *Catal. Today*, 280, 51, 2017.
45. Moniz, S.J.A., Shevlin, S.A., Martin, D.J., Guo, Z.-X., Tang, J., Visible-light driven heterojunction photocatalysts for water splitting - A critical review. *Energ. Environ. Sci.*, 8, 731, 2015.
46. Guo, Z., Li, P., Che, H., Wang, G., Wu, C., Zhang, X., Mu, J., One-dimensional spindle-like $\text{BiVO}_4/\text{TiO}_2$ nanofibers heterojunction nanocomposites with enhanced visible light photocatalytic properties. *Ceram. Int.*, 42, 4517, 2016.
47. Pilosh, Y., Turkevych, I., Mawatari, K., Asai, T., Hisatomi, T., Uemura, J., Tosa, M., Shimamura, K., Kubota, J., Domen, K., Kitamori, T., Nanostructured $\text{WO}_3/\text{BiVO}_4$ Photoanodes for efficient photoelectrochemical water splitting. *Small*, 10, 3692, 2014.
48. Xie, M., Fu, X., Jing, L., Luan, P., Feng, Y., Fu, H., Long-lived, visible-light-excited charge carriers of $\text{TiO}_2/\text{BiVO}_4$ nanocomposites and their unexpected photoactivity for water splitting. *Adv. Energy Mater.*, 4, 1300995, 2014.
49. Monfort, O., Roch, T., Gregor, M., Satrapinskyy, L., Raptis, D., Lianos, P., Plesch, G., Photooxidative properties of various $\text{BiVO}_4/\text{TiO}_2$ layered composite films and study of their photocatalytic mechanism in pollutant degradation. *J. Environ. Chem. Eng.*, 5, 5143, 2017.
50. Monfort, O., Raptis, D., Satrapinskyy, L., Roch, T., Plesch, G., Lianos, P., Production of hydrogen by water splitting in a photoelectrochemical cell using a $\text{BiVO}_4/\text{TiO}_2$ layered photoanode. *Electrochim. Acta*, 251, 244, 2017.
51. Zhang, H., Cheng, C., Three-dimensional FTO/ TiO_2 / BiVO_4 composite inverse opals photoanode with excellent photoelectrochemical performance. *ACS Energ. Lett.*, 2, 813, 2017.
52. Ho-Kimura, S., Moniz, S.J. A., Handoko, A.D., Tang, J., Enhanced photoelectrochemical water splitting by nanostructured $\text{BiVO}_4\text{-TiO}_2$ composite electrodes. *J. Mater. Chem. A*, 2, 3948, 2014.
53. Resasco, J., Zhang, H., Kornienko, N., Becknell, N., Lee, H., Guo, J., Briseno, A.L., Yang, P., $\text{TiO}_2/\text{BiVO}_4$ nanowire heterostructure photoanodes based on type II band alignment. *ACS Central Sci.*, 2, 80, 2016.
54. Lianos, P., Review of recent trends in photoelectrocatalytic conversion of solar energy to electricity and hydrogen. *Appl. Catal. B-Environ.*, 210, 235, 2017.

Copper-Based Chalcopyrite and Kesterite Materials for Solar Hydrogen Generation

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Abstract

Photoelectrochemical (PEC) water splitting process to generate hydrogen gas using nanomaterials is one of the promising techniques. Nanomaterials are advantageous in PEC process because they can tune their bandgaps by controlling the size and morphology. Copper-based chalcopyrites and kesterites are two important representatives of ternary and quaternary semiconductor nanomaterials. Owing to the unique materials' properties for PEC water splitting applications, these types of semiconductors have attracted a lot of attention recently.

This chapter is categorized into two main parts, individually presenting chalcopyrite and kesterite materials to be used as photoelectrodes in solar water splitting process. The first part introduces the basic material properties of chalcopyrite CuInS/Se₂ semiconducting material, the synthesis and thin film fabrication techniques, and finally the PEC properties. The most suitable conditions for the formation of nanocrystals with desired properties and preferable thin film deposition methods to improve photoconversion efficiency have been discussed in detail. In the second part, the synthesis and thin film fabrication techniques for copper-based quaternary compounds in kesterite phase have been discussed. The pros and cons of both nanocrystal synthesis and the thin film deposition methods have been highlighted in terms of optoelectronic properties and high photoconversion efficiency.

Keywords: Chalcopyrite, hydrogen, kesterite, photoelectrochemical water splitting, thin films

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7.1 Introduction

The global population growth and increased energy consumption cause serious environmental problems such as energy shortage, greenhouse effect, and pollution. Therefore, searching for alternative fuels to overcome the energy challenge is the rising trend in developed countries. The common alternative fuels such as biodiesel, electricity, ethanol, methanol, hydrogen, solar energy, and wind are being replaced with nonrenewable sources to decrease the tension in energy shortage [1]. Among these fuels, hydrogen is the most practical option as it is one of the most abundant elements in the universe. Besides, it is classified as “green energy” since the only by-product is water after burning it in an internal combustion engine.

One of the recent interests for sustainable hydrogen production is photoelectrochemical (PEC) water splitting in which energy is utilized directly from sunlight [2]. In a solar water splitting process, a semiconductor electrode is used in a photoelectrochemical cell to capture and convert the photon energy from sunlight to generate hydrogen and oxygen. For a successful water splitting process, the semiconductor material used as a photoelectrode in a photoelectrochemical cell must have three major requirements: a suitable bandgap range for water hydrolysis (greater than 1.23 eV), high absorption coefficient, and stability against photocorrosion. A great variety of scientific reports on seeking suitable semiconductor materials to be employed as photoelectrodes have been published in the last decade. Copper-based ternary and quaternary compounds are such semiconductors with proper visible light activity. The classification of semiconductors is shown in Table 7.1.

Recently, ternary and quaternary semiconductors have attracted much more interest due to the nontoxic nature as compared to binary semiconductors. The enormously growing interest on synthesis of these

Table 7.1 Classification of binary, ternary, and quaternary sulfide semiconductors

Group	Type	Example	Most stable phase
II-VI	Binary	CdS	Wurtzite
I-III-VI	Ternary	CuInS ₂	Chalcopyrite
I-II-III-VI	Quaternary	CuInZnS	
I-II-VI-VI		Cu ₄ ZnSnS ₄	Kesterite

semiconductors to be used in photoelectrochemical applications in the recent years has led us to archive and represent significant and essential research reports in this field. Thus, this section focuses on the recent developments on the synthesis methods, material properties, and photoelectrochemical characteristics of chalcopyrites and kesterites, which are the most common crystal phases of ternary and quaternary semiconductors.

7.2 Chalcopyrite I-III-VI₂ Semiconductors

7.2.1 Material Properties

Cu-based ternary I-III-VI₂ compounds, in particular CuInS₂, CuInSe₂ as well as their hybrid derivatives CuIn(S,Se)₂, are the semiconductor materials with high application potentials in photocatalysis [3], solar voltaic cells [4, 5], and water splitting devices [6, 7] owing to their highly favorable optoelectronic properties [8, 9]. The highly advantageous properties of CuInS/Se₂ compounds to be used as photoelectrodes in solar water splitting process arise from their high absorption coefficients ($\sim 10^5$) and relatively narrow bandgaps (Table 7.2) which match well with the solar spectrum. In addition, CuInS/Se₂ in nanocrystal form can also show efficient size-dependent photoluminescence.

This ternary semiconductor is known to have three crystal structures: chalcopyrite, wurtzite, and zincblende [10–14]. The chalcopyrite crystal structure is the most commonly existing and stable phase, whereas wurtzite and zincblende are metastable phases at room temperature [15, 16]. The chalcopyrite CuFeSe₂ mineral that crystallizes in the tetragonal crystal system with space group $I\bar{4}2d$ (eight atoms per primitive unit cell) is the phase prototype for copper-based chalcopyrite (Figure 7.1). Each anion is coordinated by two I and two III cations, whereas each cation is tetrahedral coordinated by four anions. The slight tetragonal lattice distortion leading to a lattice parameters ratio of $c/2a \sim 1.004$ contributes to the identification of chalcopyrite crystal phase in X-ray diffraction analysis.

Table 7.2 Bandgaps, crystal structures, and lattice parameters of the selected bulk ternary semiconductors [8].

Material	Bandgap at 300K (eV)	Lattice parameters
CuInS ₂	1.53	$a = 5.52, c = 11.12$
CuInSe ₂	1.05	$a = 5.61, c = 11.02$

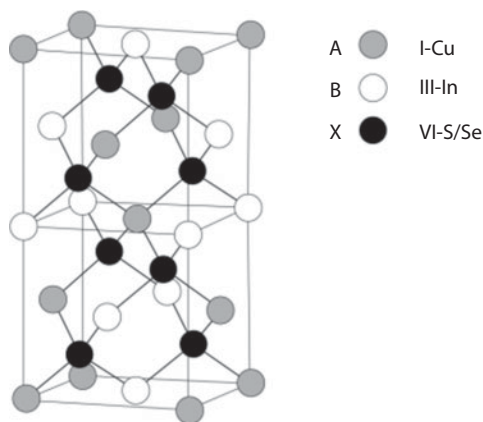


Figure 7.1 Crystal structure of the chalcopyrite CuInS/Se_2 unit cell.

Ternary chalcopyrite semiconductors can tolerate a large range of chemical ratio without changing the crystal structure [17, 18]. The lattice parameters and bandgap values of the ternary semiconductors are listed in Table 7.2. The large range of chemical ratio affects p-type or n-type conductivity nature of the semiconductors, and thus, they can be used as both photocathodes and photoanodes in photoelectrochemical cells [19]. Most of the CuInS_2 synthetic methods reported in the literature yield material with p-type semiconductivity, thus used as photocathodes in PEC water splitting. However, some colloidal methods yield n-type CuInS_2 that are Cu-poor nanocrystals [19–23]. Courtel *et al.* reported the n-type CuInS_2 nanoparticle synthesis by using N-methyl-imidazole, as a solvent and complexing agent [23].

Chalcopyrite CuInS/Se_2 , with the tunable bandgap range, has received great interest for solar energy conversion as both photocatalysts and photocathodes as it exhibited encouraging conversion efficiency by eliminating toxic elements.

Efficiency of the conversion of sunlight into the chemical energy is the key factor of a PEC water splitting process. The applied bias photon to current conversion efficiency (ABPE) is used to distinguish the photoresponse efficiency of a photoelectrode material under an applied voltage. Applied bias photon-to-current efficiency (ABPE) for photocathode was calculated from the data according to the following equation:

$$ABPE(\%) = \frac{J_{photo}(1.23 - V_{bias})}{P_{light}} \times 100 \quad (7.1)$$

where J_{photo} ($mA\ cm^{-2}$) is the measured photocurrent density, V_{bias} (V) is the bias voltage measured by the reversible hydrogen electrode (RHE), and $P_{AM\ 1.5}$ is the photon flux of the AM 1.5 simulated sunlight ($100\ mW\ cm^{-2}$).

Another energy parameter is the quantum efficiency such as the incident photon-to-current efficiency (IPCE) measured at fixed incident wavelengths that are often used to evaluate performance of a photoelectrode in a water splitting process. The IPCE is defined as the number of photo-generated charge carriers contributing to the photocurrent per incident photon, which can be represented by the following equation:

$$IPCE(\lambda) = \frac{\text{Total energy of converted electrons}}{\text{Total energy of incident photons}} \quad (7.2)$$

$$= \frac{\left(\frac{J_{photo}(\lambda)}{e} \right) \times \left(\frac{hc}{\lambda} \right)}{P(\lambda)} \times 100\% \quad (7.3)$$

where J_{photo} is the photocurrent density at that particular wavelength of incident light ($mA\ cm^{-2}$; e is the charge of an electron ($1.602 \times 10^{-19}C$); h is Planck's constant ($6.626 \times 10^{-34}\ J\ s$); c is the speed of light ($3.0 \times 10^{17}nm\ s^{-1}$); λ is the wavelength of the incident light (nm); $P(\lambda)$ is the incident light intensity at that specific wavelength ($mW\ cm^{-2}$)

7.2.2 Synthesis Techniques of Chalcopyrite CuInS/Se₂ Nanocrystals

Since the better control in nanocrystal size and shape can be provided by wet chemical methods, major efforts have been focused on the direct synthesis of CuInS/Se₂ nanoparticles in the past two decades. Therefore, most of the previous reports have been based on preparing the powder-type and transferring the powders to a substrate to form a thin-film photoelectrode. In this section, the wet chemical methods, e.g., hot-injection, heat-up, solvothermal process, etc., are summarized for an overview of the parameters in accomplished synthesis and characteristics of resulting nanocrystals.

The studies on the synthesis of CuInS/Se₂ nanocrystals by wet chemical methods have confirmed that the size, size distribution, shape, and crystal phase of the resulting nanocrystals can be controlled by the following reaction parameters in wet chemical methods: (i) the reaction temperature and duration, (ii) the injection temperature of the ligand into the metallic precursor solutions in the case of hot-injection methods, (iii) the reactivity and

the concentration of precursors, (iv) the effect of solvent, surfactant, stabilizers, and pH. Among all the wet chemical synthesis processes, hot-injection and heat-up methods are known to result in the best crystal size and shape for CuInS/Se₂ nanocrystals (see Figure 7.2). The first literature report on hot-injection method was the synthesis of cadmium chalcogenide quantum dots in 1993 [24]. Later on, many studies have been reported on the adaptation of the method to obtain copper based I-III-VI₂ semiconductor materials.

In a wet chemical synthesis process for CuInS/Se₂ nanocrystals in desired size, shape, and phase, the first step is regulating the reactivity of two cations; hard Lewis acid, In⁺³ and soft Lewis acid, Cu⁺² [25]. If the reactivity of the cationic precursors is not balanced, the formation of copper sulfide interferes the growth of chalcopyrite CuInS₂ nanocrystals. The use of appropriate ligands and stabilizer compounds may help to overcome this challenge [8, 26]. Addition of stabilizer compounds such as thiols and carboxylic acids helps to regulate the activity of copper and indium cations [27]. In general, the CuInS/Se₂ nanocrystal synthesis is conducted using a variety of metal salts and sulfur sources in organic solvents in which they are also used as capping agents [28, 29]. Additionally, to organic solvents, water-based reaction conditions have also been reported as alternative and greener chemical synthesis methods [30–35].

The commonly used sulfur and selenium sources in the synthesis of CuInS/Se₂ are 1-dodacanethiol (DDT), thiourea (TU)/ selenurea (SU), and elemental sulfur/selenium powders. Using DDT as a sulfur source results in metal thiolates, which decomposes during heating to form the corresponding metal sulfides. Tang *et al.* reported CuInS₂ nanoplates in the presence of DDT as a ligand and capping agent to form chalcopyrite nanoparticles with 8.5nm diameter [36]. In the presence of alcohols as solvents, the synthesis of CuInS₂ nanocrystal from TU leads to the formation of nanoparticles in bigger size (> 100 nm) [37, 38]. CuInSe₂ nanocrystals in trigonal shape with relatively smaller size (~20 nm) were reported by Ko *et al.* by using this method with the corresponding selenide precursors, SU, and oleylamine (OLA) as a solvent [39]. TEM images of CuInSe₂ nanocrystals confirm the formation of trigonal-shaped nanocrystals (see Figure 7.2). In the presence of OLA solvent, using elemental sulfur or selenium, relatively small particle formation is observed because the particle size growth is suppressed by OLA [40, 41]. The particles size can be increased by employing phosphine-based complexing agents such as trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), and trioctylphospite (TOOP) under same conditions (reaction time and temperature) [42].

Nose *et al.* reported the study on the formation of CuInS₂ nanoparticles from the metallic precursors in octadecene (ODE) and compared the

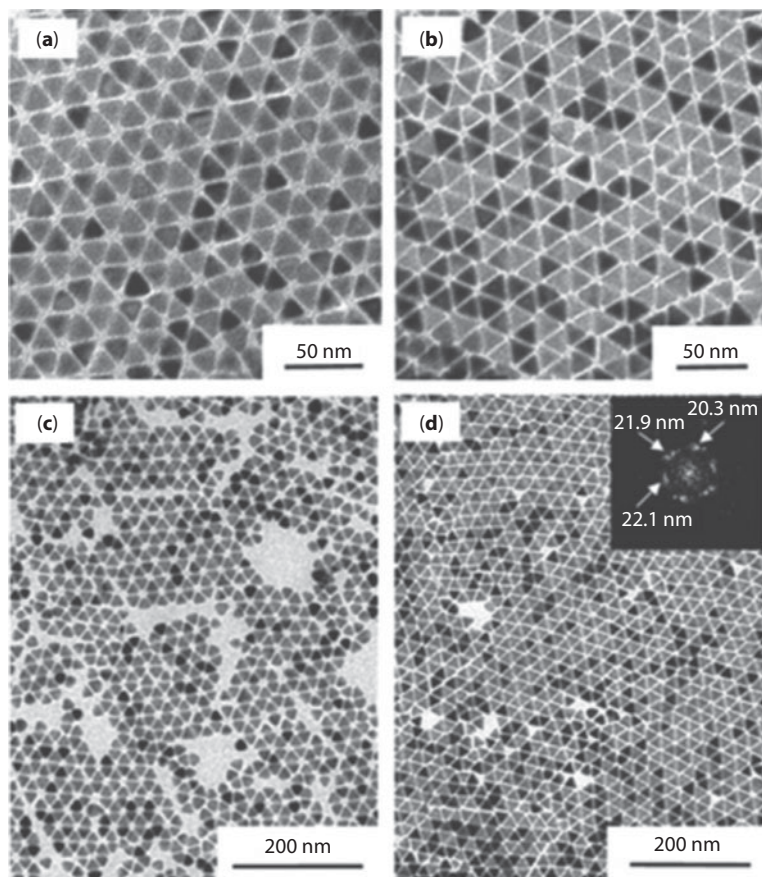


Figure 7.2 TEM images of trigonal CuInSe_2 nanocrystals synthesized at different OLA ratios [39] (Reprinted with permission from ACS, 2009).

effects of OLA and TOOP as stabilizers [43]. When TOOP is used as the complex ligand of the metallic monomer, the nucleation starts from the large number of nuclei because of the weak ligand nature resulting in chalcopyrite nanocrystals in ~ 5 nm size. However, by utilizing OLA with the metallic monomer, nucleation becomes difficult due to high bond strength between the monomer and OLA; the consumption of the metallic monomer is very low during the nucleation and yields wurtzite nanocrystals. On the other hand, use of dioctylphosphine oxide (DOPO) with TOPO and elemental selenium results in nanowires since DOPO acts as a weaker surfactant than OLA and promotes anisotropic growth [44]. Replacing OLA with ethylenediamine (EDA) as a surfactant yields large nanoparticles or nanorods [45–48]. Pure chalcopyrite CuInSe_2 nanoparticles in plate-like

and rod-like morphology have been prepared via microwave-enhanced solvothermal route in ethylenediamine (EDA) [47].

7.2.2.1 Hot-Injection Method

Panthani *et al.* applied the hot-injection method for the synthesis of chalcopyrite $\text{CuInS}_2/\text{Se}_2$ from metal precursors and elemental sulfur in the presence of OLA as capping ligand [41]. In this study, the diameter of the resulting spherical-shaped nanocrystals in the range of 8–15 nm has been obtained by controlling OLA/(Cu + In) mole ratios. Almost a decade later, Liu *et al.* studied CuInS_2 nanocrystal synthesis by hot-injection method with altering dose of OLA to obtain CuInS_2 nanocrystals with tunable bandgap. Bandgap values of the resulting nanocrystals vary from 1.44 to 1.91 as the crystal structure changes from zincblende to chalcopyrite phase with increasing amount of OLA [49].

7.2.2.2 Heat-Up (Noninjection) Method

The heat-up (noninjection) process is more convenient on a large-scale synthesis of nanocrystals for controlling elemental ratio, size, and morphology [50–58]. The only difference from the hot-injection method is that precursors can be added into a reaction vessel and heated to desired temperature by mixing. Lower reaction temperature in the process can help to prevent aggregation. In addition, to improve the quality of the resulting nanocrystals in terms of size and shape and prevent aggregation, researchers focused on using CuI instead of $\text{Cu}(\text{ac})_2$ [53, 56]. Because the iodide and hexanthiols are soft bases, they can coordinate to soft acid, Cu^+ , rather than to acetate ion as a hard base. Lefrançois *et al.* described the synthesis of CuInS_2 nanocrystals from tert-butylthiol (TBT) as sulfur source and surface ligand to yield 5-nm-sized nanocrystals [56]. Hahn *et al.* reported CuInSe_2 nanoparticles by a solution process using copper chloride, indium chloride, and selenium as the precursors and oleic acid as the solvent [59].

7.2.2.3 Thermal Decomposition Method

The thermal decomposition method is easier to handle for the synthesis of monodisperse nanocrystals. In the method, usually single-source precursors are used to form nanocrystals. The first case of the formation of chalcopyrite CuInS_2 nanoparticles from a single-source precursor, $(\text{PPh}_3)_2\text{CuIn}(\text{SET})_4$, in the presence of hexanthiol has been reported in 2004 [60]. The method produced nanocrystals between 2 and 4 nm

with a controllable surface chemistry in a noncoordinating solvent dioctyl phthalate at high temperature. The presence of alkanethiols in the reaction mixture leads the formation of nanocrystalline colloid, while the aggregated nanocrystals form without alkanethiols [61].

7.2.2.4 Solvothermal Method

Another wet chemical method for the synthesis of CuInS/Se_2 nanocrystals is solvothermal route. The reaction proceeds usually in an autoclave, and

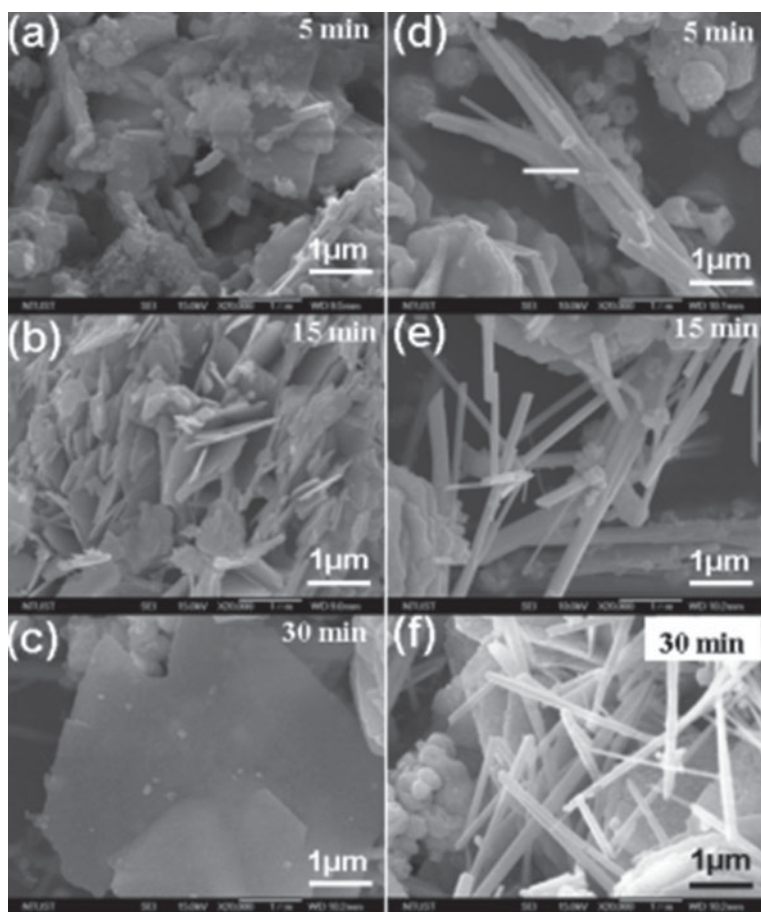


Figure 7.3 SEM images of CuInSe_2 particles synthesized by microwave-assisted solvothermal method (a–c) without pretreatment and (d–f) with pretreatment of selenium powder at different reaction times [48] (Reprinted with permission from ACS, *Chem. Mater.*, 2010).

thus, the process does not require N_2 gas flow and refluxing unlike hot-injection and heat-up processes. Wu *et al.* have prepared $CuInSe_2$ nanoparticles in spherical to nanorod morphologies via microwave-assisted solvothermal route [48]. In solvothermal route, the solvent and temperature play an important role for the formation of nanocrystals. Dimethyl formamide (DMF), octadecene (ODE), and OLA are the preferable solvents for controlling nucleation and growth of nanocrystals [62–64]. The proposed nucleation mechanism starts with the formation of $(Cu(DMF)_n)^+$ and $S(DMF)_2$ due to the complex behavior of DMF solvent to lead the formation of 15–30-nm-sized chalcopyrite $CuInS_2$ nanocrystals in spherical shape at 200 °C [63]. For the synthesis of $CuInSe_2$, selenium powder yields relatively bigger nanoparticles (~100 nm) and nanowiskers [64].

7.2.2.5 Microwave Treatment Method

Additionally, microwave treatment can be combined with both solvothermal and thermal decomposition processes to yield high-quality nanocrystals by shortening the reaction time and lower reaction temperature. Microwave-assisted (MA) synthesis has been reported by several research groups to prepare nanoparticles [65–70]. The use of microwave irradiation in the solid–liquid–solid (SLS) synthesis of nanowires has been described in the literature by Krylova *et al.* for synthesizing $CuInS_2$ nanowires [71]. The study on decomposing molecular single-source precursors (SSPs) via microwave irradiation to obtain efficient size-controlled chalcopyrite $CuInS_2$ nanoparticles in the presence of 1,2-ethanedithiol solvent at moderate temperatures (100 °C) and in 30 minutes has been reported by Sun *et al.* [72]. The nanoparticles' sizes vary between 1.8 nm to 10.8 nm as reaction temperatures were varied from 100 °C to 200 °C with the bandgaps from 2.71 eV to 1.28 eV. Zhang *et al.* reported 40x400nm sized nanorods synthesized by environmentally friendly MW heating method in deep eutectic solvent of urea/choline chloride (Figure 7.4) [73]. Sabet *et al.* widely investigated the formed $CuInSe_2$ nanocrystal size and shape depending on MW power and irradiation time, solvent, and type of Cu complex precursors [74]. While $Cu(2\text{-hydroxyacetophenone})_2$ was confirmed as the best copper complex as a precursor, ethylene glycol solvent did not have ability for the reduction of metal precursors.

7.2.3 Chalcopyrite $CuInS/Se_2$ Thin-Film Fabrication Methods

The advantage of $CuInS/Se_2$ nanocrystals to be used as absorbant layers of thin-film solar cells arises from the fact that the direct bandgap (~1.5 eV)

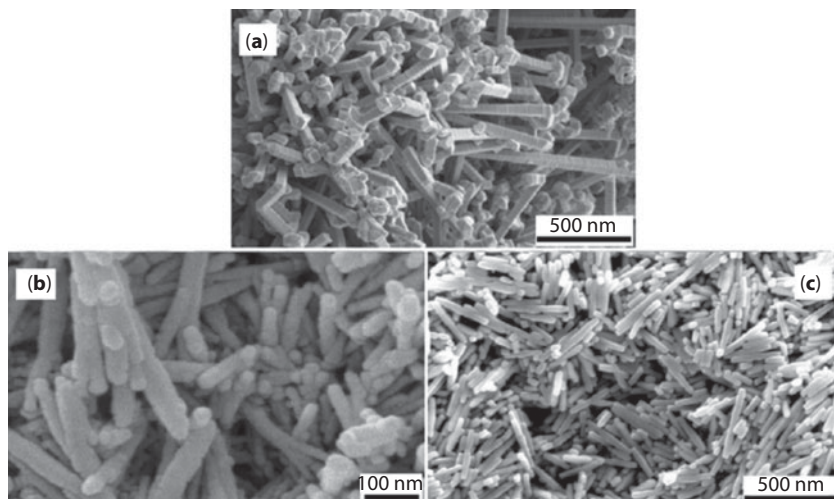


Figure 7.4 SEM images (a–c) of the CuInS_2 nanorods prepared by microwave heating method in different reaction times: (a) 10 min, (b) 15 min, and (c) 20 min [73]. (Reprinted with permission of Elsevier <http://dx.doi.org/10.1016/j.materresbull.2014.11.046>).

matches well with the solar spectrum and high stability against photocorrosion. Thus, there have been many researches about the preparation of CuInS/Se_2 thin films through chemical bath deposition [75], chemical spray deposition [76], radiofrequency reactive sputtering [77], selenization/ sulfurization of metallic alloys [78], electrodeposition [79, 80], spray pyrolysis [81], and other methods [82, 83]. In addition to these methods, the synthesized nanocrystals via wet chemical methods which were described in the previous section can be redispersed in appropriate solvents and used as “nanoink” to prepare absorbing layers [84–86]. This method is specifically convenient for the large-scale manufacture due to low production cost.

The first use of chalcopyrite materials in photovoltaic applications was reported by Wagner *et al.* in 1974. In the work, a heterojunction photovoltaic detector consists of p-type CuInSe_2 single-crystal absorber with the conjunction of n-type CdS layer [87]. However, the conversion efficiency was very low. Theoretically calculated energy conversion efficiency for CuInS_2 -based thin-film solar cells is 27–31% [88, 89]. However, the real photoconversion efficiency obtained in laboratory conditions is limited to 20% because of the light absorption limitations [90, 91]. Therefore, onward studies focused on increasing photoconversion efficiency. The CuInS/Se_2 -based thin-film fabrication techniques can be classified into two categories: nonvacuum and vacuum-based deposition techniques.

7.2.3.1 Vacuum-Based Techniques

Magnetron sputtering is most well-known vacuum technique for the thin-film fabrication [92]. Two main techniques of magnetron sputtering to obtain CuInS/Se₂ thin film have been reported [93, 94]; one is the sputtering deposition of CuInS/Se₂ thin film from the target containing Cu-In-S under the high vacuum. However, different elements may have different sputtering energy under the same sputtering power and pressure; it is therefore difficult to control the chemical composition [95]. The other technique is sputtering thin film with Cu and In targets under H₂S/Ar gas flow or annealed under sulfur- or selenium-rich environment [96–99]. Seeger *et al.* investigated the reactive magnetron sputtering process from copper and indium targets in Ar/H₂S sputtering atmospheres for the deposition of CuInS₂ absorber films. This large area deposition method is in principle suited for the preparation of absorbers of good electronic quality [96]. From the study, it is concluded that controlling of the Cu/In ratio and the film morphology is mandatory for reproducible CuInS₂ film deposition process. Guan *et al.* reported the preparation of CuInS₂ thin film on the high purity glass substrate (99.99%) via target of Cu-In alloy at a Cu/In atomic ratio of 1:1. Argon was used as the sputtering gas with a distance of 8 cm between the target and substrate. Later on, the prepared precursor films were placed in a tubular resistance furnace to prepare a CuInS₂ thin film by sulfurization heat treatment using argon gas as a protective gas to ventilate the tubular furnace at 500 °C [97].

Chemical vapor deposition (CVD) is a versatile thin film deposition method for a wide range of materials. Current methods employed for processing chalcopyrite CuInS/Se₂ thin film require techniques such as coevaporation of the elements, which involve high temperature sulfurization steps [100]. However, low temperature (<400 °C) deposition processes are needed to incorporate flexible polymer substrates. CVD is a major advancement in improving the processing of these types of solar arrays. The fundamental steps include vaporization and transport of the precursor into the reactor; diffusion of the precursor to the substrate; decomposition of the precursor; formation of CuInS/Se₂; recombination of the by-products, and desorption into the gas phase. A more detailed description of a spray CVD reactor is reported in the literature [101, 102]. Pulsed-laser deposition (PLD) is another vacuum-based deposition method for the preparation of high-quality CuInS/Se₂ thin films. It enables simple and flexible control on the composition and degree of crystallinity [103]. PLD is a thin-film deposition (specifically a physical vapor deposition, PVD) technique where a high-power pulsed-laser beam is focused to strike a target of the material that is to be deposited. This material is vaporized from

the target (in a plasma plume) which deposits it as a thin film on a substrate (such as a silicon wafer facing the target). This process can occur in ultrahigh vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to oxygenate the deposited films fully.

7.2.3.2 Nonvacuum Techniques

Thin films prepared from the application of the redispersed of nanocrystals which are synthesized by wet chemical methods to substrates are generally less expensive than those prepared by vacuum-based techniques. Therefore, a large variety of nonvacuum deposition approaches have been developed and reviewed. The direct liquid coating techniques such as doctors' blading and spin coating and some of the other key solution-based approaches including chemical bath deposition (CBD) and spray pyrolysis (SP) will be discussed in this section.

Chemical Bath Deposition (CBD)

The CBD method as technique for the preparation of thin films has many advantages, which includes low cost of the required equipment and

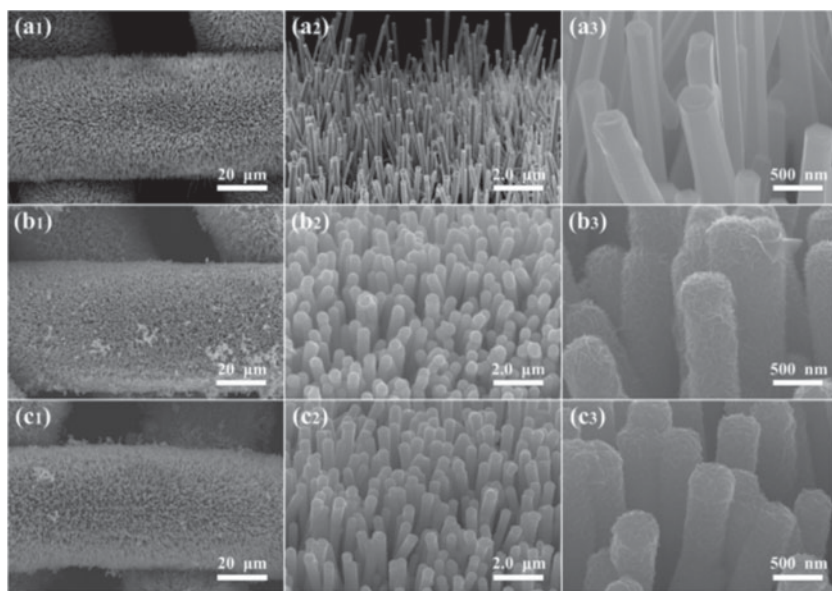


Figure 7.5 SEM images of the CuInS_2 nanowire arrays obtained with different reaction times: (a₁–a₃) 0 h, (b₁–b₃) 1 h, and (c₁–c₃) 2 h [104] (Reprinted with permission of Elsevier, <https://doi.org/10.1016/j.apcatb.2016.10.051>).

operation, simplicity, low energy consumption, and easy scalability to large area applications. Up-to-date, CBD method has been widely used to deposit many different semiconductors thin films. Li *et al.* reported the growth of the pristine Cu_2S nanowire arrays (NWAs) on Cu mesh via a gas–solid solvothermal reaction method in a Teflon autoclave-containing ethylene glycol solution of 0.15 M InCl_3 and 0.3 M thioacetamide [104].

Recently, Frank *et al.* reported a solvothermal synthesis approach that allows for preparing CuInS_2 films directly on fluorine-doped tin oxide (FTO) conductive glass substrates by involving the nontoxic biomolecule *L*-cysteine in a teflon liner autoclave at 160 °C [105]. All the CuInS_2 thin films, synthesized with different concentrations of reactants, show different film thicknesses, slightly different grain sizes, and vary in chemical composition dependent on the amount of sulfur used. Before that, Xia *et al.* reported the growth of CuInS_2 nanosheets and nanoworms on FTO glass via solvothermal process by employing hexadecyl trimethyl ammonium bromide and oxalic acid as surfactants in ethanol [106]. The nanoworm electrodes obtained in sulfur-rich environment exhibited better photoelectric performance due to their better visible-light absorption.

Direct Nanoink Coating

Spin coating technique is a simple and cost-effective way to fabricate uniform and crack-free thin film. Either the solution of precursors can be directly applied onto the substrate and annealed at high temperature to form CuInS_2 nanocrystal absorber layer [4, 107, 108], or the synthesized nanocrystals can be redispersed in a solvent to form nanoink to be coated on the surface of the substrate [109]. Zhao *et al.* reported CuIn(S,Se)_2 thin film fabrication process via spin coating from the precursor solution that contains Cu, In, and S elemental powder in mixed solvents of 1,2-ethanedithiol and 1,2-ethylenediamine (1:10 ratio) [107]. This solution deposited on Mo-coated soda-lime glass substrate via spin coater at 3000 rpm in a nitrogen-filled glove box, followed by a drying process at 300 °C on a hot plate for 5 min. The as-deposited CuInS_2 thin films were placed in a graphite box containing a certain amount of Se powders and annealed at desired temperature (525–575 °C) for 30 min in a tube furnace with double temperature zone under Ar atmosphere with a pressure of 0.03 MPa. Apart from this, the nanoink solution can be applied on thin film surface by commercial spray gun for photovoltaic applications. Akhavan *et al.* have prepared thin films via nanoink spraying method without any post-deposition treatment [109].

Doctors' blading and painting are direct nanoink coating methods for low cost and large-scale manufacture of thin film. The nanoparticles are

dispersed in solvents to create a paint or ink, which is coated onto substrates for precursor films. The CuInS_2 films are produced from the precursor by a high temperature process in which the solvents are evaporated and nanoparticles are sintered. Long *et al.* presented a study on painting ink prepared by dispersing CuInS_2 nanoflakes into polyvinylidene fluoride (PVDF)/N-methyl-2-pyrrolidone solution (NMP) with an ultrasonic process (weight ratio= 4:1:5). This ink was coated onto Mo substrate and heated to 200 °C for 30 minutes in vacuum to remove the organic compounds. Then the film was heated to 600 °C by rapid thermal process (RTP) for 1 h under argon atmosphere for crystallization and sintering [110].

Spray pyrolysis (SP)

Spray pyrolysis (SP) and ink-jet printing are versatile deposition methods that are simple, cost-effective, and can be adapted to large area deposition. Additionally, these techniques are convenient with flexible substrates compared to standard evaporation deposition. Being noncontact deposition methods, they allow the deposition of multiple layers without destroying those underlying. SP consists of spraying precursor solution on a heated substrate surface. Technically, this technique can be viewed as direct solution of metallic salts. The solvent evaporation occurs on the substrate surface and solid film growth takes place during the spraying step. It requires high substrate temperature, compensating for the cooling effect of solvent evaporation, and precursor decomposition, at the same time maintaining precisely controlled and uniform aerosol flow. Generally, the solutions consist of organometallic compounds or metal salts dissolved in aqueous or organic-based solvents. In contrast to the doctor blade technique, the solution is not required to be viscous which opens the route for binder-free solutions. In addition, the thickness of the layer can be simply adjusted by variable spraying/printing time [112]. SP has been used for the deposition of CuInS_2 [112–115]. In a study, CuInS_2 films were deposited by SP in ambient atmosphere onto substrates maintained at temperatures between 375 to 400 °C using solutions with different Cu-In-S ratios [115]. Ikeda *et al.* reported the preparation of polycrystalline CuInS_2 chalcopyrite thin films on a Mo-coated glass substrate by SP. The thin films were then annealed in a sulfur atmosphere at 500 and 600 °C. Structural and photoelectrochemical analyses of CuInS_2 films obtained by annealing at 500 °C and 600 °C revealed that a well-defined crystalline film was obtained by the 600 °C annealing [116]. CuInS_2 is deposited by spray pyrolysis technique at 350 °C by varying Cu/In ratio and annealed at 200 °C for an hour under vacuum. The stoichiometry measurements confirmed the formation of copper-rich and indium-rich CuInS_2 , in which In-rich CuInS_2 thin films

exhibited n-type conductivity, while Cu-rich CuInS_2 thin films exhibited p-type conductivity [117].

Electrodeposition

Electrodeposition is another nonvacuum preparation method, and compared with other nonvacuum techniques, it has many outstanding features such as high yield, low cost, and large scalability [80, 118, 121]. In addition, it is easier to control film composition and morphology [119]. Gunawan *et al.* reported chalcopyrite CuInS_2 semiconductor thin films fabricated by electrodeposition method for photoelectrochemical water splitting [85]. CuInS_2 film was prepared by an electrodeposition method. Uv-vis spectrophotometer test result shows that the bandgap of the electroplated film is 1.5 eV [120].

7.2.4 Applications in Photoelectrochemical Cells

CuInS_2 semiconductor layers are deposited onto glass substrates or FTO-coated glass substrates with the reactive sputtering of Cu–In metal precursors followed by the sulfurization [122]. The conversion of Cu-rich CuInS_2 to the In-rich CuInS_2 phase has been observed with an increase in the $[\text{In}]/[\text{In} + \text{Cu}]$ molar ratio in the metal precursors. A thin film with an $[\text{In}]/[\text{In} + \text{Cu}]$ molar ratio of 0.53 has a maximum photo enhancement current density of 5.81 mA/cm^2 at an applied bias of 0.4 V vs. an Ag/AgCl electrode in aqueous $\text{Na}_2\text{S}/\text{K}_2\text{SO}_3$ solution.

As mentioned in the previous section, the scalability of the photoelectrode fabrication method is an important factor for solar energy harvesting. Although the efficiency of the photocathodes prepared by vacuum evaporation methods is higher than that of the nonvacuum-based ones, the application is not very scalable. Therefore, photocathodes based on chalcopyrite CuInS_2 prepared by scalable methods are under investigation. Ikeda *et al.* have reported hydrogen evolution from water using Pt- and CdS-modified CuInS_2 photocathodes prepared from polycrystalline CuInS_2 films by electrodeposited Cu and In metallic precursors followed by sulfurization process [121]. Upon the surface modification with Pt- and CdS-modified CuInS_2 (Pt/CdS/ CuInS_2), photocathodes showed IPCEs above 20% at wavelengths ranging from 500 nm to 750 nm at $-0.37 \text{ V}_{\text{RHE}}$. PEC characterization revealed that the film was suitable for water reduction, but not for water oxidation. The high IPCE value of the CuInS_2 thin films indicated that the photoelectrodes prepared by a cost-effective liquid-based process can compete with the ones prepared by vacuum processing methods in terms of efficiency. Gunawan *et al.* reported a highly

efficient CuInS_2 -based photocathode for water reduction with a maximum applied bias photon-to-current efficiency of $\sim 2\%$ was prepared by using a novel In_2S_3 surface modifier eliminating the use of highly toxic CdS [85, 123]. A Pt- and In_2S_3 -modified CIS ($\text{Pt}/\text{In}_2\text{S}_3/\text{CIS}$) photocathode showed a photocurrent of $15.2\text{mA}/\text{cm}^2$ at 0 VRHE under AM1.5G irradiation. Xia *et al.* reached 0.25% of ABPE with photocathodes bearing CIS nanosheets and nanoworms on FTO glass (Figure 7.6) [106].

CuInS_2 nanoflakes have been synthesized by a convenient solvothermal route under the open-air condition. The resulting nanoflakes were redispersed to form ink which was coated onto Mo substrate using doctors' blade technology, and after sintering, a dense and compact CuInS_2 film was produced [111]. In this study, the photoelectrochemical (PEC) properties of the CuInS_2 thin films coated on Mo substrate were characterized. PEC performance properties have been studied in LiCl (0.1 M) solution

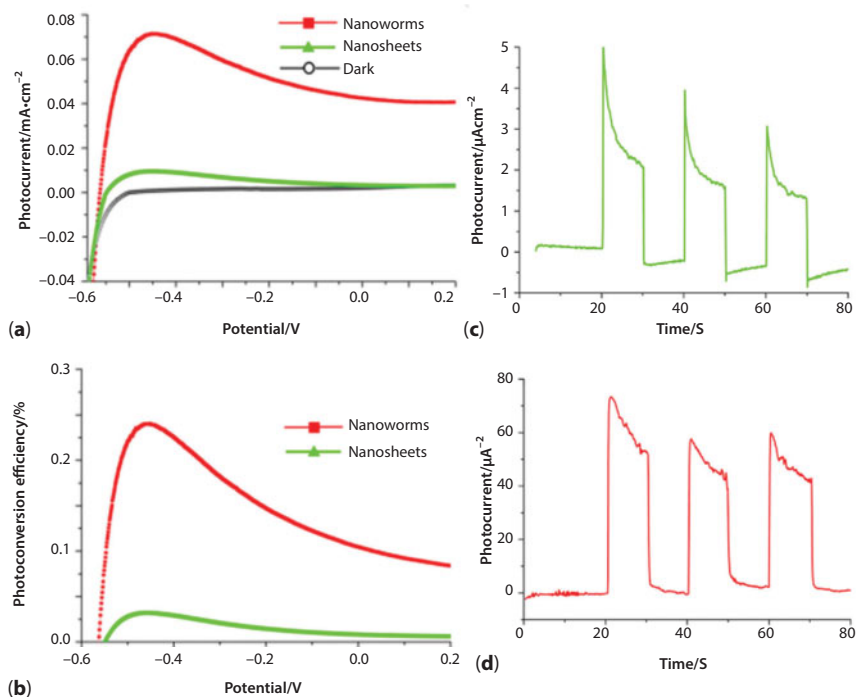


Figure 7.6 PEC properties of CuInS_2 nanosheet and nanoworm electrodes: (a) linear sweeps of the I-V characteristics, (b) photoconversion efficiency (ABPE) vs the applied potential V. Photocurrent response spectra of the synthesized CIS electrodes: (c) nanosheets, (d) nanoworms [106] (Reprinted with permission of Elsevier, <https://doi.org/10.1016/j.matchemphys.2012.08.005>).

as electrolyte by using platinum counterelectrode; the cell was illuminated by 472 nm green LED lamp and the intensity of the lamp was increased from 0 to 0.28 lum with the step of 0.005 lum. The photoelectron current increased to the intensity of the lamp which indicated the film was sensitive to light (Figure 7.7).

Li *et al.* investigated the use of CuInS_2 NWAs thin-film photocathode and reported greatly enhanced PEC performance compared to the pristine Cu_2S NWAs due to the enhanced light absorption as well as their screw-like surfaces for increased specific surface area. The $\text{CuInS}_2/\text{CdS}$ NWAs have demonstrated an optimal photocurrent of 0.71 mAcm^{-2} and an IPCE of 9.0% at 450 nm [104]. The biggest drawback for CIS-based photocathodes is instability in photocurrent. Zhao *et al.* achieved stabilization of the photocurrent and hydrogen evolution for over an hour by the deposition of an additional TiO_2 layer with an appropriate thickness on CdS-modified CuInS_2 , followed by Pt deposition, and reached a faradaic efficiency of $\sim 90\%$ [124].

Han *et al.* studied the deposition of CuInS_2 QDs on the surface of one-dimensional TiO_2 nanorod arrays by the pulsed-laser deposition (PLD) technique [103]. The CuInS_2 QDs are coated on TiO_2 nanorods/FTO substrate without any ligand engineering, and the performance of the obtained CuInS_2 QD sensitized solar cells is optimized by adjusting the laser energy. An energy conversion efficiency of 3.95% is achieved under 1-sun ($\text{AM } 1.5, 100 \text{ mW cm}^{-2}$) illumination. For the I - V characterization, a polysulfide solution consisting of 0.5 M Na_2S , 2.0 M sulfur, and 0.2 M KCl in a mixture of methanol and water solution (3:7 by volume) was used as electrolyte. For

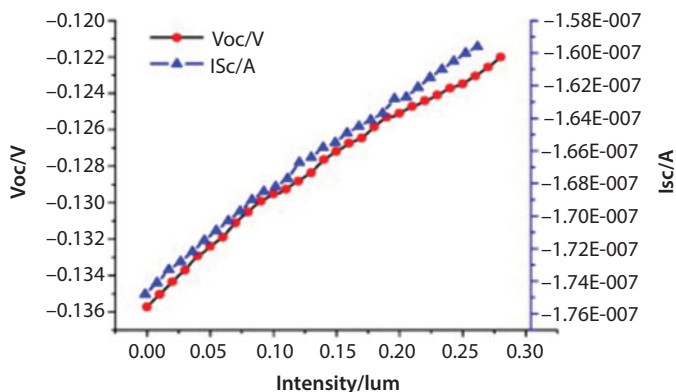


Figure 7.7 Short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) as a function of light intensity for the PEC cell of CuInS_2 thin film [111] (Reprinted with permission of Elsevier, <https://doi.org/10.1016/j.matlet.2009.10.044>).

the other photoelectric properties, the electrolyte was composed of 0.05 M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 0.95 M Na_2SO_3 aqueous solution.

Drop-casting method has been applied for coating on ITO-PET with prepared CuInS_2 nanocrystals by one-pot synthesis method (ITO-PET surface of 10.1 mm^2) [125]. PEC studies have been performed in an electrolyte containing a MV^{2+} and 0.1 M KCl. The concentration-dependent photocurrent response has been confirmed as increasing MV^{2+} gives higher photocurrent density. Another PEC study of CuInS_2 photoelectrode performed in an electrolyte containing MV^{2+} resulted in $\sim 20\%$ IPCE at 400 nm [126]. In this study, the ink of CuInS_2 nanocrystals prepared by wet chemical method was applied on FTO substrate via drop casting. After surface modification with CdS, 80% photocurrent efficiency was observed.

In summary, the performance of photocathodes based on chalcopyrite CuInS/Se_2 materials has improved rapidly with the efforts of researchers in this field (Table 7.3). Thus, chalcopyrite photocathodes are proved to be promising materials for the PEC hydrogen production system.

7.3 Cu-Based Kesterite ($\text{I}_2\text{-II-IV-VI}_4$) Semiconductors

7.3.1 Material Properties

Intensive investigations and studies have been conducted in the field of thin films based on naturally abundant quaternary copper compounds ($\text{Cu}_2\text{ZnSnX}_4$; $\text{X} = \text{S}, \text{Se}$) having the kesterite structure [127]. Denoted as $\text{CZT}(\text{S}, \text{Se})$, kesterite semiconductors are one of the most piquant materials used as absorber layers recently and therefore are perfect candidates to be used in thin-film solar cells [128]. The low-cost manufacturing, abundance on earth's crust, nontoxicity of these compounds are the main reasons for them being preferred in this application area. Moreover, it is important to note that the similar properties of $\text{CZT}(\text{S}, \text{Se})$ and CuInS_2 are an advantage due to the fact that these films are the ones exhibiting the highest power conversion efficiency of all other types of thin-film solar cells [127, 128]. However, the scarce sources and high cost of Indium (In) and Gallium (Ga) limits the further applications of CuInS_2 thin films [129]. Therefore, CZTSSs developed by replacing In atoms partially with Zn and Sn have been deeply investigated, recently. Due to its being a quaternary compound, the order of atomic arrangement is more complex in comparison to ternary CuInS_2 . According to the arrangement of atoms, CZTSSs can form two main structures known as kesterites (Figure 7.8) and stannites. However,

Table 7.3 Overview of chalcopyrite ternary semiconductors applied on photoelectrochemical cells.

Material	Deposition method	Electrolyte	$J_{sc}/(\text{mA}/\text{cm}^2)$	IPCE (%)	ABPE (%)	Ref.
CuInS ₂ /FTO	Magnetron sputtering	0.35 M Na ₂ S ₂ O/0.25 M K ₂ SO ₃ (pH 13.3)	5.81 mA/cm ² at 0.4 V (vs. an Ag/AgCl)	NA	1.20	[122]
TiO ₂ /CuInS ₂ /FTO	Pulsed-laser deposition	0.05 M Na ₂ S ₂ OH ₂ O/0.95 M Na ₂ SO ₃	17.59 mA/cm ² at 0.43 V (vs. an Ag/AgCl)	38% at 380–700 nm 0 V	3.50	[103]
CuInS ₂ /FTO	Chemical bath deposition	0.1 M Na ₂ SO ₃	72 $\mu\text{A}/\text{cm}^2$ at 0.45 V	N.A.	0.25	[106]
CdS/CuInS ₂ /Cu mesh	Chemical bath deposition	1.0 M KCl (pH 5.97)	0.71 mAcm ⁻² Ag/AgCl (0V vs. RHE).	IPCE of 9.0% at 450 nm, -0.55V	N.A.	[104]
CdS/CuInSe ₂ /FTO	Drop casting	0.02M MV ²⁺ / 0.5 M Na ₂ SO ₄ (pH 6.5)	-1.5mA/cm ² at -0.6 V vs Ag/AgCl	5–15% at 400nm, 0.5V	NA	[126]
CuInS ₂ /ITO/PET	Drop casting	MV ²⁺ /0.1 M KCl	0.20 mAcm ⁻² Ag/AgCl (0V vs. RHE).	N.A.	N.A.	[125]
Pt/CdS/CuInS/Mo	Electroplating/sulfurization	M Na ₂ SO ₄ (pH 13)	6 mA/cm ² at 0.3–0.4 V (vs Ag/AgCl)	>20% at 500–750 nm (at -0.37 VRHE in pH 4)	N.A.	[121]
Pt/CuInS ₂ /Mo	Electroplating/sulfurization	M Na ₂ SO ₄ (pH 9.0)	0.51 mA/cm ² at 0 V	25% at 500–750 nm (at -0.37 VRHE)	0.5 at 0.2V (vs) RHE	[85]
Pt/In ₂ S ₃ /CuInS ₂ /Mo	Electroplating/sulfurization	0.1 M Na ₂ SO ₄ (pH 9.0)	15.2 mA/cm ² at 0 V	37%–41% at 520–700 nm	1.97% at 0.28 VRHE	[85]
Pt/TiO ₂ /CdS/CuInS ₂	Electroplating/sulfurization	0.1 M Na ₂ HPO ₄ pH= 10	13.0 mA cm ⁻² at 0V	62% at 500–700 nm	1.82% at 0.25 VRHE	[124]

kesterites, due to having a more stable phase, are more widely preferred in PEC cell applications [130]. The nontoxic chemical composition, sustainability, optimal direct bandgap (1.4–1.6 eV), and high absorption coefficient (10^4 cm^{-1}) are the major advantages of these compounds. Despite all these advantages of quaternary kesterites, the obtained photoconversion efficiencies are still lower in comparison to other semiconductor materials. The main reason for such efficiency decay could be related to the nature of these materials that during the synthesis process tend to produce secondary phases (Cu_xS , ZnS , Sn_xS). Moreover, various point defects, vacancies and antisites could be easily formed causing the formation of deep bandgap trap states [131, 132]. Taking into consideration the fact that efficiencies of CZTSs are strongly related with their photoelectrochemical properties, lots of efforts have been put to optimize the kesterites' growth mechanism

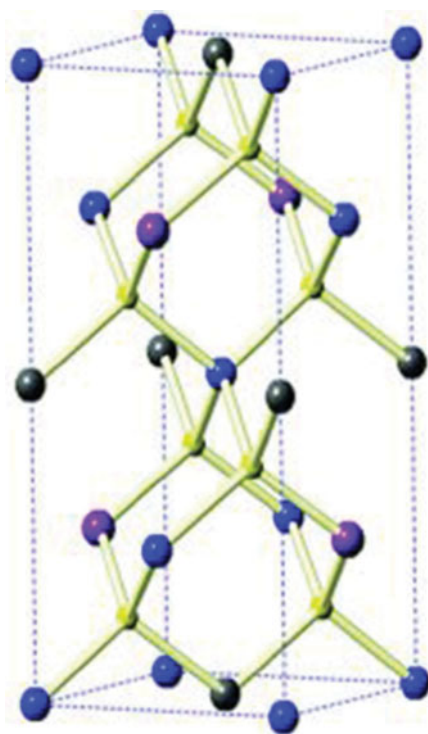


Figure 7.8 Schematic representation of kesterite crystal structure where blue-colored balls indicate copper, yellow stand for sulfur, gray for tin, and zinc atoms are shown with purple color [129]. (Reprinted with permission of Elsevier, <https://doi.org/10.1016/j.solmat.2018.03.021>).

and synthesis techniques [133]. So far, numerous methods have been developed to obtain CZTSs with decent photoelectrochemical properties. Among these methods, both the direct synthesis of kesterite nanocrystals and several vacuum and nonvacuum thin film deposition techniques have been studied deeply.

7.3.2 Synthesis Techniques of Kesterite $\text{Cu}_2\text{ZnSnS/Se}_4$ Nanocrystals

Heterostructured, multiphase materials, carrying the features of their individual compounds, are highly dependent on the interface properties as well. The synthesis of these kinds of distinctive and versatile materials requires a certain composition control at nanoscales which can only be achieved via controlling the growth solution directly [134, 135]. Besides, due to the sensitivity to point defects and phase purities, the existence of binary phases, and similar characteristic features, a precise control over the reaction steps is required. Thus, taking into consideration these requirements, several synthetic CZTS nanocrystal fabrication techniques have been studied [135–162]. Obtaining CZTSs in nanocrystalline ink forms is a desirable synthesis method which is highly applicable for large-scale device manufacturing processes. Several approaches such as hot injection, hydrothermal/solvothermal, microwave, and others have been developed as effective nanoink synthesis methods [136, 137].

7.3.2.1 Hot-Injection Method

Among the studies investigating the synthesis of evenly distributed CZTS nanocrystals in small dimensions, hot-injection method has been selected as the most suitable approach [138]. It is considered as one of the most successful methods as it is based on the surfactant-controlled nanocrystal synthesis in an organic hot solvent [139]. Various types of organic solvents have been utilized in hot-injection nanocrystal synthesis method at various reaction temperatures. Table 7.4 briefly summarizes types of solvents and reaction conditions of the most widely preferred hot-injection CZTS nanocrystal synthesis.

Kumar *et al.* reported the synthesis of colloidal CZTS nanopowders in OLA via hot-injection method by varying the initial concentration of Cu and Zn + Sn and investigating the morphological changes. The study has shown that various Cu/(Zn+Sn) ratios ranging from 0.82 to 0.48 resulted in a severe increase in particle dimensions from 20 to 150 nm, respectively. It has been concluded from this study that the decreasing Cu and increasing

Table 7.4 Summary of different CZTS nanoparticles synthesized by hot-injection method.

Solvents	Reaction parameters	Particle size (nm)	Bandgap energy	Ref.
OLA	225 °C – 0.5 h	15–25	1.5	[141]
OLA	280 °C – 1 h	10.6 ± 2.9	1.3	[142]
OLA	235 °C – 0.5 h	22.5 ± 2.0	1.52	[143]
OLA, TOPO	300 °C – 0.75 h	12.8 ± 1.8	1.5	[144]
OLA, OA, DDTI	240 °C – 1 h	20	1.4	[145]
ODE, OA	220 °C – 1 h	17	1.55	[146]
OLA, DDT	220 °C – 4 h	50	1.49	[147]
ODE, ODA, EG	220 °C – 1 h	6.5	1.5	[148]
EG	190 °C – 4 h	25–150	1.5	[149]

Zn concentrations resulted in the formation of larger particles of approximately 2 – 10 μm dimensions [141]. In one of their studies, Chen *et al.* have employed the hot-injection method in order to synthesize Cu-doped CZTSe nanocrystals at midrange temperatures and different Cu-doping contents [150]. The synthesis step has been followed by hot pressing of solid nanoparticles at 400°C and 60 mPa for 30 minutes. The morphological effects of hot pressing method have been investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis revealing that the sizes of the obtained polygon-like shaped nanoparticles (20–50 nm) after the hot-pressing step have increased up to 80 nm. This has been attributed to the agglomeration of small sized particles into one big particle under the applied temperature and pressure that resulted in the enhanced phonon-boundary scattering [150].

Mirbagheri *et al.* have also employed the hot-injection method on the synthesis of quaternary ligand-free CZTS compounds in order to obtain the desired elemental composition [151]. The synthesis method based on the utilization of metal precursors ($\text{CuCl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) at varying amounts resulted in the formation of targeted compositions. The X-ray diffraction (XRD) analysis revealed that the actual kesterite formation with their significant diffraction peaks at (112), (200), (220), (312), and (224) was obtained at the 1.02 ± 0.09 Cu/(Zn+Sn) ratio. However, it has also been noted that the composition kesterite structure obtained at

this ratio was slightly higher than actual $\text{Cu}_2\text{ZnSnS}_4$. TEM analysis showed the formation of irregular multidirectional nanoparticles with an average size of 23 nm and a standard deviation of 11 nm [151]. However, most of the studies based on hot-injection nanocrystal synthesis involve the toxic, hazardous, and expensive solvents and highly inert atmosphere making the overall synthesis highly costly.

7.3.2.2 Solvothermal/Hydrothermal Method

Solvothermal/hydrothermal CZTS nanocrystal synthesis, among other wet-chemical methods, is a highly preferred technique for the controlled synthesis of kesterite nanocrystals. This process is not limited by temperature and pressure of vessel [136]. Furthermore, the reaction does not require the N_2 atmosphere and refluxing, which are highly important parameters for the hot-injection synthesis route. Despite these advantages in the synthesis procedure, several drawbacks such as longer processing time, agglomeration, and irregular shaped nanoparticles are frequently encountered in the solvothermal nanocrystal synthesis. Gong *et al.* have performed a study based on high-quality, impurity-free solvothermal growth of kesterite CZTS nanoparticles with the diameter of approximately 9 nm [136]. A systematic control has been achieved on analyzing the effects of sulfur concentration and addition of tin (Sn) precursor. The experimental outcomes have revealed that with the increase in the amount of sulfur, the pure phase CZTS nanocrystals transform into mixed phases. The effect of Sn precursor has been analyzed by changing the Sn sources (SnI_2 , tin stearate (TNO), and $\text{Sn}(\text{Ac})_2$) in CZTS formation, revealing that the high-quality, pure, and stable kesterite phases are obtained in the presence of SnI_2 [136, 152]. Kannan *et al.* have studied the influence of various solvents (EA, water, EG, DEG, ethanol) on the morphological, optical properties, and crystallinity of hydrothermally grown CZTS nanocrystals [153]. The XRD patterns obtained from all samples confirmed the formation of kesterite structure with the characteristic diffraction peaks. However, in comparison to other types of solvents, EG revealed broader peaks which have been attributed to the smaller crystal formation (Figure 7.9). The evaluation of crystallite sizes has been performed via Scherrer's equation $D = 0.9\lambda / \beta \cos \theta$ where λ corresponds to X-ray wavelength (CuK α : $\lambda = 1.5406 \text{ \AA}$), β is the full width high maximum, and θ is the diffraction angle. The obtained crystallite sizes confirmed that the utilization of EG as solvent resulted in the formation of smallest crystallites (7 nm) and that the effect of solvent is highly distinguishable.

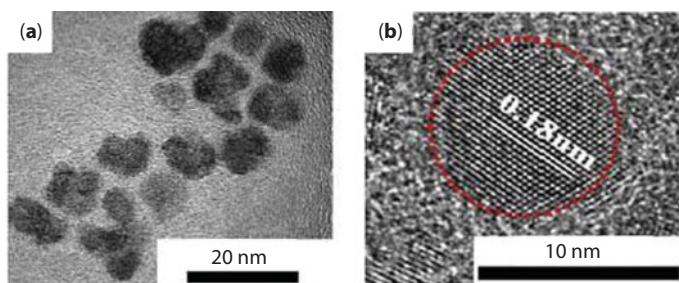


Figure 7.9 (a) TEM and (b) HRTEM image of solvothermally grown CZTS nanoparticles [136] (Reprinted with permission of Elsevier <https://doi.org/10.1016/j.jallcom.2015.12.181>).

7.3.2.3 Microwave-Assisted Chemical Synthesis

The fast reaction period, controllable, and efficient heating are among the major advantages of microwave-assisted chemical synthesis (MACS) compared to other techniques studied so far. Although the utilization of this method in the synthesis of inorganic nanoparticles is still not so popular, several studies have been performed to investigate nanocrystal properties. Vallejo *et al.* have synthesized kesterite CZTS nanoparticles via MACS technique and analyzed the effect of precursor concentration, reaction time, and solvent on the obtained crystalline structures [154]. Triethanolamine has been selected as the solvent, and the reaction periods of 0.5, 1.0, and 1.5 hours have been investigated. The XRD and Raman analysis have shown that the Cu and Zn content of 0.5 and 1.0 h samples are higher due to the intense crystallinity and well-defined peaks both in XRD and Raman spectra, respectively. However, the increase in reaction period causes decomposition in the CZTS kesterite phase, resulting in a decay of the Cu and Zn contents. The TEM images revealed the presence of CZTS nanoparticles measuring between 6 and 8 nm which is distinguishably small in comparison to other studies reported in literature (Figure 7.10) [154–157]. Despite all, there are still some parameters that need to be improved in MACS synthesis which are of wide particle size distribution and poor crystallinity [137].

7.3.2.4 Additional Novel Approaches to CZTS Nanocrystal Syntheses

In addition to the most common and widespread nanocrystal synthesis techniques, there have been other new approaches in the literature as well.

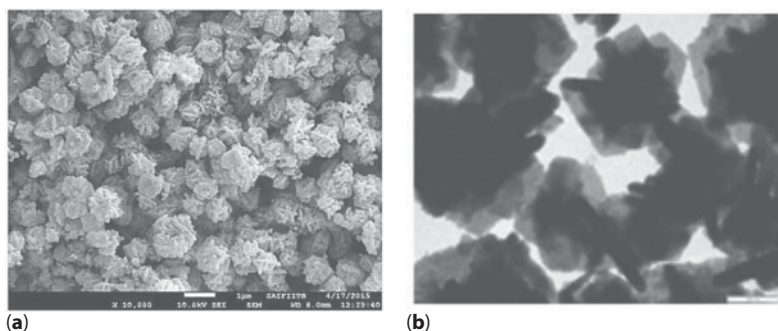


Figure 7.10 (a) SEM and (b) TEM images of the synthesized CZTS powder by microwave irradiation [156]. Reprinted with permission of Elsevier, <https://doi.org/10.1016/j.matpr.2016.06.028>).

In one of the studies, Das *et al.* handled the subject of large-scale CZTS single nanocrystal growth by vertical gradient freeze (VGF) technique [158]. The growth of kesterite single crystals is a highly challenging application. Various methods such as solution fusion [159], travelling heater [160], and iodine transport [161] have been tested, but the major problems like insufficient yield and reproducibility could not be exceeded. The VGF growth takes place inside a vertical furnace with three temperature zones taken independently under control (Figure 7.11a). The synthesis has taken place by using pure, elemental Cu, Zn, Sn, S, and Se under approximately 1100 °C and 100 °C temperature gradient between the hottest and coldest region of furnace. The XRD spectra have shown strong and sharp crystalline peaks with extremely low FWHM confirming the formation of large crystallites. The applied method has successfully formed the bulk $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ crystals in multigram amounts with a novel approach (Figure 7.11 b,c) [158].

Another research conducted by Chong *et al.* has focused on the improvement of crystallinity of CZTS nanocrystals by SiO_2 loading and high temperature calcination aiming for better H_2 evolution [162]. The kesterite nanocrystal synthesis has been carried out by typical hot-injection method. The prepared CZTS containing solution has been mixed with the solution containing SiO_2 spheres (Stöber method) [163]. The postsulfurization of the precipitated nanoparticles has taken place in argon atmosphere under vacuum, and the final outcome, CZTS/ SiO_2 nanoparticles, has been obtained. The TEM images have demonstrated that pristine CZTS nanocrystals with irregular shapes have a size distribution between 10 and 30 nm.

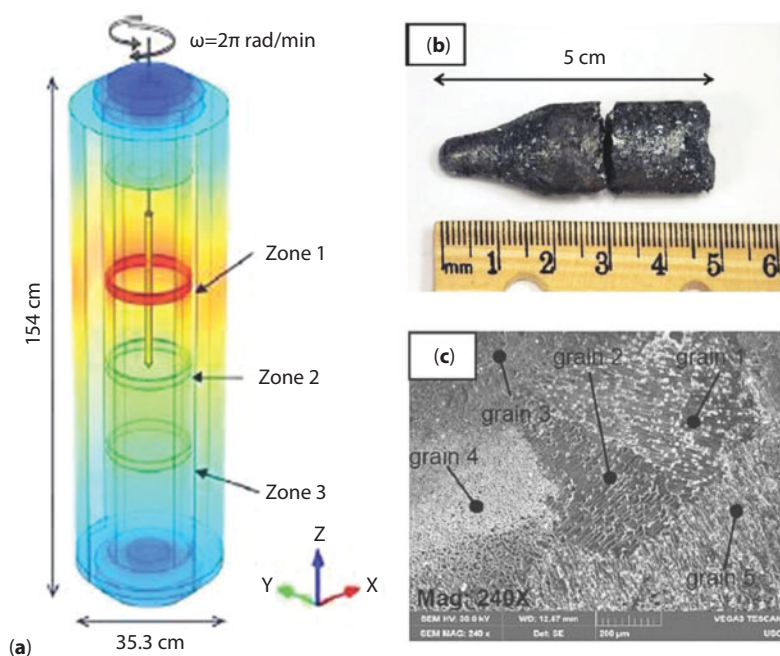


Figure 7.11 (a) 3D scheme of VGF furnace for crystal growth, (b) image of CZTSSe ingot and (c) SEM image obtained from wafer cut showing the presence of polycrystalline grains [158] (Reprinted with permission of Elsevier, <http://dx.doi.org/10.1016/j.materresbull.2014.04.073>).

7.3.3 Kesterite $\text{Cu}_2\text{ZnSnS}_4$ Thin-Film Fabrication Methods

CZTS thin-film deposition techniques have been thoroughly investigated due to their being successful candidates as solar absorber layers. As in a general approach, kesterite thin-film deposition techniques can be classified into two main categories: vacuum-based and nonvacuum-based.

7.3.3.1 Vacuum-Based Techniques

Vacuum-based thin film deposition methods are one of the mostly studied techniques as they provide controllability on the composition of the film and allow to study their specific aspects. Sputtering, chemical vapor deposition (CVD), thermal evaporation, and pulsed-laser deposition (PLD) are among the most common vacuum-based approaches investigated in the literature.

Sputtering

The first report on CZTS thin-film deposition via argon beam from a pressed metal target has been introduced by Ito and Nakazawa in 1988

[164]. This has turned to the pioneering work that launched the proceeding studies based on CZTS thin-film deposition by sputtering technique. Magnetron sputtering is a highly preferred deposition process for the preparation of thin films and solar cells due to its easy adaptability to large-scale productions. The deposition rate can be easily controlled by effectively utilizing the pure raw material itself. The film preparation can be divided into two steps where (I) the first step is based on the sputtering of metal precursors at desired deposition conditions followed by (II) the annealing at elevated temperatures in either sulfur or selenium atmosphere [133]. Jimbo *et al.* were the first to propose the substrate rotation during the sputtering process to obtain homogeneously deposited, uniform precursor layers [165]. Instead of utilizing pure metallic precursors, Seol *et al.* have been able to obtain a $\text{Cu}_2\text{ZnSnS}_4$ thin film by sequentially sputtering Cu_2S , ZnS , and SnS_2 and further annealing in Ar/S_2 mixed atmosphere at 400°C [166]. The effect of changes in the elemental ratio of Cu/Zn/Sn has been investigated by different research groups and resulted in the

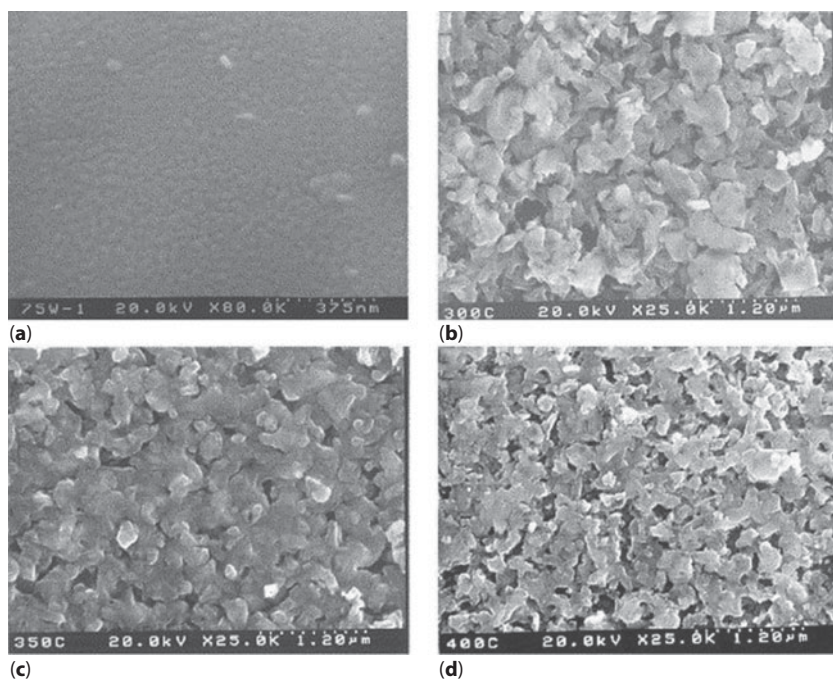


Figure 7.12 Effect of annealing temperature on surface morphology of CZTS thin films deposited by sputtering technique; (a) as-deposited (b) 300°C (c) 350°C (d) 400°C [166] (Reprinted with permission of Elsevier, [https://doi.org/10.1016/S0927-0248\(02\)00127-7](https://doi.org/10.1016/S0927-0248(02)00127-7)).

formation of composition maps that helped to determine efficient kesterite phases (Figure 7.12). It has been demonstrated that CZTS thin films with Cu-poor and Zn-rich elemental ratios have better efficiencies and hydrogen generation performances [167]. Another significant study conducted by Wibowo *et al.* has investigated a single-step CZTSe thin-film preparation by using binary selenides and eliminating further chalcogenation step. The substrate temperature maintained at 150 °C has been selected as the most successful deposition condition for the achievement of uniform film with proper stoichiometric ratios [168].

However, the limitations of cosputtering such as the formation of secondary phases and the control that needs to be maintained on the precursor ratios must be improved. At that point, the sequential deposition of metallic precursors has been proposed as an alternative method to overcome the challenges of cosputtering [169–178]. However, it has been further established by Valakh *et al.* that the small energy barrier between Cu and Zn causes a Cu/Zn surface disorder, resulting in the formation of irregular kesterite symmetry [179].

Evaporation

Evaporation is another class of widely preferred vacuum-based CZTS thin-film formation methods [180–184]. This highly controllable deposition technique provided the acquisition of thin films with large grain sizes and low levels of impurities [180]. Primarily, the studies investigating this technique were based on sequential evaporation of Cu/Sn/Zn at 150 °C followed by a postsulfurization at 500 °C in H₂S atmosphere [181]. Further improvements of the evaporation process have led to the utilization of

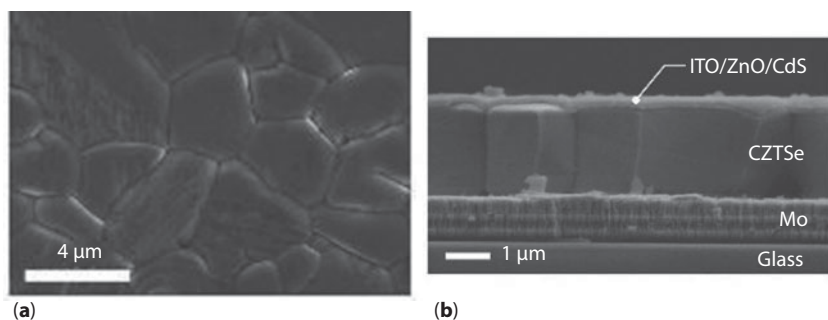


Figure 7.13 SEM images of CZTSe thin films grown by thermal coevaporation technique; (a) plain view of kesterite film with large grain sizes, (b) cross-sectional image of the device showing the layered structure [185]. (Reprinted with permission of Wiley, <https://doi.org/10.1002/aenm.201401372>).

ZnS as the source of Zn which resulted in the increase in the efficiency increase [182]. For the very first time, Katagiri *et al.* have introduced the Na-doping to the kesterite films via Na_2S addition [183]. This has caused a major improvement in the performances making a splash in power conversion efficiency. Simultaneously, a significant number of studies have been focused on the coevaporation technique for CZTS thin films. However, some major problems such as reevaporation of SnSe at temperatures above 350 °C, formation of volatile Zn phases at about 400 °C, and the decomposition of the kesterite film have been frequently encountered. In order to avoid such kinds of drawbacks, Wang *et al.* have reduced the annealing period of thin films to 5 minutes under sulfur-rich atmosphere at 540 °C (Figure 7.13) [184].

Pulsed-Laser Deposition

Pulsed-laser deposition (PLD), being a relatively novel technique, is a thin-film deposition method having several significant advantages such as easy stoichiometric control, operation at low temperatures, and good-quality thin films [185]. The method is easy to handle and has a high deposition rate and tunable incident power energy [186]. In addition, it is highly sensitive to the substrate temperature and laser density parameters which have an influence on the CZTSSe film properties. In the very first study using PLD technique for the deposition of CZTS kesterite thin films by Katsuhiko *et al.*, a target from Cu_2S , ZnS, SnS_2 , and Se powders has been prepared and deposition has taken place at 20 Hz frequency in order to obtain good crystalline properties [187]. Proceeding studies have focused on efficiency improvements by changing the type and temperature of substrate, gas pressure, or deposition frequencies [188, 189]. Since the acquisition of multicomponent films at desired stoichiometric ratio is possible in PLD technique, studies reporting low efficiencies attribute this to the unsuccessful postsulfurization and/or selenization processes. Therefore, further investigations for the improvement of efficiencies of PLD techniques are still in progress.

7.3.3.2 Nonvacuum Techniques

In comparison to vacuum-based techniques, nonvacuum deposition processes of CZTS thin films have several significant benefits such as low deposition cost, film uniformity, and mass production. Spray pyrolysis, spin coating, electrodeposition, and successive ionic layer adsorption and reaction (SILAR) are the most common nonvacuum deposition processes studied in literature [132, 188–190].

Spray Pyrolysis

Spray pyrolysis (SP), among other nonvacuum-based processes studied so far, has been the most attracting technique. Its applicability to different system scales, low cost, and versatility are the main reasons for preference. However, controlled morphology and phase purity are the main challenges confronted in the utilization of SP technique for the formation of CZTS thin films. Taking into consideration these pros and cons of SP deposition, Moholkar *et al.* have investigated the ways of avoiding the formation of undesired secondary phases and the effects of changing Cu concentrations on the properties of thin films (Figure 7.14) [190]. All the metal chlorides of Cu, Zn, and Sn were used as their primary sources, and thiourea has been selected as the source of sulfur. The sulfur amount has been incorporated into the solution in excess amounts in order to prevent the precipitation of solution and to avoid a major loss of sulfur during SP process. The obtained results investigating the effects of Cu amounts at various molarities (0.15, 0.20, 0.25 and 0.30M) have demonstrated a perfect crystallinity at 0.25M with strong and sharp kesterite phase peaks. The 0.30M concentration of copper chloride resulted in the formation of undesired phase of copper anilite giving the overall film an amorphous nature. Besides, 0.25M of copper source led to the formation of larger grains, thus decreasing the number of grain boundaries and minority carrier diffusion length having an ultimate impact on the photoconversion efficiency values (1.09%). Similar studies based on SP deposition technique have focused on the performance enhancement by changing experimental variables, but the efficiencies could not exceed those obtained by vacuum-based methods [191–194]. Recently, a remarkable study by Sayed *et al.* has increased the efficiencies of SP-deposited CZTSSe thin-film solar cells to about 7% by silver incorporation [195]. Silver (Ag) has been selected as a successful dopant for having unique properties both as absorber layer and as solar cell device. By varying the amount of Ag of the precursor solution, the effect of the amount of dopant has been investigated as well. The XRD analysis has shown a distinguishable enhancement in the crystallinity of CZTS thin films after the Ag incorporation. Besides, the properties of films as absorber layers have increased by almost 60% after the doping step.

Direct Nanoink Coating

Direct nanoink coating methods have been developed as an alternative low-cost approach for the thin-film deposition techniques from the synthesized nanocrystals. These methods are mainly categorized into two deposition techniques which are spin coating and doctor blade. The prepared and centrifuged CZTSSe nanocrystals are generally dispersed in

suitable solvents (toluene, hexanethiol, EG, DEG) to form nanoinks which are further coated on substrates [196]. Although the properties of nanocrystals can be successfully tailored, their transformation into thin films is quite challenging due to them being highly nonuniform and containing voids [197]. Miskin *et al.* achieved the highest photoconversion efficiency by modifying the technique of nanoink synthesis [198]. As a major difference in the synthesis process, during the fabrication of nanocrystals, sulfur has been primarily introduced into the system, thus causing the cation to be exposed into a sulfur-rich environment. Singh *et al.* have reported another nanoink coating technique where CZTS thin films are obtained by drop-casting method in order to form nanorod morphologies under controlled solvent evaporation [199].

Electrodeposition

Electrodeposition (ED) or electroplating is an environmentally friendly and inexpensive CZTS thin-film deposition technique. The reusability and recyclability of the electrolyte solution makes the process suitable and promising for industrial applications [200]. A considerable number of studies have focused on the electrodeposited CZTS thin films and their properties [200–208]. It is worth mentioning that for CZTS thin films, electrodeposition of copper, zinc, and tin takes place at room temperature which is a remarkable advantage in the area of energy conservation. The ED step is followed by the postchalcogenization of thin films under S or Se rich atmosphere to obtain final kesterite structure. Studies based on electroplating of kesterites are mainly categorized into two deposition techniques which are stack layer (Cu/Sn/Zn) and alloy layer (Cu-Zn-Sn) deposition [200]. In general, the highest kesterite film quality with a significant performance has been obtained in Zn-rich and Cu-poor films that avoid the formation of secondary, undesirable phases and are highly uniform throughout the film [201–203]. In stack CZTS film deposition by electroplating, varying the thickness and deposition time of each layer can help to control the overall film composition. However, a frequently encountered problem in stacked ED of CZTS thin films is the inhomogeneity of film layers that are highly dependent on the preceding bottom layers and the postannealing step [204, 205].

In comparison, the alloy electrodeposition technique has reached higher efficiency values by avoiding the formation of secondary phases. Nevertheless, another challenge encountered in this deposition technique is the control over the composition of alloy which is highly difficult due to the significant differences between the reduction potentials of Cu, Sn, and Zn. Lee *et al.*, Mkawi *et al.*, Slupska, and Ozga *et al.* have studied on several

methods such as utilizing low-cost citrate or tartrate salts, increasing the deposition potential/current density or acidic baths with low pH values in order to increase the efficiencies of ED-deposited CZTS thin films [206–208]. Recently, Ge *et al.* have demonstrated that the composition of the deposited thin film can be adjusted by mass transport, where higher Zn deposition can be achieved as a result of Cu and Sn ions reaching their diffusion limited rates. Moreover, it has been shown that electrodeposited metal precursors contain several impurities causing a performance decay which could be avoided by postannealing in the ambience containing hydrogen and sulfur together [200].

Successive Ionic Layer Adsorption and Reaction

Another common nonvacuum CZTS thin-film deposition technique that has been recently studied is the successive ionic layer adsorption and reaction (SILAR). In comparison to the nonvacuum techniques that require high amounts of energy, SILAR is a relatively low cost and eco-friendly method that does not require the utilization of toxic gases and solvents [209]. SILAR deposition method, similar to electrodeposition mentioned above, can be applied by two different methods that are (I) simultaneous deposition and (II) sequential stacking of sulfide precursors [210]. Analyzing both methods of deposition, studies have shown that sequential deposition in contrast to simultaneous one is a more successful method for the formation of uniform kesterite thin films. A precise control on stoichiometry can be easily achieved; however, longer time is spent on the sequential deposition of each layer which makes the process unsuitable for large-scale industrial applications. On the other hand, simultaneous thin-film deposition via SILAR method is highly difficult to control due to different adsorptivities of each element inside one bath. Additionally, the formation of nonuniform, porous film with poor crystallinity makes this deposition method highly undesirable [210]. In one of their studies, Kobayashi *et al.* and Araki *et al.* have investigated the effects of type (sulfide compound or metallic) and order of stacking layers in CZTS thin films [211, 212]. It has been demonstrated that using binary sulfides as sources of Cu, Sn, and Zn is a disadvantageous way due to the decomposition of precursor during the reaction and the resulting loss of Zn and Sn from the composition [212]. As an alternative path for resolving these problems, primarily deposited metallic precursors have been further annealed under sulfur or selenium atmosphere. However, it is highly challenging to obtain uniform Zn and Sn due to them being volatile and as a result forms defects and voids in the overall structure. Recently, Suryawanshi *et al.* have developed a new technique based on the preparation of CZTS kesterite films by

sulfurizing $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ film deposited via stacking SILAR method where the perfect film uniformity and smoothness could be achieved [210].

7.3.4 Applications in Photoelectrochemical Cells

Kesterite semiconductors are highly employable for absorber layer applications in photoelectrochemical solar cells due to their low cost and environmentally friendly nature. The utilization of CZTS nanocrystals for hydrogen production has gradually increased the demand for these materials, recently. The most significant photoelectrochemical (PEC) performances of CZTS nanocrystals obtained so far are summarized in Table 7.5 (Figure 7.15) [213–226].

In one of the first studies performed in this field, Scragg *et al.* have deposited CZTS thin films by electroplating method followed by postsulfurization step [213]. The PEC analysis has been conducted in a three-electrode standard cell inside 0.2M $\text{Eu}(\text{NO}_3)_3$ (pH 2.3), which is an electron scavenging electrolyte. The resulting thin film has been determined to be p-type, with the doping density of 10^{16} cm^{-3} and bandgap of 1.49 eV.

Riha *et al.* have synthesized CZTS nanocrystals via hot-injection method and further fabricated them into thin film by drop casting. The photoelectrochemical performances of these films have been tested in aqueous electrolyte (0.1M KCl and 0.1M $\text{Eu}(\text{NO}_3)_3$) and the highest IPCE performance of 10.1% has been evaluated at $\text{Eu}(\text{NO}_3)_3$ electrolyte solution [215]. Among similar direct nanoink coating techniques, Tiong *et al.* have used doctor-blade deposition technique in order to form CZTS thin films [216]. Although the PEC performances have not been reported in this study, the stability analysis showed a constant current density performance within 340 seconds.

Almost a decade ago, Yokoyama *et al.* have studied the photoelectrochemical water splitting performances of CZTS thin films deposited on Mo-coated soda lime glass by cosputtering method. Incident photon-to-electron conversion efficiencies (IPCE%) have been measured under 300W Xe lamp in the 0.1M Na_2SO_4 electrolyte solution [217].

7.4 Concluding Remarks

The most common approaches for the synthesis of the copper-based ternary and quaternary semiconductors in chalcopyrite and kesterite phases have been proposed, and their basic material and optoelectronic properties have been discussed. The comparison has been made for the most

Table 7.5 PEC performance summary of different CZTS nanoparticles synthesized by hot.

Photoelectrode	Deposition method	Electrolyte properties	J (mA cm ⁻²)	IPCE%	Ref.
CZTS	Electroplating	0.2M Eu(NO ₃) ₃ (pH 2.3)	0.1 at -0.4VAg/AgCl	N.A.	[213]
CZTS	Electrodeposition	0.2M Eu(NO ₃) ₃	0.15 at -0.5VSCE	N.A.	[214]
CZTS	Drop casting	0.1M KCl and 0.1M Eu(NO ₃) ₃	0.3 at -0.5VAg/AgCl	10.1% at 500nm	[215]
CZTS	Doctor blade	0.2M Eu(NO ₃) ₃ (pH 2.3)	0.2 at -0.3VAg/AgCl	N.A.	[216]
Pt/TiO ₂ /CdS/CZTS	Cosputtering	0.1M Na ₂ SO ₄ (pH 9.5)	5.6 at 0.22 VRHE	8.1% at 600nm	[217]
CZTS	Ultrasonic spray pyrolysis	0.5M Na ₂ SO ₄ (pH 6.5)	0.77 at -0.7VSCE	N.A.	[218]
CZTS	Electrodeposition	0.5M Na ₂ SO ₄ (pH 6)	0.25 at -0.4VRHE	2.75% at 330nm	[219]
CZTS/CdS/TiO ₂	Spin coating	0.2M Na ₂ SO ₄	0.165 at 0 VRHE	5% at 380nm	[220]
Pt/CdS/CZTS	Electroplating	0.1M Na ₂ SO ₄ (pH 9.5)	6 at -0.35 V _{RHE}	13.5% at 600nm	[221]
(Cu ₂ Sn) _{0.45} Zn _{1.65} S ₃	Electrodeposition	0.1M Na ₂ SO ₄ (pH 3)	0.2 at -0.24 VRHE	5 % at 500nm	[222]
CZTS	Direct nanoink coating	0.5M Na ₂ SO ₄	2.16 at 1.0 VSCE	7% at 300nm	[223]
CZTS	Spin coating	0.5M Na ₂ SO ₄ (pH 9.5)	1.32 at 0 VRHE	N.A.	[224]
CZTS/CdS/MV	Doctor blade	50mM Eu(NO ₃) ₃	0.075 at -0.5 VAg/AgCl	N.A.	[225]
CZTS-Ag ₂ S	Spin coating	1M Eu(NO ₃) ₃	0.58 at 0.5 VAg/AgCl	N.A.	[226]

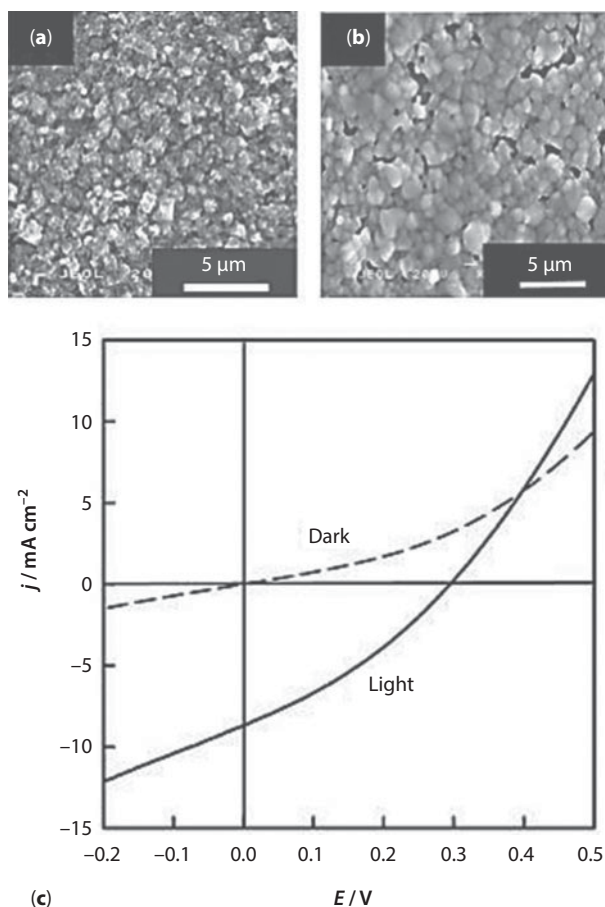


Figure 7.14 (a,b) Top and cross-sectional SEM images of $\text{Cu}_2\text{ZnSnS}_4$ thin films grown on Mo glass substrate and (c) J-V performance under illuminated and dark conditions [189] (Reprinted with permission of Wiley, <https://doi.org/10.1002/pssb.200879539>).

suitable process conditions for the synthesis of nanocrystals with tunable bandgap and high crystallinity. For the industrial applications, several thin film deposition techniques, under classification of vacuum and non-vacuum systems have been compared. Power conversion efficiencies have been taken as the major performance comparison parameter. Despite the tremendous development in the field, there are still some limitations that need to be focused on. The desired materials properties such as composition, morphology, size, bandgap, and high crystallinity should be controlled precisely during the synthesis methods. High-efficiency solar cells are expected for large area applications. Therefore, the material properties should be enhanced to achieve better photoconversion efficiency.

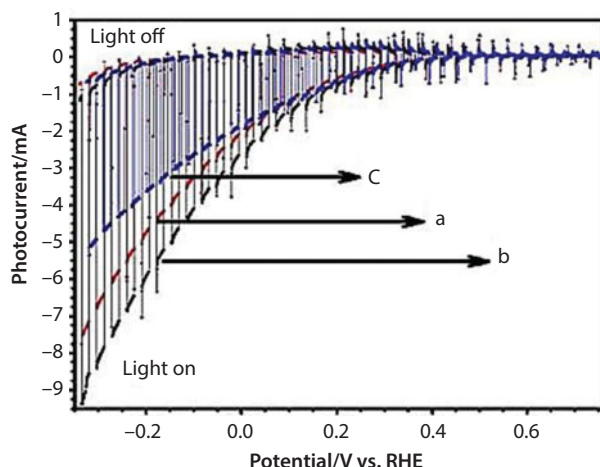


Figure 7.15 Photocurrent CZTS electrodes vs. RHE under 300 W Xe lamp. The Zn precursors were electroplated in pH = 6 (a), 9 (b), and 11 (c) solutions [221]. Reprinted with permission of Elsevier, <https://doi.org/10.1016/j.cplett.2010.03.081>.

References

1. Johnston, B., Mayo, M.C., Khare, A. Hydrogen: The Energy Source for the 21st Century, *Technovation*, 25, 2005.
2. Bard, A.J., Fox, M.A. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen, *Acc. Chem. Res.*, 28(3), 141, 1995.
3. Yu, H.T., Quan, X., Zhang, Y.B., Ma, N., Chen, S., Zhao, H.M. Electrochemically Assisted Photocatalytic Inactivation of *Escherichia coli* under Visible Light Using a ZnIn_2S_4 Film Electrode, *Langmuir*, 24, 7599, 2008.
4. Weil, B.D., Connor, S.T., Cui, Y. CuInS_2 Solar Cells by Air-Stable Ink Rolling, *J. Am. Chem. Soc.*, 132, 6642, 2010.
5. Li, L., Coates, N., Moses, D. Solution Processed Inorganic Solar Cell Based on *in Situ* Synthesis and Film Deposition of CuInS_2 Nanocrystals, *J. Am. Chem. Soc.*, 132(1), 22, 2010.
6. Tsuji, I., Kato, H., Kudo, A. Angew. Visible-Light-Induced H_2 Evolution from an Aqueous Solution Containing Sulfide and Sulfite over a $\text{ZnS-CuInS}_2\text{-AgInS}_2$ Solid-Solution Photocatalyst, *Angew. Chem. Int. Ed.*, 117, 3631, 2005.
7. Zheng, L., Xu, Y., Song, Y., Wu, C.Z., Zhang, M., Xie, Y. Nearly Monodisperse CuInS_2 Hierarchical Microarchitectures for Photocatalytic H_2 Evolution under Visible Light, *Inorganic Chem.*, 48, 4003, 2009.
8. Aldakov, D., Lefrançois, A., Reiss, P. Ternary and quaternary metal chalcogenide nanocrystals: synthesis, properties and applications, *J. Mater. Chem. C*, 2013, 3756, 2013.
9. Leach, A.D.P., Macdonald, J.E. Optoelectronic Properties of CuInS_2 Nanocrystals and Their Origin, *J. Phys. Chem. Lett.*, 7(3), 572, 2016.

10. Marai, A.D., Djessas, K., Ayadi, Z.B., Alaya, S. Preparation and characterization of CuInSe₂ nanoparticles elaborated by novel solvothermal protocol using DMF as a solvent, *J. Alloys Compounds*, 648, 1038, 2015.
11. Guo, J., Changa, G., Zhanga, W., Liua, X., He, Y. Facile synthesis of CuInS₂ nanoparticles using different alcohol amines as solvent, *Chem. Phys. Lett.*, 647, 51, 2016.
12. Bera, P., Seok, S. Facile synthesis of nanocrystalline wurtzite Cu-In-S by amine-assisted decomposition of precursors, *J. Solid State Chem.* 183, 1872, 2010.
13. Guo, J., Zhou, W.H., Li, M., Hou, Z.L., Jiao, J., Zhou, Z.J., Wu, S.X. Synthesis of bullet-like wurtzite CuInS₂ nanocrystals under atmospheric conditions, *J. Crystal Growth*, 359, 72, 2012.
14. Guo, J., Chang, G., Zhang, W., Liu, X., Zhou, T., He, Y. Mild solution-based method for synthesizing wurtzite CuInS₂ nanoplates at low temperature, *Mater. Lett.*, 123, 169, 2014.
15. Benbelgacem, J., Marai, A.B., Mendil, R., Medjnoun, K., Djessas, K. Synthesis of CuInS₂ nanoparticles by solvothermal process using dimethylformamide as a solvent, *J. Alloys Compounds*, 692, 966, 2017.
16. Thomas, S.R., Chen, C.-W., Date, M., Wang, Y.-C., Tsai, H.-W., Wang, Z.M., Yu-Lun Chueh. Recent developments in the synthesis of nanostructured chalcopyrite materials and their applications: a review, *R. Soc. Chem. Adv.*, 6, 60643, 2016.
17. Bachmann, K.J., Fearhailey, M. Phase relations in the Cu, In, Se system and the properties of CuInSe₂ single crystals, *Appl. Phys. Lett.*, 44(4), 408, 1984.
18. Chen, B., Chang, S., Li, D., Chen, L., Wang, Y., Chen, T., Zhou, B., Zhong, H., Rogach, A.L. Template Synthesis of CuInS₂ Nanocrystals from In₂S₃ Nanoplates and Their Application as Counter Electrodes in Dye-Sensitized Solar Cells, *Chem. Mater.* 27, 5949, 2015.
19. Mitchell, K., Fahrenbruch, A.L., Bube, R.H. Photovoltaic determination of optical-absorption coefficient in CdTe, *J. Appl. Phys.*, 48(2), 829, 1977.
20. Meese, J.M., Manthuruthil, J.C., Locker, D.R.B. Bull. CuInS₂ diodes for solar energy conversion, *Am. Phys. Soc.*, 20, 696, 1975.
21. Klaer, J., Siemer, K., Luck, I., Braunig, D. 9.2% efficient CuInS₂ mini-module *Thin Solid Films*, 387(1-2), 169, 2001.
22. Unold, T., Sieber, I., Ellmer, K. Efficient CuInS₂ solar cells by reactive magnetron sputtering, *Appl. Phys. Lett.*, 88(21), 13502, 2006.
23. Courtel, F.M., Paynter, R.W., Marsan, B., Morin, M. Synthesis, Characterization, and Growth Mechanism of n-Type CuInS₂ Colloidal Particles, *Chem. Mater.*, 21(16), 3552, 2009.
24. Murrang, C.B., Norris, D.B., Bawendi, M.G. Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites, *J. Am. Chem. Soc.*, 115, 8706, 1993.
25. Olesiak, J.K., Weller, H. Synthesis and Application of Colloidal CuInS₂ Semiconductor Nanocrystals, *Appl. Mater. Interfaces*, 5, 12221, 2013.

26. Liu, L., Li, H., Liu, Z., Xie, Y.-H. Structure and band gap tunable CuInS_2 nanocrystal synthesized by hot-injection method with altering the dose of oleylamine, *Mater. Design*, 149, 145, 2018.
27. Xie, R., Rutherford, M., Peng, X. Formation of high-quality I-III-VI semiconductor nanocrystals by tuning relative reactivity of cationic precursors, *J. Am. Chem. Soc.*, 131, 5691, 2009.
28. Vahidshad, Y., Ghasemzadeha, R., Irajizadb, A., Mirkazemia, S.M. Synthesis and Characterization of Copper Indium Sulfide Chalcopyrite Structure with Hot Injection Method, *J. Nanostructures*, 3, 145, 2013.
29. Mourdikoudis, S., Liz-Marzán, L.M. Oleylamine in Nanoparticle Synthesis, *Chem. Mater.*, 25(9), 1465, 2013.
30. Bensebaa, F., Durand, C., Aouadou, A., Scoles, L., Du, X., Wang, D., Page, Y.L. A new green synthesis method of CuInS_2 and CuInSe_2 nanoparticles and their integration into thin films, *J. Nanoparticle Res.*, 12, 1897, 2010.
31. Liu, Q., Zhao, Z., Lin, Y., Guo, P., Li, S., Pan, P., Ji, X. Alloyed $(\text{ZnS})(x)(\text{Cu}_2\text{SnS}_3)(1-x)$ and $(\text{CuInS}_2)(x)(\text{Cu}_2\text{SnS}_3)(1-x)$ nanocrystals with arbitrary composition and broad tunable band gaps, *Chem. Commun.*, 47, 964, 2011.
32. Liu, S., Zhang, H., Qiao, Y., Su, X. One-pot synthesis of ternary CuInS_2 quantum dots with near-infrared fluorescence in aqueous solution, *RSC Adv.*, 2, 819, 2012.
33. Wang, M., Liu, X., Cao, C., Shi, C. Synthesis of band-gap tunable Cu-In-S ternary nanocrystals in aqueous solution, *RSC Adv.*, 2, 2666, 2012.
34. Chen, Y., Li, S., Huang, L., Pan, D. Green and facile synthesis of water-soluble Cu-In-S/ZnS core/shell quantum dots, *Inorganic Chem.*, 52, 7819, 2013.
35. Luo, J., Wei, H., Huang, Q., Hu, X., Zhao, H., Yu, R., Li, D., Luo, Y., Meng, Q. Highly efficient core-shell CuInS_2 -Mn doped CdS quantum dot sensitized solar cells, *Chem. Commun.*, 49, 3881, 2013.
36. Tang, A., Hu, Z., Yin, Z., Yang, C., Teng, F. One-pot synthesis of CuInS_2 nanocrystals using different anions to engineer their morphology and crystal phase, *Dalton Trans.*, 44, 9251, 2015.
37. Yu, C., Yuand, J.C., Wen, H., Zhang, C. A mild solvothermal route for preparation of cubic-like CuInS_2 crystals, *Mater. Lett.*, 63(23), 1984, 2009.
38. Das, K., Panda, S.K., Gorai, S., Mishra, P., Chaudhuri, S. Effect of Cu/In molar ratio on the microstructural and optical properties of microcrystalline CuInS_2 prepared by solvothermal route, *Mater. Res. Bull.*, 43, 2742, 2006.
39. Koo, B., Patel, R.N., Korgel, B.A. Synthesis of CuInSe_2 nanocrystals with trigonal pyramidal shape, *J. Am. Chem. Soc.*, 131, 3134, 2009.
40. Uehara, M., Watanabe, K., Tajiri, Y., Nakamura, H., Maeda, H. Synthesis of CuInS_2 fluorescent nanocrystals and enhancement of fluorescence by controlling crystal defect, *J. Chem. Phys.*, 2008, 50, 193–200.
41. Panthani, M.G., Akhavan, V., Goodfellow, B., Schmidtke, J.P., Dunn, L., Dodabalapur, A., Barbara, P.F., Korgel, B.A. Synthesis of CuInS_2 , CuInSe_2 , and $\text{Cu}(\text{In}_x\text{Ga}(1-x))\text{Se}_2$ (CIGS) nanocrystal “inks” for printable photovoltaics, *J. Am. Chem. Soc.*, 130, 16770, 2008.

42. He, J.J., Zhou, W.-H., Li, M., Hou, Z.L., Du, Y.-F., Wu, S.-X. One-pot route for preparation of monodisperse CuInS₂ nanocrystals, *Mater. Lett.*, 66, 96, 2012.
43. Nose, K., Soma, Y., Omata, T., Otsuka Y-Matsuo, S. Synthesis of Ternary CuInS₂ Nanocrystals; Phase Determination by Complex Ligand Species, *Chem. Mater.*, 21, 2607, 2009
44. Wark, S.E., Hsia, C.H., Luo, Z., Son, D.H. Surfactant effect on the formation of CuInSe₂ nanowires in solution phase synthesis, *J. Mater. Chem.*, 21, 11618, 2011.
45. Jiang, Y., Wu, Y., Mo, X., Yu, W., Xie, Y., Qian, Y. Elemental Solvothermal Reaction to Produce Ternary Semiconductor CuInE₂ (E = S, Se) Nanorods, *Inorganic Chem.*, 39, 2964, 2000.
46. Chen, H., Yu, S.-M., Shin, D.-W., Yoo, J.-B. Solvothermal Synthesis and Characterization of Chalcopyrite CuInSe₂ Nanoparticles, *Nanoscale Res. Lett.*, 5, 217, 2009.
47. Seo, Y.-H., Lee, B.-S., Jo, Y., Kim, H.-G., Choi, Y., Ahn, S.J. et al. Facile Microwave-Assited Synthesis of Multiphase CuInSe₂ Nanoparticles and Role of Secondary CuSe Phase on Photovoltaic Device Performance", *The Journal of Physical Chemistry C*, 117, 9529, 2013.
48. Wu, C.-C., Shiau, C.-Y., Ayele, D.W., Su, W.-N., Cheng, M.-Y., Chiu, C.-Y., Hwang, B. Rapid Microwave-Enhanced Solvothermal Process for Synthesis of CuInSe₂ Particles and Its Morphologic Manipulation, *Chem. Mater.*, 22, 4185, 2010.
49. Li, B., Xie, Y., Huang, J., Qian, Y. Synthesis by a solvothermal route and characterization of CuInSe₂ nanowhiskers and nanoparticles, *Adv. Mater.*, 11, 1456, 1999.
50. Tang, X., Cheng, W., Shi, E., Choo, G., Xue, J. Synthesis of CuInS₂-ZnS alloyed nanocubes with high luminescence, *Chem. Commun.*, 47, 5217, 2011.
51. Shi, L., Yin, P., Wang, L., Qian, Y. Fabrication of single-crystalline CuInS₂ nanowires array via a diethylenetriamine-thermal route, *Crystal Eng. Commun.*, 14, 7217, 2012.
52. Shi, L., Pei, C., Li, Q. Ordered arrays of shape tunable CuInS(2) nanostructures, from nanotubes to nano test tubes and nanowires, *Nanoscale*, 2, 2126, 2010.
53. Li, L., Pandey, A., Werder, D.J., Khanal, B.P., Pietryga, J.M., Klimov, V.I. Efficient synthesis of highly luminescent copper indium sulfide-based core/shell nanocrystals with surprisingly long-lived emission, *J. Am. Chem. Soc.*, 133, 1176, 2011.
54. Li, L., Daou, T.J., Texier, I., Chi, T.T.K., Liem, N.Q., Reiss, P. Highly Luminescent CuInS₂/ZnS Core/Shell Nanocrystals: Cadmium-Free Quantum Dots for In Vivo Imaging, *Chem. Mater.*, 21, 2422, 2009.
55. Cherfouh, H., Fellahi, O., Hadjersi, T., Marsan, B. CuInS₂/SiNWs/Si composite material for application as potential photoelectrode for photoelectrochemical hydrogen generation, *Int. J. Hydrogen Energy*, 43, 3431, 2018.
56. Lefrançois, A., Pouget, S., Vaure, L., Haro, M.L., Reiss, P. Direct Synthesis of Highly Conductive tert-Butylthiol-Capped CuInS₂ Nanocrystals, *Eur. J. Chem. Phys. Phys. Chem.*, 17, 654, 2016.

57. Dierick, R., Capon, B., Damm, H., Flamee, S., Arickx, P., Bruneel, E., Van Genechten, D., Van Bael, M., Hardy, A., Detavernier, C., Hens, Z. Annealing of sulfide stabilized colloidal semiconductor nanocrystals, *J. Mater. Chem. C*, 2, 178, 2014.
58. Li, J., Shen, H., Zhou, C., Li, N., Wang, H., Li, L.S. J. Inorganic Sn-X complex ligands capped CuInS₂ nanocrystals with high electron mobility, *Nanoparticle Res.*, 16, 2802, 2014.
59. Hahn, J.-S., Park, G., Lee, J., Shim, J. Synthesis of CuInSe₂ nanoparticles in an oleic acid solution for application in thin film solar cells, *J. Ind. Eng. Chem.*, 21, 754, 2015.
60. Castro, S.L., Bailey, S.G., Raffaele, R.P. Synthesis and Characterization of Colloidal CuInS₂ Nanoparticles from a Molecular Single-Source Precursor, *J. Phys. Chem. B*, 108, 12429, 2004.
61. Castro, S.L., Bailey, S.G., Raffaele, R.P. Nanocrystalline Chalcopyrite Materials (CuInS₂ and CuInSe₂) via Low-Temperature Pyrolysis of Molecular Single-Source Precursors, *Chem. Mater.*, 15, 3142, 2003.
62. Yue, W., Wei, F., He, C., Wu, D., Tang, N., Qiao, Q. L-Cysteine assisted-synthesis of 3D In₂S₃ for 3D CuInS₂ and its application in hybrid solar cells, *RSC Adv.*, 7, 37578, 2017.
63. Benbelgacem, J., Marai, A.B. Synthesis of CuInS₂ nanoparticles by solvothermal process using dimethylformamide as a solvent, *J. Alloys Compounds*, 692, 966, 2017.
64. Li, B., Xie, Y., Huang, J., Qian, Y. Synthesis by a solvothermal route and characterization of CuInSe₂ nanowhiskers and nanoparticles, *Adv. Mater.*, 11, 1456, 1999.
65. Gardner, J.S., Shurdha, E., Wang, C.M., Lau, L.D., Rodriguez, R.G., Pak, J.J. Rapid synthesis and size control of CuInS₂ semi-conductor nanoparticles using microwave irradiation, *J. Nanoparticle Res.*, 10, 633, 2008.
66. Pein, A., Baghbanzadeh, M., Rath, T., Haas, W., Maier, E., Amenitsch, H., Hofer, F., Kappe, C.O., Trimmel, G. Investigation of the formation of CuInS₂ nanoparticles by the oleylamine route: comparison of microwave-assisted and conventional syntheses, *Inorganic Chem.*, 50, 193, 2011.
67. Hosseinpour-Mashkani, S.M., Mohandes, F., Salavati-Niasari, M., Venkateswara-Rao, K. Microwave-assisted synthesis and photovoltaic measurements of CuInS₂ nanoparticles prepared by using metal-organic precursors, *Mater. Res. Bull.*, 47, 3148, 2012.
68. Bensebaa, F., Durand, C., Aouadou, A., Scoles, L., Du, X., Wang, D., Le Page, Y. A new green synthesis method of CuInS₂ and CuInSe₂ nanoparticles and their integration into thin films, *J. Nanoparticle Res.*, 12, 1897, 2010.
69. Mousavi-Kamazani, M., Salavati-Niasari, M. A simple microwave approach for synthesis and characterization of Ag₂S-AgInS₂ nanocomposites, *Composites B*, 56, 490, 2014.
70. Mousavi-Kamazani, M., Salavati-Niasari, M., Sadeghinia, M. Synthesis and characterization of Cu₂S nanostructures via cyclic microwave radiation, *Superlattices Microstruct.*, 63, 248, 2013.

71. Krylova, G., Yashan, H., Hauck, J.G., Burns, P.C., McGinn, P.J., Na, C. Microwave-assisted solution liquid-solid synthesis of single-crystal copper indium sulfide nanowires, *Crystal Growth Design*, 15, 2859, 2015.
72. Sun, C., Gardner, J.S., Shurdha, E., Margulieux, K.R., Westover, R.D., Lau, L., Long, G., Bajracharya, C., Wang, C., Thurber, A., Punnoose, A., Rodriguez, R.G., Pak, J.J. A high-yield synthesis of chalcopyrite CuInS_2 nanoparticles with exceptional size control, *J. Nanomater.*, Article ID 748567, 2009.
73. Zhang, J., Chen, J.C., Li, Q. Microwave heating synthesis and formation mechanism of chalcopyrite structured CuInS_2 nanorods in deep eutectic solvent, *Mater. Res. Bull.*, 63, 88, 2015.
74. Sabet, M., Salavati-Niasari, M., Ghanbari, D., Amiri, O., Mir, N., Dadkhah, M. Synthesis and characterization of CuInSe_2 nanocrystals via facile microwave approach and study of their behavior in solar cell, *Mater. Sci. Semiconductor Process*, 25, 98, 2014.
75. Pathan, H.M., Lokhande, C.D. Chemical deposition and characterization of copper indium disulphide thin films, *Appl. Surf. Sci.*, 239, 11, 2004.
76. Hehemann, D.G., Lau, J.E., Harris, J.D., Hoops, M.D., Duffy, O.V., Fanwick, P.E., Khan, O., Jin, M.H.-C., Hepp, A.F. Synthesis, characterization and decomposition studies of tris(N,N-dibenzylidithiocarbamate)indium(III): chemical spray deposition of polycrystalline CuInS_2 on copper films, *Mater. Sci. Eng. B*, 116, 381, 2005.
77. He, Y.B., Kraemer, T., Polity, A., Hardt, M., Meyer, B.K., Influence of the Preparation Conditions on the Properties of CuInS_2 Films Deposited by One-Stage RF Reactive Sputtering, *Thin Solid Films*, 431–432, 126–130, 2003.
78. Bekker, J., Alberts, V., Leitch, A.W.R., Botha, J.R. Influence of the preparation conditions on the properties of CuInS_2 films deposited by one-stage RF reactive sputtering, *Thin Solid Films*, 431–432, 116–121, 2003.
79. Martinez, A.M., Arriaga, L.G., Fernandez, A.M., Cano, U. Band edges determination of CuInS_2 thin films prepared by electrodeposition, *Mater. Chem. Phys.*, 88, 417, 2004.
80. Li, L., Gao, G., Li, Q., Ma, Y., Liu, C., Wang, H. Deposition Mechanism and Characterizations of CuInS_2 film Prepared by One-Step Electro-deposition, *J. Mater. Sci.: Mater. Electron.* 27, 2108, 2016.
81. Krunks, M., Kijatkina, O., Rebane, H., Oja, I., Mikli, V., Mere, A. Composition of CuInS_2 thin films prepared by spray pyrolysis, *Thin Solid Films*, 403–404, 71, 2002.
82. Bini, S., Bindu, K., Lakshmi, M., Kartha, C.S., Vijayakumar, K.P., Kashiwaba, Y., Abe, T. Preparation of CuInS_2 thin films using CBD Cu_xS films, *Renew. Energy*, 20, 405, 2000.
83. Lokhande, C.D., Barkschat, A., Tributsch, H. Contact angle measurements: an empirical diagnostic method for evaluation of thin film solar cell absorbers (CuInS_2) Solar Energy, *Mater. Solar Cells*, 79, 293, 2003.
84. Jiang, J., Yu, S., Gong, Y., Yan, W., Zhang, R., Liu, S., Huang, W., Xin, H. 10.3% Efficient $\text{CuIn}(\text{S},\text{Se})_2$ Solar Cells from DMF Molecular Solution with the Absorber Selenized under High Argon Pressure, *Solar RRL*, 1800044, 2018.

85. Gunawan, A.H., Widiyabdari, H., Septina, W., Ikeda, S. Surface modifications of chalcopyrite CuInS_2 thin films for photoanodes in photoelectrochemical water splitting under sunlight irradiation, *IOP Conf. Ser. Mater. Sci. Eng.*, 172, 012021, 2017.
86. Yang, H., Jiang, P. Large-Scale Colloidal Self-Assembly by Doctor Blade Coating, *Langmuir*, 26, 13173, 2010.
87. Wagner, S., Shay, J.L., Migliorato, P. $\text{CuInSe}_2/\text{CdS}$ heterojunction photovoltaic detectors, *Appl. Phys. Lett.*, 25, 434, 1974.
88. Connor, S.T., Hsu, C.M., Weil, B.D., Aloni, S., Cui, Y. Phase transformation of biphasic $\text{Cu}_2\text{S-CuInS}_2$ to monophasic CuInS_2 nanorods, *J. Am. Chem. Soc.*, 131, 4962, 2009.
89. Yan, Z., Zhao, Y., Zhuang, M., Liu, J., Wei, A. J. Solvothermal Synthesis of CuInS_2 Powders and CuInS_2 Thin Films for Solar Cell Application, *Mater. Sci. Mater. Electronics*, 24, 5055, 2013.
90. Zhong, H.Z., Zhou, Y., Ye, M.F., He, Y.J., Ye, J.P., He, C., Yang, C.H., Li, Y.F. Controlled Synthesis and Optical Properties of Colloidal Ternary Chalcogenide CuInS_2 Nanocrystals, *Chem. Mater.*, 20, 6434, 2008.
91. Siebentritt, S. What limits the efficiency of chalcopyrite solar cells, *Solar Energy Mater. Solar Cells*, 95, 1471, 2011.
92. Meyer, N., Meeder, A., Schmid, D. Pilot production of large-area CuInS_2 -based solar modules, *Thin Solid Films*, 515, 5979, 2007.
93. He, Y.B., Krost, A., Blasing, J., Kriegseis, W., Polity, A., Mayer, B.K., Kisieloieski, C. Quasi-Epitaxial Growth of Thick CuInS_2 film by RF reactive sputtering with a thin epilayer buffer, *Thin Solid Films*, 451, 229, 2004.
94. He, Y.B., Kriegseis, W., Kramer, T., Deposition of CuInS_2 thin films by RF reactive sputtering with a ZnO:Al buffer layer, *J. Phys. Chem. Solids*, 64(9–10), 2075, 2003.
95. He, Y., Dissertation: Justus-Liebig-Universität, Gießen, 2003.
96. Seeger, S., Ellmer, K. Reactive magnetron sputtering of CuInS_2 absorbers for thin film solar cells: Problems and prospects, *Thin Solid Films*, 517, 3143, 2009.
97. Guan, R., Wang, X., Sun, Q., J. Structural and Optical Properties of CuInS_2 Thin Films Prepared by Magnetron Sputtering and Sulfurization Heat Treatment, *Nanomater.*, 2015, Article ID 579489, 2015.
98. Shao, L., Changa, K.-H., Hwanga, H.-L. The one-step vacuum growth of high-quality CuInS_2 thin film suitable for photovoltaic applications, *Mater. Sci. Semiconductor Process*, 6, 397, 2003.
99. Ellmer, K., Hinze, J., Klaer, J. Copper indium disulfide solar cell absorbers prepared in a one-step process by reactive magnetron sputtering from copper and indium targets, *Thin Solid Films*, 413, 92, 2002.
100. Siemer, K., Klaer, J., Luck, I., Bruns, J., Klenk, R., Bräunig, D. Efficient CuInS_2 solar cells from a rapid thermal process, *Solar Energy Mater. Solar Cells*, 67, 166, 2001.
101. Harris, J.D., Hehemann, D.G., Cowen, J.E., Hepp, A.F., Raffael, R.P., Hollingsworth, J.A. *Using Single Source Precursors and Spray Chemical*

- Vapor Deposition to Grow Thin-Film CuInS₂*, In *Proceeding of the 28th IEEE Photovoltaic Specialists Conference*, Anchorage, AK, 563, 2000.
102. Hollingsworth, J.A., Banger, K.K., Jin, M.H.-C., Harris, J.D., Cowen, J.E., Bohannon, E.W., Switzer, J.A., Buhro, W.E., Hepp, A.F. Single source precursors for fabrication of I–III–VI₂ thin-film solar cells via spray CVD, *Thin Solid Films* 431, 63, 2003
 103. Han, M., Guo, W.H., Yu, L., Li, B., Jia, J. J. Pulsed laser deposition of CuInS₂ quantum dots on one-dimensional TiO₂ nanorod arrays and their photoelectrochemical characteristics, *Power Sources*, 318, 121, 2016.
 104. Li, M., Zhao, R., Su, Y., Hu, J., Yang, Z., Zhang, Y., Synthesis of CuInS₂ nanowire arrays via solution transformation of Cu₂S self-template for enhanced photoelectrochemical performance, *Appl. Catal. B Environ.*, 203, 715, 2017.
 105. Frank, A., Wochnik, A.S., Bein, T., Scheu, C. A biomolecular-assisted, cost efficient route for growing tunable CuInS₂ films for green energy applications, *RSC Adv.*, 7, 20219, 2017.
 106. Xia, J., Liu, Y., Qiu, X., Mao, Y., He, J., Chen, L. Solvothermal Synthesis of Nanostructured CuInS₂ Thin Films on FTO substrates and Their Photoelectrochemical Properties, *Mater. Chem. Phys.*, 136, 823, 2012.
 107. Zhao, Z., Qi, Y., Chen, Q., Zheng, X., Hao, Q., Zhang, W., Mao, J., Liu, C., Liu, H. A biomolecule-assisted, cost-efficient route for growing tunable CuInS₂ films for green energy application, *Ceramics Int.*, 43, 6257, 2017.
 108. Weil, B.D., Connor, S.T., Cui, Y. CuInS₂ Solar Cells by Air-Stable Ink Rolling, *J. Am. Chem. Soc.*, 132, 6642, 2010.
 109. Akhavan, V.A., Panthani, M.G., Goodfellow, B.W., Reid, D.K., Korgel, B.A. Thickness-limited performance of CuInSe₂ nanocrystal photovoltaic devices, *Optoelectronic Express*, 18, 411, 2010.
 110. Rajendara, V., Dayakar, T., Satish, B., Subramanyam, K., Prashanthi, Y. Synthesis and characterization of CuInS₂ nanoparticles as potential candidates for photocatalyst and photovoltaic materials, *Chalcogenide Lett*, 13, 467, 2016.
 111. Long, F., Wang, W.M., Tao, H.C., Jia, T., Li, X.M., Zou, Z.G., Fu, Z. Solvothermal synthesis, nanocrystal print and photoelectrochemical properties of CuInS₂ thin film, *Mater. Lett.*, 64, 195, 2010.
 112. Sankir, N.D., Aydin, E., Ugur, E., Sankir, M. Non-toxic and environmentally friendly route for preparation of copper indium sulfide based thin film solar cells, *J. Alloys Compounds*, 640, 468, 2015.
 113. Aydin, E., Sankir, N.D. Photovoltaic Performance and Impedance Spectroscopy Analysis of CuInS₂ Thin Film Solar Cells Deposited on Polyimide Foil via Spray Pyrolysis, *Int. J. Electrochem. Sci.*, 12, 9626, 2017
 114. Oja, I., Nanu, M., Katerski, A., Krunk, M., Mere, A., Raudoja, J., Goossens, A. Crystal quality studies of CuInS₂ films prepared by spray pyrolysis, *Thin Solid Films*, 82, 480, 2005.

115. Sahal, M., Marí, B., Mollar, M., CuInS₂ thin films obtained by spray pyrolysis for photovoltaic applications, *Thin Solid Films*, 517, 2202, 2009.
116. Ikeda, S., Nonogaki, M., Septina, W., Gunawan, G., Harada, T., Matsumura, M. Fabrication of CuInS₂ and Cu(In,Ga)S₂ thin films by a facile spray pyrolysis and their photovoltaic and photoelectrochemical properties, *Catal. Sci. Technol.*, 3, 1849, 2013
117. Yukawa, T., Kuwabara, K., Koumoto, K. Electrodeposition of CuInS₂ from aqueous solution (II) electrodeposition of CuInS₂ film, *Thin Solid Films*, 286, 151, 1996.
118. Lincot, D., Guillemoles, J.F., Taunier, S., Guimard, D., Sixx-Kurdi, J., Chaumont, A., Roussel, O., Ramdani, O., Hubert, C., Fauvarque, J.P., Bodereau, N., Parissi, L., Panheleux, P., Fanouillere, P., Naghavi, N., Grand, P.P., Benfarah, M., Mogensen, P., Kerrec, O. Chalcopyrite thin film solar cells by electrodeposition, *Solar Energy*, 77, p. 725, 2004.
119. Rakitin, V.V., Novikov, G.F. Third-generation solar cells based on quaternary copper compounds with the kesterite-type structure, *Russian Chemical Reviews*, 86(2), 99, 2017.
120. Libo, L., Qi, L., Heng, W., Xiuchun, Y., Haiyan, T., Jingchen, X., Wentao, W., Preparation of Copper Indium Sulfide Film by Electro-Deposition Method, *Rare Mater. Eng.*, 44(6), 1374, 2015.
121. Ikeda, S., Nakamura, T., Lee, S.M., Yagi, T., Harada, T., Minegishi, T., Matsumura, M. Photoreduction of water by using modified CuInS₂ electrodes, *Chem. Sus. Chem.* 4, 262, 2011.
122. Cheng, K.-W., Wu, Y.-C., Hu, Y.-T. Ternary CuInS₂ photoelectrodes created using the sulfurization of Cu–In metal precursors for photoelectrochemical applications, *Mater. Res. Bull.*, 48(7), 2457, 2013.
123. Gunawan, Septina, W., Ikeda, S., Harada, T., Minegishi, T., Domen, K., Matsumura, M. Platinum and indium sulfide-modified CuInS₂ as efficient photocathodes for photoelectrochemical water splitting, *Chem. Commun.*, 8941, 2014.
124. Zhao, J., Minegishi, T., Zhang, L., Zhong, M., Gunawan, R., Nakabayashi, M., Ma, G., Hisatomi, T., Katayama, M., Ikeda, S. Enhancement of Solar Hydrogen Evolution from Water by Surface Modification with CdS and TiO₂ on Porous CuInS₂ Photocathodes Prepared by and Electrodeposition-Sulfurization Method, *Angew. Chem. Int. Ed.*, 53, 11808, 2014.
125. Tapley A., Vaccarello D., Hedges J., Jia F, Love D. A. and Ding Z. Preparation and characterization of CuInS₂ nanocrystals for photovoltaic materials, *Phys. Chem. Chem. Phys.* 15, 1431, 2013.
126. Ye, H., Park, H.S., Akhavan, V.A., Goodfellow, B.W., Panthani, M.G., Korgel, B.A., Bard, A.J. Photoelectrochemical Characterization of CuInSe₂ and Cu(In_{1-x}Ga_x)Se₂ Thin Films for Solar Cells, *J. Phys. Chem C*, 115(1), 234, 2011.
127. Vaccarello, D., Hedges, J., Tapley, A., Love, D.A., Ding, Z. Dynamic aspects of CuInS₂ light absorbing nanocrystal thin films, *J. Electroanal. Chem.*, 738, 35, 2015.

128. Amano, F., Ebin, T., Ohtani, B. Photoelectrochemical Hydrogen Evolution Using Copper-Indium-Sulfide Nanocrystalline Film Electrodes, *Electrochemistry*, 79, 804, 2011.
129. Vanalakar, S.A., Patil, P.S., Kim, J.H. Third-generation solar cells based on quaternary copper compounds with the kesterite-type structure, *Solar Energy Mater. Solar Cells*, 182, 204, 2018.
130. Wang, J., Yu, N., Zhang, Y., Zhu, Y., Fu, L., Zhang, P., Gao, L., Wu, Y. Recent trends in direct solution coating of kesterite absorber layers in solar cells, *J. Alloys Compounds*, 688, 923, 2016.
131. Romanyuk, Y.E., Fella, C.M., Uhl, A.R., Werner, M., Tiwari, A.T., Schnabel, T., Ahlswede, E. Recent trends in direct solution coating of kesterite absorber layers in solar cells, *Solar Energy Mater. Solar Cells*, 119, 181, 2013.
132. Chen, S., Yang, J.H., Gong, X.G., Walsh, A., Wei, S.H. Intrinsic point defects and complexes in the quaternary kesterite semiconductor $\text{Cu}_2\text{ZnSnS}_4$, *Phys. Rev. B*, 81, 245204, 2010.
133. Romero, M.J., Hui, D., Teeter, G., Yan, Y., Al-Jassim, M.M. Comparative study of the luminescence and intrinsic point defects in the kesterite $\text{Cu}_2\text{ZnSnS}_4$ and chalcopyrite $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films used in photovoltaic applications, *Phys. Rev. B*, 84, 16, 2011.
134. Wang, D., Zhao, W., Zhang, Y., Liu, S. Path towards high-efficient kesterite solar cells, *J. Energy Chem.*, 2017.
135. Yu, X., Shavel, A., An, X., Luo, Z., Ibáñez, M., Cabot, A. $\text{Cu}_2\text{ZnSnS}_4$ -Pt and $\text{Cu}_2\text{ZnSnS}_4$ -Au Heterostructured Nanoparticles for Photocatalytic Water Splitting and Pollutant Degradation, *J. Am. Chem. Soc.*, 136, 9236, 2014.
136. Gong, Z., Han, Q., Li, J., Hou, L., Bukhtiar, A., Yang, S., Zou, B. A solvothermal route to synthesize kesterite $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals for solution-processed solar cells, *J. Alloys Compounds*, 663, 617, 2016.
137. Ikeda, S., Nakamura, T., Harada, T., Matsumura, M. Multicomponent sulfides as narrow gap hydrogen evolution photocatalysts, *Phys. Chem. Chem. Phys.*, 12, 13943, 2010.
138. Suryawanshi, M., Shin, S.W., Ghorpade, U., Song, D., Hong, C.W., Han, S.-S., Heo, J., Kang, S.H., Kim, J.H. A facile and green synthesis of colloidal $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals and their application in highly efficient solar water splitting, *J. Mater. Chem. A*, 5, 4695, 2017.
139. Vanalakara, S.A., Patil, P.S., Kim, J.H. Recent advances in synthesis of $\text{Cu}_2\text{FeSnS}_4$ materials for solar cell applications: A review, *Solar Energy Mater. Solar Cells*, 182, 204, 2018.
140. Ghorpade, U., Suryawanshi, M., Shin, S.W., Gurav, K., Patil, P., Pawar, S., Hong, C.W., Kim, J.H., Kolekar, S. Towards environmentally benign approaches for the synthesis of CZTSSe nanocrystals by a hot injection method: a status review, *Chem. Commun.*, 50, 11258, 2014.
141. Kumar, S., Kumar, V., Mikli, V., Varema, T., Altosaar, M., Grossberg, M. Study of CZTS nano-powder synthesis by hot injection method by variation of Cu and Zn concentrations, *Energy Proc.*, 102, 136, 2016.

142. Mourdikoudis, S., Liz-Marzan, L.M. Oleylamine in Nanoparticle Synthesis, *Chem. Mater.*, 25, 1465, 2013.
143. Guo, Q., Hillhouse, H.W., Agrawal, R. Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystal Ink and Its Use for Solar Cells, *J. Am. Chem. Soc.*, 131, 11672, 2009.
144. Steinhagen, C., Panthani, M.G., Akhavan, V., Goodfellow, B., Koo, B., Korgel, B.A. Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals for Use in Low-Cost Photovoltaics, *J. Am. Chem. Soc.*, 131, 12554, 2009.
145. Wei, M., Du, Q., Wang, D., Liu, W., Jiang, G., Zhu, C. Synthesis of spindle-like kesterite $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles using thiorea as sulfur source, *Mater. Lett.*, 79, 177, 2012.
146. Riha, S.C., Parkinson, B.A., Prieto, A.L., Solution-Based Synthesis and Characterization of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals, *J. Am. Chem. Soc.*, 131, 12054, 2009.
147. Lu, X., Zhuang, Z., Peng, Q., Li, Y. Wurtzite $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals: a novel quaternary semiconductor, *Chem. Commun.*, 47, 3141, 2011.
148. Zou, C., Zhang, L., Lin, D., Yang, Y., Li, Q., Xu, X., Chen, X., Huang, S. Facile synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals, *CrystEngComm*, 13, 3310, 2011.
149. Li, M., Zhou, W.H., Guo, J., Zhou, Y.L., Hou, Z.L., Jiao, J., Zhou, Z.J., Du, Z.L., Wu, S.X. Synthesis of Pure Metastable Wurtzite CZTS Nanocrystals by Facile One-Pot Method, *J. Phys. Chem. C*, 116, 26507, 2012.
150. Chen, D., Zhao, Y., Chen, Y., Wang, B., Wang, Y., Zhou, J., Liang, Z. Hot-Injection Synthesis of Cu-Doped $\text{Cu}_2\text{ZnSnSe}_4$ Nanocrystals to Reach Thermoelectric zT of 0.70 at 450 °C, *ACS Appl. Mater. Interfaces*, 7, 24403, 2015.
151. Mirbagheri, N., Engberg, S., Crovetto, A., Simonsen, S.B., Hansen, O., Lam, Y.M., Schou, Synthesis of ligand-free CZTS nanoparticles via a facile hot injection route, *J. Nanotechnology*, 27, 185603, 2016.
152. Tiong, V.T., Bell, J., Wang, H. Beilstein One-step synthesis of high quality kesterite $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals – a hydrothermal approach, *J. Nanotechnol.*, 5, 438, 2014.
153. Kannan, A.G., Manjulavalli, T.E., Chandrasekaran, Influence of solvent on the properties of CZTS nanoparticles, *J. Proc. Eng.*, 141, 15, 2016.
154. Vallejo, O.R., Sánchez, M., Pal, M., Espinal, R., Llorca, J., Sebastian, P.J. Synthesis and characterization of nanoparticles of CZTSe by microwave-assisted chemical synthesis, *Mater. Res. Express*, 3, 125017, 2016.
155. Du, Y.F., Zhou, W.H., Zhou, Y.L., Li, P.W., Fan, J.Q., He, J.J., Wu, S.X. Solvothermal synthesis and characterization of quaternary $\text{Cu}_2\text{ZnSnSe}_4$ particles, *Mater. Sci. Semiconductor Process.*, 15, 214, 2012.
156. Patro, B., Vijaylakshmi, S., Reddy, R.K., Sharma, P. Microwave-assisted solvothermal synthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanocrystals for photovoltaic applications, *Mater. Today Proc.*, 3, 2786, 2016.
157. Shei, S.C., Lee, P.Y. Synthesis of CZTSe Nanocrystal Prepared by a Facile Route in Coordinating Solvent From Elemental Sources, *IEEE Trans. Nanotechnol.*, 12, 532, 2013.

158. Das, S., Mandal, K.C. Growth and characterization of kesterite $\text{Cu}_2\text{ZnSn}(\text{SxSe}_1 - \text{x})_4$ crystals for photovoltaic applications, *Mater. Res. Bull.*, 57, 135, 2014.
159. Oleksyuk, I.D., Gulay, L.D., Dydchak, I.V., Piskach, L.V., Parasyuk, O.V., Marchuk, O.V. Single crystal preparation and crystal structure of the $\text{Cu}_2\text{Zn}/\text{Cd,Hg/SnSe}_4$ compounds, *J. Alloys Compounds*, 340, 141, 2002.
160. Nagaoka, A., Yoshino, K., Taniguchi, H., Taniyama, T., Miyake, H. Growth of $\text{Cu}_2\text{ZnSnS}_4$ Single Crystal by Traveling Heater Method, *Japanese J. Appl. Phys.*, 50, 128001, 2011.
161. Colombara, D., Delsante, S., Borzone, G., Mitchels, J.M., Molloy, K.C., Thomas, L.H., Mendis, B.G., Cummings, C.Y., Marken, F., Peter, L.M. Crystal growth of $\text{Cu}_2\text{ZnSnS}_4$ solar cell absorber by chemical vapor transport with I_2 , *J. Crystal Growth*, 364, 101, 2013.
162. Chong, R., Wang, X., Chang, Z., Zhou, W, Wu, S. SiO_2 loading combined with high temperature calcination of kesterite $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals towards enhanced photocatalytic H_2 evolution, *Int. J. Hydrogen Energy*, 42, 20703, 2017.
163. Stöber, W., Fink, A., Bohn, E. Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interface Sci.*, 26, 62, 1968.
164. Ito, K., Nakazawa, T. Electrical and Optical Properties of Stannite-Type Quaternary Semiconductor Thin Films, *Japanese J. Appl. Phys.*, 27, 2094, 1988.
165. Jimbo, K., Kimura, R., Kamimura, T., Yamada, S., Maw, W.S., Araki, H., Oishi, K., Katagiri, H. $\text{Cu}_2\text{ZnSnS}_4$ -type thin film solar cells using abundant materials, *Thin Solid Film*, 515, 5997, 2007.
166. Seol, J.-S., Lee, S.-Y., Lee, J.-C., Nam, H.-D., Kim, K.-H. Electrical and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films prepared by rf magnetron sputtering process, *Solar Energy Mater. Solar Cells*, 75, 155, 2003.
167. Katagiri, H., Jimbo, K., Tahara, M., Araki, H., Oishi, K. The Influence of the Composition Ratio on CZTS-based Thin Film Solar Cells, *Mater. Res. Soc. Symp. Proc.*, 1165, M04-01, 2009.
168. Webowo, R.A., Kim, W.S., Lee, E.S., Munir, B., Kim, K.H. Single step preparation of quaternary $\text{Cu}_2\text{ZnSnSe}_4$ thin films by RF magnetron sputtering from binary chalcogenide targets, *J. Phys. Chem. Solids*, 68, 1908, 2007.
169. Fairbrother, A., Fontané, X., Izquierdo-Roca, V., Espíndola-Rodríguez, M., López-Marino, S., Placidi, M., Calvo-Barrio, L., Pérez-Rodríguez, A., Saucedo, E. On the formation mechanisms of Zn-rich $\text{Cu}_2\text{ZnSnS}_4$ films prepared by sulfurization of metallic stacks, *Solar Energy Mater. Solar Cells*, 112, 97, 2013.
170. Fairbrother, A., Fontané, X., Izquierdo-Roca, V., Espíndola-Rodríguez, M., López-Marino, S., Placidi, M., López-García, L., Pérez-Rodríguez, A., Saucedo, E. Single-Step Sulfo-Selenization Method to Synthesize $\text{Cu}_2\text{ZnSn}(\text{SySe}_1 - \text{y})_4$ Absorbers from Metallic Stack Precursors, *Chemphyschem*, 14, 1836, 2013.
171. Dimitrievska, M., Fairbrother, A., Gunder, R., Gurieva, G., Xie, H., Saucedo, E., Perez-Rodriguez, A., Izquierdo-Roca, V., Schorr, S. Role of S and Se atoms

- on the microstructural properties of kesterite $\text{Cu}_2\text{ZnSn}(\text{SxSe1-x})_4$ thin film solar cells, *Phys. Chem. Chem. Phys.*, 18, 8692, 2016.
172. Márquez, J., Neuschitzer, M., Dimitrievska, M., Gunder, R., Haass, S., Werner, M., Romanyuk, Y.E., Schorr, S., Pearsall, N.M., Forbes, I. Systematic compositional changes and their influence on lattice and optoelectronic properties of $\text{Cu}_2\text{ZnSnSe}_4$ kesterite solar cells, *Solar Energy Mater. Solar Cells*, 144, 579, 2016.
 173. Fernandes, P.A., Salomé, P.M.P., da Cunha, A.F. Precursors' order effect on the properties of sulfurized $\text{Cu}_2\text{ZnSnS}_4$ thin films, *Semiconductor Sci. Technol.*, 24, 105013, 2009.
 174. Araki, H., Mikaduki, A., Kubo, Y., Sato, T., Jimbo, K., Maw, W.S., Katagiri, H., Yamazaki, M., Oishi, K., Takeuchi, A. Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of stacked metallic layers, *Thin Solid Films*, 517, 1457, 2008.
 175. Fairbrother, A., Fourdrinier, L., Fontané, X., Izquierdo-Roca, V., Dimitrievska, M., Pérez-Rodríguez, A., Saucedo, E. Precursor Stack Ordering Effects in $\text{Cu}_2\text{ZnSnSe}_4$ Thin Films Prepared by Rapid Thermal Processing, *J. Phys. Chem. C*, 118, 17291, 2014.
 176. Scragg, J.J., Ericson, T., Fontané, X., Izquierdo-Roca, V., Pérez-Rodríguez, A., Kubart, T., Edoff, M., Platzer-Björkman, C. Rapid annealing of reactively sputtered precursors for $\text{Cu}_2\text{ZnSnS}_4$ solar cells, *Progress Photovoltaics Res. Appl.*, 22, 10, 2014.
 177. Fairbrother, A., García-Hemme, E., Izquierdo-Roca, V., Fontané, X., Pulgarín-Agudelo, F.A., Vigil-Galán, O., Pérez-Rodríguez, A., Saucedo, E. Development of a Selective Chemical Etch To Improve the Conversion Efficiency of Zn-Rich $\text{Cu}_2\text{ZnSnS}_4$ Solar Cells, *J. Am. Chem. Soc.*, 134, 8018, 2012.
 178. Fairbrother, A., Fontané, X., Izquierdo-Roca, V., Placidi, M., Sylla, D., Espindola-Rodriguez, M., López-Mariño, S., Pulgarín, F.A., Vigil-Galán, O., Pérez-Rodríguez, A., Saucedo, E. Secondary phase formation in Zn-rich $\text{Cu}_2\text{ZnSnSe}_4$ -based solar cells annealed in low pressure and temperature conditions, *Progress Photovoltaics Res. Appl.*, 22, 479, 2014.
 179. Valakh, M.Y., Kolomys, O.F., Ponomaryov, S.S., Yukhymchuk, V.O., Babichuk, I.S., Izquierdo-Roca, V., Saucedo, E., Perez-Rodriguez, A., Morante, J.R., Schorr, S., Bodnar, I.V. Raman scattering and disorder effect in $\text{Cu}_2\text{ZnSnS}_4$, *Phys. Status Solidi (RRL) Rapid Res. Lett.*, 7, 258, 2013.
 180. Mitzi, D.B., Gunawan, O., Todorov, T.K., Wang, K., Guha, S. The path towards a high-performance solution-processed kesterite solar cell, *Solar Energy Mater. Solar Cells*, 95, 1421, 2011
 181. Katagiri, H., Sasaguchi, N., Hando, S., Hoshino, S., Ohashi, J., Yokota, T. Preparation and evaluation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of E-B evaporated precursors, *Solar Energy Mater. Solar Cells*, 49, 407, 1997.
 182. Katagiri, H., Saitoh, K., Washio, T., Shinohara, H., Kurumadani, T., Miyajima, S. Development of thin film solar cell based on $\text{Cu}_2\text{ZnSnS}_4$ thin films, *Solar Energy Mater. Solar Cells*, 65, 141, 2001.

183. Katagiri, H., Jimbo, K., Monya, K., Tsuchida, K, Solar cell without environmental pollution by using CZTS thin film, *Proc. World Conf. Photovoltaics Energy Conversion III*, 2874, 2003.
184. Wang, K., Gunawan, O., Todorov, T., Shin, B., Chey, S.J., Bojarczuk, N.A., Mitzi, D., Guha, S. Thermally evaporated $\text{Cu}_2\text{ZnSnS}_4$ solar cells, *Appl. Phys. Lett.*, 97, 143508, 2010.
185. Lee, Y.S., Gershon, T., Gunawan, O., Todorov, T.K., Gokmen, T., Virgus, Y., Guha, S. $\text{Cu}_2\text{ZnSnSe}_4$ Thin-Film Solar Cells by Thermal Co-evaporation with 11.6% Efficiency and Improved Minority Carrier Diffusion Length, *Adv. Energy Mater.*, 5, 1401372, 2015.
186. He, J., Sun, L., Ding, N., Kong, H., Zuo, S., Chen, S., Chen, Y., Yang, P., Chu, J. Single-step preparation and characterization of $\text{Cu}_2\text{ZnSn}(\text{SxSe1-x})_4$ thin films deposited by pulsed laser deposition method, *J. Alloys Compounds*, 529, 34, 2012.
187. Katsuhiko, M., Kunihiro, T., Hisao, U. Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ Thin-Film Solar Cell Prepared by Pulsed Laser Deposition, *Japanese J. Appl. Phys.*, 46, 5780, 2007.
188. Vanalakar, S.A., Agawane, G.L., Shin, S.W., Suryawanshi, M.P., Gurav, K.V., Jeon, K.S., Patil, P.S., Jeong, C.W., Kim, J.Y., Kim, J.H. A review on pulsed laser deposited CZTS thin films for solar cell applications, *J. Alloys Compounds*, 619, 109, 2015.
189. Scragg, J.J., Dale, P.J., Colombara, D., Peter, L.M. Thermodynamic aspects of the synthesis of thin-film materials for solar cells, *Chemphyschem*, 13, 3035, 2012.
190. Moholkar, A.V., Shinde, S.S., Babar, A.R., Sim, K.-U., Lee, H.K., Rajpure, K.Y., Patil, P.S., Bhosale, C.H., Kim, J.H. Synthesis and characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films grown by PLD: Solar cells, *J. Alloys Compounds*, 509, 7439, 2011.
191. Cazzaniga, A., Crovetto, A., Yan, C., Sun, K., Hao, X., Estelrich, J.R., Canulescu, S., Stamate, E., Pryds, N., Hansen, O., Schou, J. Ultra-thin $\text{Cu}_2\text{ZnSnS}_4$ solar cell by pulsed laser deposition, *Solar Energy Mater. Solar Cells*, 166, 91, 2017.
192. Patil, S.J., Lokhande, V.C., Lee, D.-W., Lokhande, C.D. Electrochemical impedance analysis of spray deposited CZTS thin film: Effect of Se introduction, *Optical Mater.*, 58, 418, 2016.
193. Bhosale, S.M., Suryawanshi, M.P., Gaikwad, M.A., Bhosale, P.N., Kim, J.H., Moholkar, A.V., Influence of growth temperatures on the properties of photoactive CZTS thin films using a spray pyrolysis technique, *Mater. Lett.*, 129, 153, 2014.
194. Huang, S., Luo, W., Zou, Z. Band positions and photoelectrochemical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films by the ultrasonic spray pyrolysis method, *J. Phys. D Appl. Phys.*, 46, 235108, 2013.
195. Sayed, M.H., Schoneberg, J., Parisi, J., Gütay, L. Influence of silver incorporation on CZTSSe solar cells grown by spray pyrolysis, *Mater. Sci. Semiconductor Process.*, 76, 31, 2018.

196. Steinhagen, C., Panthani, M.G., Akhavan, V., Goodfellow, B., Koo, B., Korgel, B.A. Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals for Use in Low-Cost Photovoltaics, *J. Am. Chem. Soc.*, 131, 12554, 2009.
197. Guo, Q., Hillhouse, H.W., Agrawal, R. Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystal Ink and Its Use for Solar Cells, *J. Am. Chem. Soc.*, 131, 11672, 2009.
198. Miskin, C.K., Yang, W.-C., Hages, C.J., Carter, N.J., Joglekar, C.S., Stach, E.A., Agrawal, R. 9.0% efficient $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells from selenized nanoparticle inks, *Progress Photovoltaics Res. Appl.*, 23, 654, 2015.
199. Singh, M., Jiu, J., Suganuma, K., Kim, J.H. Non-toxic precursor solution route for fabrication of CZTS solar cell based on all layers solution processed, *J. Alloys Compounds*, 646, 497, 2015.
200. Ge, J., Yan, Y. Controllable Multinary Alloy Electrodeposition for Thin-Film Solar Cell Fabrication: A Case Study of Kesterite $\text{Cu}_2\text{ZnSnS}_4$, *iScience*, 1, 55, 2018.
201. Fairbrother, A., Dimitrievska, M., Sanchez, Y., Izquierdo-Roca, V., Perez-Rodriguez, A., Saucedo, E. Compositional paradigms in multinary compound systems for photovoltaic applications: a case study of kesterites, *J. Mater. Chem. A*, 3, 9451, 2015.
202. Tai, K.F., Gunawan, O., Kuwahara, M., Chen, S., Mhaisalkar, S.G., Huan, C.H.A., Mitzi, D.B. Fill Factor Losses in $\text{Cu}_2\text{ZnSn}(\text{SxSe1-x})_4$ Solar Cells: Insights from Physical and Electrical Characterization of Devices and Exfoliated Films, *Adv. Energy Mater.*, 6, 1501609, 2016.
203. Vauche, L., Risch, L., Sa'nchez, Y., Dimitrievska, M., Pasquinelli, M., Goislar de Monsabert, T., Grand, P.P., Jaime-Ferrer, S., Saucedo, E. 8.2% pure selenide kesterite thin-film solar cells from large-area electrodeposited precursors, *Progress Photovoltaics*, 24, 38, 2016.
204. Scragg, J.J., Berg, D.M., Dale, P.J. A 3.2% efficient Kesterite device from electrodeposited stacked elemental layers, *J. Electroanal. Chem.*, 646, 52, 2010.
205. Guo, L., Zhu, Y., Gunawan, O., Gokmen, T., Deline, V.R., Ahmed, S., Romankiw, L.T., Deligianni, H. Electrodeposited $\text{Cu}_2\text{ZnSnSe}_4$ thin film solar cell with 7% power conversion efficiency, *Progress Photovoltaics*, 22, 58, 2014.
206. Lee, K.D., Seo, S.-W., Lee, D.-K., Kim, H., Jeong, J.-H., Ko, M.J., Kim, B., Kim, D.H., Kim, J.Y. Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films via electrochemical deposition and rapid thermal annealing, *Thin Solid Films*, 546, 294, 2013.
207. Mkawi, E.M., Ibrahim, K., Ali, M.K.M., Farrukh, M.A., Mohamed, A.S., Allam, N.K. Effect of complexing agents on the electrodeposition of Cu-Zn-Sn metal precursors and corresponding $\text{Cu}_2\text{ZnSnS}_4$ -based solar cells, *J. Electroanal. Chem.*, 735, 129, 2014.
208. Slupska, M., Ozga, P. Electrodeposition of Sn-Zn-Cu alloys from citrate solutions, *Electrochim. Acta*, 141, 149, 2014.
209. Suryawanshi, M.P., Shin, S.W., Ghorpade, U.V., Gurav, K.V., Hong, C.W., Agawane, G.L., Vanalakar, S.A., Moona, J.H., Jae Ho Yun, Patil, P.S., Jin Hyeok Kim, Moholkar, A.V. Improved photoelectrochemical performance

- of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films prepared using modified successive ionic layer adsorption and reaction (SILAR) sequence, *Electrochim. Acta*, 150, 136, 2014.
210. Suryawanshi, M.P., Shin, S.W., Ghorpade, U.V., Gurav, K.V., Hong, C.W., Patil, P.S., Moholkar, A.V., Kim, J.H. Improved solar cell performance of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films prepared by sulfurizing stacked precursor thin films via SILAR method, *J. Alloys Compounds*, 671, 509, 2016.
 211. Kobayashi, T., Jimbo, K., Tsuchida, K., Shinoda, S., Oyanagi, T., Katagiri, H. Investigation of $\text{Cu}_2\text{ZnSnS}_4$ -Based Thin Film Solar Cells Using Abundant Materials, *Japanese J. Appl Phys.*, 44, 783, 2005.296 Photoelectrochemical Solar Cells
 212. Araki, H., Mikaduki, A., Kubo, Y., Sato, T., Jimbo, K., Maw, W.S., Katagiri, H., Yamazaki, M., Katagiri, H., Sasaguchi, N., Hando, S., Hoshino, S., Ohashi, J., Yokota, T. Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of stacked metallic layers, *Thin Solid Films*, 517, 1457, 2008.
 213. Scragg, J.J., Dale, P.J., Peter, L.M., Zoppi, G., Forbes, I. New routes to sustainable photovoltaics: evaluation of $\text{Cu}_2\text{ZnSnS}_4$ as an alternative absorber material, *Phys. Status Solidi B*, 245, 1772, 2008.
 214. Pawar, S.M., Pawar, B.S., Moholkar, A.V., Choi, D.S., Yun, J.H., Moon, J.H., Kolekar, S.S., Kim, J.H. Single step electrosynthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films for solar cell application, *Electrochim. Acta*, 55, 4057, 2010.
 215. Riha, S.C., Fredrick, S.J., Sambur, J.B., Liu, Y., Prieto, A.L., Parkinson, B.A. Photoelectrochemical Characterization of Nanocrystalline Thin-Film $\text{Cu}_2\text{ZnSnS}_4$ Photocathodes, *Am. Chem. Soc. Appl. Mater. Interfaces*, 3, 58, 2011.
 216. Tiong, W.T., Zhang, Y., Bell, J., Wang, H. Phase-selective hydrothermal synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals: the effect of the sulphur precursor, *CrystEngComm*, 16, 4306, 2014.
 217. Yokoyama, D., Minegishi, T., Jimbo, K., Hisatomi, T., Ma, G., Katayama, M., Kubota, J., Katagiri, H., Domen, K. H_2 Evolution from Water on Modified $\text{Cu}_2\text{ZnSnS}_4$ Photoelectrode under Solar Light, *Appl. Phys. Express*, 3, 101202, 2010.
 218. Huang, S., Luo, W., Zou, Z. Band positions and photoelectrochemical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films by the ultrasonic spray pyrolysis method, *J. Phys. D Appl. Phys.*, 46, 235108, 2013.
 219. Guan, Z., Luo, W., Zou, Z. Formation mechanism of ZnS impurities and their effect on photoelectrochemical properties on a $\text{Cu}_2\text{ZnSnS}_4$ photocathode, *CrystEngComm*, 16, 2929, 2014.
 220. Wang, J., Zhang, P., Song, X., Gao, L. $\text{Cu}_2\text{ZnSnS}_4$ thin films: spin coating synthesis and photoelectrochemistry, *RSC Adv.*, 4, 21318, 2014.
 221. Ma, G., Minegishi, T., Yokoyama, D., Kubota, J., Domen, K. Photoelectrochemical hydrogen production on $\text{Cu}_2\text{ZnSnS}_4$ /Mo-mesh thin-film electrodes prepared by electroplating, *Chem. Phys. Lett.*, 501, 619, 2011.

222. Chen, Y., Chuang, C.H., Lin, K.C., Shen, S., McCleese, C., Guo, L., Burda, C. Synthesis and Photoelectrochemical Properties of $(\text{Cu}_2\text{Sn})_x\text{Zn}_{3(1-x)}\text{S}_3$ Nanocrystal Films, *J. Phys. Chem. C*, 118, 11954, 2014.
223. Zhu, L., Tao, J., Tao, H., Chen, S., Shen, Y., Xu, A., Jiang, J., Pan, L. In-situ growth of $\text{Cu}_2\text{ZnSnS}_4$ nanosheets on TiO_2 nanowires for enhanced photoelectrochemical performance, *J. Alloys Compounds*, 649, 704, 2015.
224. Li, B.J., Yin, P.F., Zhou, Y.Z., Gao, Z.M., Ling, T., Du, X.W. Single crystalline $\text{Cu}_2\text{ZnSnS}_4$ nanosheet arrays for efficient photochemical hydrogen generation, *RSC Adv.*, 5, p. 2543, 2015.
225. Guijarro, N., Prevot, M.S., Sivula, K. Enhancing the Charge Separation in Nanocrystalline $\text{Cu}_2\text{ZnSnS}_4$ Photocathodes for Photoelectrochemical Application: The Role of Surface Modifications, *J. Phys. Chem. Lett.*, 5, 3902, 2014.
226. Yu, X., Liu, J., Genc, A., Ibanez, M., Luo, Z., Shavel, A., Arbiol, J., Zhang, G., Zhang, Y., Cabot, A. $\text{Cu}_2\text{ZnSnS}_4$ -Ag₂S Nanoscale p-n Heterostructures as Sensitizers for Photoelectrochemical Water Splitting, *Langmuir*, 31, 10555, 2015.

Eutectic Composites for Photoelectrochemical Solar Cells (PSCs)

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Abstract

The answer to increasing world energy consumption comes from renewable sources. Example of such is solar energy, which not only offers direct conversion into electrical current but also offers a possibility to store energy in form of hydrogen bonds. This chapter focuses on the application of emerging class of materials — eutectic composites for photoelectrochemical solar cells (PSCs). Eutectic composites provide many advantageous properties for photoelectrochemistry.

Keywords: Photoelectrochemical solar cells (PSCs), eutectic composites, TiO_2 , SrTiO_3 , WO_3

8.1 Introduction

Photoelectrochemical solar cells (PSCs) have a plethora of applications in catalysis including hydrogen production and reduction of pollutants such as CO_2 or organic compounds in wastewater. Recently, the idea of utilizing eutectic composites as light absorbing layer in PSC has been introduced. Eutectic composites are characterized by the formation of two or more nonmixable crystals from a completely mixable melt, which leads to formation of self-organized micro/nanostructures. Directionally solidified eutectics (DSE) may be defined as composite materials with a complex and homogeneous micro- or nanostructure which controls their

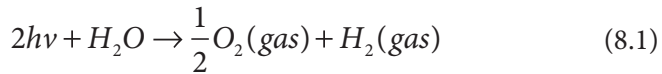
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properties. Eutectic composites exhibit the unusual characteristic of being both monolith and multicomponent/multiphase in nature with sharp, clean, and strong interfaces. Eutectic composites can enhance the efficiency of water splitting due to matched photoresponse to the solar spectrum, suitable band energies, efficient separation of the photogenerated charges, and good stability under PSC conditions. The research on SrTiO_3 - TiO_2 and WO_3 - TiO_2 eutectic materials obtained by the micro-pulling-down method proved that eutectic systems can be utilized for photoelectrochemical hydrogen production. In the case of SrTiO_3 - TiO_2 , the generated photocurrents upon light irradiation up to 8.5 mA/cm^2 have been achieved. For WO_3 - TiO_2 , the performed cyclic voltammetry experiments demonstrated electrodes photocurrent of 4.3 mA/cm^2 at 1.7 V versus normal hydrogen electrode (NHE) under 6 suns illumination. During 3000 s long measurements, a good quality and high stability of WO_3 - TiO_2 electrodes was confirmed with only $3 \text{ } \mu\text{A/cm}^2$ per minute decrease of photocurrent. Finally, we have demonstrated that measured photocurrents strongly depend on the electrode thickness. In this chapter, we demonstrate working principles of photoelectrochemical hydrogen production, drawbacks, and advantages of utilizing eutectic composites for this application. The following issues will be addressed: (1) the photoelectrolysis of water as a source of hydrogen, (2) experimental methods of study of the photoactive materials such as electrochemical (Mott–Schottky plots) and photoelectrochemical determination of the flat-band potential, impedance spectroscopy, band-gap determination by optical spectroscopy, (3) eutectic composites, (4) methods of obtaining eutectic composites, (5) eutectic composites used for photoelectrochemical water splitting, (6) other potential eutectic composites, and (7) modification of the properties of eutectic composites. The influence of the material modification on the electronic, optical, and photoelectrochemical properties will be described.

8.2 The Photoelectrolysis of Water as a Source of Hydrogen

Among the many methods widely employed for hydrogen production, water photoelectrolysis upon solar irradiation is considered as the most attractive from the point of view of ecological safety. True renewable, sustainable, and pollution-free energy sources require the use of only water and natural light for their fabrication and operation. However, to become practically viable, the process of water splitting has to attain at least 10% conversion efficiency. At the moment, this aim is far from being reached in simple systems.

Photoelectrolysis of water is based on light-induced dissociation of a water molecule H_2O into gaseous oxygen and hydrogen according to a globally expressed reaction:



where $h\nu$ represents the photon energy.

This absorbed photon energy should amount to at least 1.23 eV ($\lambda < 1000$ nm), but water is transparent to light over this wavelength range. Therefore, a semiconducting photoelectrode (PE) is required to assist in the process following the well-known scheme:

$$h\nu \rightarrow e' + h \quad (8.2)$$

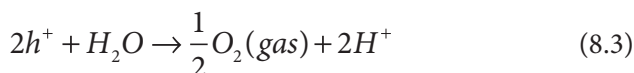
A photon with an energy $h\nu$, equal to or higher than the bandgap energy, E_g , of a semiconductor is absorbed promoting electrons e' into the conduction band (CB) and electron holes h into the valence band (VB). Therefore, the semiconducting electrode is the most important element of a device for photoelectrolysis, i.e., a photoelectrochemical solar cell (PSC). As a consequence, in order to run this process efficiently, the following conditions have to be fulfilled:

- (i) Minimum energy: $E_{H_2O}^{\circ}(25^{\circ}C)_{\min} = 1.23$ eV
- (ii) Practical energy (+overpotential and losses): $E_{H_2O}^{\circ}(25^{\circ}C)_{\text{prac}} = 1.6\text{--}2.0$ eV
- (iii) Efficient utilization of sunlight: $UV > h\nu_{(\text{vis})} > IR$ and $h\nu \geq E_g$
- (iv) Band edges relative to the vacuum level: $E_{H^{+}/H_2}^{\circ} < E_{CB}^g$ and $E_{O_2/H_2O}^{\circ} > E_{VB}^g$
- (v) Low recombination rate of photoexcited electron–hole pairs
- (vi) Optimized electrical resistivity
- (vii) Fast transfer of electrical charges from the semiconductor to the electrolyte
- (viii) High stability and resistivity to corrosion and photocorrosion
- (ix) Low cost and availability

The principle of operation of different types of PSC is shown in Figure 8.1. The most typical is a solution with an n-type semiconductor acting as a photoanode immersed in liquid electrolyte, known since the pioneering work of Fujishima and Honda [1]. A second electrode, typically metallic when n-type semiconducting photoanode, is applied, completing

the electronic circuit. The original work of Fujishima and Honda [1, 2] also included a permeable membrane (Figure 8.1a) in order to impose pH bias ($\Delta\text{pH} = 2.3$).

In such a basic PSC system (Figure 8.1b), water is oxidized at the n-type photoanode according to:



when the valence band maximum of the photoanode semiconductor is below the O_2/H_2O potential.

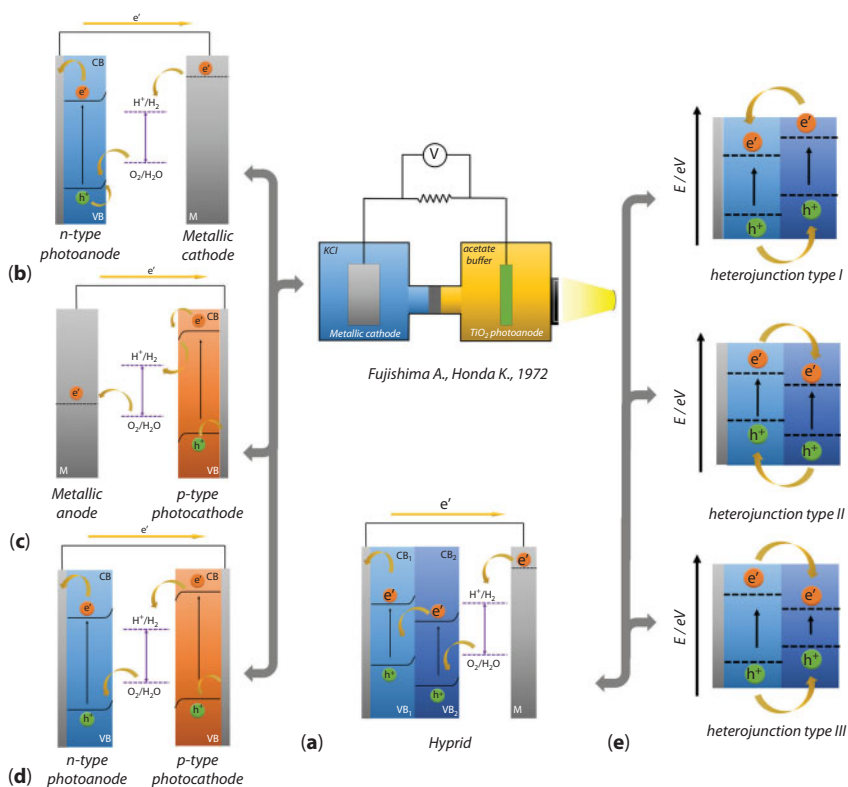
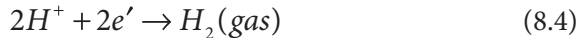


Figure 8.1 Different configurations of photoelectrochemical solar cells (PSCs); (a) original setup of Fujishima and Honda [1], (b) illuminated n-type photoelectrode PE as a photoanode, (c) illuminated p-type photoelectrode PE as a photocathode, (d) illuminated n-type photoanode and p-type photocathode, (e) hybrid photoanode based on single or multiple heterojunctions of types I, II, and III with different relative positions of conduction and valence band edges.

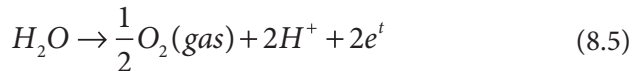
H^+ ions migrate through the electrolyte from the anode to the metallic cathode, and electrons produced in reaction (8.2) reach the back side of the photoanode upon which they are transported by an external circuit toward the cathode.

In close vicinity to the cathode surface, H^+ ions are reduced to form hydrogen via the reaction:



provided that the conduction band minimum of PE is above the H^+/H_2 potential.

Different arrangements of the electrodes in PSC are possible. For example, p-type semiconducting material can be used as a photocathode, as demonstrated in Figure 8.1c. In this case, the photoelectrolysis is carried out according to the following scheme: evolution of hydrogen according to reaction (8.4) occurs at the p-type photocathode illuminated with light, while oxygen is produced at the metallic anode:



In order to drive reaction (8.4), the electrode p-type material has to be chosen so that the minimum of its conduction band lies above the H^+/H_2 potential.

As one can easily observe, there is a development of a space charge region (SCR) at the interface between the electrode and the liquid electrolyte resulting in so-called band bending. In the case of n-type photoanode, the conduction and valence bands bend upward due to depletion layer formation. The opposite effect is seen for a p-type photocathode.

Simultaneous application of both n-type photoanode and p-type photocathode has been also proposed as shown in Figure 8.1d [3, 4]. The advantage of such a configuration is that both electrodes, being illuminated simultaneously, participate in the water splitting. One can anticipate that still better performance in terms of process efficiency occurs with the use of a hybrid photoanode based on two or more semiconducting layers with different configurations of the electronic band edges (Figure 8.1e). Three cases of heterojunctions, depending on the direction of charge transfer, are usually reported in the literature [5, 6]. When both the conduction band minimum and valence band maximum of one semiconductor are above those of the other one, electrons and holes are separated in space by moving in different directions (type I and type II). For type III heterostructures,

electrons and holes transfer from one material to the other without spatial charge separation. Only the type I configuration is suitable for hydrogen evolution because of the proper position of the band edges with respect to redox potential levels.

8.3 Experimental Methods for Studying Photoactive Materials Such as Electrochemical (Mott–Schottky Plots) and Photoelectrochemical Determination of the Flat-Band Potential, Impedance Spectroscopy, and Bandgap by Optical Spectroscopy

The most important parameters that determine the performance of PSC are:

- a) flat-band potential
- b) fundamental bandgap of the semiconductor
- c) recombination/relaxation rate of photoinduced charge carriers

This means that the efficiency of process of the photoelectrolysis is strongly affected by a proper compromise between sometimes conflicting requirements imposed for (a–c).

- a) Flat-band potential is a term that denotes specific conditions under which band bending, normally formed at the interface semiconductor–electrolyte disappears. Determination of the flat-band potential V_{fb} provides information about alignment of the conduction and valence band edges with respect to the redox potential levels of the electrolyte.

There are numerous experimental methods for flat-band potential estimation. They include illuminated OCP (open circuit potential), Mott–Schottky analysis without illumination, and the photocurrent onset. However, due to certain limitations of each technique, values of V_{fb} resulting from these different methods can be in slight disagreement.

Figure 8.2 illustrates the standard approach to the experimental evaluation of the flat-band potential, the methods of analysis of the results, and comparison of the V_{fb} values derived from different techniques for three semiconductors

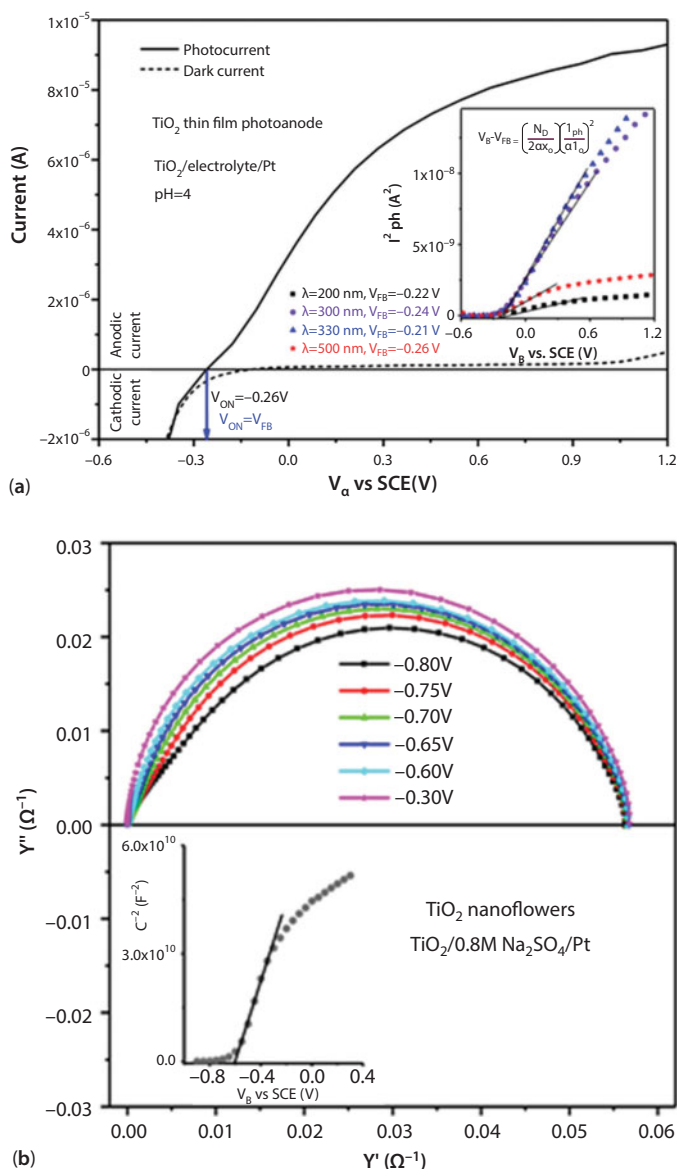


Figure 8.2 Experimental methods for flat-band potential V_{FB} determination; (a) photocurrent under illumination with white light and dark current I as a function of the applied bias voltage V_B (the inset illustrates the more accurate method proposed by Butler [7] based on photocurrent measurements under monochromatic light); (b) complex plane admittance plots (Nyquist plots) for a TiO_2 -nanostructured photoanode without illumination at different imposed bias potentials V_B ; analysis of the inverse square of the capacitance (C^{-2}) as a function of V_B allows determination of V_{FB} ; (c) Mott-Schottky plots ($1/C^2$ vs. V_B) taken at constant frequency for different pH of the electrolyte; the inset

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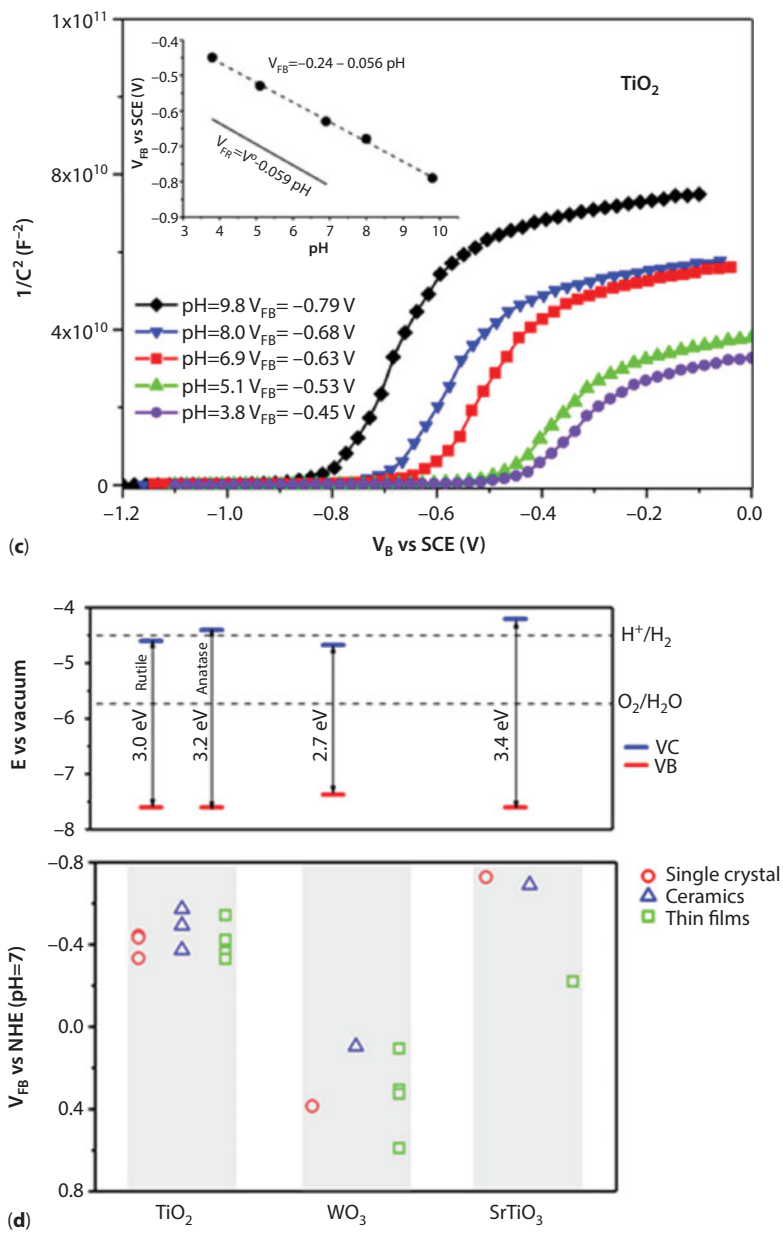


Figure 8.2 (Continued) shows the experimental dependence of the flat-band potential on pH (points) in relation to the theoretical (linear) Nernst behavior; (d) comparison of the experimental data for V_{FB} derived from different techniques for three semiconducting photoelectrodes TiO_2 , WO_3 , and SrTiO_3 . The influence of the form (e.g., single crystal, polycrystalline, ceramic, or thin film) on the results is shown [6, 8–12].

TiO_2 , WO_3 , and SrTiO_3 which are frequently used as photoelectrodes in PSC. Moreover, Figure 8.2a shows an example of the basic photoelectrochemical I-V characteristics from which it is possible to estimate the fundamental properties of the photoelectrode, such as its potential for photocurrent onset as well as its ability to generate photocurrent at a given potential. White or monochromatic light with a well-defined wavelength is applied for illumination of the PE. In order to perform efficiently, the onset of the photocurrent should appear at a negative potential.

As shown in Figure 8.2a, the photocurrent I_{ph} approaches the dark current at V_{fb} . The photocurrent onset is the simplest but not always most accurate measure of the flat-band potential V_{fb} . In the vicinity of V_{fb} , not only the space charge layer disappears but also the recombination process may suppress the photocurrent. This is a source of a systematic error in V_{fb} determination. Therefore, a more accurate method, proposed by Butler [7], is based on the following formula:

$$V_B - V_{\text{fb}} = \left(\frac{N_D}{2e\epsilon\epsilon_0} \right) \left(\frac{I_{\text{ph}}}{\alpha I_0} \right)^2 \quad (8.6)$$

where V_B is the applied (bias) voltage, I_0 is the intensity of the incident radiation, α stands for the light absorption coefficient, e is the electron charge, N_D denotes the donor density, ϵ is the dielectric constant of the semiconductor, and ϵ_0 is the vacuum permittivity.

When the semiconductor is illuminated with the monochromatic light of a wavelength λ smaller than λ_G corresponding to the bandgap, the linear relationship between I_{ph}^2 and V_B holds. As shown in the inset of Figure 8.2a, the experimental I_{ph}^2 vs. V_B quite closely follows the linear dependence predicted by Eq. 6; thus their common intercept with the potential axis gives $V_{\text{fb}} = -0.24$ V vs. SCE close to the -0.26 V determined for the photocurrent onset.

Figure 8.2b and c indicates how impedance spectroscopy (IS) can be used to determine electrical properties not only of the semiconducting photoelectrode but also the PE interface with the liquid electrolyte without illumination. Impedance spectroscopy is a valuable experimental tool for providing

information about charge transfer phenomena, double layer properties, carrier generation, and recombination processes, etc. Usually, the impedance or admittance spectra are measured over a wide range of frequencies (as shown in Figure 8.2b), but, in the case of photoelectrochemical measurements, the spectra are studied as a function of the bias voltage of the PSC. The space charge capacitance C_{sc} can be determined from the so-called Mott-Schottky equation:

$$C_{sc}^{-2} = \left(\frac{2}{\epsilon \epsilon_o e N_D S^2} \right) \left(V_B - V_{Fb} - \frac{kT}{e} \right) \quad (8.7)$$

where T is the absolute temperature, k is the Boltzmann constant, and S is an area of the electrode.

According to equation (8.7), C_{sc}^{-2} vs. V_B is linear and is referred to as a Mott-Schottky plot (Figure 8.2b). Assuming that kT/e is negligible at room temperature, V_{Fb} can be found from the intercept of the fitted linear dependence C_{sc}^{-2} vs. V_B with the bias voltage axis. The slope of the Mott-Schottky plot delivers information about the donor density N_D . From that, the width W of the depletion layer can be calculated using the following relationship:

$$W = \left(\frac{2 \epsilon \epsilon_o \left(V_B - V_{Fb} - \frac{kT}{e} \right)}{e^2 N_D} \right)^{1/2} \quad (8.8)$$

There are several ways to determine the electrical parameters such as capacitance and resistance. The most general procedure is to use the equivalent circuit and to fit its parameters to the impedance spectra over the full range of frequencies. This was done in the case of Figure 8.2b. However, a much simpler approach involves measurements of the impedance at a single frequency as a function of the bias voltage V_B (Figure 8.2c). In this case, one has to make sure that the results concerning the flat-band potential are independent of the frequency. It has been proven before [13] that a simple equivalent circuit containing C and R connected in series can be used to derive the flat-band potential from

the intercept of the linear part of the C^{-2} vs. V_B dependence. Dutoit *et al.* [14] have shown that the plots obtained by means of a simple equivalent circuit often exhibit frequency-dependent slopes but have a common intercept.

Moreover, Figure 8.2c illustrates how the pH of the liquid electrolyte affects the flat-band potential. The inset of this figure presents the linear dependence of V_{Fb} vs. pH, the slope of which is very close to the value theoretically predicted by Nernst equation at room temperature:

$$V_{Fb} = V_{Fb}^0 - 0.059 \text{ pH} \quad (8.9)$$

This is a consequence of the fact that V_{Fb} is not only a characteristic constant of the semiconductor but is also affected by the properties of the electrolyte. Changes in V_{Fb} follow the potential drops within the Helmholtz layer, the intermediate layer between the space charge regions of the semiconductor and electrolyte [15]. The potential drop across the Helmholtz layer is sensitive to the electrolyte composition. This effect is caused by the adsorption/desorption of mostly H^+ and OH^- ions at the semiconductor surface. V_{Fb}^0 is affected by the crystallographic structure and by the form of the electrode material (e.g., thin film, single crystal or polycrystalline ceramic).

Figure 8.2d summarizes the data obtained for the most frequently used TiO_2 , WO_3 , and $SrTiO_3$ semiconducting photoanodes. When one compares the V_{Fb} for single crystals, it is clear that the highest negative value of about -0.6 eV (pH=7) correlates well with the position of the minimum of the conduction band CB in $SrTiO_3$ with respect to the H^+/H_2 potential. Smaller but still negative V_{Fb} is obtained for anatase TiO_2 , while the positive V_{Fb} is characteristic for WO_3 . Due to the unsuitable position of the CB minimum of WO_3 with respect to H^+/H_2 potential, this semiconducting material, when configured as a photoanode, will work inefficiently in a PSC, requiring some potential bias.

- b) Bandgap energy E_g , i.e., the separation between the maximum of the valence band VB and the minimum of the conduction band CB, is a fundamental parameter characterizing the electronic structure of a semiconductor which is particularly important for photoelectrochemical applications.

Efficient utilization of sunlight requires that the bandgap of the photoelectrode should fall within the range of photon energies from 1.6 to 2.0 eV. Unfortunately, until now there has been no practical demonstration of a suitable photoelectrode material that could fulfill all the requirements (i-ix) especially as those semiconductors that have a well-adapted bandgap are usually unstable in liquid electrolytes. Typically, wide-bandgap materials such as TiO_2 are used but with UV radiation instead of the much more suitable visible range of the AM 1.5G solar spectrum because they are resistive to corrosion and photocorrosion.

The bandgap of semiconductors can be evaluated by means of several experimental techniques among which spectrophotometry, ellipsometry, and photoelectrochemical methods play the most important role. All-optical methods such as spectrophotometry rely on the determination of the optical constants, i.e., the refractive index $n(\lambda)$ and absorption coefficient $\alpha(\lambda)$. The spectral dependence of the absorption coefficient is then analyzed to establish the energy of the optical transition from VB to CB attributed to the fundamental bandgap.

As shown in Figure 8.3a, depending on the form of a semiconducting material, either both transmittance $T(\lambda)$ and specular reflectance coefficient are measured (thin films, single crystals) or only total reflectance coefficient $R(\lambda)$ is determined by means of an integrating sphere (polycrystalline ceramics). In both methods, the wavelength dependence of the absorbance has to be analyzed within the region of the fundamental absorption edge in order to calculate the bandgap energy (Figure 8.3b).

The methods of analysis of the spectrophotometric data are either based on the calculation of the first derivative $dR/d\lambda$ or the Kubelka–Munk model as shown in Figure 8.3b. The maximum in the differential reflectance spectrum is very sensitive to the optical transitions, and its position can be interpreted as the bandgap E_g [16]. On the other hand, the Kubelka–Munk K-M or $F(R)$ method offers great advantages [17]. The K-M method is based on the following function:

$$F(R) = \frac{(1-R)^2}{2R} \quad (8.10)$$

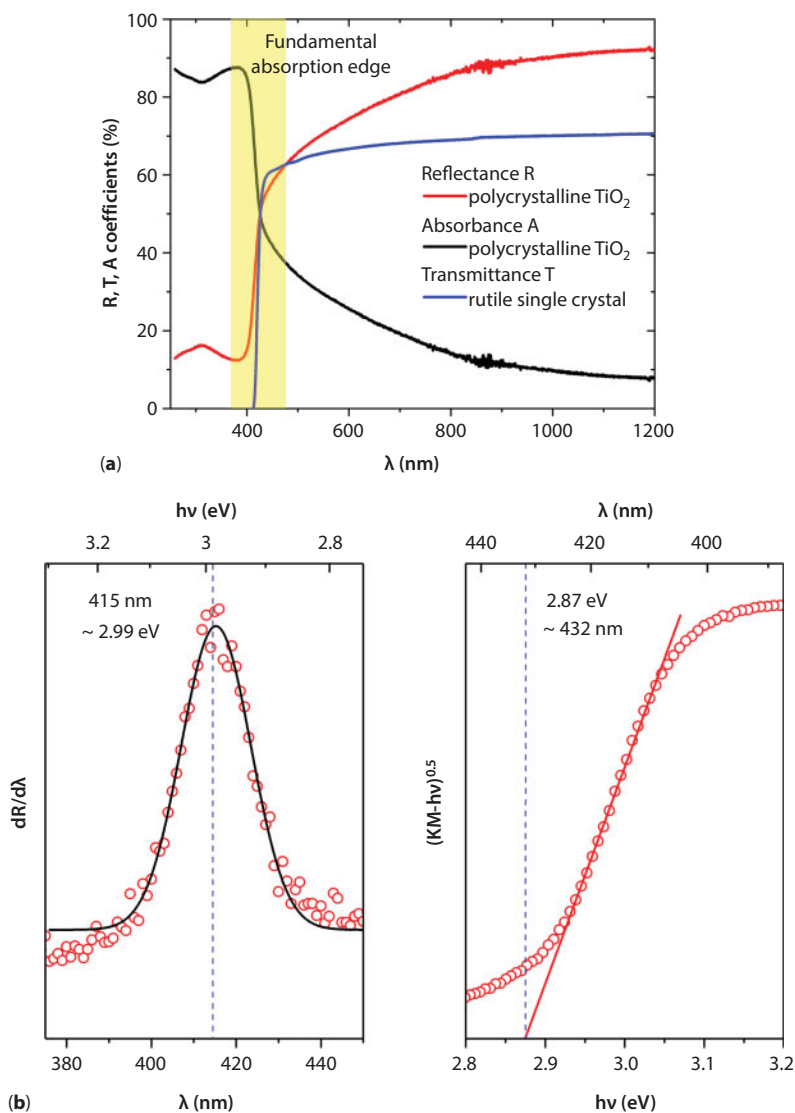


Figure 8.3 Experimental methods for energy bandgap E_g determination; (a) spectral dependence of the total reflectance $R(\lambda)$ for polycrystalline TiO_2 compared to that of the transmittance coefficient $T(\lambda)$ for single crystal of TiO_2 ; absorbance A of polycrystalline TiO_2 decreases sharply within the wavelength λ range corresponding to the fundamental absorption edge; (b) methods of analysis of the experimental spectra by means of the first derivative of reflectance $dR/d\lambda$ and Kubelka–Munk model; (c) normalized photocurrent as a function of wavelength λ with the method of analysis given in the inset; (d) comparison of the experimental data for E_g derived from different methods of analysis for three semiconducting photoelectrodes TiO_2 , WO_3 , and SrTiO_3 [19–34].

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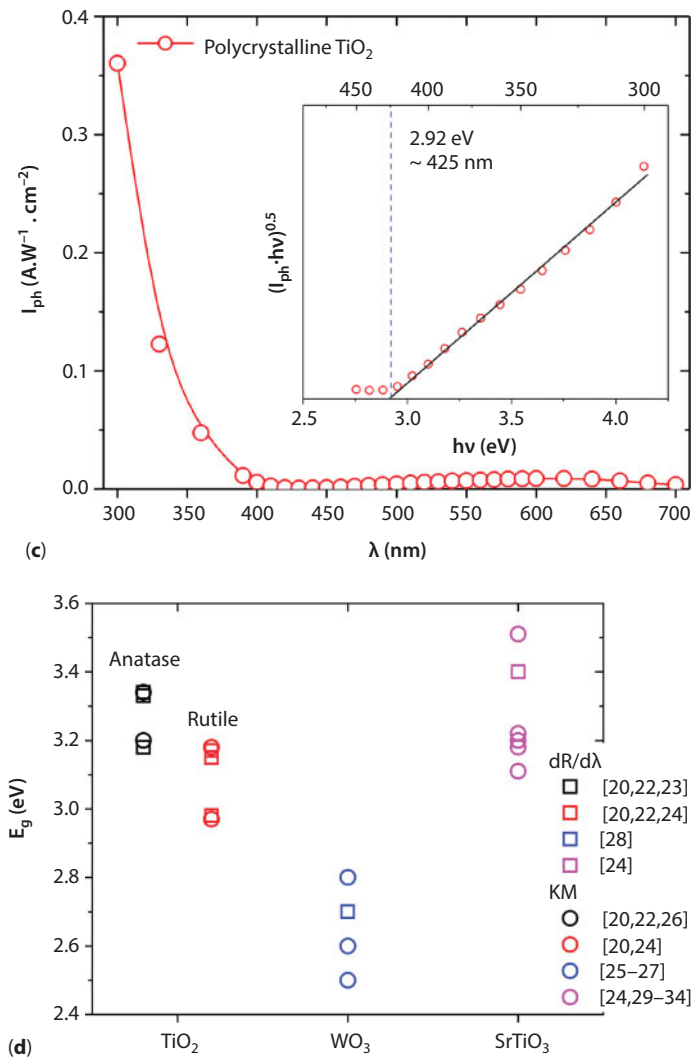


Figure 8.3 (Continued)

where R is the reflectance and $F(R)$ is proportional to the absorption coefficient α . This approach is usually applied to high light scattering materials. A modified Kubelka–Munk function can be obtained by multiplying the $F(R)$ function by $h\nu$, using the corresponding coefficient γ associated with an electronic transition as follows:

$$(F(R) \cdot h\nu)^\gamma \tag{8.11}$$

The coefficient γ can take different values, e.g., 1/2 for indirect allowed transitions, 1/3 for indirect forbidden transitions, 2 for direct allowed transitions, and 2/3 for direct forbidden transitions. By plotting (11) as a function of the photon energy in eV, the bandgap of the semiconductor can be obtained.

This approach allows determination of the effective absorption assuming that the scattering is independent of wavelength over this narrow range.

Values of the bandgap energy E_g of about 2.93–2.99 eV obtained from these two methods for TiO_2 polycrystalline samples remain in very good agreement.

Alternative experimental method for bandgap determination based on the spectral dependence of the photocurrent density J_{ph} is demonstrated in Figure 8.3c. For an n-type semiconductor in contact with electrolyte, assuming an electron diffusion length L_n much smaller than the thickness of the PE, one can obtain the relation known as the Gärtner equation [18]:

$$J_{ph} = eF(1 - R) \left(1 - \frac{\exp(-\alpha W)}{1 + \alpha L_n} \right) \quad (8.12)$$

where F is the flux density of incident photons, α is absorption coefficient, and W is the width of SCR.

If we consider the special case of weak absorption, when $\alpha W \ll 1$ and $\alpha L_n \ll 1$, the relation (8.12) can be rewritten as:

$$J_{ph} = eF(1 - R)(L_n + W)\alpha \quad (8.13)$$

From equation (8.13), it is clearly seen that the photocurrent density is proportional to the absorption coefficient. Therefore, from the intercept of the linear dependence of $(I_{ph} h\nu)^2$ vs. $h\nu$ with the photon energy axis at $I_{ph}=0$, a bandgap energy of 2.92 eV is obtained in accordance with the results of Figure 8.3b.

Figure 8.3d summarizes the data obtained from different methods for the most frequently used TiO_2 , WO_3 , and SrTiO_3 semiconducting photoanodes. In all cases, there is a big scatter of values of E_g of about 0.2–0.4 eV due to differences in

the microstructure and form of the materials. The biggest E_g of about 3.4 eV corresponds to SrTiO_3 , while the smallest is observed for WO_3 . The bandgap of WO_3 (E_g of about 2.7 eV) matches quite well the visible range of the light spectrum, but the main disadvantage of WO_3 , mentioned before, is its unsuitable alignment of CB and VB edges with respect to the redox potential of H_2O .

- c) Recombination of photoinduced charge carriers cannot be avoided but should be limited at all cost because it prevents the photogenerated carriers from reaching the electrode surface where they can participate in redox reactions. In order to reduce the inherent recombination, a certain electric field has to be formed at the electrode/electrolyte interface that will spatially separate the electrons from holes. Recombination is detrimental to the process of water splitting and its characteristic transient time constants (Figure 8.4) can be determined either from photoluminescence experiments [35] or from the kinetics of the photocurrent change upon a sudden impulse of light [8]. Depending on a time scale, different relaxation processes can take place as shown in Figure 8.4a [36]. One should distinguish between charge carrier trapping when electron and holes are trapped in shallow and deep levels within the bandgap occurring on a picosecond time scale, and recombination of electrons and holes already trapped in these states on much longer time scales, extending even to microseconds.

Figure 8.4b shows the kinetics of the photocurrent changes corresponding to successive sudden switching on and off the white light. In this case, we deal with relaxation processes on much longer time scales. The process of relaxation is controlled by the following kinetic equation

$$D = \exp\left(\frac{-t}{\tau}\right) \quad (8.14)$$

where D is defined as:

$$D = \frac{I_t - I_f}{I_i - I_f} \quad (8.15)$$

where t denotes time, τ is a parameter defined as a transient time constant, I is either the photoanode or cathodic current, and the subscripts t and f are related to the initial and final (steady) state. Two different types of photocurrent responses

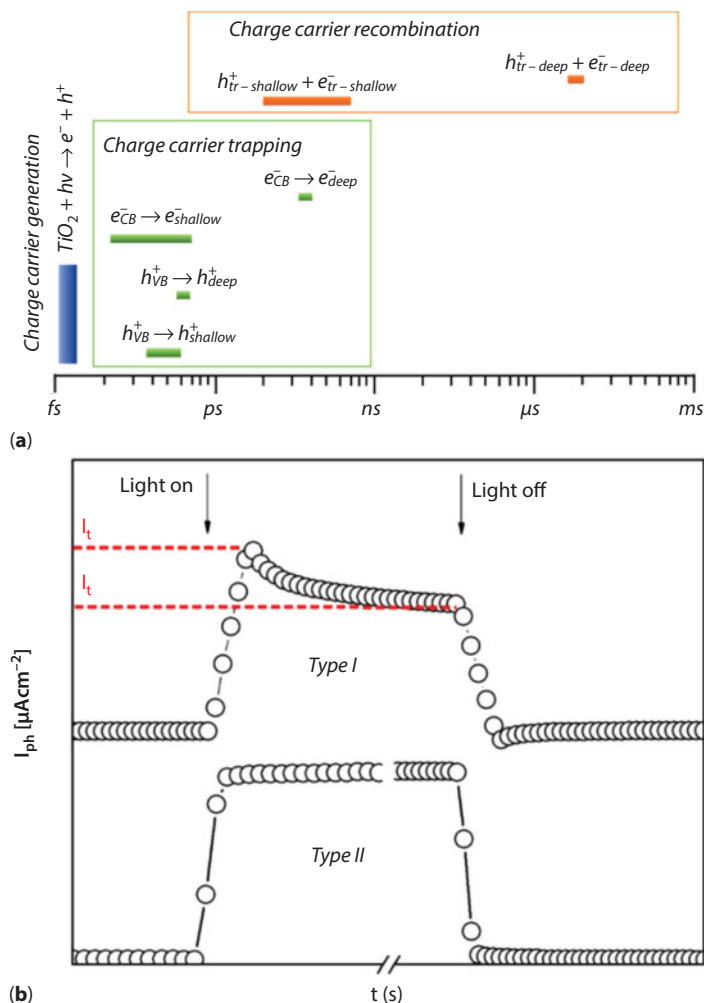


Figure 8.4 Experimental methods for transient time constants determination; (a) different time scales corresponding to electron and hole trapping and recombination mechanisms [36]; (b) two types of kinetics of the photocurrent rise and decay for TiO_2 ; (c) methods of analysis leading to the determination of the relaxation time; (d) comparison of the time transients obtained from different methods for three semiconducting photoelectrodes: TiO_2 , WO_3 , and SrTiO_3 [10, 35,38–42].

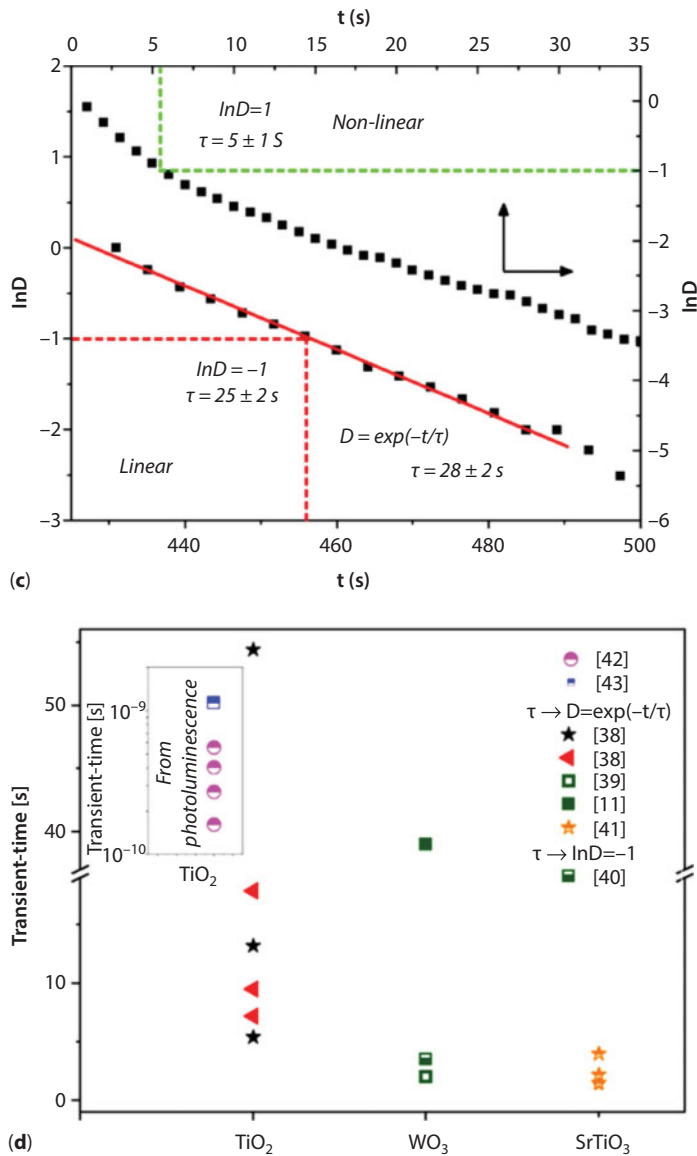


Figure 8.4 (Continued)

I and II are seen. In case I, two spikes are clearly seen, anodic and cathodic ones. They are due to fast processes of electron-hole separation followed by surface recombination of charge carriers. In case II, no such spikes can be observed,

which indicates that the relaxation processes are slower due to deep trapping.

Figure 8.4c shows $\ln D$ vs. t plots for two cases: linear and nonlinear dependence. In the case of linear dependence, the relaxation constant τ can be easily extracted from the linear fit of eq. 14 to the experimental data. However, for nonlinear dependence of $\ln D$ vs. t , the transient time constant has been defined as the time at which $\ln D = -1$ [37].

Figure 8.4d recapitulates the experimental data obtained for transient constants. Transient time constants obtained from the kinetics of the photocurrent switching (Figure 8.4b) are much longer than those obtained from photoluminescence decay. The former should be treated as relaxation times, while the latter reflects the much faster process of recombination of electrons and holes from shallow and deep traps within the bandgap. No particular differences in the relaxation constants related to the choice of the semiconductors TiO_2 , WO_3 , SrTiO_3 can be seen. The scatter of data is due to different methods of analysis and experimental conditions of measurements.

d) Conversion efficiency

The energy conversion efficiency is the ultimate performance indicator of a PSC cell. It is affected by all three parameters discussed above, but when the bandgap of a chosen semiconducting photoelectrode is correctly matched to the visible range of the electromagnetic radiation, there still remains the recombination rate of the photocarriers: electron and holes, acting as a limiting factor.

There are different measures of the energy conversion efficiency [43]:

- (i) the standard solar-to-hydrogen conversion efficiency (η_{STH})
- (ii) applied bias photon-to-current efficiency (ABPE)
- (iii) faradaic efficiency
- (iv) quantum efficiencies, e.g.
 - incident photon-to-current conversion efficiency (IPCS)
 - absorbed photon-to-current conversion efficiency (APCE)

Detailed information about these measures is given in Table 8.1.

Table 8.1 Various energy conversion efficiencies and their definitions.

Energy conversion efficiency	Definition	Comments
Standard solar-to-hydrogen conversion, η_{STH}	$\frac{\Delta G \cdot r_{\text{H}_2}}{P_{\text{sun}} \cdot S}$	Valid under $V_{\text{B}}=0$, and AM1.5 G irradiation, benchmark efficiency
Applied bias photon-to current, ABPE	$\frac{J_{\text{ph}} (1.23 - V_{\text{B}})}{P_{\text{light}}}$	Valid under external bias $V_{\text{B}} \neq 0$, diagnostic efficiency
Faradaic efficiency	$\frac{\text{Oxygen evolution measured}}{\frac{J_{\text{photo}} \cdot S \cdot t}{4eN_{\text{A}}}} \cdot 100\%$	Verifies that the photocurrent is due to water splitting not to the photocorrosion
Quantum efficiencies: Incident photon-to-current efficiency IPCE Absorbed photon-to-current efficiency APCE	$\frac{J_{\text{photo}}(\lambda)}{e} \cdot \frac{hc}{\lambda} \cdot 100\%$ $\frac{\text{IPCE}(\lambda)}{1 - R - T} \cdot 100\%$	Measured at fixed wavelength, diagnostic efficiency

The standard solar-to-hydrogen conversion efficiency can be expressed as the ratio of the total energy generated and the total energy input from sunlight irradiation (AM 1.5G, 100 mW cm⁻²):

$$\eta_{\text{STH}} = \frac{\text{Total energy generated}}{\text{Total energy input}} = \frac{\Delta G \cdot r_{\text{H}_2}}{P_{\text{sun}} \cdot S} \quad (8.16)$$

where ΔG is the Gibbs free energy (237 kJ mol⁻¹), r_{H_2} is the rate of hydrogen production in moles per second, P_{sun} is the incident light intensity (100 mW cm⁻²), and S is the illuminated area of the photoelectrode (cm²).

In fact, η_{STH} efficiency is the most important parameter for characterizing a PSC device with which all PSC devices can be reliably ranked against each other. η_{STH} is the best of all the efficiency metrics as it describes the overall efficiency of a PSC water splitting device exposed to broadband solar irradiance, e.g., air mass 1.5 under zero-bias conditions.

When an external bias is applied to the PSC system, the electrical energy must be subtracted and thus the applied bias photon-to-current efficiency (ABPE) is frequently used:

$$\begin{aligned} ABPE &= \frac{\text{Electrical (output power - input power)}}{\text{Power of incident light}} \\ &= \frac{J_{ph}(V_{redox} - V_B)}{P_{light}} \end{aligned} \quad (8.17)$$

where V_{redox} is the redox potential for water splitting (1.23 V vs. NHE); V_B refers to the actual potential difference between the working and the counterelectrode; P_{light} is the light intensity (100 mW cm^{-2}), and J_{ph} is the generated photocurrent density.

Determination of the faradaic efficiency is the most useful method for verifying that the generated photocurrent is, in fact, due to water splitting and not photocorrosion of the electrodes nor other side reactions. It is defined as the ratio of the actual evolved gas divided by the theoretically evolved gas based on the measured photocurrent.

$$\begin{aligned} \text{Faradaic efficiency} &= \frac{\text{Experimental gas evolution}}{\text{Theoretical gas evolution}} \\ &= \frac{\text{Oxygen evolution measured}}{\text{Gas evolution based on the photocurrent}} \\ &= \frac{\text{Oxygen evolution measured}}{\frac{J_{photo} \cdot S \cdot T}{4eN_A} \cdot 100\%} \end{aligned} \quad (8.18)$$

The unit of gas evolution is moles; J_{photo} is the photocurrent density (S cm^{-2}) generated during the measurement time T (seconds); S is the illumination area of the photoelectrode (cm^2); e is the charge of an electron ($1.602 \times 10^{-19} \text{ C}$); and N_A is the Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$). The amounts of evolved gases can be analyzed by gas chromatography (GC) or, in the case of oxygen, by using a suitable oxygen electrode or fluorescence detector.

Quantum efficiencies such as the incident photon-to-current efficiency (IPCE) and the absorbed photon-to-current conversion efficiency (APCE) are measured at fixed incident wavelengths and are often used as a diagnostic tool of a photoelectrode for water splitting.

The IPCE is defined as the number of photogenerated charge carriers contributing to the photocurrent per incident photon, which can be represented by the following equation:

$$\begin{aligned} IPCE(\lambda) &= \frac{\text{Total number of photoinduced pairs } e - h}{\text{Total number of incident photons}} \\ &= \frac{J_{\text{photo}}(\lambda) \cdot \frac{hc}{\lambda}}{P(\lambda)} \cdot 100\% \end{aligned} \quad (8.19)$$

where J_{photo} is the photocurrent density at that particular wavelength of incident light (mA cm^{-2}); e is the charge of an electron ($1.602 \times 10^{-19} \text{ C}$); h is Planck's constant ($6.626 \times 10^{-34} \text{ J s}$); c is the speed of light ($3.0 \times 10^8 \times 10^9 \text{ nm s}^{-1}$); λ is the wavelength of the incident light (nm); and $P(\lambda)$ is the incident light intensity at that specific wavelength (mW cm^{-2}). In the calculation of IPCE, optical losses such as reflection and transmission are neglected, despite potentially having a large impact on the IPCE. In order to correct for these optical losses, the absorbed photon-to-current conversion efficiency (APCE) is often used to determine the quantum efficiency. The APCE is defined as the number of photogenerated charge carriers contributing to the photocurrent per absorbed photon, which is termed the internal quantum efficiency, and it can be expressed using the following equation:

$$APCE(\lambda) = \frac{IPCE(\lambda)}{A(\lambda)} = \frac{IPCE(\lambda)}{1 - R - T} 100\% \quad (8.20)$$

where A , R , and T are the optical absorption, reflection, and transmission, respectively.

Figure 8.5 shows the spectral dependence of solar irradiance AM1.5 G and the method for determining the theoretical efficiency $J_{\lambda_g}/J_{\text{total}}$ resulting from the ratio of the integral taken between the curve and below the straight line drawn at λ_g (J_{λ_g}) normalized to the total integral below the same curve J_{total} . The inset in Figure 8.5 demonstrates how the η_{STH} efficiency is related to the bandgap of the semiconducting photoelectrode. The very well-known PE material — TiO_2 cannot achieve the η_{STH} required for practical applications because of its wide bandgap.

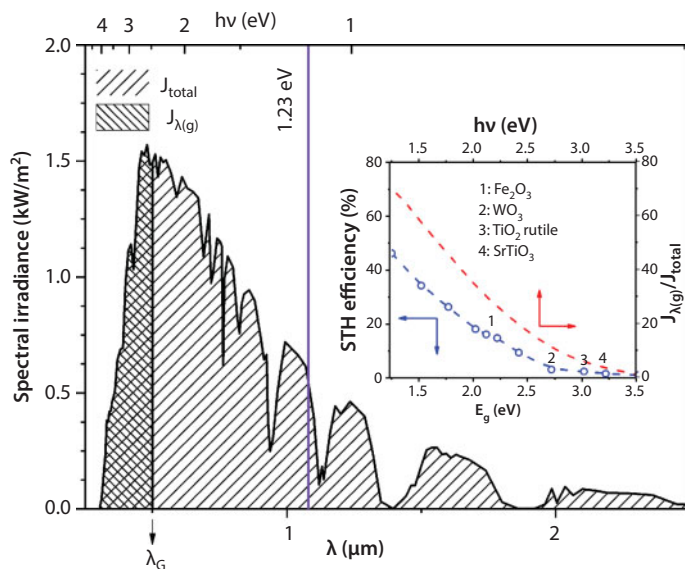


Figure 8.5 Spectral irradiance for AM1.5G air mass spectrum; λ_g is the wavelength corresponding to the bandgap E_g of PE. The inset shows the η_{STH} efficiency as a function of the bandgap of PE.

8.4 Eutectic Composites

As it was previously mentioned, there is not perfect semiconducting material that meets all requirements for efficient photoelectrochemical water splitting. Common materials in PSC can be divided into two groups:

- photoelectrochemically stable, absorbing only UV radiation, i.e.: TiO_2 , SrTiO_3 , ZnO , SnO_2 , BaTiO_3 ,
- photoelectrochemically unstable, absorbing visible light, i.e.: Cu_2O , CuO , CdSe , CdTe , InP , GaAs .

Current modifications of semiconducting materials aim at developing materials with high stability and enhanced absorption. This is investigated by introducing composite materials such as dye-sensitized solar cells, various heterostructures, and recently proposed eutectic composites [29, 30]. Eutectic composites are solid mixtures of at least two components which are mixable in the liquid and separate in the solid state. Eutectic composites crystallize at much lower melting temperature than its component phases.

What makes eutectic composites so attractive is the unique possibility of combining various phases together in an almost “on-demand” fashion enabling adjusting the components and the composite to an application of interest. Collection of phases from which a eutectic composite can be made of is vast, including alkali salts, metals, semiconductors, oxides, and materials demonstrating various properties as, i.e., superconducting, nonlinear, optically active, and others. Eutectic microstructures can be either regular or irregular, with precipitates ranging in sizes from hundreds of micrometers to nanometers, including a plethora of geometrical motifs such as (i) lamellar, (ii) rodlike, (iii) broken lamellar, (iv) globular, (v) spiral, and others. Even though most of research on eutectic composites concerns binary systems, ternary and quaternary systems are also available broadening available material combinations [44].

Historically, recognition of eutectic composites as functional materials began with the use of eutectic alloys of carbon-iron and metal-metal systems with excellent mechanical properties. However, the area of investigation concerning functional properties of eutectic composites has currently entered new frontiers.

The ability to combine various phases together including even so different materials as metals and oxides as well as the ability to form various micro/nanostructures especially the regular ones like lamellar/layered or fibrous/rodlike leads to multiphase composites with interesting properties. This combined with the ability to control the size of the precipitates by the growth rate offers a unique opportunity to obtain composite materials with designed light–matter interaction. Thus, eutectic composites recently started to be used as demonstration of the novel material concepts, such as photonic crystals, plasmonic materials, and metamaterials, by material scientists using the directional solidification.

Photonic crystals require periodic structures; thus lamellar and rodlike eutectic structures were originally proposed and demonstrated as “natural” photonic crystals [45–47]. Later the eutectic solidification was proposed as a potential method for manufacturing materials [48, 49], and already a composite with features mimicking pivotal for metamaterial structures was reported [49]. On the other hand, recently, a Bi_2O_3 -Ag composite was demonstrated as the first eutectic-based plasmonic materials in which, through the monotectic and eutectic reactions, silver was distributed within the whole volume of the composite, and upon the postannealing process, silver nanoparticles were formed. Silver nanoparticles placed in the Bi_2O_3 matrix gave rise to the localized surface plasmon resonance (LSPR), which position and intensity could be tuned when applying different annealing conditions [50–52].

Apparent tendency of exploiting the structures formed upon eutectic solidification for light–matter interaction and availability of component

phases have been explored in perspective of obtaining eutectic materials for energy applications. Laguna-Bercero *et al.* [53, 54] have reported a promising method of obtaining Ni-ZrO₂ anode for solid oxide fuel cells by treatment of eutectic NiO₂-ZrO₂ in reducing atmosphere, thus obtaining a highly porous cermet composite. Oliete *et al.* [55] proposed Al₂O₃/Y_{3-x}Er_xAl₅O₁₂ systems as thermal emitters, which could be used in photovoltaics to increase efficiency of devices.

The particularly interesting properties of eutectic composites in the perspective of solar energy conversion include (Figure 8.6) (i) high crystallinity (as single crystals) [56], (ii) sharp interfaces between the component phases [57], (iii) possibility of designing materials with various component materials enabling broadband absorption (UV-Vis), (iv) utilizing phases which are difficult to achieve or are unavailable in another way, as well as (v) ability to tune eutectic properties according to the application. In perspective of employing eutectic composites in devices carrying out

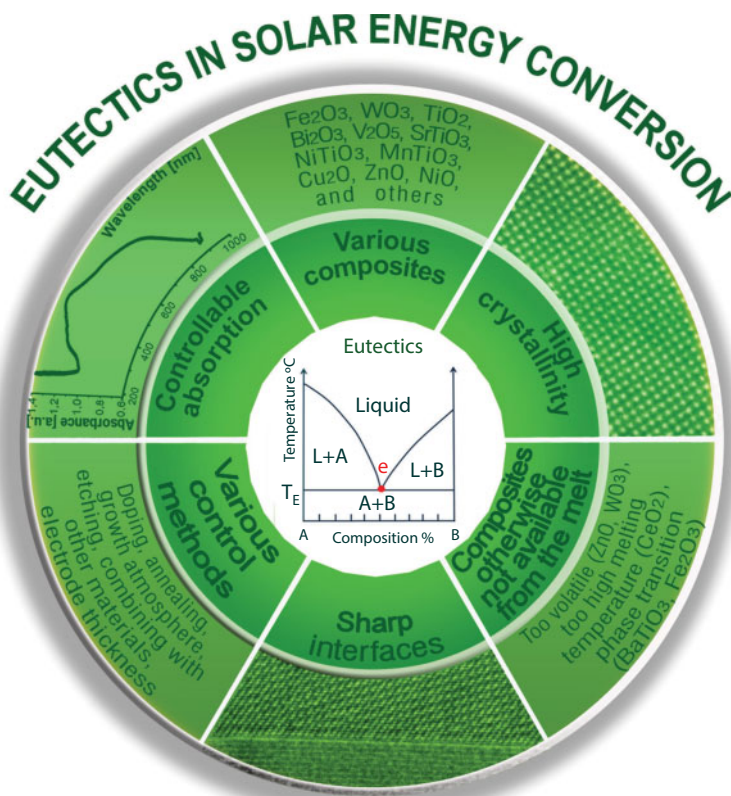


Figure 8.6 Diagram showing particularly interesting properties of eutectic composites for solar energy conversion applications.

photoelectrochemical water splitting, apparent advantage arises from a variety of phases that can constitute such composite. Most importantly, these phases can be potentially selected to form a eutectic system with bandgap energies covering significant part of the solar spectrum. And additionally the phases can be combined in such a way as to enable assisted charge-carrier separation through a design of relative positions of conduction and valence band edges of the eutectic component phases [29].

8.5 Methods of Obtaining Eutectic Composites

Eutectic materials obtained at industrial scale are predominantly grains of eutectics used as abrasive media. Process of fabricating these grains begins with melting of raw materials by fusion techniques realized in arc furnaces. Second stage is cooling of molten material which is carried out on inert receptor-like steel balls. Apparent advantage of using steel balls is the fact that by adjusting their size, cooling speed can be controlled and thus the size of obtained grains. Steel balls can also be easily removed from the reaction environment using magnets. Once the melt has solidified, material is crushed and sieved to obtain desired sizes of grains.

Czochralski and Bridgman were the first techniques used to obtain eutectic ceramics in bulk, yet they provide limited thermal gradients that are crucial in terms of having control over the microstructure. Therefore, new methods were developed that provided larger thermal gradients and ability to fabricate various sample shapes like fibres, tubes, and ribbons [44].

On the other hand, obtaining relatively big areas of eutectic layers is possible using processing the material with a laser beam. This approach involves preparation of hot-pressed pellets constituting eutectic composition first, which are then resolidified using high-power laser beam with diameter of ca. 1 cm. Drawbacks of this method include distorted microstructure due to curved solidification front, and significant temperature stress imposed on the sample often resulting in cracks. Notable examples include such composites as $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}\text{-ZrO}_2$ [58], $\text{WC-W}_2\text{C}$ [59], and $\text{B}_4\text{C-TiB}_2$ [60].

Variant of floating zone method (FZ) called flux-feeding floating zone (FFFZ) was also reported as a viable way of obtaining superconductive $\text{Sr}_2\text{RuO}_4\text{-Sr}_3\text{Ru}_2\text{O}_7$ eutectic composites [61]. Employing FZ most often results in good refinement of the eutectic structure as well as low impurity concentration in the material due to absence of crucible. This method is based on establishing a molten zone between a seed crystal and feeding rod using radiation from halogen/xenon bulbs. The molten zone travels when both seed crystal and feeding rod are moved, thus the term “floating zone.”

The FFFZ is useful whenever the constituent is too volatile, due to employing a feeding rod rich in the constituting phase to compensate for its evaporation, rather than using a stoichiometric feeding rod. Excess of volatile phase initiates its flux into melt zone, enabling its incorporation in the final crystal.

For smaller scale and purposes of investigating new eutectic compositions, several methods of obtaining eutectic materials are used and new are being developed.

Kim *et al.* [62] have proposed a novel approach called template-directed eutectic solidification. This method is a multistep process that involves creating a silica template which is then mounted on a steep holder. Raw material composition is set on top of the template in the holder and placed inside a furnace. Upon heating, molten material enters voids in the silica template forming unique eutectic microstructure. Altering the template allows controlling and tailoring microstructure of eutectic composites fabricated this way. This technique is especially promising in terms of obtaining photonic crystals on a large surface for solar cells or light-emitting diodes.

Recently, low-melting eutectic materials of alkali salts have been employed to explore a promising method of printing filaments on a substrate [63]. The idea behind high-operating-temperature direct ink writing developed by Boley *et al.* [63] is similar to 3D additive manufacturing. Device used to realize growth of eutectic AgCl-KCl filaments consists of so-called “print-head” comprising a heating coil, graphite nozzle, and thermal insulator, all mounted up on a 3D stage. In this method, the substrate remains stationary, while the eutectic ink heated up to 700 °C is released from a moving, heated shaper with a nozzle to print eutectic filaments. By altering printing speed and temperature, one can tailor microstructure directly. Boley *et al.* [63] stress that upon optimization of the setup, patterning of various materials with controlled lamellar spacing is possible for application in optics, including polymers, other eutectic compositions, and glasses.

The micro-pulling-down method (μ -PD) was introduced by T. Fukuda as an accelerated method for obtaining crystalline materials in small quantities [64]. Since 1994, when this method was first reported, it was proven feasible for obtaining single crystals [65], multiphase composites [66], glasses [67], or even organic materials [68, 69]. Techniques of directional solidification from melt-like Czochralski or Bridgman–Stockman require days or even weeks to obtain a crystal, whereas μ -PD process takes as long as several hours. This way multiple samples of various materials can be obtained readily at a small expense.

The centerpiece of any μ -PD furnace is a crucible. Crucibles can be made out of various materials such as Al_2O_3 or ZrO_2 ceramics, graphite, or noble metals like platinum or iridium. Selection of an appropriate crucible

is usually related to melt's reactivity with crucible material and melting temperature of used eutectic composite. At the bottom of every μ -PD crucible, there is a die with a narrow nozzle. The die determines the shape and size of growth zone and thus the grown/solidified material's dimensions. Most widely used shapes of dies are circular, conical, and rectangular, and the size of the die may enable obtaining also larger pieces of materials as it has been reported previously for the SrTiO_3 - TiO_2 eutectic composite, when larger rectangular shaper was applied [70].

Crucibles in many μ -PD setups are heated via high-frequency alternating electric field-emitting (radio frequency "RF") coils that surround the crucible. This alternating field forces dipoles present in dielectric crucible to rapidly reorient producing heat. Apart from RF heating, resistive heating is used as an alternative. An example of the scheme of thermal system and view of the inside of the growth chamber are presented in Figure 8.7.

Directional solidification methods of obtaining eutectic composites are not the only ones available, but in the perspective of potential applications, these methods are often associated with very interesting properties of eutectic materials. Directional solidification enables control over microstructure of obtained eutectic composite by varying parameters of growth.

8.6 Eutectic Composites used for Photoelectrochemical Water Splitting

Recently, Wysmulek *et al.* [29] and Kolodziejak *et al.* [30] demonstrated new photoelectrodes for hydrogen generation, through water splitting, utilizing eutectic composites as the electrode active part. The authors

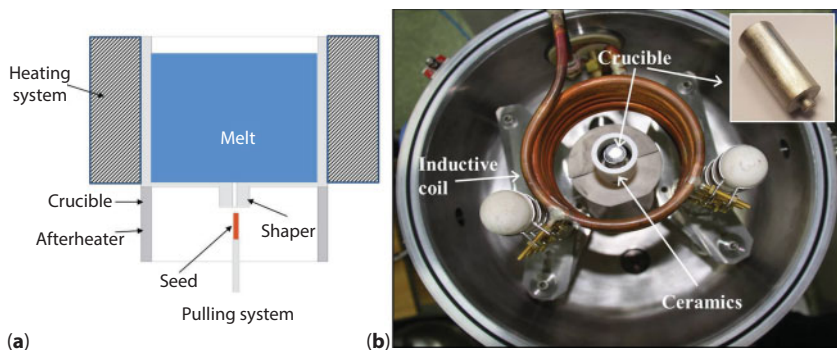


Figure 8.7 The micro-pulling-down method: (a) scheme of the chamber inside used for the growth of eutectic composites; (b) view of the inside of the growth chamber.

combined in these eutectic material phases which were already broadly investigated as active materials for water splitting such as absorbing UV light TiO_2 , and SrTiO_3 , and absorbing visible light WO_3 . Thus the photoanodes were made of SrTiO_3 - TiO_2 and WO_3 - TiO_2 eutectic composites, which were produced using the micro-pulling-down method (Figure 8.8). The WO_3 - TiO_2 eutectic composite was made using a composition containing 36% mol. of TiO_2 and 64% mol. of WO_3 [71], while SrTiO_3 - TiO_2 77 mol. % of TiO_2 and 23 mol. % of SrO [72] (Figure 8.8a,b). Both eutectic

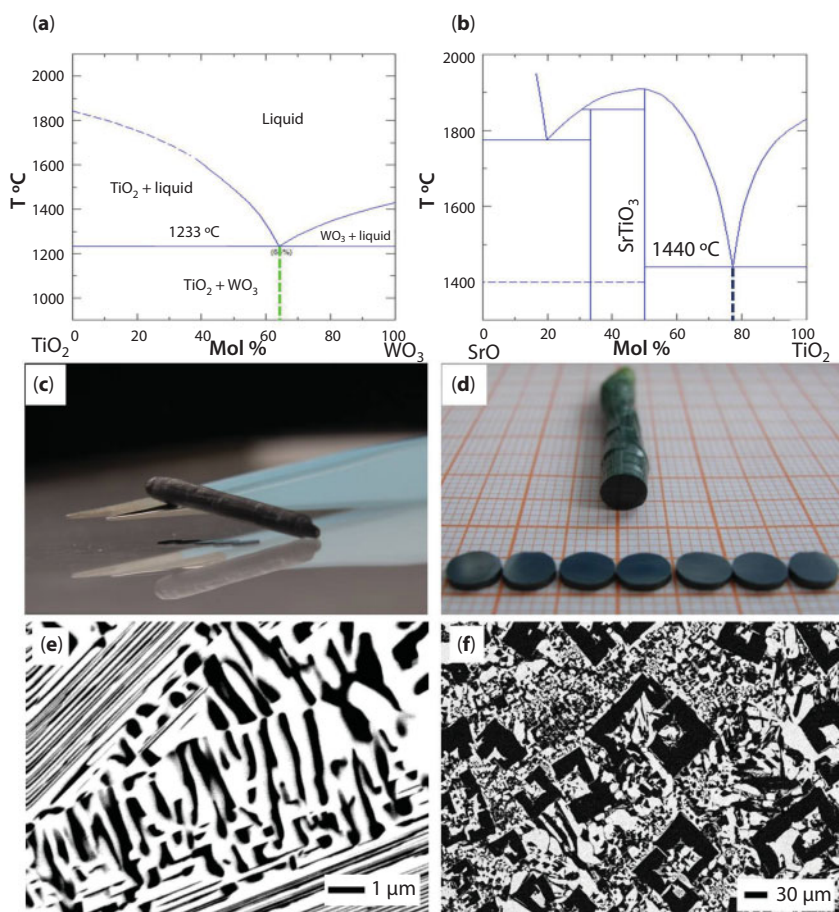


Figure 8.8 TiO_2 - WO_3 (a, c, e) and TiO_2 - SrTiO_3 (b, d, f) eutectic composites used as photoactive materials in the PSC photoanodes. The phase diagrams with eutectic composition and eutectic temperature for TiO_2 - WO_3 (a) and TiO_2 - SrTiO_3 (b). As-grown eutectic rods TiO_2 - WO_3 (c) and TiO_2 - SrTiO_3 (d), and SEM picture of eutectic microstructures, where TiO_2 is shown in black, while WO_3 (e) and SrTiO_3 phases are in white (f).

materials (Figure 8.8c,d) contain the TiO_2 phase, and in both of them, TiO_2 forms precipitate embedded in a matrix of the other material, WO_3 or SrTiO_3 (Figure 8e,f). However, in both of these composites, TiO_2 is in a different allotropic form, as well as it shows different geometrical motifs. In the case of WO_3 - TiO_2 eutectic composite, TiO_2 is in the form of anatase, and the composite demonstrates two types of TiO_2 precipitates, very narrow elongated ones (ca. 100–200 nm in width) and bigger less regular ones. While in the case of SrTiO_3 - TiO_2 material, TiO_2 is present in the form of a rutile and it forms a fractal microstructure with the TiO_2 precipitates all growing in the [001] crystallographic orientation in which it has a fourfold symmetry.

Although the gas evolution kinetics for TiO_2 is very good, the optical absorption edge is as high as 3.12 eV (397 nm) in eutectic SrTiO_3 - TiO_2 [29], limiting the overall performance. Commonly, one functionalizes nanostructured TiO_2 by dye sensitizing, by which photons from visible spectral range can be utilized. However, utilizing eutectic composite in which TiO_2 is combined with a phase-absorbing visible light, such as WO_3 can widen the absorption range and can be used as an alternative method. In Figure 8.9, bandgaps are shown for TiO_2 - WO_3 and TiO_2 - SrTiO_3 eutectic composites revealing in both of them double bandgap, which in both cases widens the absorption range.

On the other hand, combining different phases in one composite can help us to design band edges of the component materials in respect to each other and the gas evolution reactions in a favorable way. For example, rutile TiO_2 is in most cases n-type doped, which shifts its conduction band below the hydrogen evolution reaction (Figure 8.10). Thus, hydrogen generation in such a process is unfavorable as additional bias should be applied to

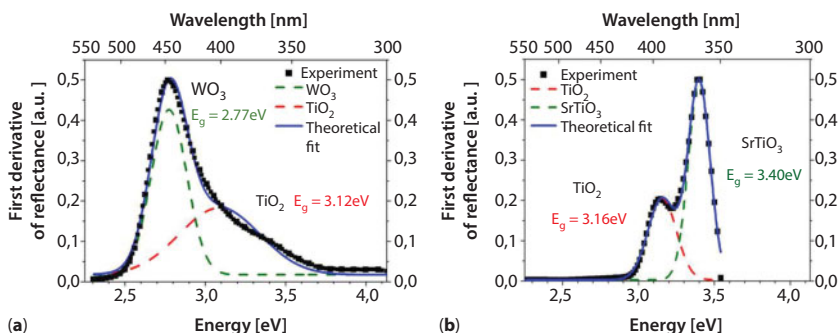


Figure 8.9 Double optical bandgaps in eutectic composites enabling broader absorption range: (a) TiO_2 - WO_3 , (b) TiO_2 - SrTiO_3 . Optical bandgaps were determined from first derivative of the diffuse reflectance measurements [29, 30].

achieve efficient charge separation. Thus in order to overcome this problem, SrTiO_3 is often used in combination with TiO_2 , for photoelectrochemical water splitting under zero bias conditions, and this idea stands behind utilization of the eutectic SrTiO_3 - TiO_2 for the PSC photoanode [29]. In Figure 8.10, positions of the bandgaps in SrTiO_3 and TiO_2 are shown relative to the hydrogen and oxygen evolution reactions [6, 73].

The photocurrent densities which have been demonstrated for the WO_3 - TiO_2 eutectic-based photoanode reached 4.4 mA/cm^2 under 600 mW/cm^2 irradiance [57], a sevenfold increase compared to nanostructured WO_3/TiO_2 thin-film photoanodes studied by Khare *et al.* [74]. In contrast to the WO_3 , the SrTiO_3 bandgap is much broader ($E_g = 3.4 \text{ eV}$) (Figure 8.9b), and one would expect decrease of photocurrent response with respect to WO_3 - TiO_2 system due to the weaker absorption of visible light. This is, however, not the case. The highest values of photocurrent densities recorded for SrTiO_3 - TiO_2 eutectic samples reach 8.5 mA/cm^2 at 600 mW/cm^2 and 1 V vs NHE, which are comparable to results obtained for nanostructured $\text{SrTiO}_3/\text{TiO}_2$ composites previously reported: 0.8 mA/cm^2 at 100 mW/cm^2 [75], 1.4 mA/cm^2 at 100 mW/cm^2 [76]. It is worth noting that after 30 h of stability testing of SrTiO_3 - TiO_2 eutectic electrode, the photocurrent increased by 44% what was explained by increased surface area and decreased reflectance caused by selective etching [29].

To further increase the efficiency, the thickness of the active material must be adjusted so to maximize the light absorption (increase the thickness) and minimize the recombination losses (decrease the thickness). By the Lambert-Beer law, 95% of photons are absorbed in the layer of thickness $3/\alpha(\lambda)$ ($\alpha(\lambda)$ — the absorption coefficient at wavelength λ). With α in the order of 10^4 - 10^6 cm^{-1} depending on the type of the fundamental

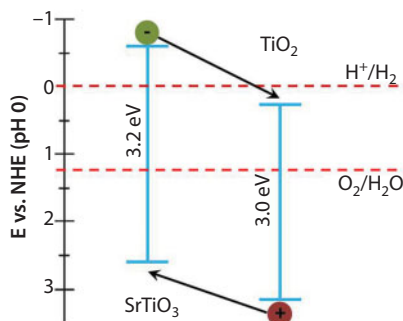


Figure 8.10 Band positioning in n- TiO_2 and SrTiO_3 at pH = 0 with respect to the normal hydrogen electrode potential ($E \text{ vs. NHE}$). [29].

transition (indirect or direct), this implies a penetration depth of 30 nm–3 μm . The charge-carrier mean free path for high-quality semiconductors usually does not exceed 1 μm and in defected structures drops to 1–10 nm.

The bulk character of the eutectic-based photoelectrodes results from the fabrication process, where thickly cut slices (>100 μm) must be grinded, lapped, and polished. Nevertheless, even for changes in thickness from 23 μm to 10 μm , a 13% rise in photocurrent can be observed.

8.7 Other Potential Eutectic Composites

There is a wide variety of possible eutectic composites. In order to simplify the search of eutectic composites, we focus only on double eutectic composites containing TiO_2 phase, which potentially could find application in photoelectrochemical water splitting.

PbO-TiO₂. In PbO-TiO₂ system, there are two eutectic points with corresponding compositions: first at 13.94 mol. % of TiO₂ and 82.06 mol. % of PbO giving following eutectic composites PbTiO₃-PbO at 838°C and second at 59.43 mol. % of TiO₂ and 40.57 mol. % of PbO giving PbTiO₃-TiO₂ at 1240°C [77]. PbTiO₃ phase has quite large bandgap of 3.88 eV absorbing UV light [78], while depending on the PbO polymorphs, its bandgap can change from 1.9 eV (α -PbO) [79] to 2.8 eV (β -PbO) [80].

Bi₂O₃-TiO₂. Generally, bismuth oxides have narrow bandgap allowing absorption of visible light. The complex phase diagram of Bi₂O₃-TiO₂ presents only one eutectic point at 97 mol. % of Bi₂O₃ and 3 mol. % TiO₂ crystallizing at 835°C giving mixture of Bi₂O₃ and Bi₁₂TiO₂₀ [81]. The estimated indirect bandgaps for Bi₂O₃ and Bi₁₂TiO₂₀ are 2.7 and 2.4 eV, respectively [82].

FeO-TiO₂. The FeO-TiO₂ system has two eutectic points at 14 and 44 mol. % of TiO₂, at 1312 and 1373°C, respectively. In the first case, eutectic composite consists of FeO and Fe₂TiO₄ and, in the second, Fe₂TiO₄ and FeTiO₃ [83]. FeTiO₃ is p-type semiconductor with a bandgap of 2.6–2.9 eV [84], while the bandgap of Fe₂TiO₄ is 2.1 eV [85].

V₂O₃-TiO₂. This system has three eutectic points at 40, 62.3, and 80 wt. % of TiO₂. Eutectic composites consists of V₂TiO₅-V₂Ti₂O₇, V₂Ti₂O₇-V₂Ti₃O₉, and V₂Ti₃O₉-TiO₂ [86]. There are very little published papers dealing with such composites, especially, their application in photoelectrochemical

water splitting, but pure vanadium oxide is p-type semiconductor absorbing green light (bandgap, 2.3 eV) [87].

MgO-TiO₂. MgO-TiO₂ system has two eutectic points at 72 and 86 wt. % of TiO₂ giving following composites MgTiO₃-MgTi₂O₅ and MgTi₂O₅-TiO₂ [88]. The bandgaps of MgTiO₃ is 3.7 eV and MgTi₂O₅ is 3.4 eV [89].

BaO-TiO₂. In BaO-TiO₂ system, there is one eutectic composition at 68.72 mol. % of TiO₂ at 1312°C. At this point, the eutectic composite is made of BaTiO₃ phase and Ba₆Ti₁₇O₄₀ phase [90]. Barium titanate is common material with bandgap of 3.2 eV, but it is difficult to find any information about the second phase.

TiO₂-Nb₂O₅. This system presents three eutectic points with compositions: 42, 62, and 83.3 mol. % of Nb₂O₅ at temperature around 1445, 1430, and 1440°C, respectively [91]. Despite TiO₂ and Nb₂O₅, eutectic composites have TiNb₂O₇ and Ti₂Nb₁₀O₂₉. More complex titanium niobates are subjects as anodes in lithium ion batteries [92].

8.8 Modification of the Properties of Eutectic Composites

Another important advantage of eutectic composites is the fact that their properties can be modified in several ways, for example, by (i) doping, (ii) change of the growth parameters, (iii) postgrowth annealing in various atmospheres, and (iv) surface engineering by selective etching and surface enriching by deposition of various materials.

- (i) Doping. Doping can effectively affect the photoelectrochemical properties of the material. This can be achieved in two ways: doping for improving photoactivity and/or doping for bandgap modification. The improved photoactivity through the doping can be achieved by change of pore size, density of hydroxyl groups, acidity, adsorption, and desorption rates. For materials with large bandgap absorbing UV light (only 5% of the spectrum of solar light), doping is used to decrease bandgap allowing absorption of broader spectrum of sunlight. Doping can also be used to improve charge carrier transport by the enhancement of conductivity. However, it should be kept in mind that the high level of

dopants increases the density of defects which may serve as recombination centers negatively influencing the properties. Examples of materials and already-used dopants for improving their PSC performance are listed in Table 8.2.

- (ii) Change of the growth parameters. Important growth parameters that influence the eutectic composite are the growth rate and the growth atmosphere. The growth rate affects the size of precipitates in the eutectic micro/nanostructure enabling, in the same eutectic composition, adjusting their dimensions from micron to nano. The growth atmosphere can influence the oxidation state of particular elements, as well as influences the presence and the concentration of oxygen vacancies in the material. Additionally, the important role in the crystallization process takes the crystallographic orientation of used seed; the crystallizing material adopts the crystallographic orientation from the seed.
- (iii) Postgrowth annealing. The influence of postgrowth annealing is similar to the influence of the atmosphere present during the growth. During the annealing process, it is necessary to define time, temperature, heating/cooling rates, and the atmosphere in order to control surface morphology, reduction/oxidation of ions, and the oxygen vacancy

Table 8.2 Examples of dopants used for improving PSC properties of SrTiO_3 , TiO_2 , Fe_2O_3 , WO_3 , and BiVO_4 .

Material	Dopants	Effects
SrTiO_3	Cr [93], Au [93], Pt [93], Ag [93], N [94], Nb [95]	VIS sensitivity
	Cr [93]	↑ photocurrent
	Nb [95]	↑ IPCE
TiO_2	Cr [96], Cu [97], Bi [98], V [99], Fe [100]	VIS sensitivity
	Fe [100]	↑ O_2 evolution rate
Fe_2O_3	Ta [101], Cr [102], Ti [102], W [102], Mo [102]	↑ photocurrent
WO_3	Fe [103], Yb [104], Gd [105]	↑ photocurrent
BiVO_4	Mo [106], W [106], Sn [106]	↑ photocurrent

concentration. Oxygen vacancy concentration plays an important role in semiconducting bandgap structure by narrowing its value for higher oxygen vacancy concentrations [107]. However, unwanted phase transition or thermal decomposition should be avoided.

- (iv) Surface engineering. In addition to the surface modification by thermal treatment, eutectic composites can be engineered by selective etching. By proper choice of acidic/basic solution, one phase in eutectic composite is etched faster than other providing micro- or nanopores at the eutectic surface [48, 49]. This enlarges the surface area of the material interacting with the electrolyte and allows absorption of larger portion of light by multiscattering [108]. The other surface engineering is cocatalyst loading. Cocatalysts are typically placed on the material surface in insular-like form or in continuous layer form. The role of cocatalyst is to enhance water oxidation rates by providing reduction or oxidation active sites, to avoid photocorrosion by fast hole transfer at the semiconducting/electrolyte interface and to decrease recombination probability and applied external potential. The commonly used cocatalysts are the following: RhO_2 , RuO_2 , Co-Pt, Mo, CoBi, Ni, NiO, and Ir.

8.9 Conclusions

Photoelectrochemical water splitting is a promising approach for the development of sustainable energy sources. Even though plans for a photoelectrochemical device are simple, commercial application still remains to be seen. This is mainly related with scale-up tendencies, which require simultaneously low-cost, STH efficiency over 10% and at least 10 years of stable operation [96]. In this chapter, we described main parameters that are used by the photoelectrochemical community to assess new materials for PSC devices.

Many materials used for photoelectrochemical water splitting do not meet all requirements for efficient and economic hydrogen production. Recently, eutectic materials were investigated and demonstrated as potential new photoactive materials for photoelectrochemical splitting. Directionally solidified eutectic composites have many applications spanning from high-strength structural materials, optical elements, to clean energy solutions due to their ability to constitute a synergetic combination

of various phases in a material. At the same time, eutectic materials offer excellent chemical and thermal stability, especially in the case of oxide composites. We also review various methods of obtaining eutectic composites — a crucial aspect in the perspective of fabricating photoactive layers. Optimal thickness should take into consideration the diffusion length of minority charge carriers; that is why materials obtained in bulk are troublesome to process mechanically to a desired layer thickness. Therefore, new high-operating temperature methods of obtaining thin layers of eutectic materials are being sought, such as the one developed at the Institute of Electronic Materials Technology [109].

Many advantages associated with inherent characteristics of this particular class of materials make them interesting candidates for efficient water splitting. Properties such as high crystallinity, sharp interfaces, and most importantly the plethora of available phases are the cornerstone for the development of new promising eutectic composites for solar energy conversion, as well as the optimization of compositions presented herein. The initial investigations reported by Wysmulek *et al.* [29] and Kolodziejek *et al.* [30] show untapped potential of eutectic composites for PSC cells. Development of other compositions and optimization of SrTiO_3 - TiO_2 and WO_3 - TiO_2 eutectic materials could potentially lead to interesting results and final applications.

References

1. Fujishima, A., Honda, K., Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, 37–38, 1972.
2. Fujishima, A., Honda, K., Kikuchi, S., Photosensitized electrolytic oxidation on semiconducting n-Type TiO_2 electrode. *J. Soc. Chem. Ind. Japan*, 72, 108–113, 1969.
3. Minggu, L.J., Wan Daud, W.R., Kassim, M.B., An overview of photocells and photoreactors for photoelectrochemical water splitting. *Int. J. Hydrogen Energy*, 35, 5233–5244, 2010.
4. Hisatomi, T., Kubota, J., Domen, K., Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.*, 43, 7520–7535, 2014.
5. Ma, Y., Wang, X., Jia, Y., Chen, X., Han, H., Li, C., Titanium dioxide-based nanomaterials for photocatalytic fuel generations. *Chem. Rev.*, 114, 9987–10043, 2014.
6. Marschall, R., Semiconductor composites: Strategies for enhancing charge carrier separation to improve photocatalytic activity. *Adv. Funct. Mater.*, 24, 2421–2440, 2014.

7. Butler, M.A., Photoelectrolysis and physical properties of the semiconducting electrode WO_3 . *J. Appl. Phys.*, 48, 1914–1920, 1977.
8. Radecka, M., Rekas, M., Trenczek-Zajac, A., Zakrzewska, K., Importance of the band gap energy and flat band potential for application of modified TiO_2 photoanodes in water photolysis. *J. Power Sources*, 181, 46–55, 2008.
9. Watanabe, T., Fujishima, A., Honda, K., Photoelectrochemical reactions at SrTiO_3 single crystal electrode. *Bull. Chem. Soc. Jpn.*, 49, 355–358, 1976.
10. Radecka, M., Sobas, P., Wierzbicka, M., Rekas, M., Photoelectrochemical properties of undoped and Ti-doped WO_3 . *Phys. B Condens. Matter.*, 364, 85–92, 2005.
11. Pinheiro, A.N., Firmiano, E.G.S., Rabelo, A.C., Dalmaschio, C.J., Leite, E.R., Revisiting SrTiO_3 as a photoanode for water splitting: development of thin films with enhanced charge separation under standard solar irradiation. *RSC Adv.*, 4, 2029–2036, 2014.
12. Ham, Y., Minegishi, T., Hisatomi, T., Domen, K., A SrTiO_3 photoanode prepared by the particle transfer method for oxygen evolution from water with high quantum efficiencies. *Chem. Commun.*, 52, 5011–5014, 2016.
13. Radecka, M., Wierzbicka, M., Rekas, M. Photoelectrochemical cell studied by impedance spectroscopy. *Phys. B Condens. Matter.*, 351, 121–128, 2004.
14. Dutoit, E.C., Van Meirhaeghe, R.L., Gomes, W.P., Bunsenges, B., (No title available). *Phys. Chem. - Int. J. Phys. Chem.*, 79, 1206, 1975.
15. Pleskov, Y.V., Gurevich, Y.Y., *Semiconductor Photoelectrochemistry*, New York & London, 1986.
16. Radecka, M., Rekas, M., Kusior, E., Zakrzewska, K., Heel, A., Michalow, K., *et al.*, TiO_2 -based nanopowders and thin films for photocatalytical applications. *J. Nanosci. Nanotechnol.*, 10, 1032–1042, 2010.
17. López, R., Gómez, R., Band-gap energy estimation from diffuse reflectance measurements on sol-gel and commercial TiO_2 : A comparative study. *J. Sol-Gel Sci. Technol.*, 61, 1–7, 2012.
18. Memming, R., *Semiconducting Electrochemistry*, Wiley-VHC Verlag GmbH, 2001.
19. Trenczek-Zajac, A., Radecka, M., Jasinski, M., Michalow, K.A., Rekas, M., Kusior, E., *et al.*, Influence of Cr on structural and optical properties of TiO_2 :Cr nanopowders prepared by flame spray synthesis. *J. Power Sources*, 194, 104–111, 2009.
20. Radecka, M., Trenczek-Zajac, A., Zakrzewska, K., Rekas, M., Effect of oxygen nonstoichiometry on photo-electrochemical properties of TiO_{2-x} . *J. Power Sources*, 173, 816–821, 2007.
21. Cardona, M., Optical properties and band structure of SrTiO_3 and BaTiO_3 . *Phys. Rev.*, 140, A651–A655, 1965.
22. Živojinović, J., Pavlović, V.P., Kosanović, D., Marković, S., Krstić, J., Blagojević, V.A., *et al.*, The influence of mechanical activation on structural evolution of nanocrystalline SrTiO_3 powders. *J. Alloys Compd.*, 695, 863–870, 2017.

23. Wang, J., Yin, S., Zhang, Q., Saito, F., Sato, T., Mechanochemical synthesis of $\text{SrTiO}_3\text{-xFx}$ with high visible light photocatalytic activities for nitrogen monoxide destruction. *J. Mater. Chem.*, 13, 2348–2352, 2003.
24. Ehsan, M.F., Ashiq, M.N., Bi, F., Bi, Y., Palanisamy, S., He, T., Preparation and characterization of $\text{SrTiO}_3\text{-ZnTe}$ nanocomposites for the visible-light photo-conversion of carbon dioxide to methane. *RSC Adv.*, 4, 48411–48418, 2014.
25. Ha, M.N., Zhu, F., Liu, Z., Wang, L., Liu, L., Lu, G., *et al.*, Morphology-controlled synthesis of $\text{SrTiO}_3/\text{TiO}_2$ heterostructures and their photocatalytic performance for water splitting. *RSC Adv.*, 6, 21111–21118, 2016.
26. Pasierb, P., Komornicki, S., Radecka, M., Structural and optical properties of $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ thin films prepared by rf sputtering. *Thin Solid Films*, 324, 134–140, 1998.
27. Trenczek-Zajac, A., Kusior, A., Lacz, A., Radecka, M., Zakrzewska, K., TiO_2 flower-like nanostructures decorated with CdS/PbS nanoparticles, *Mater. Res. Bull.*, 60, 28–37, 2014.
28. Kusior, A., Klich-Kafel, J., Trenczek-Zajac, A., Swierczek, K., Radecka, M., Zakrzewska, K., $\text{TiO}_2\text{-SnO}_2$ nanomaterials for gas sensing and photocatalysis. *J. Eur. Ceram. Soc.*, 33, 2285–2290, 2013.
29. Wysmulek, K., Sar, J., Osewski, P., Orlinski, K., Kolodziejak, K., Trenczek-Zajac, A., *et al.*, A $\text{SrTiO}_3\text{-TiO}_2$ eutectic composite as a stable photoanode material for photoelectrochemical hydrogen production. *Appl. Catal. B Environ.*, 206, 538–546, 2017.
30. Kolodziejak, K., Sar, J., Wysmulek, K., Osewski, P., Warczak, M., Sadkowski, A., *et al.*, When eutectic composites meet photoelectrochemistry – highly stable and efficient UV – visible hybrid photoanodes. *J. Catal.*, 352, 93–101.
31. Kwong, W.L., Qiu, H., Nakaruk, A., Koshy, P., Sorrell, C.C., Photoelectrochemical properties of WO_3 thin films prepared by electrodeposition. *Energy Proc.*, 34, 617–626, 2013.
32. Enesca, A., Andronic, L., Duta, A., Manolache, S., Optical properties and chemical stability of WO_3 and TiO_2 thin films photocatalysts. *Rom. J. Inf. Sci. Technol.*, 10, 269–277, 2007.
33. Zhou, B., Han, S., Raja, R., Somorjai, G.A., *Nanotechnology in Catalysis*, 3, Springer, 2007.
34. Komornicki, S., Radecka, M., Sobaś, P., Structural, electrical and optical properties of $\text{TiO}_2\text{-WO}_3$ polycrystalline ceramics. *Mater. Res. Bull.*, 39, 2007–2017, 2004.
35. Fujihara, K., Izumi, S., Ohno, T., Matsumura, M., Time-resolved photoluminescence of particulate TiO_2 photocatalysts suspended in aqueous solutions. *J. Photochem. Photobiol. A Chem.*, 132, 99–104, 2000.
36. Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., *et al.*, Understanding TiO_2 photocatalysis: Mechanisms and materials. *Chem. Rev.*, 114, 9919–9986, 2014.
37. Tafalla, D., Salvador, P., Benito, R.M., Kinetic approach to the photocurrent transients in water photoelectrolysis at n- TiO_2 electrodes II. Analysis of the photocurrent-time dependence. *J. Electrochem. Soc.*, 137, 1810–1815, 1990.

38. Kusior, A., Wnuk, A., Trenczek-Zajac, A., Zakrzewska, K., Radecka, M., TiO₂ nanostructures for photoelectrochemical cells (PECs). *Int. J. Hydrogen Energy*, 40, 4936–4944, 2015.
39. Yousefzadeh, S., Reyhani, A., Naseri, N., Moshfegh, A.Z., MWCNT/WO₃ nanocomposite photoanode for visible light induced water splitting. *J. Solid State Chem.*, 204, 341–347, 2013.
40. Liu, Y., He, H., Li, J., Li, W., Yang, Y., Li, Y., *et al.*, Preparation and enhanced photoelectrochemical performance of a p–n heterojunction CuFe₂O₄/WO₃ nanocomposite film. *RSC Adv.*, 5, 99378–99384, 2015.
41. Shen, H., Lu, Y., Wang, Y., Pan, Z., Cao, G., Yan, X., *et al.*, Low temperature hydrothermal synthesis of SrTiO₃ nanoparticles without alkali and their effective photocatalytic activity. *J. Adv. Ceram.*, 5, 298–307, 2016.
42. Chakraborty, A.K., Qi, Z., Chai, S.Y., Lee, C., Park, S.Y., Jang, D.J., *et al.*, Formation of highly crystallized TiO₂(B) and its photocatalytic behavior. *Appl. Catal. B Environ.*, 93, 368–375, 2010.
43. Chen, Z., Dinh, H.N., Miller, E., *Photoelectrochemical Water Splitting*, 2013.
44. Llorca, J., Orera, V.M., Directionally solidified eutectic ceramic oxides. *Prog. Mater. Sci.*, 51, 711–809, 2006.
45. Pawlak, D.A., Lerondel, G., Dmytruk, I., Kagamitani, Y., Durbin, S., Royer, P., *et al.*, Second order self-organized pattern of terbium-scandium-aluminum garnet and terbium-scandium perovskite eutectic. *J. Appl. Phys.*, 91, 9731–9736, 2002.
46. Merino, R.I., Pena, J.I., Larrea, A., de la Fuente, G.F., Orera, V.M., Melt grown composite ceramics obtained by directional solidification: structural and functional applications. *Recent Res. Dev. Mater. Sci.*, 4, 1–24, 2003.
47. Kulkarni, A.A., Kohanek, J., Tyler, K.I., Hanson, E., Kim, D.-U., Thornton, K., *et al.*, Template-directed solidification of eutectic optical materials. *Adv. Opt. Mater.*, 1800071, 1–20, 2018.
48. Pawlak, D.A., Kolodziejak, K., Turczynski, S., Kisielewski, J., Rożniatowski, K., Diduszko, R., *et al.*, Self-organized, rodlike, micrometer-scale microstructure of Tb₃Sc₂Al₃O₁₂–TbScO₃:Pr Eutectic. *Chem. Mater.*, 18, 2450–2457, 2006.
49. Pawlak, D.A., Turczynski, S., Gajc, M., Kolodziejak, K., Diduszko, R., Rożniatowski, K., *et al.*, How far are we from making metamaterials by self-organization? The microstructure of highly anisotropic particles with an SRR-like geometry. *Adv. Funct. Mater.*, 20, 1116–1124.
50. Sadecka, K., Toudert, J., Surma, H.B., Pawlak, D.A., Temperature and atmosphere tunability of the nanoplasmonic resonance of a volumetric eutectic-based Bi₂O₃–Ag metamaterial. *Opt. Express.*, 23, 19098, 2015.
51. Sadecka, K., Gajc, M., Orlinski, K., Surma, H.B., Klos, A., Jozwik-Biala, I., *et al.*, When eutectics meet plasmonics: Nanoplasmonic, volumetric, self-organized, silver-based eutectic. *Adv. Opt. Mater.*, 3, 381–389, 2015.
52. Deska, R., Sadecka, K., Olesiak-Bañska, J., Matczyszyn, K., Pawlak, D.A., Samoć, M., Nonlinear plasmonics in eutectic composites: Second harmonic generation and two-photon luminescence in a volumetric Bi₂O₃–Ag metamaterial. *Appl. Phys. Lett.*, 110, 031102, 2017.

53. Laguna-Bercero, M.A., Larrea, A., Peña, J.I., Merino, R.I., Orera, V.M., Structured porous Ni- and Co-YSZ cermets fabricated from directionally solidified eutectic composites. *J. Eur. Ceram. Soc.*, 25, 1455–1462, 2005.
54. Laguna-Bercero, M.A., Larrea, Á., Merino, R.I., Peña, J.I., Orera, V.M., Stability of channeled Ni-YSZ cermets produced from self-assembled NiO-YSZ directionally solidified eutectics. *J. Am. Ceram. Soc.*, 88, 3215–3217, 2005.
55. Oliete, P.B., Orera, A., Sanjuán, M.L., Merino, R.I., Selective thermal emission of directionally solidified $\text{Al}_2\text{O}_3/\text{Y}_3-\text{xEr}_x\text{Al}_5\text{O}_{12}$ eutectics: Influence of the microstructure, temperature and erbium content. *Sol. Energy Mater. Sol. Cells.*, 174, 460–468, 2018.
56. Feng, J., Luo, W., Fang, T., Lv, H., Wang, Z., Gao, J., *et al.*, Highly photo-responsive LaTiO_2N photoanodes by improvement of charge carrier transport among film particles. *Adv. Funct. Mater.*, 24, 3535–3542, 2014.
57. Pinaud, B.A., Vesborg, P.C.K., Jaramillo, T.F., Effect of film morphology and thickness on charge transport in $\text{Ta}_3\text{N}_5/\text{Ta}$ photoanodes for solar water splitting. *J. Phys. Chem. C*, 116, 15918–15924, 2012.
58. Peña, J.I., Larsson, M., Merino, R.I., de Francisco, I., Orera, V.M., Lorca, J.L., *et al.*, Processing, microstructure and mechanical properties of directionally-solidified $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}\text{-ZrO}_2$ ternary eutectics. *J. Eur. Ceram. Soc.*, 26, 3113–3121, 2006.
59. Chen, W.T., Meredith, C.H., Dickey, E.C., Growth and Microstructure-dependent hardness of directionally solidified WC-W2C eutectoid ceramics. *J. Am. Ceram. Soc.*, 98, 2191–2196, 2015.
60. Polotai, A.V., Foreman, J.F., Dickey, E.C., Meinert, K., Laser surface processing of $\text{B}_4\text{C-TiB}_2$ eutectic. *Int. J. Appl. Ceram. Technol.*, 5, 610–617, 2008.
61. Fittipaldi, R., Vecchione, A., Fusanobori, S., Takizawa, K., Yaguchi, H., Hooper, J., *et al.*, Crystal growth of the new $\text{Sr}_2\text{RuO}_4\text{-Sr}_3\text{Ru}_2\text{O}_7$ eutectic system by a floating-zone method. *J. Cryst. Growth.*, 282, 152–159, 2005.
62. Kim, J., Aagesen, L.K., Choi, J.H., Choi, J., Kim, H.S., Liu, J., *et al.*, Template-directed directionally solidified 3D mesostructured AgCl-KCl eutectic photonic crystals. *Adv. Mater.*, 27, 4551–4559, 2015.
63. Boley, J.W., Chaudhary, K., Ober, T.J., Khorasaninejad, M., Chen, W.T., Hanson, E., *et al.*, High-operating-temperature direct ink writing of meso-scale eutectic architectures. *Adv. Mater.*, 29, 1–8, 2017.
64. Yoon, D.H., Yonenaga, I., Fukuda, T., Ohnishi, N. Crystal growth of dislocation-free LiNbO_3 single crystals by micro pulling down method. *J. Cryst. Growth*, 142, 339–343, 1994.
65. Yoon, D.-H., Fukuda, T., Characterization of LiNbO_3 micro single crystals grown by the micro-pulling-down method. *J. Cryst. Growth*, 144, 201–206, 1994.
66. Kolodziejek, K., Gajc, M., Sar, J., Diduszko, R., Rozniatowski, K., Pawlak, D.A., Synthesis and structural study of a self-organized $\text{MnTiO}_3\text{-TiO}_2$ eutectic. *J. Alloys Compd.*, 659, 152–158, 2016.

67. Gajc, M., Surma, H.B., Klos, A., Sadecka, K., Orlinski, K., Nikolaenko, A.E., *et al.*, Nanoparticle direct doping: Novel method for manufacturing three-dimensional bulk plasmonic nanocomposites. *Adv. Funct. Mater.*, 23, 3443–3451, 2013.
68. Yamaji, A., Kurosawa, S., Ohashi, Y., Yokota, Y., Kamada, K., Yoshikawa, A., Crystal growth and optical properties of organic crystals for neutron scintillators. *Plasma Fusion Res.*, 13, 1–4, 2018.
69. Raczekiewicz, M., Klos, A., Osewski, P., Gajc, M., Pawlak, D.A., Utilizing the micro-pulling down method as a manufacturing method of organic crystals, on the example of vanillin (MHBA), Poster session on DSEC V Conference in Warsaw, Poland, 3–7 April 2016, (n.d.).
70. Bienkowski, K., Turczynski, S., Diduszko, R., Gajc, M., Gorecka, E., Pawlak, D.A., Growth of a plate-shaped SrTiO_3 - TiO_2 eutectic. *Cryst. Growth Des.*, 11, 3935–3940, 2011.
71. Chang, L.L.Y., Scroger, M.G., Phillips, B., High-temperature, condensed-phase equilibria in the system Ti-W-O. *J. Less Common Met.*, 12, 51–56, 1967.
72. Roy, R., Pennsylvania State University, University Park, Pennsylvania, 1957.
73. Scanlon, D.O., Dunnill, C.W., Buckeridge, J., Shevlin, S.A., Logsdail, A.J., Woodley, S.M., *et al.*, Band alignment of rutile and anatase TiO_2 . *Nat. Mater.*, 12, 798–801, 2013.
74. Khare, C., Sliozberg, K., Meyer, R., Savan, A., Schuhmann, W., Ludwig, A., Layered WO_3/TiO_2 nanostructures with enhanced photocurrent densities. *Int. J. Hydrogen Energy*, 38, 15954–15964, 2013.
75. Shang, Q. Yu, T., Tan, X., Zhang, Z., Zou, Y., Zhang, L., *et al.*, Enhanced photoelectrochemical performance of $\{001\}\text{TiO}_2/\{001\}\text{SrTiO}_3$ epitaxial heterostructures. *J. Solid State Electrochem.*, 20, 123–132, 2016.
76. Park, S., Kim, S., Kim, H.J., Lee, C.W., Song, H.J., Seo, S.W., *et al.*, Hierarchical assembly of TiO_2 - SrTiO_3 heterostructures on conductive SnO_2 backbone nanobelts for enhanced photoelectrochemical and photocatalytic performance. *J. Hazard. Mater.*, 275, 10–18, 2014.
77. Elisa, M.A., Abadir, M.F., Gandalla, A.M., The system TiO_2 -PbO in air. *Trans. Br. Ceram. Soc.*, 79, 100–104, 1980.
78. Zelezny, V., Chvostova, D., Simek, D., Maca, F., Masek, J., Setter, N., *et al.*, The variation of PbTiO_3 bandgap at ferroelectric phase transition. *J. Phys. Condens. Matter.*, 28, 1–8, 2016.
79. Thangaraju, B., Kaliannan, P., Optical and structural studies on spray deposited α -PbO thin films. *Semicond. Sci. Technol.*, 15, 542–545.
80. Chen, K., Wang, C., Lee, Y., Liu, H., Physicochemical and engineering aspects nanoplates and nanostars of B-PbO formed at the air/water interface. *Colloids Surf. A Physicochem. Eng. Asp.*, 373, 124–129, 2011.
81. Levin, E.M., Roth, R.S., Polymorphism of bismuth sesquioxide. II. Effect of oxide additions on the polymorphism of Bi_2O_3 . *J. Res. Natl. Bur. Stand. - A. Phys. Chem.*, 68, 197–206.

82. Yao, W.F., Wang, H., Xu, X.H., Cheng, X.F., Huang, J., Shang, S.X., *et al.*, Photocatalytic property of bismuth titanate Bi_2TiO_5 crystals. *Appl. Catalysis A Gen.*, 243, 185–190, 2013.
83. Eriksson, G., Pelton, A.D., Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the MnO-TiO_2 , MgO-TiO_2 , FeO-TiO_2 , $\text{Ti}_2\text{O}_3\text{-TiO}_2$, $\text{Na}_2\text{O-TiO}_2$, and $\text{K}_2\text{O-TiO}_2$ systems. *Metall. Trans. B.*, 24B, 795–805, 1993.
84. Gao, B., Kim, Y.J., Chakraborty, A.K., Lee, W.I., Efficient decomposition of organic compounds with $\text{FeTiO}_3/\text{TiO}_2$ heterojunction under visible light irradiation. *Appl. Catal. B Environ. Environ.*, 83, 202–207, 2008.
85. Morosin, B., Baughmn, R.J., Ginley, D.S., Butler, M.A., The influence of crystal structure on the photoresponse of iron-titanium oxide electrodes. *J. Appl. Crystallogr.*, 11, 121–124, 1978.
86. Najjar, M.S., Muan, A., Stable solid phases involving $\text{V}_2\text{O}_5\text{-TiO}_2$ and mixtures of said phases, US Pat. 5, 049,537, 1991.
87. Su, J., Zou, X.-X., Li, G.-D., Wei, X., Yan, C., Wang, Y.-N., *et al.*, Macroporous $\text{V}_2\text{O}_5\text{-BiVO}_4$ composites: Effect of heterojunction on the behavior of photo-generated charges. *J. Phys. Chem. C.*, 115, 8064–8071, 2011.
88. Woermann, E., Brezny, B., Muan, A., Magnesium-oxygen-titanium ternary alloy phase diagram. *Am. J. Sci.*, 267A, 463–479, 1969.
89. Qu, Y., Zhou, W., Xie, Y., Jiang, L., Wang, J., Tian, G., *et al.*, A novel phase-mixed $\text{MgTiO}_3\text{-MgTi}_2\text{O}_5$ heterogeneous nanorod for high efficiency photocatalytic hydrogen production. *Chem. Commun.*, 49, 8510–8512, 2013.
90. O'Bryan, H.M., Thomson, J., $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase equilibria. *J. Am. Ceram. Soc.*, 66, 66–68, 1983.
91. Babich, T.G., Zagorodnyuk, A.V., Teterin, G.A., Khodos, M.Y., Zhirnova, A.P., (No title available). *Zhurnal Neorg. Khimii.*, 33, 996–999, 1988.
92. Yu, H., Lan, H., Yan, L., Qian, S., Cheng, X., Zhu, H., *et al.*, TiNb_2O_7 hollow nanofiber anode with superior electrochemical performance in rechargeable lithium ion batteries. *Nano Energy*, 38, 109–117, 2017.
93. Wang, F., Di Valentin, C., Pacchioni, G., Doping of WO_3 for photocatalytic water splitting: Hints from density functional theory. *J. Phys. Chem. C.*, 116, 8901–8909, 2012.
94. Zou, F., Jiang, Z., Qin, X., Zhao, Y., Jiang, L., Zhi, J., Template-free synthesis of mesoporous N-doped SrTiO_3 perovskite with high visible-light-driven photocatalytic activity. *Chem. Commun.*, 48, 8514–8516, 2012.
95. Yin, J., Ye, J., Zou, Z., Enhanced photoelectrolysis of water with photoanode Nb:SrTiO_3 . *Appl. Phys. Lett.*, 85, 689–691, 2004.
96. Li, X., Guo, Z., He, T., The doping mechanism of Cr into TiO_2 and its influence on the photocatalytic performance. *Phys. Chem. Chem. Phys.*, 15, 20037–20045, 2013.
97. Cui, R., Jiang, Z., Yao, Z., Influence of Cu^{2+} doping on the photocatalytic activity of TiO_2 film. *Key Eng. Mater.*, 372, 1483–1485, 2008.

98. Zuo, H., Sun, J., Den, K., Su, R., Wei, F., Wang, D., Preparation and characterization of Bi³⁺-TiO₂ and its photocatalytic activity. *Chem. Eng. Technol.*, 25, 577–582, 2007.
99. Khan, M., Song, Y., Chen, N., Cao, W., Effect of V doping concentration on the electronic structure, optical and photocatalytic properties of nano-sized V-doped anatase TiO₂. *Mater. Chem. Phys.*, 142, 148–153, 2013.
100. Wang, X.H., Li, J., Kamiyama, H., Katada, M., Ohashi, N., Moriyoshi, Y., *et al.*, Pyrogenic iron(III)-doped TiO₂ nanopowders synthesized in RF thermal plasma: Phase formation, defect structure, band gap, and magnetic properties. *J. Am. Chem. Soc.*, 127, 10982–10990, 2005.
101. Fu, Y., Dong, C., Zhou, Z., Lee, W., Chen, J., Guo, P., *et al.*, Solution growth of Ta-doped hematite nanorods for efficient photoelectrochemical water splitting: a tradeoff between electronic structure and nanostructure evolution. *Phys. Chem. Chem. Phys.*, 17, 3846–53, 2016.
102. Su, J., Wang, J., Liu, C., Feng, B., Chen, Y., Guo, L., On the role of metal atom doping in hematite for improved photoelectrochemical properties: a comparison study. *RSC Adv.*, 6, 101745–101751, 2016.
103. Zhang, T., Zhu, Z., Chen, H., Bai, Y., Xiao, S., Zheng, X., *et al.*, Iron-doping-enhanced photoelectrochemical water splitting performance of nanostructured WO₃: a combined experimental and theoretical study. *Nanoscale*, 7, 2933–2940, 2014.
104. Liew, S.L., Zhang, Z., Goh, T.W.G., Subramanian, G.S., Seng, H.L.D., Hor, T.S.A., *et al.*, Yb-doped WO₃ photocatalysts for water oxidation with visible light. *Int. J. Hydrogen Energy*, 39, 4291–4298, 2014.
105. Liu, Y., Li, J., Li, W., Yang, Y., Li, Y., Chen, Q., Enhancement of the photoelectrochemical performance of WO₃ vertical arrays film for solar water splitting by Gadolinium doping. *J. Phys. Chem. C.*, 119, 14834–14842, 2015.
106. Luo, W., Wang, J., Zhao, X., Zhao, Z., Li, Z., Zou, Z., Formation energy and photoelectrochemical properties of BiVO₄ after doping at Bi³⁺ or V⁵⁺ sites with higher valence metal ions. *Phys. Chem. Chem. Phys.*, 15, 1006–1013, 2013.
107. Macdonald, D.D., The point defect model for the passive state. *J. Electrochem. Soc.*, 139, 3434–3449, 1992.
108. Lewis, N.S., Crabtree, G., Nozik, A.J., Wasielewski, M.R., Alivisatos, P., Basic research needs for solar energy utilization, 2005. http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf.
109. Klos, A., Lobodzinski, W., Pawlak, D.A., Stefanski, A., Osewski, P., A method of manufacturing thin layers of eutectic composites, 2015.

Part III

PHOTOELECTROCHEMICAL RELATED SYSTEMS

Implementation of Multijunction Solar Cells in Integrated Devices for the Generation of Solar Fuels

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Abstract

A promising approach to produce hydrogen and other value-added fuels is the use of photo-electrocatalytic cells for the direct conversion of water and/or CO₂ using solar energy. In the present contribution the applications of multijunction solar cells in photoelectrochemical devices for hydrogen production are addressed. Integrated PEC devices are composed of a 'traditional' photovoltaics (PV) cell combined with an electrochemical (EC) cell, allowing to produce chemical fuels as reaction products only by using sunlight energy. The requirements for PEC devices and strategies for photoelectrode development are discussed, including fundamental considerations for bias-free water splitting. An overview of several successful concepts reported in recent years is presented. The results on the photovoltaic development of multijunction silicon based photoelectrodes are overviewed, focusing on a wide range of photovoltages and photocurrents in various systems. Prototype integrated PEC systems based of multijunction solar cells are presented, including employed catalytic materials, stability, and performance, i.e. the solar to hydrogen efficiency (STH) range of these state of the art devices.

The paths of device upscaling beyond laboratory size and the influence of varied illumination conditions close to those obtained outdoor are also addressed. This includes the effects of spectral quality and intensity on the performance of both

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photoelectrodes and PEC devices. Finally, pathways towards the application of multijunction based photoelectrodes for CO_2 conversion will be briefly outlined.

Keywords: Si solar cells, multijunction solar cells, integrated PV-EC devices, water splitting, solar fuels

9.1 Introduction

The size of fossil fuel reserves is not sufficient to cover the energy demand of our societies in the future, even if the energy utilization would stagnate on today's level [1, 2]. Additionally, the associated emission of the greenhouse gas CO_2 can lead to unpredictable climate changes on earth. Nature's own processes of fuel generation based on biomass utilization are considered to be not efficient to replenish the used resources on a short time scale.

Artificial photosynthesis utilizing semiconductor materials in a liquid environment to realize a water splitting process may be viewed as the "holy grail" of photoelectrochemistry since the first experiments reported in 1972 by Fujishima and Honda [3]. They used an n- TiO_2 photoanode irradiated with ultraviolet (UV) light to split water into hydrogen and oxygen but with inherent practical shortcomings: TiO_2 only absorbs light in the ultraviolet region, which is only a minor part of the solar spectrum. In addition, the energy bands are not in the right positions to split water directly, and the obtained quantum efficiency of about 0.1% is very low. These parameters remain critical for a technical device, which is envisaged as an inorganic leaf producing hydrogen on one and oxygen on the other side when submerged in water and irradiated by sunlight [4].

Since 1972, intensive research on photoelectrochemical H_2O splitting has started and several other more or less efficient devices for water splitting have been presented, but they also serve mainly as a proof of principle, because of different shortcomings in their design: Heller and Vadimsky presented in 1981 an electric efficiency of 12% for hydrogen generation based on p-InP photoelectrode covered with Pt metal islands, but the material was not very stable in contact with the electrolyte and it did not deliver enough voltage to drive the bias-free water splitting process; an additional bias voltage had to be supplied [5]. Recently, p-InP materials and their applications in the water splitting have been evaluated in detail by Lewerenz *et al.* [6] A device with ability to provide more than 1.3 V, which is needed for the water splitting process, and demonstrating an efficiency of 12.4% was shown by Khaselev and Turner in 1998 [7]. The device was based on p-GaInP photocathode supported by a GaAs solar cell to generate the necessary total photovoltage, but it suffers also from stability

problems and high production costs. Nevertheless, it showed the possibility of employing a tandem cell arrangement to overcome the single small band gap semiconductor limitation on photovoltage. Such a system would allow to achieve higher both theoretical and practical conversion efficiencies [8]. A tandem device based on AlGaAs and Si cells was presented by Licht *et al.* in 2000, [9] where an efficiency of 18.3% was demonstrated at a photopotential of 1.36 V. A triple-junction solar cell based on thin film silicon was presented by Reece *et al.* in 2011, reaching an efficiency for H_2 generation between 2.5% and 4.7% [10]. But even for this case, the estimated costs per kg hydrogen were still considerable despite using cheap thin-film solar cells and the long-term stability was not sufficient.

All the examples noted above demonstrate the general applicability of the concept of photoelectrochemical water splitting, but in many cases the devices do not deliver the required voltage for water splitting and are usually not economically competitive to standard processes for hydrogen production from natural gas. Therefore, the challenge is to identify specifically adjusted materials or material combinations, which demonstrate appropriate stability in an electrochemical environment, are efficient for the water splitting process, and are inexpensive and available in sufficient quantities to realize simple device configurations at low costs.

In this contribution, we will present our consideration and approach to the multijunction structures, as exemplarily shown in Figure 9.1, as efficient bias-free photoelectrochemical cell. Previous experiments seem to indicate that single absorber devices either do not generate enough voltage to drive the water splitting reaction on its own or that the band gap is by far too large to obtain reasonable solar conversion efficiencies due to the low intensity of the solar radiation in this wavelength regime. Tandem or multiple junction cells, as schematically shown in Figure 9.1 and representing the approach, offer here decisive advantages: First, they can absorb different wavelengths in the high-intensity part of the solar spectrum, and second, they are able to deliver a larger working voltage [11–15]. Therefore, the theoretical efficiency limit is much higher than for single absorber structures. Multijunction cells made from silicon and its alloys fulfill, additionally, the above stated requirements, because the material itself is abundant, they can be manufactured as thin-film devices with reduced material costs, they may provide a high stability, and last but not least silicon-based photovoltaics and electronics is a proven technology nowadays.

The integrated photovoltaic-biased electrolysis device, schematically illustrated in Figure 9.1, can offer the advantage that the voltage and the current generated by the photovoltaic device under illumination are available for the electrolysis independent of the energy band positions at

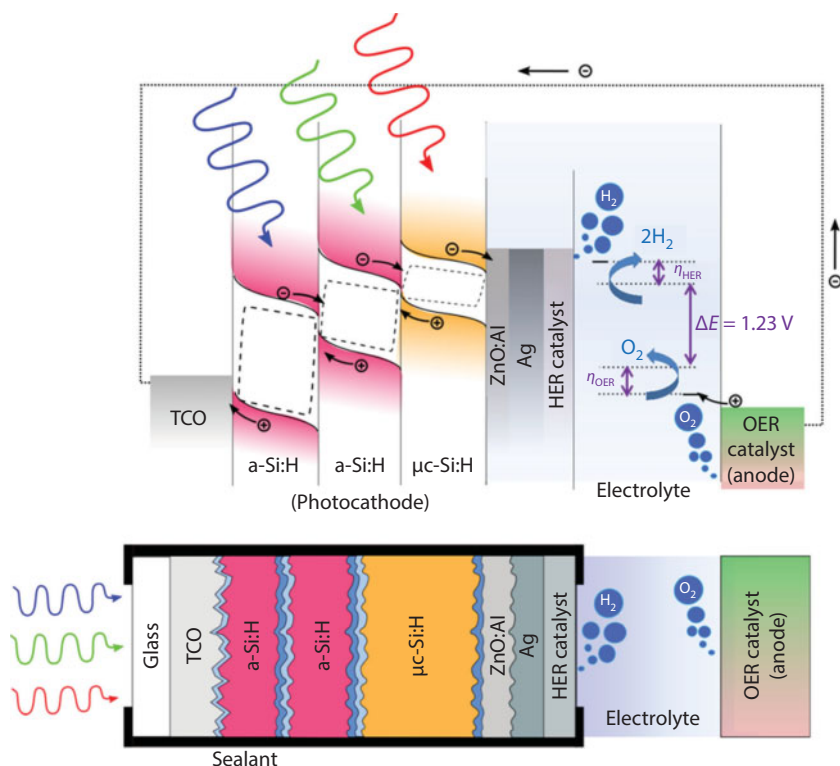


Figure 9.1 Band diagram illustration of a multijunction photovoltaic cells made from thin-film silicon for photoelectrochemical water splitting with its main parts (adapted from Ref. (16)): the multijunction photocathode (a-Si:H/a-Si:H/ μ c-Si:H shown as an example) under bias-free illumination condition, an HER catalyst layer at the photocathode/electrolyte interface, the electrolyte, and the anode with the OER catalyst. The energy levels for the HER and OER and the corresponding reactions are shown. Hydrogen evolution occurs at the rear side of the photocathode and oxygen occurs at the anode side. $\Delta E = 1.23$ V is the thermodynamic potential required for water electrolysis at 25 °C. η_{HER} and η_{OER} indicate the overpotentials for the HER and OER, respectively.

the solid/liquid interface. Opposite to the case of photovoltaic-assisted photocatalysis, [17] the photovoltaic and the catalyst materials could be developed independently. Therefore, the photovoltaic part and the electrochemical part of the entire device, for example the catalyst materials for the H_2 (HER) and the O_2 evolution reaction (OER), respectively, can be tuned and integrated in a flexible manner. Note that the device configuration shown in Figure 9.1 has also an advantage that the incident illumination directly enters the photovoltaic device and is not attenuated by the surrounding electrolyte medium, by catalyst materials or gas bubbles.

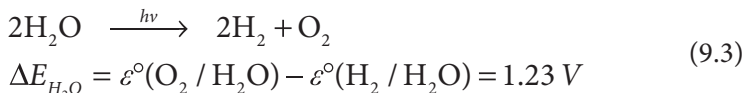
Nevertheless, the chemical durability aspects should be considered, as the photovoltaic cell should avoid the direct contact with the electrolyte. This can be realized using protective oxide and metal layers [18].

The exploration of multijunction photovoltaic cells made from silicon for photoelectrochemical water splitting has been around for almost 20 years now [19–27]. They can be used in a wired or wireless (artificial leaf) arrangement and are comprised in most cases by two or more active thin-film silicon (a-Si:H, $\mu\text{c-Si:H}$) or silicon alloy layers [28–33]. The solar to hydrogen conversion efficiencies are reported of being just a few to nearly 10%.

For absorption of the incident photons, semiconductor structures are preferably used as they can provide optimal results for broadband charge carrier generation. In order to provide the photovoltage required for water splitting reaction, wide bandgap compound semiconductor structures or low bandgap multijunction structures should be considered. Overall, the photovoltaic converter system must provide a difference in the chemical potentials of electrons and holes $D\mu_{e-h}^*$ for nonequilibrium conditions under illumination, equivalent to the usable (operative) photovoltage U_{ph}^{op} of the converter, of more than 1.5 V, which corresponds to an open-circuit photovoltage of about U_{ph}^{oc} of 1.7–1.9 V, as will be discussed in more detail below. As additional condition for high conversion efficiencies, the quantum efficiencies of the absorbed photons should approach 1, which means that every absorbed photon should produce one light-induced extra electron–hole pair, which must be effectively separated from each other leading to a maximized operational photocurrent j_{ph}^{op} . The value of U_{ph} delivered by the PV converter for light-induced water splitting without adding an additional artificial bias must exceed the difference of the electrochemical potentials of the reductive and oxidative water splitting reactions with adapted overpotential values, providing appropriate exchange currents and minimizing resistive losses in the circuit $j_{ph} \times R$. This will define a minimum operational photovoltage U_{ph}^{op} , which must be provided by the converter in the working photoelectrochemical device. Note that in the case of photovoltaic cells generating power output, there is no lower limit of U_{ph} . It is thus evident that the majority of the prominent photovoltaic devices having bandgaps below 1.5 eV do not provide the photovoltage needed for H_2O splitting.

In the water splitting process, multiple electrons have to be transferred. The hydrogen evolution reaction (HER) consumes four electrons in order to form two molecules of H_2 . These four electrons are produced in the oxygen evolution reaction (OER), where two molecules of H_2O yield one molecule of O_2 , four protons as well as four electrons. Therefore the overall process involves the transfer of four (or two) electrons, respectively, to split

two (or one) molecules of water. The potentials needed for the water splitting reaction in acidic media are given as follows:



Since the reaction contains H^+ (OH^-), the pH takes part in the equilibrium and leads to a negative shift of the redox potentials given at $\text{pH} = 0$ ($1 \text{ N } [\text{H}^+]$) according to 59 mV per pH. Considering the alignment of the band edge positions to the OER/HER half cells redox potentials, the shift caused by the pH has to be included. If the surface is oxidic, the pH shift of 59 mV/pH may also have an effect on the band edge position of the semiconductor. However, a reduced shift (or no shift) of band edges is expected for less ionic or more covalent semiconductors. Additionally, the shift of the band edges due to the trapping of charge carriers during illumination could be expected [34–37].

The photovoltaic device under illumination must provide the total sufficient voltage required to drive the reaction:

$$U_{ph}^{op} > \Delta E^{op} = \Delta E_{\text{H}_2\text{O}} + \eta_c + \eta_a + i_{ph} \cdot R \quad (9.4)$$

The operational photovoltage must be above the values of thermodynamic potential of the water splitting reaction $\Delta E_{\text{H}_2\text{O}}$ 1.23 V. Additionally, potential losses related to sufficient photocurrents should be taken into account, which are at first the gradients of the electrochemical potentials of electrons and holes $\Delta_n E_F^*$ and $\Delta_p E_F^*$ to drive the charge carrier separation, this value can be approximated by $U_{ph}^{oc} - U_{mpp}$. To be added are the overvoltages η_c and η_a for the HER and OER, respectively, needed for the provided current densities (approximated as 0.05 and 0.3 V, respectively, for typical PV current densities of 20 mA/cm²). And finally the Ohmic losses in the circuit $i_{ph} \cdot R$, e.g., the resistance of the electrolyte solution between cathode and anode to carry the photocurrent i_{ph} must be made as small as possible. Thus the photovoltaic converter must provide an operational photovoltage U_{ph}^{op} of at least 1.6 V assuming optimistic values for the values on the right-hand side of equation (9.4) ($1.2 + 0.05 + 0.3 + 0.05 \text{ V}$). The photovoltage of the PV converter at the MPP in relation to the thermodynamic H_2O splitting

potential multiplied with the achieved photocurrent at this point provides a realistic upper value for an estimate of the H_2 (STH) conversion efficiency:

$$\eta_{STH} = \Delta E_{H_2O} \cdot \frac{j_{ph}}{P_{hv}} < U_{ph}^{op} \cdot \frac{j_{ph}}{P_{hv}} \quad \text{with } U_{ph}^{op} > \Delta E_{H_2O} = 1.23 \text{ V} \quad (9.5)$$

These results indicate that for highly efficient photoelectrochemical H_2O splitting devices the PV converter's U_{MPP} must be larger, but as close as possible to ΔE^{op} (see eq. (9.4)). If the photovoltage $U_{MPP} = U_{ph}^{op}$ produced by the PV converter is much larger compared to the difference ΔE_{H_2O} of the reversible half-cell reaction potentials of $\varepsilon^\circ(H_2O/O_2) - \varepsilon^\circ(H_2/H_2O)$, any kinetic limitations of the water splitting reactions may be avoided. But this extra potential is translated directly into an energy transformation loss as the thermodynamic potential difference $\Delta E_{H_2O} = \varepsilon^\circ(H_2O/O_2) - \varepsilon^\circ(H_2/H_2O)$ of 1.23 V is equivalent to the energy stored in the H_2 formation (fuel production). A larger operational photovoltage applied to the EC converter system leads to a reduced η_{STH} . This behavior is different to an electric power producing PV converter, where both i_{ph} and U_{ph} can be used to increase the performance value.

9.2 Multijunction Solar Cells as Photoelectrodes

Multijunction device architectures, such as tandem or triple structure, have been suggested as promising photovoltaic device structure for advanced thin-film solar cells, [38–45] which would also provide a good basis of an efficient photoelectrochemical structure. While the examples of applicable semiconductor materials with the bandgap around 2.3 eV and sufficient charge carrier mobilities were reported in the extensive literature, [46, 47] none has demonstrated the sufficient photovoltages (close to 1.9 V), which would be needed for efficient water splitting process. As an alternative configuration of the device, the combination of two or more different absorber materials with different bandgaps may be considered, which will absorb different parts of the incident spectrum. Such tandem (multiple junction cell) structures may be arranged in the form of classical semiconductor tandem solar cells as shown in Figure 9.1. Considering tandem device architectures, including also triple or quadruple arrangements, [30, 48–52] would have the advantage that the given photovoltage will be the sum of the several coupled photovoltaic subcells. The photovoltages of the system would thus add up to the operating photovoltage for H_2O splitting. Like photovoltaic tandem solar

cells, such devices are able to provide higher conversion efficiencies with the further advantage for photoelectrolysis devices, as discussed here, that also narrow bandgap semiconductors can be used to deliver part of the needed potential difference of electrons and holes for the water splitting reaction under illumination. To achieve high overall photocurrents, the two (three, four) separate photovoltaic subcells must be matched to each other, [39–41] since the subcell with the lowest photocurrent determines the overall current through the entire device. These conditions are also true for all other arrangements in which, e.g., two photoelectrochemical cells are directly combined as photoanode and photocathode in the water splitting device. It is therefore not reasonable, for example, to couple in series-connection PV converters with high photocurrents to low photocurrent PEC converters. In general, all the arguments given for the single absorber solar cell are also true for the multijunction cell. The photovoltaic part of the system must be optimized in a comparable manner independent of a possible application as electricity-producing photovoltaic cell or fuel-producing photoelectrochemical cell. This simplifies to the fact that only good PV tandem arrangements will provide competitive PEC tandem arrangements. It should also be noted that an appropriate interface engineering of the active semiconductor junction in contact to the electrolyte may be needed in the development of the water splitting devices. Broadly similar to the functionality of passivation layers in the photovoltaic devices, [53] an electronic passivation layer [18] may shift the detrimental states out of the bandgap region by chemical bond formation. A proper adjustment of energy levels across the junction during the photoelectrochemical HER or OER reactions should be taken into account for achieving high conversion efficiencies.

As already discussed above, the photovoltage needed for bias-free water splitting varies with the used catalysts. The photocurrent at the respective required operation voltage U_{ph}^{op} determines the solar-to-hydrogen device efficiency (see eq. (9.5)). It is therefore important to develop photovoltaic structures, which provide a wide voltage (U_{ph}^{oc} and U_{MPP}) range together with high photocurrents. The high photovoltage/high photocurrent combination can be achieved by utilizing multijunction solar cells made of thin-film amorphous (a-Si:H) and microcrystalline (μ c-Si:H) silicon. Implementation of a-Si:H and μ c-Si:H absorber materials allows for a more accurate tuning of the photovoltaic parameters and, additionally, results in an improved stability against degradation under prolonged illumination, known as Staebler-Wronski effect [54–56], as compared to amorphous silicon-based structures. In the following sections of our contribution, first the results on the photovoltaic development of single and multijunction solar cells are presented. The applicability of the multijunction solar cells as photocathodes in an integrated PV-EC device is presented with Pt and Ni

catalyst layers, respectively, on top of the solar cells for the HER and a RuO_2 counterelectrode for the OER. Additionally, the relevant aspects of the integrated photovoltaic-electrochemical device performance, such as catalysis, electrochemical stability, and electrolyte influence, will be addressed.

In order to close the high photovoltage/high photocurrent gap, particularly present in thin-film silicon solar cells, it is relevant to have a possibility to increase the open-circuit voltage (U_{ph}^{oc}) without notably impairing the short-circuit current (i_{ph}^{sc}), and therefore, the overall efficiency of the devices. In the case of single-junction solar cells ($\mu\text{c-Si:H}$ and a-Si:H), it is possible to tune the U_{ph}^{oc} by adjusting the electronic and material properties of the absorber layers. For example, the improvement of the U_{ph}^{oc} could be achieved by the several routes[49, 57, 58]: (i) variation in the absorber layer thickness (intrinsic $\mu\text{c-Si:H}$), (ii) control of layer crystallinity by adjusting the SiH_4 flow during deposition of the intrinsic $\mu\text{c-Si:H}$ absorber layer, and (iii) incorporation of thin amorphous silicon buffer layer at the n-i interface of the $\mu\text{c-Si:H}$ solar cell. This leads to the improvement of U_{ph}^{oc} in the single junction solar cells utilizing $\mu\text{c-Si:H}$ absorber layers. Figure 9.2(a) shows the U_{ph}^{oc} measured in $\mu\text{c-Si:H}$ solar cell as a function of the crystallinity of the $\mu\text{c-Si:H}$ absorber layers for the range of absorber layer thickness. By reducing the thickness of the $\mu\text{c-Si:H}$ absorber layer, the general trend indicates that U_{ph}^{oc} can be increased for a given crystallinity, as shown in Figure 9.2(a). Overall, the results indicate that thinner absorber layers tend to increase the U_{ph}^{oc} values, especially in the moderate crystallinity range, indicating the tunability of the U_{ph}^{oc} in $\mu\text{c-Si:H}$ cells by around 100 mV up to a maximum value of 600 mV. The optimization of the a-Si:H single-junction solar cells can be conducted as a function of silane concentration and the substrate temperature during the deposition. In total, the U_{ph}^{oc} in a-Si:H single junction solar cells can be systematically tuned over approximately 150 mV by varying both parameters during the deposition of the intrinsic a-Si:H absorber layers. Both parameters influence the hydrogen content in the intrinsic material, which in turn influences the optical bandgap E_G [49, 59]. To elucidate the $U_{ph}^{oc}-E_G$ relationship, Figure 9.2(b) shows the U_{ph}^{oc} of the a-Si:H solar cells as a function of the E_G of the respective a-Si:H absorber layers. As one would expect, the U_{ph}^{oc} increases with the E_G of the absorber layer.

The open-circuit voltage (U_{ph}^{oc}) can also be tuned by alloying of the silicon absorber layer with, for example, O, C, and Ge. The bandgaps of a-SiOx:H , a-SiC:H , and a-SiGe:H materials can be adjusted in a flexible way, and the corresponding solar cells can reach high U_{ph}^{oc} values above 1 V [29, 60].

Solar cells utilizing the a-Si:H and $\mu\text{c-Si:H}$ absorber layers can be implemented in multijunction solar devices. It was shown that the U_{ph}^{oc} of these solar cells can be tuned in both large (600 mV) and small (50 mV) steps from 1.5 to 2.8 V in U_{ph}^{oc} and from 1.2 to 2.3 V in U_{MPP} without significantly

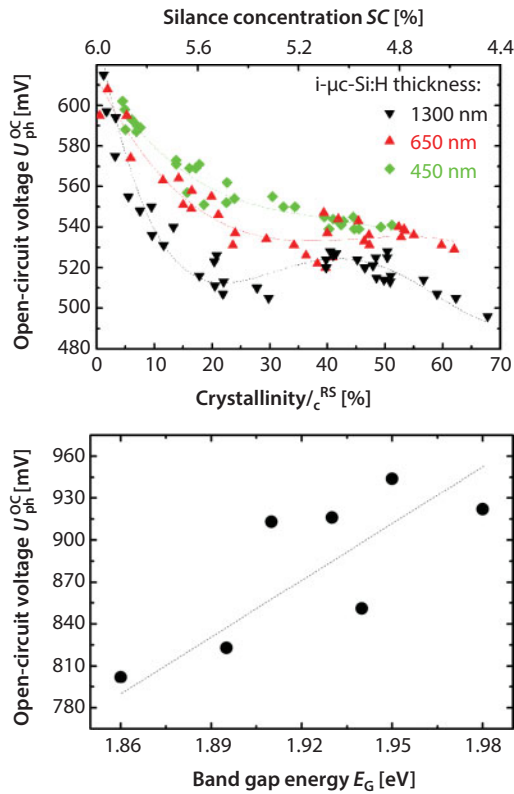


Figure 9.2 (a): Open-circuit voltage U_{ph}^{oc} of $\mu\text{c-Si:H}$ single-junction solar cells as a function of the crystallinity I_c^{RS} of the intrinsic $\mu\text{c-Si:H}$ absorber layers (arrow on the upper x-axis illustrates the corresponding trend for silane concentration SC). Absorber layer thicknesses of 1300 nm (pointing down triangles), 650 nm (pointing up triangles), and 450 nm (green diamonds) were investigated. The dashed lines serve as a guide to the eye. (b): Open-circuit voltage U_{ph}^{oc} of a-Si:H single-junction solar cells as a function of optical bandgap E_G of the respective intrinsic a-Si:H absorber layers. The dotted line serves as a guide to the eye (adapted from Ref. [16, 57]).

impairing the device efficiency. Figure 9.3 displays the achieved j_{ph}^{sc} as a function of U_{ph}^{oc} of the developed single- and multijunction solar cells. It nicely shows the $U_{ph}^{oc} - j_{ph}^{sc}$ tradeoff of thin-film silicon solar cells mentioned earlier. As a consequence, the development routes addressed above allow to tune the U_{ph}^{oc} of the photovoltaic cells over a wide range while keeping the device efficiency over 11 % for the multijunction solar cells. The high efficiency of 13.6% in combination with a high U_{ph}^{oc} of 2.3 V can be achieved with the triple-junction solar cells utilizing a-Si:H and $\mu\text{c-Si:H}$ absorber layers. In the case of quadruple-junction solar cells utilizing

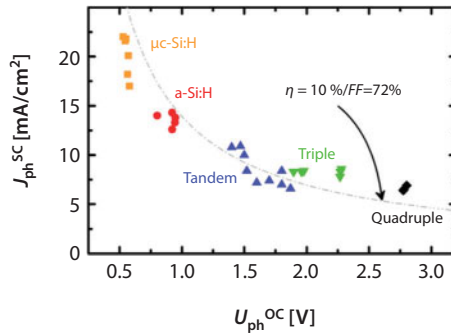


Figure 9.3 Open-circuit voltages U_{ph}^{oc} as a function of the short-circuit photocurrent densities j_{ph}^{sc} of the developed a-Si:H- and μc -Si:H-based single- and multijunction solar cells. The gray dotted line indicates a photovoltaic efficiency η_{pv} of 10 % assuming a FF of 72% (adapted from Refs. [16, 58]).

a-SiC:H, a-Si:H, a-SiGe:H, and μc -Si:H absorber layers, a high U_{ph}^{oc} of 3.0 V was reported [61]. Theoretical predictions for the quadruple-junction solar cells based on thin-film silicon layers yield 19.8% efficiency [62], indicating that multijunction thin-film silicon solar cells are attractive functional devices for photovoltaic and environmental applications.

In order to reach the high efficiencies in high-voltage cells discussed here, it is necessary to carefully adjust the individual subcell current densities in the device. It is important to “match” the photocurrent densities, i.e., to equally distribute the total current among the subcells in a multijunction solar cell in order to avoid current limitation. The matching in subcells with respect to the photocurrent could be achieved by integrating microcrystalline silicon oxide [38–42] as doped intermediate reflecting layers and by adjusting the thicknesses of the subcell absorber layers [57]. The current matching can be evaluated by means of quantum efficiency measurements. Exemplarily, Figure 9.4 shows the quantum efficiency measurement of a quadruple-junction solar cell. The subcell photocurrent densities were reasonably good distributed in the cell, as all subcells provide similar photocurrent densities [58].

The ability to vary the photovoltaic parameters over a wider range, as presented in Figure 9.3, is vital to fulfill the specific requirements of various PV-EC systems with different catalyst overpotential losses, i.e., when different voltage requirements are implied. To elucidate this further, figure illustrates the effect of overpotential losses on the solar-to-hydrogen (STH) efficiency of a PV-EC device based on the developed multijunction solar cells. The illuminated j - V curves of the tandem-, triple-, and quadruple-junction solar cells are plotted and linked to the theoretical operation

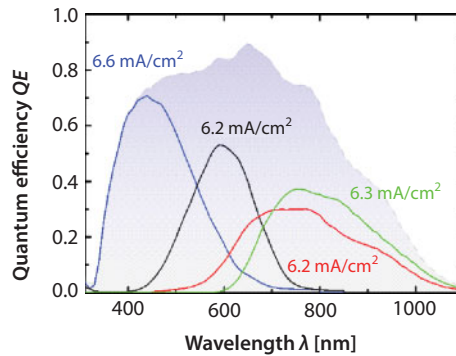


Figure 9.4 Quantum efficiency curves of the a-Si:H/a-Si:H/ μ c-Si:H/ μ c-Si:H quadruple-junction solar cell Q3. Subcell current densities calculated from the QE curves are placed near the related measurements and the blue shaded area gives the total QE. Adapted from Ref. [16, 58].

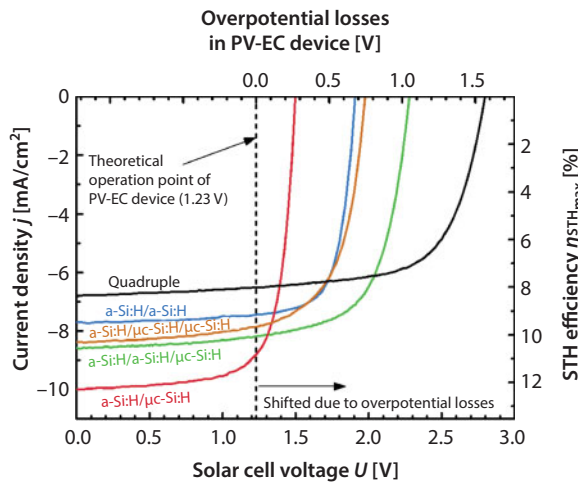


Figure 9.5 Illustration of the achievable solar-to-hydrogen efficiency η_{STHmax} in PV-EC devices for water splitting based on thin-film silicon solar cells (adapted from Refs. 16, 58). The illuminated j - U curves of tandem-, triple-, and quadruple-junction solar cells are linked with the theoretical operation point of a PV-EC device at 1.23 V (without overpotential losses) shown as dashed vertical line. The overpotential losses are plotted on the top x-axis and shift the operation point toward higher voltages. The right y-axis depicts the achievable STH efficiency as a function of the respective photocurrent density at a certain overpotential multiplied by the value of 1.23.

point of a PV-EC device. The PV-EC device operates in its operation point when both electrodes are shorted. In an ideal system without overpotential losses, the PV-EC device would operate at a voltage of 1.23 V of the solar cell, indicated by a straight vertical dashed line in figure.

In real systems, the presence of the overpotential losses causes that the operation point is shifted toward more positive bias, as indicated in figure. The photocurrent density j_{ph}^{op} at this required voltage can be used to estimate a maximum STH efficiency η_{STHmax} (under the assumption of 100 % faradaic efficiency) of the PV-EC device. Under an assumption that the photovoltaic parameters of the solar cells are not changing when the solar cells are incorporated in the integrated PV-EC device, figure then allows to illustratively predict the performance of PV-EC devices based on the various types of multijunction solar cells. On the right y-axis, the maximum STH efficiency is plotted and can be found at the crossing point of the photovoltaic j - U curve with the operation point line at the corresponding overpotential value indicated in the top x-axis. As indicated in figure, a-Si:H/ μ c-Si:H tandem junction could provide a maximum STH efficiency over 10 % when the integrated PV-EC device would function without any overpotential losses. When the losses are taken into account, high-voltage triple- and quadruple-junction photocathodes would be needed for a working device.

Another important aspect related with thin-film silicon solar cells is the effect of light-induced degradation (LID) on the performance of the solar cells. Especially, a-Si:H and its alloys can suffer from the LID, which mainly causes additional metastable electronic defects in the absorber layer. As a consequence, the efficiency of thin-film silicon solar cells can decrease when exposed to light over significant periods of time. This effect, known as Staebler-Wronski effect, has been intensively investigated [54, 55, 63]. It was demonstrated that the quadruple, the a-Si:H/ μ c-Si:H/ μ c-Si:H triple, and the a-Si:H/ μ c-Si:H tandem-junction solar cells exhibit a high stability against LID, as the relative degradation in efficiency is below 5 % for all cells after 1000 hours of illumination. Among these solar cells, the quadruple cell, which has an initial efficiency of 12.9 %, shows the highest stabilized conversion efficiency of 12.4 %. Additionally, if an antireflection foil is attached to the solar cell, an initial efficiency of 13.2 % and a stabilized efficiency of 12.6 % can be obtained on this type of solar cell, respectively. The conversion efficiencies of the a-Si:H/a-Si:H tandem and the a-Si:H/a-Si:H/ μ c-Si:H triple junction cell, for their part, decrease by approximately 16 % and 12 % after prolonged light soaking, respectively.

9.3 PV-EC Devices Based on Multijunction Solar Cells

To investigate the complete PV-EC device characteristics, two-electrode measurements have to be conducted and are presented in this section.

Figure 9.6 depicts the voltammograms in two-electrode configuration of the real PV-EC devices based on various types of multijunction solar cells (see Figure 9.6). The measurements were conducted in 0.1 M KOH and Pt was used as HER catalyst layer (approximately 150 nm) on top of the solar cell Ag contacts.

In general, it should be noted that the shape of the curves shown in Figure 9.6 is different from the photovoltaic j - U curves presented in figure 9.5. It is evident that the FF and U_{ph}^{oc} are reduced, which is likely due to the electrolyte resistance and the overpotential losses at the electrode surfaces. The modeling of the photocurrent-voltage characteristics was presented elsewhere [64]. As could be predicted from Figure 9.5, the measurements shown in Figure 9.6 confirm that the photovoltage generated by the a-Si:H/ μ c-Si:H tandem photocathode is not sufficient to operate this device in its maximum power point (MPP) under real operating conditions. Although, the device provides the highest J_{ph}^{sc} of all investigated solar cell types (see Figure 9.6), it only operates at a j_{ph}^{op} of 0.5 mA/cm² in the PV-EC device configuration. This result demonstrates that the U_{ph}^{oc} of 1.5 V provided by the a-Si:H/ μ c-Si:H solar cell is the minimum output voltage required to run this specific PV-EC device (Pt and RuO₂ as HER and OER catalyst, respectively, and 0.1 M KOH electrolyte solution) bias-free. For the a-Si:H/a-Si:H-based device, the operation point lies in the current slope of its voltammogram, and the generated j_{ph}^{op} is 4.8 mA/cm². Although the

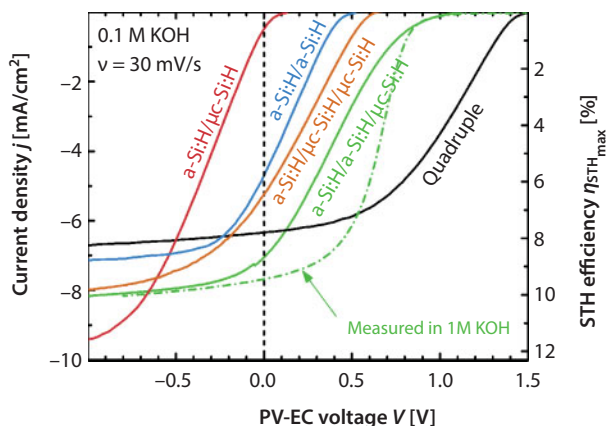


Figure 9.6 Linear sweep voltammetry measurements of the PV-EC devices based on thin-film silicon multijunction photocathodes with a 150-nm-thick Pt layer as HER catalyst on top of the Ag contact and a RuO₂ counterelectrode for the OER reaction. The measurements were conducted in 0.1 M KOH at a scan rate of 30 mV/s. The right y-axis depicts the achievable STH efficiency as a function of the photocurrent density at 0 V applied bias multiplied by the value of 1.23. Figure adapted from Refs. 16, 58.

a-Si:H/ μ c-Si:H/ μ c-Si:H triple-junction devices provides a higher U_{ph}^{oc} , and consequently a higher $E_{onset,cat}$ (as apparent from Figure 9.5), the j_{ph}^{op} is not increased compared to the a-Si:H/a-Si:H tandem devices. Here, further increase in the fill factor of the a-Si:H/ μ c-Si:H/ μ c-Si:H solar cell could help to reach the MPP photocurrent under short-circuit condition and thus would result in an improved performance and a higher STH efficiency. The highest operation photocurrent density j_{ph}^{op} is achieved with a-Si:H/a-Si:H/ μ c-Si:H-based integrated device. The device operates close to its MPP at 7.1 mA/cm², which corresponds to an estimated STH efficiency of 8.7 %. When this device is operated in 1 M KOH electrolyte, an even higher operation photocurrent density is achieved and the device provides an estimated STH efficiency of 9.5 %. For the best PV-EC devices, the PV performance parameters of $U_{ph}^{oc} = 2.3$ V, $j_{ph}^{sc} = 8.6$ mA/cm², $U_{MPP} = 1.9$ V, and $j_{MPP} = 7.4$ mA/cm² can be compared to the STH PV-EC performance parameters $U_{ph}^{op} = 1.9$ V and $j_{ph}^{op} = 7.7$ mA/cm² to get a quantitative measure for the losses related to the photoelectrochemical H₂O splitting for rather optimized conditions. The operation point of the quadruple-junction device is in the current plateau region at 6.3 mA/cm². Albeit the corresponding 7.6 % STH efficiency is reduced relative to the a-Si:H/a-Si:H/ μ c-Si:H device for the used catalyst materials, the j_{ph}^{op} of the device is located in a sufficiently flat region of the voltammogram (current plateau

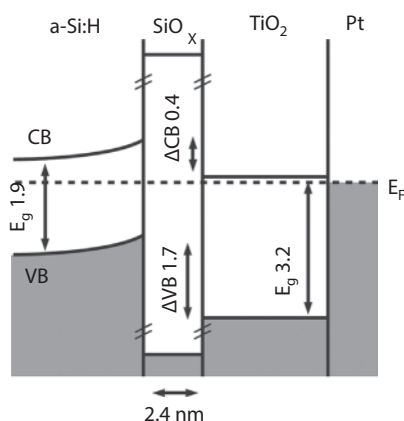


Figure 9.7 Band alignment of the interface between an a-Si:H/a-Si:H solar cell, TiO₂ and Pt in the dark on the basis of core line positions of the XPS measurements (adapted from Ref. [18]). Indicated values are in eV. The conduction band minimum (CB), the valence band maximum (VB), the band gaps (E_g), and the Fermi level (E_F) are shown. The conduction band offset (ΔCB) and the valence band offset (ΔVB) are indicated between a-Si:H and the TiO₂ buffer layer.

region). Therefore, this device offers some excess voltage, which additionally results a higher flexibility in selecting various catalyst materials (for example, nonprecious) for the HER and OER, respectively.

TiO₂ is well known for its chemical stability in aqueous electrolytes and may be considered as a potential protection layer for thin-film silicon multijunction cell [65]. When the Ag layer is replaced by TiO₂ layer, so that the TiO₂ layer is in direct contact to the solar cell silicon layers, stability and interface experiments can be conducted by, for example, XPS analysis [65, 66]. Note that when the Ag layer (acting as an optical back reflector contact) is removed, the reduction in the photovoltaic performance of the solar cells is expected. Nevertheless, based on the results of the interface studies, a band line-up can be constructed for dark conditions, which gives information about the charge transfer properties of the interface (see Figure 9.7). The electronic transport across the buffer layer is sustained by electrons, which are generated in the solar cell on the left side of the schematic structure and are consumed in the HER, which is located at the Pt catalyst. The Pt catalyst forms an ohmic contact to the TiO₂ buffer layer due to the higher doping level of the n⁺-TiO₂ layer. Therefore, no potential loss can be expected at this interface. The interface between a-Si:H and TiO₂ exhibits only a small conduction band offset, which is negative for electrons traveling from the tandem cell into the buffer layer. Hence, the band line-up of TiO₂ to the tandem solar cell seems favorable, which was also observed on crystalline silicon [18, 66].

An optimized catalyst is also necessary to achieve a high solar to fuel efficiency. Such a catalyst must show a good adhesion to a contact layer, a high electrochemical activity, and a high selectivity toward the targeted product, which is of utmost importance for the CO₂ reduction reaction (CO₂RR) process (see Section 4). In contrast to pure water reduction, which solely generates H₂ (and O₂) as reaction product, CO₂RR can generate numerous products (CO, CH₄, CH₃OH, etc.) depending on the chosen catalyst. Additionally, the reaction pathways for CO₂RR are more complex and involve multielectron steps and thus, higher overpotentials to occur. In this regard, enlarging the active area to increase the activity and consequently reduce the required overpotential presents an efficient approach for CO₂RR and water splitting. Furthermore, the deposition of large surface area catalyst materials enables to increase the specific mass activity and thus to reduce material and energy consumption during production. The deposition process itself must be “soft” in order to avoid damaging the multijunction solar cell. The cost of the catalyst material also plays a significant role [67]. For water splitting, it is well known that Pt exhibits the highest performance toward H₂ production. Regarding CO₂RR, catalysts such as

Au, Ag (for CO production), and In (for formic acid production) possess superior catalytic behavior. However, in view of commercial application at large scale, such expensive and rare materials are not ideal. More adequate candidates are Ni (for HER) and Zn or Cu (for CO₂RR), as they are cheaper and earth-abundant [68]. Besides pure metallic catalysts, the HER can also be driven by cost-effective compound catalyst materials such as MoS₂ [69] and Mo₂C, [70, 71] for instance. In order to allow an efficient overall water splitting or CO₂RR process, the OER needs to be taken into account as well. For this anodic reaction, metal oxides, such as Co₃O₄, NiO_x, IrO₂, and RuO₂, are prominent candidates. For these catalyst materials, there is a tradeoff between performance and cost, similar as for the catalysts for the cathodic water splitting or CO₂R reaction, respectively. Accordingly the performance of a PEC device will significantly be affected by the choice of the catalyst. In Figure 9.8, the influence of different HER and OER catalyst materials on the water splitting performance for an a-Si:H/a-Si:H, an a-Si:H/a-Si:H/ μ c-Si:H, and an a-Si:H/a-Si:H/ μ c-Si:H/ μ c-Si:H based PEC device is presented. The photocurrent–voltage curves in Figure 9.8(a)–(c) were calculated using an empirical serial circuit model, presented in Ref. [64] and [72]. The empirical input data for the catalytic properties of the investigated catalysts (Tafel slope and exchange current density) can be found in Ref. [72].

HER and OER catalysts, such as Pt and RuO₂, respectively, led to the highest calculated photocurrent densities j_{op} at 0 V applied bias, and thus, to the highest STH values. When cost-effective and more earth-abundant material combinations are used to catalyze the HER and OER reactions, which suffer from lower reaction kinetics, i.e., higher overpotential losses, a clear shift of the onset potential for cathodic current in negative bias direction was observed. In the case of the a-Si:H/a-Si:H- and a-Si:H/a-Si:H/ μ c-Si:H-based devices, this significantly affected the j_{op} of the voltammograms. For the a-Si:H/a-Si:H devices, the STH efficiency decreased from 6.2 % for a Pt/RuO₂ catalyst combination to 1.5 % for a MoS₂/Co₃O₄ combination (see Figure 9.8(a)). Due to the higher photovoltages of the a-Si:H/a-Si:H/ μ c-Si:H cell, which led to higher-onset potentials for cathodic current, the operation point of the corresponding PV-EC devices was shifted more to the MPP (see Figure 9.8(b)). In this region of the voltammograms, the decrease in STH efficiency (from 9.0 % to 7.0 %) was less pronounced compared to the a-Si:H/a-Si:H-based devices. Finally, as shown in Figure 9.8(c), the j_{op} values for the quadruple based PV-EC devices remained nearly unaffected by the variation of the HER and OER catalysts. In spite of the fact that the STH efficiency for the Pt/RuO₂ catalyst combination ($\eta_{STHmax} = 7.8$ %) was lower compared to the a-Si:H/a-Si:H/ μ c-Si:H device ($\eta_{STHmax} = 9.0$ %), the quadruple-based device provided

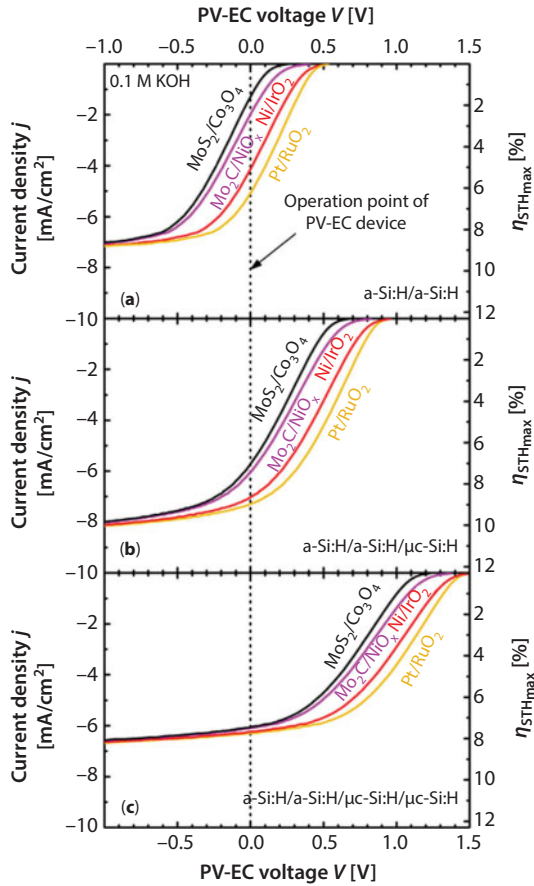


Figure 9.8 Calculated voltammograms of a-Si:H/a-Si:H (a), a-Si:H/a-Si:H/ μ c-Si:H (b), and quadruple junction (c) based PEC devices with varying HER and OER catalysts. The HER/OER catalyst combinations are Pt/RuO₂ (yellow curves), Ni/IrO₂ (red curves), Mo₂/NiO_x (purple curves), and MoS₂/Co₃O₄ (black curves). The measurements were simulated for a 0.1 M KOH electrolyte (56 Ω). The respective solar cell type is indicated in the corresponding figure. The right ordinate depicts the achievable STH efficiency as a function of the photocurrent density at 0 V applied bias. Adapted from Ref. [16].

enough excess voltage to compensate the overpotential losses of the cost-effective and earth-abundant catalyst materials. For the MoS₂/Co₃O₄ HER/OER catalyst combination, the STH efficiency only slightly decreased to a minimum STH efficiency of 7.5 %.

Overall, this result elucidates the importance in PV-EC devices to adapt the photovoltaic to the electrochemical properties and vice versa. In this regard, the tunability of the photovoltaic parameters, especially of the

U_{ph}^{oc} , is a vital feature and offers a lot of freedom in the design of all kinds of photoelectrochemical devices.

The effect of light-induced degradation (LID) on the solar-to-hydrogen efficiency for silicon-based water splitting devices has been examined recently in the Refs. [49] and [73]. In both studies, it has been found that the effect of LID is less pronounced in the photoelectrochemical configuration under typical operation conditions than in the pure photovoltaic configuration. The thin-film $\mu\text{c-Si:H/a-Si:H}$ solar cells show only minor degradation effects below 5% in PV-EC devices. Nevertheless, for the a-Si:H/a-Si:H - and $\text{a-Si:H/a-Si:H}/\mu\text{c-Si:H}$ -based PV-EC devices, the impact of LID needs to be taken into account also in the PV-EC configuration.

Figure 9.9 shows the photocurrent density at 0 V applied bias measured over a period of time for the integrated PV-EC devices utilizing quadruple-junction solar cell ($\text{a-Si:H/a-Si:H}/\mu\text{c-Si:H}$) with a Ni HER catalyst and a Pt HER catalyst in 0.1 M and 1 M KOH, respectively. It can be seen that in the case of 0.1 M KOH a stable photocurrent of around 6.1 mA/cm² and 7.0 mA/cm², respectively, can be measured for both PV-EC devices over the course of 4 hours (approximately 15000 s) [58]. Note that the fluctuations in the measured currents are likely due to the formation and detachment of hydrogen bubbles at the catalyst surface.

The results obtained for 1 M KOH indicate that these devices do not function for more than approximately 0.5 and 1 hour with the Ni and the Pt HER catalyst, respectively. This also indicates that a change in the pH value from approximately 13 (0.1 M KOH) to approximately 14 (1 M KOH) can notably impact the stability of the integrated devices.

It should be noted that the excess photovoltage offered by the quadruple-junction solar cell can be considered as an additional advantage. It can be seen in Figure 9.9 (black curves) that the increase in the concentration of solution does not influence the measured photocurrent values. For this device, utilizing high-voltage solar cell, an operation photocurrent of j_{ph}^{op} of around 6 mA/cm² is obtained for the experiments performed in 0.1 M and 1 M KOH solution, respectively. This behavior is expected since the integrated device operates already in the plateau region of the current, so that an increase in U_{MPP} will not lead to a change in j_{ph}^{op} .

The behavior discussed above indicates that the high-voltage quadruple-junction solar cells are beneficial when inexpensive catalyst materials are utilized and additionally can be used in low concentration solutions without significant reduction in the device performance and efficiency, and therefore, can offer an increased long-term stability of the device. Concerning the stability against LID, the quadruple-junction solar cell might offer an additional advantage [49].

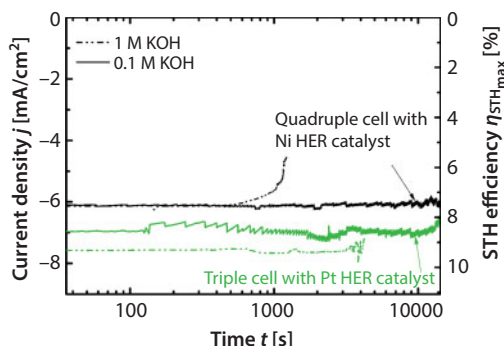


Figure 9.9 Chronoamperometric data evaluating the long-term stability of the triple- and the quadruple-junction solar cells integrated in the PV-EC devices with Pt and Ni catalyst layers (on top of Ag contacts), respectively, at 0 V applied bias. Adapted from Refs. [16, 58]. The measurements were conducted in 0.1 M (solid curves) and in 1 M KOH (dotted curves) under AM 1.5 illumination ($100\text{mW}/\text{cm}^2$). RuO_2 was used as counterelectrode for the OER reaction. The right y-axis depicts the achievable STH efficiency as a function of the photocurrent density at 0 V applied bias multiplied by the value of 1.23.

9.4 Promising Device Designs, Future Prospects

Considering any commercial realization of the PV-EC devices and their suitability for outdoor applications, the device area has to be upscaled considerably. The practical PV-EC devices are typically demonstrated on areas below 1 cm^2 [74]. When the solar water-splitting devices are scaled to practical areas $\gg 1\text{ cm}^2$, a number of scientific technological challenges have to be considered. These are, for instance, on the solar cell side, the scalability of the photovoltaic cell which are attended by ohmic losses, related to the current collection of a large area solar cell through the front electrode of the device. Concerning the implementation in the PV-EC device, the PV cell needs to be fully protected against the corrosive electrolyte in order to ensure long-term stability. Different fully scalable concepts employing thin-film silicon solar cells and lateral interconnection of the subcells and/or the design of appropriate grid contact patterns to reduce resistive losses were presented [75] to overcome the ohmic losses occurring in the upscaled photovoltaic cells. The protection of the solar cell against the electrolyte can be realized by using metal sheet electrodes instead of thin deposited protection (buffer) layers with additional catalysts. Remarkably, an integrated photovoltaic–electrochemical module with an active area of 64 cm^2 and a long-term stable solar-to-hydrogen efficiency close to 5% was realized based on multijunction a-Si:H/a-Si:H/ $\mu\text{c-Si:H}$ photovoltaic cell combined with noble metal catalysts in alkaline media [75].

Furthermore, if the PV-EC device is to be used outdoors, the device performance will be influenced by the illumination conditions. The performance of the prototype devices is typically evaluated under standard test conditions (STC), which means a temperature of 25 °C and an illumination intensity of 1 sun (1000 W/m²) of the AM1.5 G spectrum. However, this set of conditions only represents one option among a wide range of possible conditions. For example, due to clouds and other varying weather conditions, the illumination intensity is often below 1 sun, whereas, on sunny days, system temperatures of 60 °C and more may occur [76, 77]. Additionally, the spectral quality of the incident light changes during the season[78] and the day time[79] and differs for the geographical locations. For instance, during winter time on the northern hemisphere, the incident illumination spectra are shifted toward longer wavelengths (red shift), while during summer time a shift toward short wavelengths (blue shift) occurs. Varying illumination conditions (intensity and spectral) can be considered as a possible influence on the device performance. Especially the varying spectral quality of the incident illumination spectrum has to be considered, since each subcell in a multijunction cell stack has different optical properties and will react differently to the adjusted spectral conditions.⁸⁰

The spectral quality can be presented in terms of average photon energy (APE), which is defined as the total energy in a spectrum (spectral irradiance) divided by the total number of photons it contains (photon flux density):

$$APE = hc \frac{\int_a^b E(\lambda) d\lambda}{\int_a^b \lambda E(\lambda) d\lambda} \quad (9.6)$$

Herein h stands for the Planck constant, c is the speed of light, E is the spectral irradiance, and λ is the wavelength. (a) and (b) define the wavelength range of the incident spectrum, typically between 300 nm (=a) and 1100 nm (=b). The AM 1.5G spectrum has in this case an average photon energy of 1.71 eV. In order to investigate the influence of the incident illumination spectrum on the PV-EC device performance, the APE has to be varied. The variation can be achieved by using a set of high-power LEDs allowing a wide range of APEs to be studied. Exemplary, Figure 9.10(a) shows the external quantum efficiencies [81] in the wavelength range from 300 to 1100 nm of an a-Si:H/a-Si:H/ μ c-Si:H triple-junction cell. The a-Si:H top cell mainly absorbs in the short wavelength range (300–600

nm), while the a-Si:H middle cell shows the highest quantum efficiencies in a wavelength range from 400 to 750 nm. The μ c-Si:H bottom cell primarily absorbs in the long wavelength range (600–1100 nm). The subcells show subcell currents in the range of 7.1–7.3 mA/cm² (lowest subcell current: middle cell) and are therefore current matched under standard test conditions. Figure 9.10(b) shows the spectral irradiance of a set of LEDs, which can be used to vary the spectral composition and therefore the average photon energy of the incident illumination spectrum. Comparing the wavelengths of Figure 9.10(a) and (b), one can see that the blue LED will mainly influence the top cell, whereas the green LED will have an effect on both a-Si:H cells. In the case of the red LED, the effect will possibly be on the middle and bottom cell, while the infrared LED will only influence the μ c-Si:H bottom cell.

Figure 9.10(c) shows a possible spectral modification toward a short wavelength rich spectrum (dashed curve). The black curve shows the initial AM1.5 G spectrum, which is used for the illumination under standard test conditions. The average photon energy of the AM1.5 G spectrum is 1.71 eV as mentioned before. The spectrum can be shifted toward higher APEs—enriched in the short wavelength range—by using the blue LED (465 nm). Therefore, the blue LED light (465 nm) is added while the intensity of the AM1.5 G spectrum is reduced in a way that the overall intensity of the incident spectrum is constant (1 sun = 1000 W/m²), resulting in an APE of 1.75 eV for the blue shifted spectrum. The same spectral modification was realized for the four LEDs, yielding an APE ranging from 1.69 to 1.75 eV. For comparison, an annual APE variation of 0.06 eV was reported in the literature [76].

These spectral variations can significantly influence the performance of the used multijunction Si thin-film solar cell and therefore the corresponding solar-to-hydrogen efficiency values. The current–voltage curves of the PV-EC devices were measured under the modified spectra with an APE range of 1.69–1.75 eV. According to equation (9.5), the upper limit of the solar-to-hydrogen efficiency can be calculated using the current density at the operation point under zero bias (J_{OP} for $V = 0$ V) for the different illumination conditions. Figure 9.11 shows the solar-to-hydrogen efficiencies measured under the varied APE spectra [81] normalized to the solar-to-hydrogen efficiency measured under AM1.5 G (1.71 eV) plotted versus the APE range investigated (1.69–1.75 eV) for two different catalyst systems (system (a): Pt/IrO_x; system (b): Ni_xMo_yN_z/Co-Fe LDH). It is evident that an increase in the average photon energy of the spectrum results in a higher solar-to-hydrogen efficiency. This effect is especially pronounced for the red and green rich spectra which mainly influence the middle a-Si:H cell in the triple-junction cell stack. As mentioned before, the subcell current of

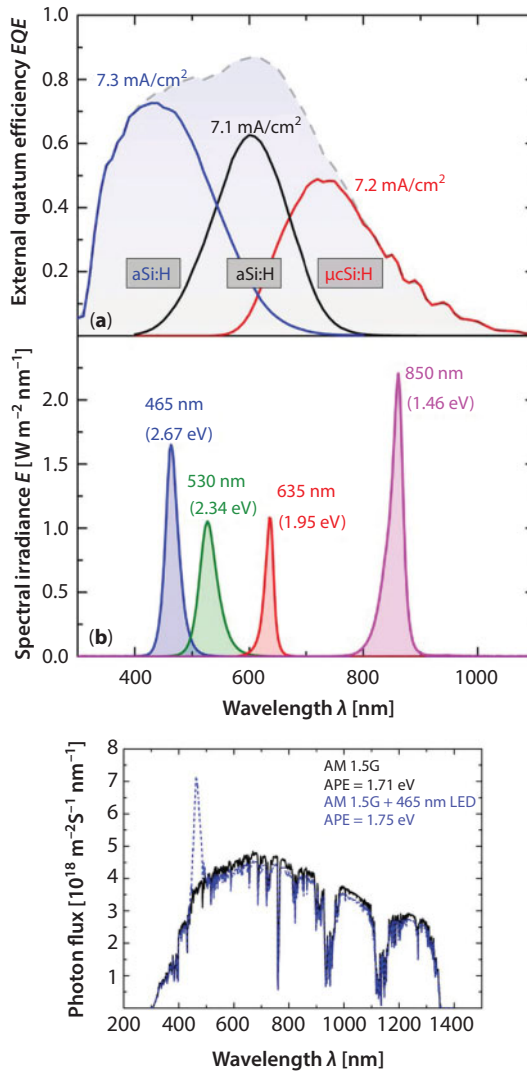


Figure 9.10 (a) EQE of the $\text{aSi:H/a-Si:H}/\mu\text{c-Si:H}$ solar cell, together with J_{QE} values calculated for each subcell, indicating that the device current J_{SC} under STC is limited is the middle subcell ($J_{\text{QE}} = 7.1 \text{ mA/cm}^2$). (b) Spectral irradiance of a set of LEDs with different wavelengths to address the different subcells in the triple cell stack and to vary the average photon energy of the spectrum. (c) Example of spectral modifications. Black curve: AM1.5G spectrum (STC) with an average photon energy of 1.71 eV; dashed curve: modified “blue rich” spectrum with increased average photon energy of 1.75 eV. Adapted from Ref. [81].

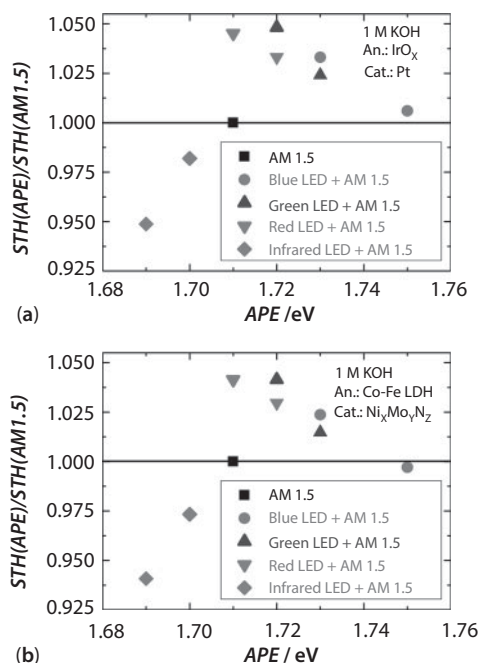


Figure 9.11 Normalized solar-to-hydrogen efficiency plotted versus the average photon energy of the incident spectrum: (a) Pt/IrO_x and (b) Ni_xMo_yN_z/Co-Fe LDH. The symbols illustrate, which LED was used to modify the spectrum to achieve the given APE values, adapted from ref [81].

the middle cell limits the overall cell stack current density, due to the variation in wavelength, the middle subcell current is enhanced and not limiting under red and green shifted spectra, leading to high STH efficiencies. Low average photon energy spectra—as for example during winter—lead to decreased solar-to-hydrogen efficiencies. In this case, the enhanced long wavelength regions affect the μ c-Si:H bottom cell, whereas the top and middle cell react to the decreased intensity in the short wavelength range. Overall the difference in solar-to-hydrogen efficiency caused by varied illumination spectra is close to 1% (absolute) in solar-to-hydrogen efficiency. Therefore the PV-EC devices have to be carefully adjusted for the outdoor application toward the illumination conditions at the operation side rather than to laboratory conditions.

Among the photoelectrochemical reactions for solar fuel production, the direct solar reduction of CO₂ to liquid organic substances, such as carbon monoxide (CO) [82], methane (CH₄) [83], or formic acid (CH₂O₂) [84], has recently attracted considerable attention due to the higher energy

density and accessible storage advantages compared with hydrogen energy [85]. Several device assemblies based on various catalysts and light absorbers for CO_2 reduction with varying levels of integration have been demonstrated experimentally [86–91]. In this process, however, particularly the cathodic half reaction suffers significant kinetic overpotentials, which have been considered much more difficult than the hydrogen generation reaction in the water splitting process, as already explained in Section 3. The overpotentials depend largely on the nature of the used catalysts and on the additional constraint that electrochemical CO_2 reduction must be performed at near-neutral pH (due to CO_2 solubility limitations in strong acidic or alkaline solutions). Hence, a voltage of at least 2.0 V is demanded to drive an efficient fuel production via CO_2RR . Additionally, the product selectivity at the electrodes is highly potential-dependent, i.e., a number of different products can be generated by reduction processes depending on the applied potential. This must be accounted for when defining the required photoelectrode operating potential [90]. As shown by Urbain *et al.*, [90] the series connection of four silicon heterojunction solar cells led to a photovoltage of 2.5 V, enabling bias-free CO_2 conversion into syngas ($\text{CO} + \text{H}_2$) at an operation current density of 5 mA/cm^2 (crossing point of PV and EC curves in Figure 9.12). Figure 9.12 illustrates the effect of series connection of Si heterojunction solar cells and the influence of the membrane and electrolyte choice for the complete CO_2RR system. As apparent from this plot, the series connection of PV cells, however, does not allow to precisely adjust the photovoltage, i.e., in small 100 mV steps. In this regard, multijunction thin-film silicon solar cells offer a much more flexible solution. As discussed, the deposition process can be adjusted in order to systematically adapt the solar cell output voltage to the required voltage of the complete solar CO_2RR system.

9.5 Summary and Conclusions

In the present contribution, we have summarized the major aspects relevant for the design architecture of PV-EC devices and have overviewed the key achievements, which have been obtained in recent years with electrochemical cells (PV-EC devices) applying multijunction photoelectrodes.

Bias-free water splitting will only be possible if the performance of the PV component provides the photovoltage needed to drive the oxygen and the hydrogen evolution reaction as given by their electrochemical potentials and compensate for additional losses due to the respective overpotentials and other possible series resistances within the circuit. Adding up

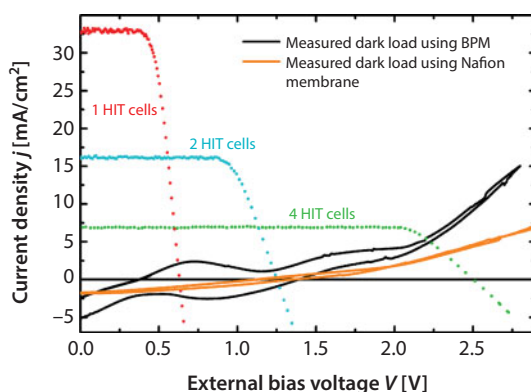


Figure 9.12 Overall polarization characteristics for CO_2RR reaction and OER using a cathode made of Cu foam and Zn catalysts and a photoanode made of series-connected Si heterojunction solar cells connected to an Ni foam. The device was measured in two different configurations: (i) with a bipolar membrane, where 0.5 M KHCO_3 (pH=7.5) was used as catholyte and 1 M KOH (pH=13.7) as anolyte solution (black curve), (ii) with a Nafion membrane, where 0.5 M KHCO_3 was used as catholyte and anolyte solution (orange curve). The measurements were conducted with a 20 ml/min , CO_2 and electrolyte flow rate and 10 mV s^{-1} scan rate. The overlaid current density–voltage characteristics of the applied Si heterojunction solar cell as single (red dotted curve) and as series-connected (two cells, blue dotted curve; four cells, green dotted curve) photovoltaic devices were measured under simulated AM 1.5G illumination. Adapted from Ref. [90].

these relevant potential differences leads to a minimum open-circuit photovoltage of about 1.9 V ; this value is higher than the usually discussed value of about $1.5\text{--}1.6\text{ V}$: The difference of $U_{\text{ph}}^{\text{oc}}$ to the operation voltage of the PEC $U_{\text{ph}}^{\text{op}}$ cell with reasonable photocurrents, which is close to the photovoltage at the maximum power points U^{MPP} , must be considered in addition. From such considerations, it is clear that only multijunction cells will provide a reasonable conversion yield for bias-free direct light-induced H_2 evolution by H_2O splitting.

The solar-to- H_2 STH conversion efficiency is finally given by the photocurrent density, which flows at the operation photovoltage point of the current voltage curve obtained without a potentiostat or bias voltage in a two-electrode arrangement. It is clear that the photovoltage onset must be situated beyond the reversible H_2 evolution potential (RHE) for photocathodes or the reversible O_2 evolution potential (ROE) for photoanodes; in cases where only an increased photocurrent is noticed in between the RHE and the ROE, only a partial contribution to the overall needed water dissociation potential is provided by the photoelectrode (even worse are cases, which are shifted in their photocurrent onsets outside of the RHE

and ROE). Clearly the photocurrent density at $U_{\text{ph}}^{\text{op}}$ is valid for the STH efficiency, which is situated at the intersection point of the PV current-voltage curve with the electrolyzer two-electrode current-voltage curve. This operational photocurrent $j_{\text{ph}}^{\text{op}}$ reached at $U_{\text{ph}}^{\text{op}}$ must approach values as defined by the bandgap of the absorber(s) and the optimized quantum efficiencies of the PV device. In rather ideal cases, this photocurrent is identical to the photocurrent measured in the respective PV cell close to U^{MPP} . Or in other words, if the PV component of the photoelectrochemical cell cannot deliver high photocurrents approaching quantum efficiencies of 1 and the needed photovoltages, one cannot expect working or competitive PEC devices. The anticipated performance can be checked in preliminary experiments by investigating the performance of regenerative PEC cells with reversible and fast redox couples before complex interface engineering steps have been started.

As is evident from the overview of multijunction solar cells presented here that the PV component must be adjusted to the conditions of the PV-EC cell to realize the highest performance, which may be possible with a given system. The overall performance follows indeed the expected series connection of the components photovoltaic cell and electrolyzer, and if additional unexpected losses are observed, e.g., in the photocurrent onset (reduced photopotentials), these can be related to additional series resistances in the cell, e.g., due to weakly conducting interfacial layers in the device or high series resistances in the electrolyte. An STH efficiency of 9.5 % was obtained with the triple-junction device made of a-Si:H/a-Si:H/ $\mu\text{c-Si:H}$, applying relatively expensive noble metals as cocatalysts [58]. But as was also shown, if quadruple-junction solar cells are used which provide higher photovoltages, even nonnoble metals can be applied. Additionally, the stability of these devices is still an issue but can be improved by using passivation layers as, e.g., TiO_2 . Furthermore, thin-film silicon photocathodes with precisely adjustable photovoltages up to 2.8 V represent ideal photoelectrodes for applications in photoelectrochemical CO_2 reduction.

Overall, these results can be taken as promising perspective for direct light-induced water splitting and the production of a storable solar fuel by an artificial leaf approach. The possibilities of device upscaling beyond laboratory size and the paths to predict the performance in the outdoor conditions (such as the effects of spectral quality) were outlined, which is particularly relevant when a successful commercial realization of the PV-EC devices is considered. Given the societal importance of the challenge, the needed research money seems well spent. The route to a competitively produced fuel from solar radiation seems given; we just need the determination to follow it.

References

1. Grimes, C.A., Varghese, O.K., Ranjan, S., *Light, Water, Hydrogen*, Springer, New York, 2008.
2. Rajeshwar, K., McConnell, R., Licht, S. (Eds.), *Solar Hydrogen Generation*, Springer, New York, 2008.
3. Fujishima, A., Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature*, 238, 37–38, 1972.
4. Nocera, D.G. The Artificial Leaf, *Acc. Chem. Res.*, 45, 767–776, 2012.
5. Heller, A., Vadimsky, R.G. Efficient Solar to Chemical Conversion: 12% Efficient Photoassisted Electrolysis in the [p-type InP(Ru)]/HCl-KCl/Pt(Rh) Cell, *Phys. Rev. Lett.*, 46, 1153, 1981.
6. Lewerenz, H.J., Heine, C., Skorupska, K., Szabo, N., Hannappel, T., Vo-Dinh, T., Campbell, S.A., Klemm, H.W., Munoz, A.G. Photoelectrocatalysis: principles, nanoemitter applications and routes to bio-inspired systems, *Energy Environ. Sci.*, 3, 748–760, 2010.
7. Khaselev, O., Turner, J.A. A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting, *Science*, 280, 425–427, 1998.
8. Lewerenz, H.-J., Jungblut, H., *Photovoltaik Grundlagen und Anwendungen*, Springer, Berlin, 1995.
9. Licht, S., Wang, B., Mukerji, S., Soga, T., Umeno, M., Tributsch, H. Efficient Solar Water Splitting, Exemplified by RuO₂-Catalyzed AlGaAs/Si Photoelectrolysis, *J. Phys. Chem. B*, 104, 8920–8924, 2010.
10. Reece, S.Y., Hamel, J.A., Sung, K., Jarvi, T.D., Esswein, A.J., Pijpers, J.J.H., Nocera, D.G. Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts, *Science*, 334, 645–648, 2011.
11. Bolton, J.R., Strickler, S.J., Connolly, J.S. Limiting and realizable efficiencies of solar photolysis of water, *Nature*, 316, 495–500, 1985.
12. Prévot, M.S., Sivula, K. Photoelectrochemical Tandem Cells for Solar Water Splitting, *J. Phys. Chem. C*, 117, 17879–17893, 2013.
13. Miller, E.L., DeAngelis, A., Mallory, S., Photoelectrochemical Hydrogen Production, R.V.D. Krol, M. Grätzel (Eds.), Springer, New York, pp. 205–273, 2012.
14. Seitz, L.C., Chen, Z., Forman, A.J., Pinaud, B.A., Benck, J.D., Jaramillo, T.F. Modeling practical performance limits of photoelectrochemical water splitting based on the current state of materials research, *ChemSusChem*, 7, 1372–1385, 2014.
15. Jaegermann, W., Kaiser, B., Ziegler, J., Klett, J., *Photoelectrochemical Solar Fuel Production. From Basic Principles to Advanced Devices*. S. Gimenez, J. Bisquert, (Eds.) Springer, 2016.
16. Urbain, F., Light induced water splitting using multijunction thin film silicon solar cells, *Energy and Environment*, Volume 323, Forschungszentrum Jülich, 2016

17. Pihosh, Y., Turkevych, I., Mawatari, K., Uemura, J., Kazoe, Y., Kosar, S., Makita, K., Sugaya, T., Matsui, T., Fujita, D., Tosa, M., Kondo, M., Kitamori, T. Photocatalytic generation of hydrogen by core-shell $\text{WO}_3/\text{BiVO}_4$ nanorods with ultimate water splitting efficiency, *Scientific Reports*, 5, 11141, 2015.
18. Klett, J., Ziegler, J., Radetinac, A., Kaiser, B., Schäfer, R., Jaegermann, W., Urbain, F., Becker, J.-P., Smirnov, V., Finger, F. Band engineering for efficient catalyst-substrate coupling for photoelectrochemical water splitting, *Phys. Chem. Chem. Phys.*, 18(16), 10751–10757, 2016.
19. Appleby, A.J., Delahoy, A.E., Gau, S.C., Murphy, O.J., Kapur, M., Bockris, J.O.M. An amorphous silicon-based one-unit photovoltaic electrolyzer, *Energy*, 10, 871–876, 1985.
20. Delahoy, A.E., Gau, S.C., Murphy, O.J., Kapur, M., Bockris, M.O. A one-unit photovoltaic electrolysis system based on a triple stack of amorphous silicon (pin) cells, *Int. J. Hydrogen Energ.*, 10, 113–116, 1985.
21. Lin, G.H., Kapur, M., Kainthla, R.C., Bockris, J.O.M. One step method to produce hydrogen by a triple stack amorphous silicon solar cell, *Appl. Phys. Lett.*, 55, 386–387, 1989.
22. Rocheleau, R.E., Miller, E.L., Misra, A. High-Efficiency Photoelectrochemical Hydrogen Production Using Multijunction Amorphous Silicon Photoelectrodes, *Energ. Fuel*, 12, 3–10, 1998.
23. Khaselev, O., Bansal, A., Turner, J.A. High-Efficiency Integrated Multijunction Photovoltaic/Electrolysis Systems for Hydrogen Production, *Int. J. Hydrogen Energ.*, 26, 127–132, 2001.
24. Miller, E.L., Rocheleau, R.E., Deng, X.M. Design considerations for a hybrid amorphous silicon/photoelectrochemical multijunction cell for hydrogen production, *Int. J. Hydrogen Energ.*, 28, 615–623, 2003.
25. Yamada, Y., Matsuki, N., Ohmori, T., Mametsuka, H., Kondo, M., Matsuda, A., Suzuki, E. One chip photovoltaic water electrolysis device, *Int. J. Hydrogen Energ.*, 28, 1167–1169, 2003.
26. Kelly, N.A., Gibson, T.L. Design and characterization of a robust photoelectrochemical device to generate hydrogen using solar water splitting, *Int. J. Hydrogen Energ.*, 31, 1658–1673, 2006.
27. Walter, M.G., Warren, E.L., McKone, J.R., Boettcher, S.W., Mi, Q.X., Santori, E.A., Lewis, N.S. Solar water splitting cells, *Chem. Rev.*, 110, 6446–6473, 2010.
28. Bogdanoff, P., Stellmach, D., Gabriel, O., Stannowski, B., Schlattmann, R., van de Krol, R., Fiechter, S. Artificial Leaf for Water Splitting Based on a Triple-Junction Thin-Film Silicon Solar Cell and a PEDOT: PSS/Catalyst Blend, *Energy Technol.*, 4, 230–241, 2016.
29. Zhang, Q., Li, T., Luo, J., Liu, B., Liang, J., Wang, N., Kong, X., Li, B., Wei, C., Zhao, Y., Zhang, X. Ti/Co-S catalyst covered amorphous Si-based photocathodes with high photovoltage for the HER in non-acid environments, *J. Mater. Chem. A*, 6, 811–816, 2018.
30. Ziegler, J., Kaiser, B., Jaegermann, W., Urbain, F., Becker, J.-P., Smirnov, V., Finger, F. Photoelectrochemical and Photovoltaic Characteristics of

- Amorphous-Silicon-Based Tandem Cells as Photocathodes for Water Splitting, *ChemPhysChem*, 15, 4026–4031, 2014.
31. Urbain, F., Wilken, K., Smirnov, V., Astakhov, O., Lambertz, A., Becker, J.-P., Rau, U., Ziegler, J., Kaiser, B., Jaegermann, W., Finger, F. Development of Thin Film Amorphous Silicon Tandem Junction Based Photocathodes Providing High Open-Circuit Voltages for Hydrogen Production, *Int. J. Photoenergy*, 2014, Article ID 249317, 2014.
 32. Liu, B., Jin, Z., Bai, L., Liang, J., Zhang, Q., Liu, C., Zhang, Q., Liu, C., Zhao, Zhang, X. A catalyst-free amorphous silicon-based tandem thin film photocathode with high photovoltage for solar water splitting, *J. Mater. Chem. A*, 3(30), 15583–15590, 2015.
 33. Jaegermann, W., Tributsch, H. Interfacial properties of semiconducting transition metal chalcogenides, *Progress Surf. Sci.*, 29, 1–167, 1988.
 34. Meissner, D., Memming, R., *Photocatalytic Production of Energy-rich Compounds*, G. Grassi and D. O. Hall, (Eds.) Elsevier, London, pp. 138–147, 1988.
 35. Sinn, C., Meissner, D., Memming, R. Charge Transfer Processes at WSe₂ Electrodes with pH-Controlled Stability, *J. Electrochem. Soc.*, 137, 168–172, 1990.
 36. Kühne, H.M., Tributsch, H. Energetics and dynamics of the interface of RuS₂ and implications for photoelectrolysis of water, *J. Electroanal. Chem. Interfacial Electrochem.*, 201, 263–282, 1986.
 37. Schefold, J., Kühne, H.M. Charge transfer and recombination kinetics at photoelectrodes: A quantitative evaluation of impedance measurements, *J. Electroanal. Chem. Interfacial Electrochem.*, 300, 211–233, 1991.
 38. Lambertz, A., Smirnov, V., Merdzhanova, T., Ding, K., Haas, S., Jost, G., Schropp, R.E.I., Finger, F., Rau, U. Microcrystalline silicon–oxygen alloys for application in silicon solar cells and modules, *Solar Energy Mater. Solar Cells*, 119, 134–143, 2013.
 39. Smirnov, V., Lambertz, A., Tillmanns, S., Finger, F. p- and n-type microcrystalline silicon oxide ($\mu\text{c-SiOx:H}$) for applications in thin film silicon tandem solar cells, *Canadian J. Phys.*, 92, 932–935, 2014.
 40. Shah, A., Thin-film silicon solar cells. *McEvoy's Handbook of Photovoltaics* (3rd ed.), 235–307, 2017.
 41. Kim, S., Chung, J.W., Lee, H., Park, J., Heo, Y., Lee, H. Remarkable progress in thin-film silicon solar cells using high-efficiency triple-junction technology, *Solar Energy Mater. Solar Cells*, 119, 26–35, 2013.
 42. Richter, A., Smirnov, V., Lambertz, A., Nomoto, K., Welter, K., Ding, K. Versatility of doped nanocrystalline silicon oxide for applications in silicon thin-film and heterojunction solar cells, *Solar Energy Mater. Solar Cells*, 174, 196–201, 2018.
 43. Yan, B., Yue, G., Sivec, L., Yang, J., Guha, S. Innovative dual function nc-SiOx:H layer leading to a >16% efficient multi-junction thin-film silicon solar cell, *Appl. Phys. Lett.*, 99(11), 113512, 2011.

44. Smirnov, V., Lambertz, A., Grootenok, B., Carius, R., Finger, F. Microcrystalline silicon oxide ($\mu\text{c-SiOx:H}$) alloys: A versatile material for application in thin film silicon single and tandem junction solar cells, *J. Non-crystalline Solids*, 358, 1954–1957, 2012.
45. Konagai, M. Present Status and Future Prospects of Silicon Thin-Film Solar Cells, *Japanese J. Appl. Phys.*, 50, 030001 2011.
46. Luque, A., Hegedus, S. (Eds.), *Handbook of Photovoltaic Science and Engineering*, Wiley, Chichester, 2011.
47. Green, M.A., Emery, K., Hishikawa, Y., Warta, W., Dunlop, E.D. Solar cell efficiency tables (Version 45), *Progress Photovoltaics: Res. Appl.*, 23, 1–9, 2015.
48. Urbain, F., Becker, J.P., Smirnov, V., Ziegler, J., Yang, F., Kaiser, B., Jaegermann, W., Finger, F. Influence of the operating temperature on the performance of silicon based photoelectrochemical devices for water splitting, *Mater. Sci. Semiconductor Process.*, 42, 142–146, 2016.
49. Urbain, F., Smirnov, V., Becker, J.-P., Lambertz, A., Rau, U., Finger, F. Light-induced degradation of adapted quadruple junction thin film silicon solar cells for photoelectrochemical water splitting, *Solar Energy Mater. Solar Cells*, 145, 142–147, 2016.
50. Du, B., Yang, R., He, Y., Wang, F., Huang, S. Nondestructive inspection, testing and evaluation for Si-based, thin film and multi-junction solar cells: An overview, *Renew. Sustain. Energy Rev.*, 78, 1117–1151, 2017.
51. Reynolds, S., Urbain, F., Smirnov, V. Spectral matching and outdoor solar to electrical conversion efficiency in thin-film silicon multi-junction solar cells, *J. Phys. Conf. Ser.*, 794, 012025, 2017.
52. Liu, B., Bai, L., Chen, Z., Zhang, X., Zhang, D., Zhang, X., Zhang, X. High efficiency triple junction thin film silicon solar cells with optimized electrical structure, *Progress Photovoltaics: Res. Appl.*, 23(10), 1313–1322, 2015.
53. De Wolf, S., Descoedres, A., Holman, Z.C., Ballif, C. High-efficiency silicon heterojunction solar cells: A review, *Green*, 2, 7–24, 2012.
54. Staebler, D.L., Wronski, C.R. Reversible conductivity changes in discharge-produced amorphous Si, *Appl. Phys. Lett.*, 31, 292–294, 1977.
55. Matsui, T., Bidiville, A., Maejima, K., Sai, H., Koida, T., Suezaki, T., Matsumoto, M., Saito, K., Yoshida, I., Kondo, M. High-efficiency amorphous silicon solar cells: Impact of deposition rate on metastability, *Appl. Phys. Lett.*, 106(5), 053901, 2015.
56. Smirnov, V., Urbain, F., Lambertz, A., Finger, F. High stabilized efficiency single and multi-junction thin film silicon solar cells, *Energy Proc.*, 102, 64–69, 2016.
57. Urbain, F., Smirnov, V., Becker, J.-P., Rau, U., Finger, F., Ziegler, J., Kaiser, B., Jaegermann, W. a-Si: H/ $\mu\text{c-Si:H}$ tandem junction based photocathodes with high open-circuit voltage for efficient hydrogen production, *J. Mat. Res.*, 29, 2605–2614, 2014.
58. Urbain, F., Smirnov, V., Becker, J.-P., Lambertz, A., Yang, F., Ziegler, J., Kaiser, B., Jaegermann, W., Rau, U., Finger, F. Multijunction Si photocathodes with

- tunable photovoltages from 2.0 V to 2.8 V for light induced water splitting, *Energy Environ. Sci.*, 9, 145–154, 2016.
59. Wilken, K., Diploma Thesis, Technische Universität Darmstadt, 2012.
 60. Wang, S., Smirnov, V., Chen, T., Holländer, B., Zhang, X., Xiong, S., Zhao, Y., Finger, F. Effects of oxygen incorporation in solar cells with a-SiOx: H absorber layer, *Japanese J. Appl. Phys.*, 54, 011401, 2014.
 61. Liu, B., Bai, L., Li, T., Changchun, W., Li, B., Huang, Q., Zhang, D., Wang, G., Zhao, Y., Zhang, X. High efficiency and high open-circuit voltage quadruple-junction silicon thin film solar cells for future electronic applications, *Energy Environ. Sci.*, 10, 1134, 2017.
 62. Isabella, O., Smets, A.H.M., Zeman, M. Thin-film silicon-based quadruple junction solar cells approaching 20% conversion efficiency, *Sol. Energy Mater. Sol. Cells*, 129, 82–89, 2014.
 63. Lambertz, A., Finger, F., Schropp, R.E.I., Rau, U., Smirnov, V. Preparation and measurement of highly efficient a-Si:H single junction solar cells and the advantages of $\mu\text{c-SiOx:H}$ n-layers, *Progress Photovoltaics: Res. Appl.*, 23, 939–948, 2015.
 64. Urbain, F., Smirnov, V., Becker, J.-P., Rau, U., Ziegler, J., Kaiser, B., Jaegermann, W., Finger, F. Application and modeling of an integrated amorphous silicon tandem based device for solar water splitting, *Solar Energy Mater. Solar Cells*, 140, 275–280, 2015.
 65. Muñoz-Portero, M.J., García-Antón, J., Guiñón, J.L., Leiva-García, R. Pourbaix diagrams for titanium in concentrated aqueous lithium bromide solutions at 25 °C, *Corr. Sci.*, 53, 1440–1450, 2011.
 66. Ziegler, J., Yang, F., Wagner, S., Kaiser, B., Jaegermann, W., Urbain, F., Smirnov, V., Becker, J.P., Finger, F. Interface engineering of titanium oxide protected a-Si:H/a-Si:H photoelectrodes for light induced water splitting, *Appl. Surf. Sci.* 389, 73–79, 2016.
 67. Fulton, C.C., Lucovsky, G., Nemanich, R.J. Electronic states at the interface of Ti–Si oxide on Si(100), *J. Vacuum Sci. Technol. B: Microelectron. Nanometer Struct.*, 20, 1726, 2002.
 68. Urbain, F., Smirnov, V., Becker, J.-P., Rau, U., Ziegler, J., Yang, F., Kaiser, B., Jaegermann, W., Hoch, S., Blug, M., Finger, F. Solar water splitting with earth-abundant materials using amorphous silicon photocathodes and Al/Ni contacts as hydrogen evolution catalyst, *Chem. Phys. Lett.*, 638, 25–30, 2015.
 69. Lee, J., Kwon, Y., Machunda, R. L., Lee, H.J. Electrocatalytic Recycling of CO_2 and Small Organic Molecules, *Chem. Asian J.*, 4, 1516–1523, 2009.
 70. Kibsgaard, J., Chen, Z., Reinecke, B.N., Jaramillo, T.N. Engineering the surface structure of MoS_2 to preferentially expose active edge sites for electrocatalysis, *Nat. Mater.*, 11, 963–969, 2012.
 71. Morales-Guio, C.G., Thorwarth, K., Niesen, B., Liardet, L., Patscheider, J., Ballif, C., Hu, X. Solar Hydrogen Production by Amorphous Silicon Photocathodes Coated with a Magnetron Sputter Deposited Mo_2C Catalyst, *J. Am. Chem. Soc.*, 137, 7035–7038, 2015.

72. Becker, J.P., Urbain, F., Smirnov, V., Rau, U., Ziegler, J., Kaiser, B., Jaegermann, W., Finger, F. Modeling and practical realization of thin film silicon-based integrated solar water splitting devices, *Phys. Status Solidi A*, 213, 1738–1746, 2016.
73. Urbain, F., Smirnov, V., Becker, J.P., Finger, F. Impact of Light-Induced Degradation on the Performance of Multijunction Thin-Film Silicon-Based Photoelectrochemical Water-Splitting Devices, *Acs Omega*, 1(5), 832–836, 2016.
74. Ager, J.W., Shaner, M.R., Walczak, K.A., Sharp, I.D., Ardo, S. Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting, *Energy Environ. Sci.*, 8, 2811–2824, 2015.
75. Becker, J.-P., Turan, B., Smirnov, V., Welter, K., Urbain, F., Wolff, J., Haas, S., Finger, F. A modular device for large area integrated photoelectrochemical water-splitting as a versatile tool to evaluate photoabsorbers and catalysts, *J. Mater. Chem. A*, 2017, 5, 4818.
76. Minemoto, T., Nagae, S., Takakura, H. Impact of spectral irradiance distribution and temperature on the outdoor performance of amorphous Si photovoltaic modules, *Sol. Energy Mater. Sol. Cells*, 91, 919–923, 2007.
77. Minemoto, T., Fukushige, S., Takakura, H. Difference in the outdoor performance of bulk and thin-film silicon-based photovoltaic modules, *Sol. Energy Mater. Sol. Cells*, 93, 1062–1065, 2009.
78. Cornaro, C., Andreotti, A. Influence of average photon energy index on solar irradiance characteristics and outdoor performance on photovoltaic modules, *Prog. Photovolt Res. Appl.*, 21, 996–1003, 2013.
79. Mutiara, L., Pegels, K., Reinders, A. Evaluation of Spectrally Distributed Irradiance in the Netherlands Regarding the Energy Performance of Various Pv Technologies, *Proc. IEEE 42nd Photovolt. Spec. Conf.*, p. 2719, 2015.
80. Reynolds, S., Smirnov, V. Modelling performance of two- and four-terminal thin-film silicon tandem solar cells under varying spectral conditions, *Energy Proc.*, 84, 251–260, 2015.
81. Welter, K., Smirnov, V., Becker, J.-P., Borowski, P., Hoch, S., Maljusch, A., Jaegermann, W., Finger, F. “The Influence of Operation Temperature and Variations of the Illumination on the Performance of Integrated Photoelectrochemical Water-Splitting Devices”, *ChemElectroChem*, 4, 2099–2108, 2017.
82. Rosen, J., Hutchings, G.S., Lu, Q., Rivera, S., Zhou, Y., Vlachos, D.G., Jiao, F. Mechanistic insights into the electrochemical reduction of CO₂ to CO on nanostructured Ag surfaces, *ACS Cat.*, 5, 4293–4299, 2015.
83. Wang, Y., Fan, S., Alotaibi, B., Wang, Y., Li, L., Mi, Z. A Monolithically Integrated Gallium Nitride Nanowire/Silicon Solar Cell Photocathode for Selective Carbon Dioxide Reduction to Methane, *Chem. Eur. J.*, 22, 8809 – 8813, 2016.
84. Irtem, E., Andreu, T., Parra, A., Hernández-Alonso, M.D., García-Rodríguez, S., Riesco-García, J.M., Penelas-Pérez, G., Morante, J.R. Low-energy formate

- production from CO₂ electroreduction using electrodeposited tin on GDE, *J. Mater. Chem. A*, 4, 13582–13588, 2016.
85. Habisreutinger, S.N., Schmidt-Mende, L., Stolarczyk, J.K. Photocatalytic reduction of CO₂ on TiO₂ and other semiconductors, *Angew. Chem. Int. Ed.*, 52, 7372–7408, 2013.
 86. Singh, M.R., Bell, A.T. Design of an artificial photosynthetic system for production of alcohols in high concentration from CO₂, *Energy Environ. Sci.*, 9, 193–199, 2016.
 87. Arai, T., Sato, S., Morikawa, T. A monolithic device for CO₂ photoreduction to generate liquid organic substances in a single-compartment reactor, *Energy Environ. Sci.*, 8, 1998–2002, 2015.
 88. Asadi, M., Kim, K., Liu, C., Addepalli, A.V., Abbasi, P., Yasaei, P., Phillips, P., Behranginia, A., Cerrato, J.M., Haasch, R., Zapol, P., Kumar, B., Klie, R.F., Abiade, J., Curtiss, L.A., Salehi-Khojin, A. Nanostructured transition metal dichalcogenide electrocatalysts for CO₂ reduction in ionic liquid, *Science*, 353, 467–470, 2016.
 89. Schreier, M., Heroguel, F., Steier, L., Ahmad, S., Luterbacher, J.S., Mayer, M.T., Luo, J., Gratzel, M. Solar conversion of CO₂ to CO using Earth-abundant electrocatalysts prepared by atomic layer modification of CuO, *Nat. Energy*, 2, 17087, 2017.
 90. Urbain, F., Tang, P., Carretero, N.M., Andreu, T., Gerling, L.G., Voz, C., Arbiol, J., Morante, J.R. A prototype reactor for highly selective solar-driven CO₂ reduction to synthesis gas using nanosized earth-abundant catalysts and silicon photovoltaics, *Energy Environ. Sci.*, 10, 2256–2266, 2017.
 91. Gurudayal, J., Bullock, D.F., Srankó, C.M., Towle, Y., Lum, M., Hettick, M.C., Scott, A., Javey, J., Ager. Efficient solar-driven electrochemical CO₂ reduction to hydrocarbons and oxygenates, *Energy Environ. Sci.*, 10, 2222, 2017.

Photoelectrochemical Cells: Dye-Sensitized Solar Cells

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Abstract

Energy is one of the indispensable needs of humans and economies globally, usually in the form of electricity which can be easily converted to other forms of our energy needs. Currently, there is the growing demand for energy; the challenge of the depleting non-renewable major energy source of fossil fuel; and the issue of the severe adverse environmental impact of the use of fossil fuels. Thus, the drive and research for sustainable, low cost and environmentally friendly alternative energy sources. The dye-sensitized solar cell (DSSC) has emerged as one of the viable alternative energy sources with its relatively high power conversion efficiency and low cost, and unique attributes of best performance under low light conditions and integration into building structures. However, there is still much room for improvement. Thus, this chapter broadly discusses the core principles, components, the current state and spin-offs from DSSCs and the possible future outlook of the DSSC in relation to its performance. It provides many references for more in-depth studies into more specific areas of DSSCs. Thus, the chapter aims to provide good fundamentals of DSSC to students and also serve as a quick reference and source of identifying research gaps in the DSSC field to researchers.

Keywords: DSSCs, history of DSSCs, plasmonic, hydrogen generation

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10.1 Introduction

The world population is increasing with growing and emerging economies, and fossil fuel, the major energy source (>80 % [1]), is finite, depleting, expensive, and has negative environmental impact concerns. Its most prominent environmental issue being its release of CO_2 causes global warming with negative ripple effects. These concerns have instigated the search for alternative energy sources that are renewable, low cost, eco-friendly, and sustainable. So far, common alternative energy sources include geothermal, biomass, hydropower, wind, and solar. Among these, solar seems to be the best option with the unique qualities of being clean, inexhaustible, and free of cost, with thermonuclear fusion reactions exuding abundant energy of $3.89 \times 10^{26} \text{ J s}^{-1}$ from the sun's core. While, averagely, only 1.367 KW m^{-2} (the *solar constant*) of this energy enters the Earth's atmosphere, it is nevertheless still more than enough for the world's energy need. N.S. Lewis [2] aptly puts this in perspective that, "More energy from sunlight strikes Earth in one hour than all of the energy consumed by humans in an entire year. Thus, photovoltaics (PVs) seem to be the most viable in the search for alternative energy sources." Currently, the most commercially available PVs are the solid-state *p-n* junction solar cells, most especially the Si-based (well-studied/mature first-generation PV) solar cells. These are relatively expensive due to the high crystallinity, purity, and the thick active material requirements. The second-generation (thin-film) PVs were designed in the form of thin films (1–4 μm) to reduce cost. Examples of these include amorphous and polycrystalline Si, cadmium telluride (CdTe), copper-indium-selenide/diselenide (CIS), and copper-indium-gallium-selenide/diselenide (CIGS). Then came the third-generation (with the sub-generation, Emerging PVs) PVs with novel designs over the first- and second-generation PVs to increase performance at even lower cost. These are still in their pre-/noncommercialized stages and hence are a great source of research interest. They include the dye-sensitized solar cell (DSSC) and its close relatives (organic solar cells, perovskite solar cells, and quantum-dot solar cells) and concentrating PVs [3].

A solar cell is basically a device that can convert light energy directly to electricity via the PV effect. Such a device should possess three principal features:

1. Ability to absorb light and generate electron-hole pair charge carriers
2. Separation of these charge carriers and
3. Extraction of these charge carriers to an external circuit

10.2 Brief History of Solar Cells to DSSCs

The history of solar cells began in 1839 when French physicist Alexandre-Edmond Becquerel observed the generation of electricity between two Pt electrodes immersed in an acidic solution of AgCl under illumination (first observation of the photovoltaic effect), with increasing magnitude as the intensity of the illumination increased [4]. Today, this is considered an electrochemical cell. Moser in 1887 [5] and Rigollot in 1893 [6] observed that the sensitivity of the electrodes increased when coated with a dye material. Review articles by Copeland and coworkers [7], T. Kuwana [8], M.D. Archer [9], and A.K. Jana [10] throw more light on the journey of DSSCs. In 1968, H. Gerischer *et al.* [11], using experimental data, proposed a theoretical model to explain the mechanism of dye sensitization on *n*-type ZnO and *p*-type perylene for the production of photocurrent. Then in 1971, H. Tributsch *et al.* [12] demonstrated for the first time the conversion of photon energy to electric current via electrochemical reactions of chlorophyll molecules on single-crystal ZnO, similar to photosynthesis, with efficient charge separation. Further research works were carried out with ZnO and TiO₂, especially in relation to the famous publication of A. Fujishima *et al.* [13] on TiO₂ where they used TiO₂ to split water into H₂ and O₂. In 1980, M.S. Matsumura *et al.* [14] obtained a power conversion efficiency (PCE) of 2.5 % with 562 nm light, using Al-doped porous ZnO and rose bengal dye among other works including CdS and TiO₂ using anionic, cationic, and zwitterion dyes.

Thus the PCEs of DSSCs were still low, basically from low dye loading with only ~ 1 % absorbed incident light, until the famous work of M. Gratzel *et al.* [15] in 1991, in which they used a 3D mesoporous nanocrystalline TiO₂ electrode to obtain an unprecedented PCE of 7.1 %. Since then, research in this field has spurred until the current certified record PCE of 11.9 % by Sharp [16] and uncertified record of 14.3 % by Kakiage *et al.* [17]. However, the theoretical maximum limit is 32 %, with a potential to subvert and exceed it. Moreover, an ideal 15–20 % PCE is needed to be effectively competitive commercially, thus necessitating more research in the DSSC field. Table 10.1 is a summary of significant events in the history of the DSSC.

10.3 Structure, Components, and Working Principle of the DSSC

The basic structure and working mechanism of the DSSC is as described in the following steps and shown in Figure 10.1.

Table 10.1 A summary of key events in the history of the DSSC.

Year	J_{sc} /mA cm ⁻²	V_{oc} /V	FF	PCE /%	Key materials (ECM/dye/HTM/CE)	Ref.	Comments
1839					AgCl- or AgBr-Pt/H ⁺ _(aq) /Pt	[4]	Discovery of PV effect.
1883	–	–	–	–	Metal/molten Se/Au	[100]	Great potential of PV.
1887	–	0.25	–	–	I- or Br-Ag/Erythrosine/Ag	[5]	Enhanced photocurrent generation by employing dyes.
1971	1×10^{-7} @ 670 nm	0.5	–	–	ZnO/Chlorophyll/ KCl-hydroquinone/Pt	[12]	1 st photon energy to current energy conversion.
1980	–	–	–	2.5 @ 562 nm	Al ₂ O ₃ -doped ZnO/Rose Bengal/ KI-I ₂ /Pt	[14]	First use of porous electrode DSSC.
1991	11.33	0.681	0.684	7.1	TiO ₂ /Ru-complex/I ⁻ -I ₃ ⁻ /Pt	[15]	Unprecedented high PCE invention of the Gratzel cell.
2001	6.8	0.67	0.46	2.2	TiO ₂ /Z316/ [Co(dbbip) ₂] ^{2+/3+} /Pt	[103]	Introduction of I ⁻ -I ₃ ⁻ -free 1-electron Co-based HTM DSSC.
2005	3.2	0.79	0.55	1.4	TiO ₂ /Ru-complex/ [Cu(dmp) ₂] ^{1+/2+} /Pt	[104]	Introduction of Cu-based HTM DSSC.
2006	11.9	0.66	0.68	5.1	TiO ₂ /D5/I ⁻ -I ₃ ⁻ /Pt	[101]	Pioneer work on the design of n-type D-π-A dyes.
2009	11.0	0.61	0.57	3.81	TiO ₂ /CH ₃ NH ₃ PbI ₃ /Li:I ₂ /Pt	[102]	Evolution of perovskite solar cells from DSSC.
2015	18.27	1.014	0.771	14.3	TiO ₂ / ADEKA-1 & LEG4 / [Co-(phen) ₃] ^{3+/2+} /Au-GNP	[17]	Record DSSC PCE so far.

NB: ECM: electron-conducting material; HTM: hole-conducting material.

10.3.1 The Transparent Conducting Oxide (TCO) Substrate

This is usually made of a thin layer ($\leq 1 \mu\text{m}$) of fluorine- or indium-doped tin oxide (F/ITO) coating on a transparent glass substrate.

The transparency is critical for maximum incident light passage to reach the photoelectron generating dye and the conductive F/ITO for reception of photogenerated electrons and their subsequent transport to the external circuit. Common TCOs usually have sheet resistance around $10 \Omega/\square$; however, EXEGER recently revealed that they have developed a TCO with a sheet resistance of $0.1 \Omega/\square$, thus allowing them to fabricate cells of large active areas with minimal negative effect of Joule's heat on performance.

10.3.2 The Hole Blocking Layer (HBL)

This is a thin compact layer of semiconductor electron transporting material (ETM) on the TCO to prevent short-circuiting cell from a contact between the TCO and the hole conducting material (HCM) electrolyte. It should be as thin as possible to reduce electron transport resistance through it to the minimum possible, but thick enough to prevent hole transportation through it. It can be prepared via a number of ways including chemical bath deposition (e.g., sol-gel and aqueous TiCl_4 [18]), spin coating [19], spray pyrolysis [20], atomic layer deposition [21], electrochemical deposition [22], thermal deposition [23], pulse laser deposition [24], etc.

10.3.3 The Photoanode

This is the porous layer of ETM that supports the dye/sensitizer. It receives photogenerated electrons and transports them to the TCO substrate. The

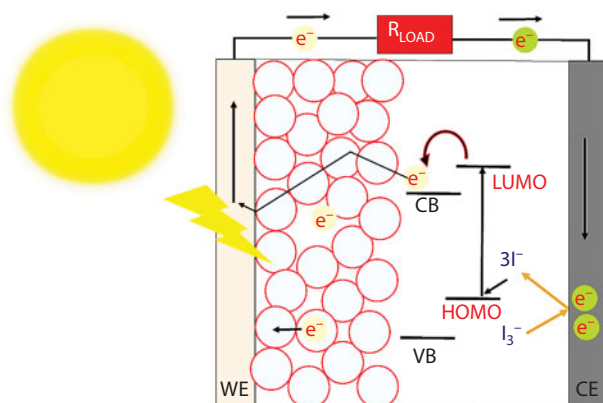


Figure 10.1 Schematic of the structure and working principle of the *n*-type DSSC.

common ETMs include ZnO , TiO_2 , SnO_2 , SrTiO_3 , Nb_2O_5 , Zn_2SnO_4 , $\text{SnO}_2@ \text{ZnO}$ core-shell, WO_3 , In_2O_3 , Ta_2O_5 , ZrO_2 , etc. [25–33], with NiO as the common p -type ETM for p -type DSSCs [34–36]. However, the best and most common ETM is TiO_2 for n -type DSSCs, with the key desirable properties of large bandgap; suitable band edge levels for charge injection and extraction; long lifetime of excited electrons; exceptional resistance to photocorrosion; nontoxicity and low cost [37–39]. Thus, further discussion on the ETM will be mainly in respect to TiO_2 . The ETM can be prepared in varied forms including nanoparticles (NPs), nanotubes (NTs), nanorods (NRs), and nanowires (NWs) as shown in Figure 10.2, or as a composite or various modifications of them. The major differences between the 1D nanostructures (NTs, NRs, and NWs) and the 3D NPs are that the 1D nanostructured ECMs have superior electron transport efficiency due to minimal or absence of intergrain boundaries but suffer relatively lower surface areas. The NPs on the other hand have lower electron transport efficiency due to the presence of many grain boundaries but have larger surface areas. However, the common and best performing DSSCs employ NPs. The photoanode typically has a thickness around $10\text{ }\mu\text{m}$. Additionally, the photoanode is expected to have a high surface area to be able to adsorb maximum optimal monolayer dye for high incident light absorbance. For efficient light harvesting (η_{LHE}), photoanode structures that scatter light (increasing the mean path of light within the cell) are desirable and designed.

Thus, various designs of the photoanode include high surface area porous morphology; hierarchical/scattering top layer morphology which increases both light scattering and surface area; plasmonic photoanodes which use the localized surface plasmon resonance (LSPR) effect of

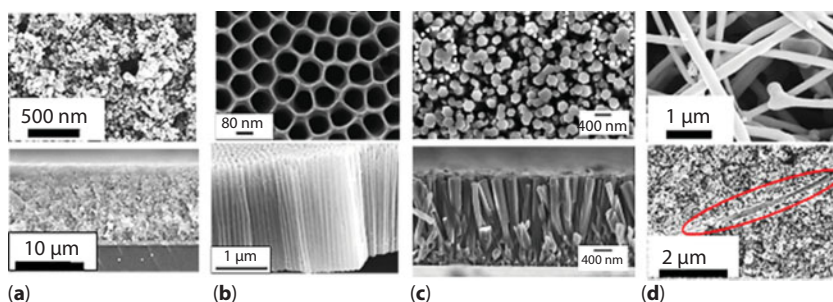


Figure 10.2 FE-SEM images of various ETM structures for DSSC photoanodes: (a) Top: surface view of TiO_2 P25 NPs; Bottom: cross-sectional view; (b) Top: surface view of TNTs; Bottom: cross-sectional view; (c) Top: surface view of ZnO NRs; Bottom: cross-sectional view (From W. K. tan et al., *nt. J. Energy Res.*, 37, 2013; with permission); and (d) Top: $\text{Ag}@ \text{TiO}_2$ NWs; Bottom: $\text{Ag}@ \text{TiO}_2$ NW located in a doped TiO_2 P25 photoanode.

subwavelength NPs to increase η_{LHE} ; and photonic crystal-modified photoanodes which also increase the η_{LHE} via the control of the reflected, diffracted, and refracted lights through the cell. Reference [40] is a good resource for further information.

The ETM is deposited via many routes with some common techniques including doctor blade coating (usually with a screen printer), spin coating, dip-coating, atomic layer deposition (ALD), electrophoretic deposition (EPD), electrochemical deposition, anodization, and thermal oxidation.

TiO₂, as the best ETM, has three natural crystalline forms: anatase, rutile (~ 98 %), and brookite, with brookite being the rarest of the three. Rutile is the thermodynamically most stable form at all temperatures with the metastable forms of anatase and brookite transitioning into rutile at temperatures around 500 and 750 °C, respectively, with other conditions such as pressure, reaction agents, and catalysts sensitively affecting these phase transitioning temperatures. Anatase and rutile have tetragonal structures, while brookite has an orthorhombic structure. Anatase is preferred for DSSs because of its superior charge transport and relatively higher surface area. Anatase and rutile have different band structures; hence a mixture of them as ETM causes trapping of charge carriers and promotes recombination processes. However, some studies have suggested that a little amount of rutile in anatase enhances performance [41–43]. Rutile as the ETM in DSSCs also gives a lower V_{oc} compared to anatase.

The bandgap of *n*-type single crystal anatase is ~ 3.2 eV with a resistivity of 10¹⁵ Ω cm [44]. Its lower conduction band (CB) edge is made of vacant Ti⁴⁺ 3d bands and the upper valence band (VB) edge made of filled O²⁻ p bands [45]. Bulk oxygen vacancies, Ti interstitials, and reduced crystal surfaces generate shallow electron traps, enabling excess electrons that can enhance conductivity, giving TiO₂ its *n*-type SC characteristics. However, at the same time, oxygen vacancies can also generate Ti³⁺ species that form a band about 0.5 eV below the CB of TiO₂, thus generating deep trap states which enable charge recombination and, thus, negatively affect device performance [44, 46]. The amount of defects can be influenced by factors such as heating and UV irradiation or oxygen-depriving conditions (processes that cause oxygen desorption) or exposure to the atmosphere (oxygen-rich) or oxonation (processes that promote oxygen adsorption, resulting in passivation). Thus, these complex defect states create a complex electron transport system in TiO₂ and consequently are difficult to investigate. However, theoretical and experimental evidence strongly support the notion that electrons are detrapped from subband states that lie deep in the tail of density of states (DOS) into the conduction band [47–49]. This also agrees with the multiple-trapping model for charge transport [50–51].

The occupation of the subband gap states at energy E_A can be determined using the Fermi-Dirac distribution function:

$$F(E_A - E_{Fn}) = 1/(1 + e^{(E_A - E_{Fn})/K_B T}) \quad (10.1)$$

the density of carriers at energy E_A (n_A) is given by, $n_A = N_A F_A$; N_A is the total number of trap sites. Using this, the density of electrons in the CB (n_{CB}) can be derived as a function of the quasi-Fermi level (E_{Fn}) as:

$$n_{CB} = N_{CB} e^{(E_A - E_{Fn})/K_B T} \quad (10.2)$$

and the conductivity of the film given by:

$$\sigma = n_{CB} e \mu \quad (10.3)$$

where μ is electron mobility, given that electron conduction takes place only in the CB.

From these relations, it can be deduced that conductivity increases with an increase of (probability of) electrons in the CB, which in turn increases as the Fermi level moves closer to the CB. Thus, any modification that eliminates deep trap states increases the conductivity of the TiO_2 ETM.

Different studies suggest that trap states are located in the bulk [48], at the interparticle grain boundaries [52] and at the particle surfaces [53–54]. Charge recombination is an interfacial phenomenon [55], hence bulk trap states are not relevant [56]. However, it is difficult to distinguish, experimentally, between interparticle grain boundaries trap states from interfacial trap states. However, the synthesis route heavily influences the type and location of defect states, with the understanding that weakly reducing synthesis conditions and annealing at low temperatures favor the formation of oxygen vacancies, while strongly reducing conditions and high temperature annealing favor the formation of titanium interstitials as the main defects states [44, 57]. Trap states can also affect the V_{oc} of a DSSC device, since V_{oc} can also be described as the energy difference between the quasi-Fermi level of the TiO_2 and the reduction potential of the HTM, with an increase in V_{oc} resulting from reduction in deep trap states and a lower V_{oc} from enhanced deep trap states (lowering of quasi-Fermi level). In addition, when trap states act as recombination centers, it leads to a decrease in J_{sc} .

At the TiO_2 -HTM interface, band bending occurs due to the formation of a space charge region (depletion layer) which provides an electric field

that separates electrons and holes. The space charge region can be cancelled by an external voltage to eliminate the band bending. This specific external voltage is known as flat-band potential, V_{FB} [58, 59]. Because this is an interfacial phenomenon, it means that surface trap states can influence this V_{FB} and thus affect effective charge separation. A negative shift in V_{FB} (upward shift of CB edge/Fermi level) can cause inefficient charge injection into the CB due to reduction in potential difference between the CB edge of TiO_2 and the lowest unoccupied molecular orbital (LUMO) of the dye, leading to lower J_{sc} and vice versa with additional consequence of possible increased charge recombination. In addition, since the sensitizer anchors to the TiO_2 surface, here again, it means the trap states can influence the dye adsorption depending on their distribution.

Thus with such a delicate and complicated electronic structure, it appears impossible to characterize the electron transport in TiO_2 . However, a high-throughput characterization and analytical approach can reveal reliable results.

TiO_2 nanostructures for the ETM can be synthesized in many ways with some of these including sol-gel, hydrothermal, solvothermal, anodization, micelle method, sonochemical, microwave synthesis, etc. [58, 59], mostly using titanium precursors like titanium alkoxides and titanium metal.

10.3.4 The Sensitizer/Dye

This functions to absorb photons from the incident light to excite electrons and subsequently inject them into the CB of the SCM. In the *p*-type DSSC, holes are injected from the highest occupied molecular orbital (HOMO) of the dye to the VB of the SCM. Thus, there are some essential characteristics a dye should have that include:

- a) It should absorb light across the visible spectrum and if possible into the NIR region.
- b) It should be photostable and also thermally and electrochemically stable.
- c) It should have an anchoring group(s) (e.g., RH_2PO_3 , RCOOH , RCOOR , RCOCl , RCOR) to strongly bind it onto the SCM surface.
- d) The energy of the excited LUMO level of the dye should be higher than that of the CB edge of the SCM for enough potential difference to drive efficient charge injection, while in the *p*-type, the HOMO of the dye should be at a more positive potential than the VB of the SCM.

- e) For efficient dye regeneration, the oxidized state level of the photosensitizer should be more positive than the redox potential of the HCM.
- f) Dye aggregation should be avoided and this can be achieved by optimizing the molecular structure of the dye or by the use of coadsorbers or optimizing the dyeing time period.

There are basically three classes of sensitizers: metal complex dyes, metal-free organic dyes, and natural organic dyes. The Ru-complex dyes have always been the best performing dyes in the order of N3 dye in the early 1990s with the highest cell PCE around 10 %; black dye in the mid-1990s with a highest PCE of about 10.4 %, and N719 since the early 2000s with a highest efficiency of about 11.2 %. However, by the early-to-mid-2000s, high-performing metal-free organic dyes had appeared on the scene with 11.5 % PCE using C259 + C239 dyes; and 11.9 % using YD2 + o-C8 porphyrin dyes + Y123 dyes. The highest PCE using porphyrin dye (SM 315) DSSC is 13.1 % and that of ADEKA-1 and LEG4 tandem sensitizers is 14.3 %, (the record laboratory DSSC PCE). These achievements have been possible from the added achievement of the development of new alternative HCMs such as the Co- and Cu-complex redox couples to replace the corrosive iodine-based HCM which also requires large-regeneration driving force (0.6 V).

A common description of the metal-free organic dye structure is donor (D)- π /linker-acceptor (A) (D— π —A) structure. The HOMO of the dye is usually associated with the donor component and the LUMO with the acceptor component which injects the electrons into the SCM, while the π system, that links the two, has a conjugated system, making it conductive via delocalization, and hence transports electrons from the donor to the acceptor. Thus, these parts can be tuned to reduce dye aggregation, retard charge recombination, enhance light absorption, and adjust the HOMO and LUMO energy levels of the dye, among other factors, to enhance η_{LHE} . However, a reverse structure is used in the *p*-type DSSC where holes are injected into the SCM and hence the anchoring group is near or part of the donor component. The current target of *p*-type DSSCs is to increase the V_{oc} to the level of the *n*-type to combine them into more efficient tandem structure DSSCs.

There are also natural sensitizers that are extracted from natural sources such as the leaves, fruits, flowers, roots, grains, husks, barks, etc. of plants and algae, among others. They are classified into the three main families of carotenoids, betalains, flavonoids/chlorophylls. Natural dyes have the main advantages of being low cost, high absorption coefficients in the visible

region, abundant in nature, facile extraction and preparation, complete biodegradability, and environmentally friendly. Their major disadvantages include low PCEs around 1 % (although combinations of these dyes have given PCEs around 4 %) and unstable DSSCs. Some suggested reference papers on sensitizers include references [60–66].

10.3.5 The HTM/Electrolyte

The HTM is responsible for receiving electrons from the CE, to be reduced, and in turn reduce the oxidized dye, effecting dye regeneration. It can be in a liquid or solid state. Although the solid state is preferred, mainly to overcome evaporation and/or leakage issues. However, the best performing HTMs are in a liquid state. Another alternative is the use of ionic liquids (ILs) such as derivatives of imidazolium salts, which have negligible vapor pressure, high conductivity, and low flammability; however, they are viscous causing lower ionic diffusion and hence lowering J_{sc} s. Nevertheless, the discovery of binary ILs like 1-ethyl-3-methylimidazolium dicyanide and 1-propyl-3-methylimidazolium iodide seems to be subverting this challenge. The standard HTM has been the I^-/I_3^- redox couple; however, it has the severe disadvantage of loss of a significant part of the cell voltage, from high dye regeneration driving force due to many intermediate reactions. Hence a new class of HTMs, the colorless Co complex redox couples with one electron reduction process, and reduction potentials closer to the energy levels of the HOMO of dyes (reduced dye regeneration driving force) have been developed to overcome this challenge [66–69]. A Co-complex HTM was used in the current record DSSC PCE of Kakiage *et al.* In addition, high-performance Cu-complex redox couples HTMs have been developed with the main advantages of faster dye regeneration, slow charge recombination, suitable redox potential, faster diffusion due to smaller Cu size, earth-abundant Cu, and faster electron self-exchange [70–73]. A typical performance comparison of the three main high-performance HTMs is shown in Table 10.2 [74].

10.3.6 The CE

This receives photogenerated electrons from the external circuit to catalyze the reduction of the HTM. The commonest efficient CE is Pt coated on a TCO. However, with the advent of the noncorrosive HTMs, the low cost and environmentally friendly carbon-based CE materials (graphite, carbon black, single-walled carbon nanotubes, multiwalled carbon nanotubes, graphene, graphene oxide, etc.) have sprung up and some actually perform

Table 10.2 Comparison of the three high-performance HTMs in DSSCs (Ref. 74; with permission).

Electrolyte (a)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
[Cu(dmbp) ₂] ^{2+ /1+}	14.4	1048	68.1	10.3
I ⁻ /I ₃ ⁻	15.8	724	70.4	8.0
[Co(bpy) ₃] ^{3+ /2+}	15.3	844	71.2	9.2

Other HCMs include Br₂/Br₃⁻; SCN⁻/(SCN)₃⁻; SeCN⁻/(SeCN)₃⁻; and the organic TEMPO.

better than the traditional good performing Pt [75–77]. The record cell of Kakiage *et al.* employed graphene nanoplatelets with the structure FTO/Au/graphene nanoplatelets.

The CE and working electrode (WE) are then sealed with either a hot-melt of plastic film (Surlyn® or Bynel®) or glass frits, usually between 25 and 50 μm to reduce internal resistance of the HTM, but not too thin to cause short circuiting. The cell is then filled with the HTM (or before sealing, especially for solid-state HTMs) and the holes sealed.

10.3.7 Electron Kinetics in an Active DSSC

The followings are typical electron dynamics time constants in a typical TiO₂-N719 dye-I⁻/I₃⁻ working DSSC cell:

1. Positive kinetics: charge injection from dye to CB of ETM—10⁻¹³ s (singlet state) and 10⁻¹¹ s (from the triplet state); charge transport through the ETM to the TCO—10⁻³s; charge relaxation in LUMO of dye and CB of ETM—10⁻¹² s; dye regeneration—10⁻⁶ s; reduction of redox species—10⁻⁵ s;
2. Negative kinetics: electron–hole recombination in dye—10⁻⁸ s; CB electron–HCM recombination—10⁻² s; CB electron–dye recombination—10⁻⁴ s

Thus, it is these variant electron kinetic time constants that are responsible for the effective charge separation in DSSCs, unlike the electric field in conventional *p-n* junction solar cells.

It is noteworthy to consider the following points in the fabrication of DSSCs for efficient and stable cells:

- Use smaller cell areas (0.25 cm² is common)
- Avoid contamination; use dedicated equipment

- Avoid humidity which can react with the anchors of dyes to the surface of the SCM
- Test many cells to ensure repeatability
- Undertake extra treatments such as TiCl_4 treatment (increases surface area and efficient charge transport) and ozonation (reduces negative trap states)
- Always wear gloves during cell preparation and characterization.

A critical point to consider in the fabrication of DSSCs is that no particular component can be necessarily considered the best in itself because DSSC is such a complex interaction of all components such that a change in one component will most often have to be optimized with all the other components to achieve high performance.

10.4 Characterization Techniques for DSSCs

This section discusses the most common techniques and the information that can be obtained from the measurements [59, 78–79]:

10.4.1 Computational Modeling

Computational modeling can be used to predict and design material properties. Density functional theory (DFT) is a popular method to investigate electronic structure due to its low computational cost, making it possible to quickly screen the effect of dopants for their suitability to increase the properties of TiO_2 . However, this method often underestimates the band-gap, leading to inaccurate predictions.

10.4.2 Morphological and Structural Studies

The structure of TiO_2 can be studied via several techniques. Electron microscopy offers the possibility to image nanostructures; with X-ray diffraction, crystal structure, average particle size, and dopant distribution can be determined; and surface area analysis for studies such as the effect of doping on surface area and dye adsorption.

10.4.2.1 Electron Microscopy

Electron microscopy makes it possible to visualize and characterize nanostructures. Scanning electron microscopy (SEM) is generally used

to study the surface topography and to measure the average particle size and film thickness. The latter can also be measured by a profilometer. If equipped with an energy dispersive X-ray (EDX) detector, the distribution of elements in the film can also be evaluated. Transmission electron microscopy (TEM) yields a higher resolution than SEM but requires extremely thin or small size samples, which makes TEM less well suited for topographic investigations. Atomic scale/high resolution mode allows imaging of the TiO_2 lattice and typically gives a better measurement of the average crystallite size; with an EDX detector, elemental composition can be evaluated.

10.4.2.2 X-Ray Diffraction

X-ray diffraction (XRD) is a precise method to determine the crystal structure of TiO_2 . It is routinely used to determine the crystal structure and the presence of impurity phases. The Rietveld refinement method allows a more detailed analysis of XRD spectra by using a least squares fit to approximate the measured profile. This way it is possible to determine the average crystallite size, D , by using the Scherrer formula:

$$D = K\lambda/\beta\cos\theta \quad (10.4)$$

where K is a dimensionless shape factor dependent on the particle shape (0.9 for spherical particles); λ is the wavelength of the X-rays; β is the full width half-maximum (FWHM) of the peak, after subtracting the instrumental line broadening; and θ is the Bragg angle. It is important to note that β and θ are in radians, whereas the instrumental output is usually in degrees. Furthermore, the interplanar spacing, d_{hkl} , can be calculated with Bragg's law:

$$d = \lambda/2\sin\theta \quad (10.5)$$

and using this interplanar spacing, the lattice parameters a and c can be calculated using the Bragg formula for a tetragonal ($a = b$) lattice:

$$1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2 \quad (10.6)$$

The change of the individual lattice parameters from impurities effect can be determined by calculating the distortion degree of the lattice using:

$$R = [2a\sqrt{(2/3)}]/c \quad (10.7)$$

Vegard's law provides an empirical method to assess the successful incorporation of a dopant. It states that there is a linear relation between the lattice distortion and the concentration of dopant. It requires that the crystal retains its lattice structure and the dopant and matrix form a solid solution.

10.4.3 Dye Adsorption

The amount of dye adsorbed on the TiO_2 surface is typically a good measure to determine how many photons will be absorbed. Dye adsorption depends on the porosity of the porous TiO_2 , which can be measured by gas adsorption. Gas adsorption isotherms are typically analyzed by the Brunauer–Emmett–Teller (BET) theory that yields the specific surface area of the material or by the Barrett–Joyner–Halenda (BJH) analysis, which yields the pore size distribution. Doping, however, often affects the adsorption of the dye to TiO_2 (in relation to the dye affinity) implying a difference in the amounts of adsorbed dye for samples with the same surface area.

In a more direct measurement, the dye can be desorbed from TiO_2 using a nonreactive solvent such as a 1:1 ethanol:1 M NaOH solvent system or 0.1 M *tetra*-butyl ammonium hydroxide (TBAOH). By comparing the optical absorbance of the extracted dye solutions to reference spectra, the amount of adsorbed dye can be estimated. A combination of the two methods can be used to calculate the average dye density.

10.4.4 Spectroscopic Techniques

By studying the interaction between light and matter, the electronic structure of the material can be determined. The bandgap, presence of defect states, and material composition can be found through these methods:

10.4.4.1 Optical (UV–Vis) Spectroscopy

This is basically used to characterize the sensitizer or photoanode's light absorbance or the SCM, especially in doping studies, to obtain the direct and indirect bandgap by determining the position of the absorption band edge. Absorbance/reflectance is usually recorded in the range of 300–800 nm. Absorbance and a direct bandgap E_g are related through:

$$\alpha E = C(E - E_g)^{1/2} \quad (10.8)$$

where α is the absorption coefficient, $E(= hc/\lambda)$ is the photon energy, and C is a proportionality constant. Sample reflectance, R , can be converted to the Kubelka–Munk function, $F(R)$, which is equivalent to the absorption coefficient in Eqn (10.8)

$$F(R) = (1 - R)^2/2R \quad (10.9)$$

Using a Tauc plot, it is possible to extract the direct and indirect band-gap. In a Tauc plot, $(F(R)E)^{1/r}$ is plotted versus E , where $r = 1/2$ for the direct bandgap and $r = 2$ for the indirect bandgap. Extrapolation of the linear part of the curve gives the bandgap energy at the intercept.

10.4.4.2 X-Ray Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy (XPS), the sample is irradiated with X-rays, and the number of escaping electrons and their energies are measured to gain information about the elemental composition and electronic state of the elements. For example, it is possible to quantify the amount of dopant in the sample and the Ti^{3+} to Ti^{4+} ratio.

10.4.4.3 FTIR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy measures optical absorption in a wide spectral range ($4400\text{--}4000\text{ cm}^{-1}$) and gives information about atomic bond vibrations. The intensity and position of the peaks of the stretching vibrations of Ti–O–Ti and Ti–O bonds give information about the purity (or conversely impurity or dopants present) of TiO_2 , and hence the interaction between TiO_2 and these foreign materials is related to the number and strength of Ti–O bonds. The size, electron affinity, and valency of the foreign material also influence the strength and orientation of neighboring Ti–O bonds.

10.4.4.4 Raman Spectroscopy

Raman spectroscopy is used to find rotational, vibrational, and other low-frequency modes in a system. A laser beam interacts with the sample modes, resulting in an up- or downshift of the photon energy. Each material has a distinct spectrum which allows the identification of impurity phases. Dopants alter the modes and in this way it is possible to measure the effect of the dopant on the TiO_2 crystal lattice. Raman spectroscopy is particularly useful to detect the formation of oxygen vacancies.

10.4.4.5 *Material Composition*

Several methods are able to determine the elemental composition in the TiO_2 photoanode with great precision. These include EDX spectroscopy, XPS spectroscopy, mass spectroscopy, or neutron activation analysis, which make use of unique “fingerprint” measurement spectra obtained upon sample irradiation.

10.4.5 **Electromagnetic Measurements**

The interaction between magnetic fields and free charges in the sample makes it possible to determine the type of conduction, carrier concentration, and trap states.

10.4.5.1 *Hall Effect Measurement*

When a magnetic field is applied on a current-carrying semiconductor, the charge carriers experience a force perpendicular to the magnetic field and the current. This is called the Hall Effect. By measuring the strength of this effect, the type of ETM (*p*- or *n*-type), and the carrier type and concentration can be determined.

10.4.5.2 *Electron Paramagnetic Resonance Analysis*

In electron paramagnetic resonance analysis (EPR), the spins of unpaired electrons are excited by microwave radiation in a magnetic field. This makes it possible to detect trapped electrons, which are unpaired, and the corresponding trap states. The technique is similar to nuclear magnetic resonance analysis (NMR) with the exception that, in NMR, nuclear spins are excited.

10.4.6 **(Photo-)Electrochemical Measurements**

By simulating real-world conditions, the performance of the solar cell can be predicted through the determination of the photovoltaic properties such as J_{sc} , V_{oc} , and FF . A wide range of measurements where the sample is subjected to periodic optical or electronic perturbations provide information about the concentration, diffusion length, and lifetime of electrons, CB position, density of trap states as well as transport and recombination processes. They include transient and decay measurements, electrochemical impedance spectroscopy (EIS), intensity-modulated photocurrent spectroscopy (IMPS), intensity-modulated photovoltage spectroscopy (IMVS), and open-circuit voltage decay (OCVD).

10.4.6.1 Photovoltaic Properties

The PCE of a solar cell is determined by measuring the current density as a function of applied voltage, under illumination. The illumination spectrum and intensity should approximate that of the sun. To this end, a standardized light source of 100 mW cm^{-2} (AM 1.5) solar simulator is used. From the current–voltage (I – V) curve, J_{sc} , V_{oc} , and FF are extracted. J_{sc} is the current in the absence of a net voltage, V_{oc} is the voltage in the absence of net current, and FF is a measure for the “squareness” of the curve and is a good indication of the resistances in the device. FF is determined by dividing the maximum power output, P_{max} , of the device by $(J_{sc} \times V_{oc})$. Parasitic resistances in the device lower FF for low voltages shunt resistances are dominating, while for high voltages the series resistance is important. These are revealed by I – V curves measured in the dark. Under dark conditions, a solar cell behaves as an ideal diode, and deviations from the ideal diode behavior arise from injected current leakage.

The quantum efficiency is defined as the ratio of incident photons of a certain energy to the charges collected. The external quantum efficiency (EQE) considers all the incident photons including those that are transmitted and reflected, whereas internal quantum efficiency (IQE) only takes the absorbed photons into account. From this, a correlation between the energy of the photon and the probability of charge collection can be found.

Lastly, the stability of the device can be tested by measuring the device efficiency over a long period of time.

10.4.6.2 Electrochemical Impedance Spectroscopy

By perturbing an applied voltage with a small sine wave modulation, the impedance can be found through the sinusoidal current response. Impedance can be defined as the frequency domain ratio of the voltage to current. This ratio is in a complex number form and the resulting function can be visualized with a Nyquist plot, where the real part of the function is plotted on the x-axis and the imaginary part on the y-axis. The system can be described by an equivalent circuit consisting of parallel and series connected circuit elements. From this, charge transfer and transport processes, and capacitance can be extracted.

10.4.6.3 Electron Transport

Because electron transport and recombination processes respond nonlinearly to different light intensities, they can be studied using a small

perturbation of light modulated onto a higher constant light intensity. The output can again be visualized with a Nyquist plot. In IMPS, a sinusoidal modulation of light intensity is applied and the photocurrent is measured as a function of this modulation.

The photocurrent response τ_{pc} depends on both the electron transport and electron recombination according to $(\tau_{pc})^{-1} = (\tau_{tr})^{-1} + (\tau_n)^{-1}$. Under short-circuit conditions, using I^-/I_3^- electrolyte, the electron lifetime, τ_n , is usually much larger than the transport time, τ_{tr} , implying $\tau_{pc} = \tau_{tr}$.

The chemical diffusion coefficient, D_n , can be derived from the transport time

$$D_n = d^2/C\tau_{tr} \quad (10.10)$$

where d is the thickness of the TiO_2 layer and C is a constant which depends on the absorption coefficient and direction of illumination.

10.4.6.4 Electron Lifetime

The measurement of the electron lifetime is similar to the electron transport, but the open-circuit potential rather than the photocurrent is measured. Under these conditions, photogenerated electrons are not extracted and will eventually recombine with holes. Using a small intensity modulation, the response time of the potential corresponds to the electron lifetime τ_n . An alternative is the OCVD method, where V_{OC} is measured as a function of time after the light source is switched off. The electron lifetime is calculated from the slope of the transient as:

$$\tau_n = kT/e (dV_{OC}/dt)^{-1} \quad (10.11)$$

The advantage of this method is that the electron lifetime can be determined for a wide potential range in just one measurement.

A third method is time-dependent charge extraction, where the lifetime is given by

$$\tau_n = Q(t)[(dQ(t))/dt]^{-1} \quad (10.12)$$

$Q(t)$ is the extracted charge after decay in the dark for the time, t , assuming recombination follows first-order kinetics.

IMVS and OCVD give similar values, while charge extraction usually gives a value that is about four times higher. This can be explained by the

fact that the former methods are based on the recombination of photoinduced excess charges, whereas the latter method gives an average lifetime for all the electrons in the TiO_2 .

10.4.6.5 *Electron Concentration*

The electron concentration can be measured through charge extraction methods, where the current is integrated over time after the light has been switched off. Alternatively, the capacity is measured. An open-circuit potential is established by a bias illumination after which a light pulse is applied. The resulting voltage rise is measured, while the transient photocurrent is measured separately under short-circuit conditions to calculate the injected charge. The capacity is given by the ratio of injected charge and voltage change. Lastly, the electron concentration can be estimated from the slope of a Mott–Schottky plot.

10.4.6.6 *Flat-Band Potential*

The flat-band potential, V_{FB} , can be derived from a Mott–Schottky plot, where the capacitance of the space charge region is measured as a function of voltage under depletion conditions. For a fit of the linear part of the curve, V_{FB} and electron density are given by the axis-intersect and the slope of the fit, respectively. The flat-band potential is usually referenced to a standardized electrode. A negative shift is indicative of an upward shift of CB, whereas a positive shift indicates a downward shift of CB.

10.4.6.7 *Charge Collection Efficiency*

The charge collection efficiency, η_{CC} , is an important parameter as it combines the results of electron transport and lifetime studies, enabling to find the ideal balance between the two. η_{CC} is given by:

$$\eta_{CC} = 1 - (\tau_{pc}/\tau_e) = 1/(1 - (\tau_{tr}/\tau_n)) \quad (10.13)$$

provided τ_{tr} and τ_n are measured at the same quasi-Fermi level. A similar parameter is the electron diffusion length, L :

$$L = \sqrt{(D_n \tau_n)} \quad (10.14)$$

which is the average diffusion distance of electrons before they recombine with holes.

10.5 Plasmonic DSSCs

From the evaluation of publications on “sensitized solar cells,” over 40 % and over 24 % were dedicated to the photoanode and sensitizer components of the DSSC, respectively [80]. These components are mainly focused on efficient light absorbance. Nevertheless, the absorbance range of DSSCs is still limited, mainly within the visible region unlike their contenders, the Si-based solar cells, which significantly absorb incident light from the visible into the NIR region. As for DSSCs, research on light harvesting has relatively been relegated. This is true to some extent and resulted in the fact that DSSCs are covering only one-third of the light spectrum. These sentiments were also expressed in the review paper of Jang *et al.* [81] on plasmonic solar cells. Nevertheless, there has been a lot of research work to increase the light-harvesting efficiency (LHE) of DSSCs with various innovative designs of the photoanode to increase efficient light absorbance. Some of these designs include large surface area porous photoanodes; hierarchically nanostructured and scattering top-layer photoanodes; aqueous TiCl_4 treatment of the TiO_2 SCM; design of new panchromatic absorbing dyes; photonic crystal photoanodes; and plasmonic photoanodes [82].

Plasmonic DSSCs were predicted to greatly increase η_{LHE} and PCE with thinner (less material) photoanode coatings, using the LSPR effect of sub-wavelength metallic nanostructures. It has the added advantage of facile preparation. However, the highest plasmonic DSSC PCE is still $< 11\%$ [83], but its predicted high potential is still viable. The main challenge of the LSPR effect is that apart from enhancing light absorbance, it also affects the electron dynamics of the DSSC. Thus, we think with the appropriate studies and understanding of these secondary effects, the application of plasmonics in DSSCs can be appropriately tuned and engineered to realize this predicted potential.

Subwavelength nanometallic structures (e.g., Ag, Au, Cu, Pt, and Pd) have delocalized CB electrons at their surface. These electrons are easily displaced to one side at the surface causing polarization of the nanostructure, and thus neutral particles of charged cloud of negative electrons and positive nuclei are formed, referred to as plasma. The restoring coulombic force between the displaced electrons and nuclei causes the electrons to oscillate about the surface in the form of plasmons. If light of similar frequency as that of the oscillating plasmons interacts with them, then resonance occurs, creating the LSPR phenomenon, as shown in Figure 10.3. The characteristics of the LSPR are affected by the size, shape, composition, and environment of the metal NP.

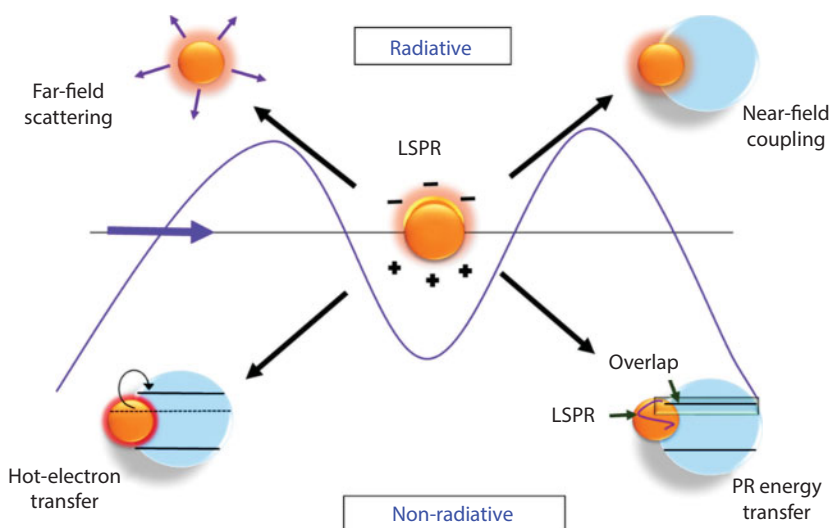


Figure 10.3 Schematic of the LSPR phenomenon and various energy transfer mechanisms (*Adapted from Ref. 83*).

Since electricity is the directional flow of charges, this LSPR generates a huge electric field which can increase the DOS of vicinal materials. The DOS of materials can also be understood as “channels” for storing and/or routing electromagnetic energy. Thus, the modification of DOS enhances light trapping and tailored emission spectra of materials [84]. In addition, the LSPR is not finite but decays over time, at the femtosecond scale [85]. When it decays, it can transfer energy in the form of photons, known as radiative transfer, or in the form of electron–hole pairs via Landau damping, referred to as nonradiative transfer [83, 86].

The radiative mechanism can be in the form of either scattering the incident, or secondary scattered light, known as far-field scattering (Figure 10.3; top left), thus increasing the light path length within the cell and its probability of being absorbed, or near-field coupling (Figure 10.3; top right) via coupling of the plasmon dipole (or higher order-pole) with vicinal materials (especially the sensitizer) to transfer the photon energy. This second radiative mechanism gives rise to the enhanced DOS.

The nonradiative mechanism has two routes too: (a) the Landau damping relaxation of the LSPR can lead to the generation of hot electron–hole pairs which can be injected to vicinal materials such as the SCM, after Fermi level equilibration and with minimal separation (≤ 2 nm). This process is described as hot-electron transfer (Figure 10.3; bottom left) and (b) via plasmon resonant energy transfer by dipole–dipole coupling with

the SCM, generating electron–hole pairs below and near the SCM CB edge. Unlike in the hot-electron transfer mechanism, here, minimal separation between the plasmonic NP and SCM; band alignment and Fermi level equilibration; and the condition for a noninsulating layer around the plasmonic NP are not essential. However, the SCM should be within the near field of the plasmonic NP, and there should be a spectral overlap between the two components.

In addition, LSPR can generate surface plasmon polaritons which can cause similar effects as LSPR and also enhance light absorbance and cell performance in the NIR of the solar spectrum [81, 86–88].

All these LSPR mechanisms can occur at the same time in a single cell but with one or more dominating over the others.

We have used 3.9- μm -thick TiO_2 nanotubes (TNTs), grown from FTO-Pt substrate, of ~ 50 nm pore size, filled with 10–50 nm Ag NPs via chemical bath immersion and subsequent reduction with UV irradiation. This was used to increase cell PCE of a pristine sample from 1.39 % to 2.03 % in the plasmonic DSSC [89]. In another work, using 23- μm -thick TiO_2 TNTs with a pore size of about 100 nm on a Pt substrate, and with similar deposition technique of Ag plasmonic NPs (10–30 nm) as above, we increased the PCE from 3.0 to 3.7 % [90]. In another work, using 13- μm -thick TiO_2 TNTs on Pt substrate with a pore size of about 100 nm and filled with 25–79 nm Ag NPs via an electrophoretic deposition technique, we were able to increase PCE from 3.70–5.01 % [91]. Based on these significant but relatively low plasmonic effect enhancements and coupled with other reported works of varying observations on the effect of plasmonic nanostructures, barring their different preparation routes and materials used [92–98], we decided to study the effects of plasmonic nanostructures on the performance of DSSCs using different Ag@ TiO_2 core–shell nanostructures of uniform size and shape NPs [18]; varying size and shape composite NPs [99]; and nanowires (NWs). The core–shell structure was used to protect the core plasmonic NPs from the high temperature (500 °C) processing of the photoanode and from the corrosive effect of the I^-/I_3^- redox couple electrolyte used.

From these studies, we observed that the plasmonic NPs unequivocally enhance light absorbance of N719 dye and have an electron-sink effect (observed by photoluminescence (PL) spectroscopy) in the trapping–detrapping of photogenerated electrons from the SCM. The trapping of electrons causes an upward shift of the CB edge of the TiO_2 , evidenced in increasing V_{oc} with increasing amount of plasmonic NPs loading. This reduces the potential difference between the LUMO of the dye and the CB edge of the TiO_2 , thus reducing charge injection efficiency, evidenced

in reducing J_{sc} and PCE with an increasing amount of plasmonic NPs loadings. However, at some optimal plasmonic NPs loadings, a lowering of the CB edge of the TiO_2 occurs, evidenced in a reduction in V_{oc} . This is understood to be due to deep trap states, thought to be catalyzed by the plasmonic NPs. This lowering of CB edge causes high efficient charge injection, evidenced in high J_{sc} , but with an accompanying exponential charge recombination, evidenced in reduced electron lifetime and charge collection efficiency. However, at this optimal concentration of plasmonic NPs, the combined effect of efficient charge generation and injection surpasses the effect of charge recombination. This leads to enhanced J_{sc} and PCE. The electron-sink effect also causes effective electron-hole separation which leads to reduced charge recombination and enhanced charge transport, evidenced in increasing FF and charge collection efficiency with increasing amount of plasmonic NPs loading.

We also found that there is usually a second optimal plasmonic NPs loading at a higher concentration than the first optimal loading. At this second optimal concentration, the enhancing effect is in the balance of the negative and positive effect of the plasmonic NPs on the key parameters of DSSC to give a net positive effect with enhanced PCE. This PCE can even be higher than that of the first optimal concentration. High charge recombination was also observed to be one of the drawbacks in plasmonic DSSCs.

Thus, armed with the knowledge of these effects, we believe a highly efficient plasmonic DSSC can be engineered. Table 10.3 below is a summary of selected published works on plasmonic DSSCs and their key performance characteristics.

10.6 Dye-Sensitized Solar Hydrogen Production

In the search for alternative sustainable energy sources, hydrogen gas (H_2) has emerged as one of the excellent clean fuels for the generation of energy. It can be obtained from water, which makes up $\sim 71\%$ of the earth's surface. Hydrogen can be used to generate electricity and power cars with more power than batteries, in fuel cells. It is also the main reagent for the preparation of synthetic fuels or the synthesis of important industrial chemical intermediates (e.g., reduction of CO_2 to CH_4 , CH_3OH , H_2NCONH_2 , etc.) [119]. Nature, in photosynthesis (which is basically a DSSC system), provides a blue print for the production of H_2 from water via splitting of water into O_2 and reduction equivalents of hydrogen to ultimately produce carbohydrates. The pioneer work of Fujishima and Honda [13] used a

Table 10.3 A summary of selected plasmonic DSSC publications over the years.

Plasmonic nanostructure	Size /nm	Ref. PCE /%	Enhanced PCE /%	Effects	Ref. (Year)
Film of Ag island	3.3–6	–	–	Enhanced light absorbance from LSPR effect.	105 (2000)
Layer-by-layer Au NPs film	30 (4 layers)	0.26	0.95	Schottky barrier reducing recombination of electrons to the dye or the electrolyte.	106 (2007)
Elliptical Au	$40 \times 120 \times 20$	–	–	LSPR-enhanced charge carrier generation.	107 (2008)
Au NPs	–	0.7	1.2	• LSPR-enhanced light absorbance. • Increased V_{oc}. • Blocks charge recombination from Schottky barrier effect.	108 (2009)
Ag@TiO ₂ and Ag@Al ₂ O ₃ @TiO ₂ film	–	–	–	Need for a pinhole-free PNP protection.	109 (2009)
Ag@TiO ₂	20	3.1 7.8	4.4 9.0	• Enhanced dye absorbance via near-field effect. • 25 % reduction in photoanode thickness.	110 (2011)
Au NPs	94 (20–94)	0.74	1.52	• > 50 nm NPs enhanced PCE via constructive interference from SPPs. • Decreasing PCE with smaller NPs due to destructive interference.	111 (2012)
AuNR@Ag ₂ S	50	5.8	7.1	• 37.6 % enhanced photocurrent generation at 600–720 nm region.	112 (2012)

(Continued)

Table 10.3 Cont.

Plasmonic nanostructure	Size /nm	Ref. PCE /%	Enhanced PCE /%	Effects	Ref. (Year)
Au@TiO ₂ NWs	160	2.98	5.40	- Enhanced electron transport. - LSPR enhancing effect.	113 (2012)
TiO ₂ @Au@TiO ₂ NPs	20	8.3	10.8	Panchromatic light harvesting and cell performance.	114 (2013)
Au@SiO ₂ triangular prisms	30–100	3.9	4.6	Panchromatic light harvesting from optimal overlap of LSPR and dye.	115 (2014)
Ag NW@TiO ₂	–	4.68	5.31	Reduced TiO ₂ /dye/electrolyte interfacial charge transfer impedance.	116 (2015)
Au NSs@SiO ₂ + Au NRs@SiO ₂	–	7.39	9.12	Enhanced broadband light harvesting.	117 (2016)
Cu-doped TiO ₂	–	6.41	8.65	- Enhancement of optical response toward visible range of solar spectrum. - Higher surface area for dye adsorption, active charge transfer sites, and reduced recombination.	118 (2017)
Ag@TiO ₂ NPs	20	4.66	5.00	- Two optimal enhancement NPs concentrated from efficient charge injection and balance of negative and positive effects. - Enhanced performance in the NIR region from direct charge injection from NPs.	18 (2017)

TiO₂ photoanode and a Pt cathode, with some external bias, to split water, using UV irradiation. However, this has a major limitation in TiO₂, with a wide bandgap, absorbing only in the narrow wavelength range of UV light, resulting in very low efficiencies.

Currently, hydrogen is mainly produced using water electrolysis (1.8–2.0 V), thermal water splitting, natural gas reforming, and coal gasification, with about 90 % produced from fossil fuels and its accompanying adverse environmental effects [120]. Thus, a clean, cost-effective, and sustainable approach will be to use the photocatalytic/solar-assisted water splitting approach by extending the photocatalyst wavelength absorbing range to include the visible and/or NIR regions. There are mainly two approaches to solar energy water splitting: (1) PV-driven electrolysis where the electricity or voltage generated using a solar cell is used to drive an electrolyzer to split water and (2) integrated system where a photocatalyst or a photochemical cell does the splitting. The former is relatively efficient but expensive (about 2.6 €/kg H₂; steam reforming of methane: 1 €/kg H₂); thus the integrated approach is more attractive [120, 121]. However, as mentioned earlier on, this approach has the major challenge of narrow absorbance range of the semiconductor photocatalyst/photoanode/photocathode, which requires an ideal bandgap, E_g , of $1.23 \text{ eV} < E_g < 3.0 \text{ eV}$ for visible light water splitting [120]. Efforts to tune the semiconductor optical absorbance into the visible region have not been particularly successful, with major issues of photocorrosion and appropriate bandgap edges alignment. On the other hand, spectral sensitization with dyes has shown some promising results and thus attracting a lot of research interests with a high reliance on the principles of DSSCs, which is a relatively established related field. Figure 10.4(a–c) shows schemes of water splitting with sensitized electrodes and electrochemical cell setups.

For spectral sensitization dye-sensitized hydrogen generation, a critical component is the dye. One key difference between these dyes and those of DSSCs is in their design to work efficiently in a water environment, unlike DSSC dyes that commonly work in organic solvents environment. It is thus very critical to control the structure of the dye: the anchor should be stable in a water medium, the dye system should be stable from hydrogenation by the generated hydrogen, and the LUMO and HOMO levels should be appropriately tuned to the CB and VB edges of the SCMs for efficient charge transfers. The dye structure should also be such as to make it hydrophilic in order not to repel the water away. On these bases, the D- π -A architecture has been found to be the most versatile and of general applicability, and with the introduction of thiopene-based spacers into the π moiety, enhanced light absorbance and long-term stability have been observed.

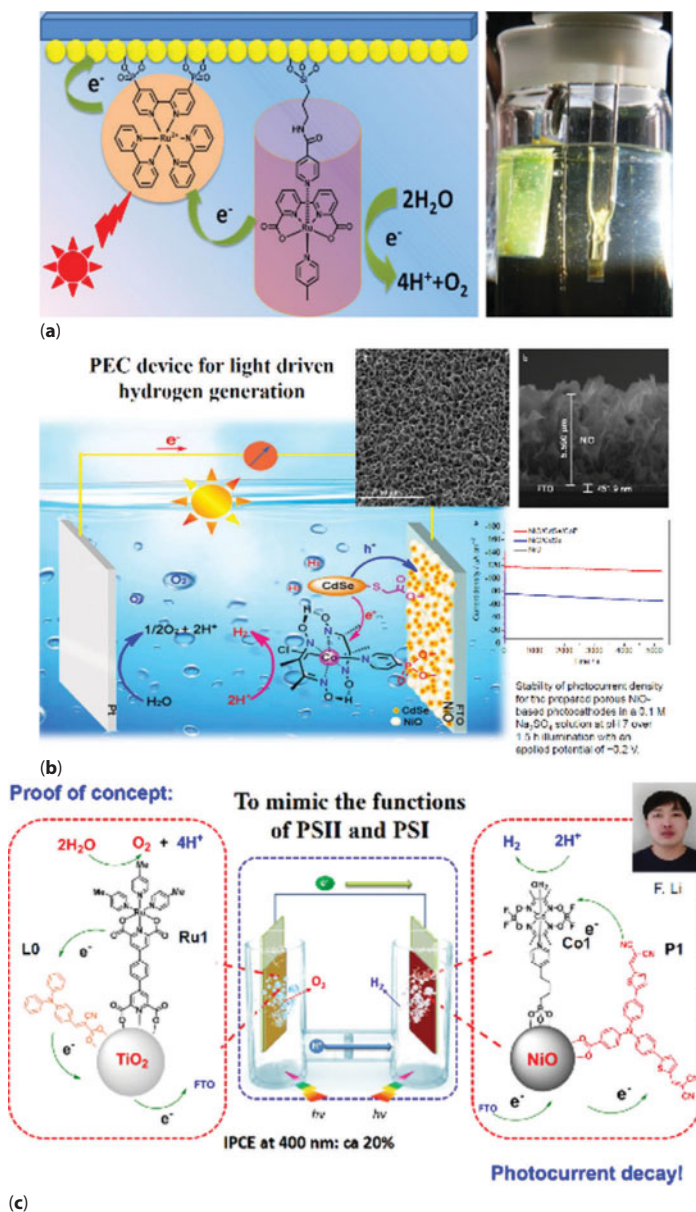


Figure 10.4 (Source: Licheng Sun, 1st Dynameo conference training and coaching, 2017) (a) A schematic and picture of water splitting using a photoactive anode based on *n*-type TiO₂ (based on Y. Gao et al., *J. Am. Chem. Soc.*, 135, 2013). (b) A schematic and SEM images of a photoactive cathode based on CdSe quantum dots-sensitized *p*-type NiO for H₂ generation (based on P. Meng et al., *J. Mater. Chem. A.*, 3, 2015). (c) A schematic of total water splitting using a Pt free Z-scheme PEC (based on, and with permission from, Fusheng Li et al., *J. Am. Chem. Soc.*, 137, 2015).

Although there have been significant achievements in dye-sensitized photocatalytic hydrogen generation/water splitting, the efficiencies are still very low, usually $< 1\%$ in terms of solar-to-hydrogen energy conversion efficiency, and still rich with many research gaps. Typical areas include research to enhance understanding of the sacrificial electron donors (e.g., EDTA and TEOA) which mainly effect dye regeneration for a continuous hydrogen production, and improvement of quick electron–hole recombination.

10.7 Applications and Future Outlook of DSSC

The followings are some facts on current DSSCs:

- Highest laboratory PCE: 14.3 % (ADEKA); modules: 9.9 % (Sony).
- Outdoor performance—production cost per kWh: a 10 % PCE rated DSSC module produces, over one year, the same amount of electricity as 14–15 % rated Si module (Sony).
- Electricity from ambient and indoor light: DSC outperforms all competitors
- Stability: >20 years outdoors accelerated testing (Dyesol, Fujikura)
- Energy payback time: <1 year (3GSolar and ECN life cycle analysis)

In addition, crystalline (mono and multi) Si-based solar cells with PCEs of 14–22.2 % (potential of 20–25 %) take the main share of the PV market (>85 %), followed by thin-film solar cells (CIGS, CdTe, a-Si, and $\mu\text{c-Si}$) with about 3–5 % market share and efficiencies of 6–16 % (potential of 12–20 %). The concentration solar cells mostly consisting of groups III–V based elements solar cells with efficiencies between 25 and 35 % (potential of 30–50 %) are trying to enter the market with many start-ups, and the emerging technologies which include DSSC, perovskite, organic-polymer, and nano-inorganics are entering the niche applications.

DSSC is now considered to be relevant and has a bright future as an emerging PV field, but the story should probably change to a complementary PV, from a competitor of low cost, to the well-established “expensive” Si PV because the price of Si production for PV has been pushed down by –99.5 % over the past 50 years. Nevertheless, DSSC is still cheaper. In addition, in terms of low-light condition performance, stability, effect of

modules inclination on performance, esthetic use, environmental friendliness, and building integrated photovoltaics (BIPVs), DSSC is the best. From an industrial point of view, high PCE is now not as critical as eco-friendliness and stability/reliability of materials. Thus, industry needs companies to produce more DSSC fabrication materials (e.g., HGlass (formerly G2E) cannot get a company to supply them 250 kg of dye per year); low-cost and diverse color dyes are needed; solventless/low solvent formulations fabrication systems (ionic liquid solvents (ILS) or inkjets) are needed; low-cost and stable (at high temperatures) TCO glass and low sheet resistance TCOs are also needed. National Research Institutes presented ambitious national targets such as about 30 % dependence on renewable energy by 2020 to 2030 from countries such as Korea and China. For example, the renewable energy targets of China are 15 % by 2020; 20 % by 2030, and 60 % by 2050, with solar energy as the main target to achieve them.

Various high-tech and fascinating applications of DSSCs are being studied: EXEGER has developed a DSSC powered E-reader with eternal battery life (a prototype that has not been charged for over 3 years). This suggests a huge market for self-sustaining devices that can rely on indoor lighting systems. They currently have a 300,000 m² factory with a target of a gigafactory of 10,000,000 m² by 2020. Thus, they will require a huge workforce. They have also developed a novel conductive layer substrate with sheet resistance of 0.1 $\Omega/\square$, compared to the common 10 $\Omega/\square$ of FTO and, hence, are able to make cells covering wide area without too much performance loss to substrate resistance. 3G solar has targets of DSSC use in wireless electronic devices to eliminate the need to use or replace or recharge batteries, with prototypes in Wi-Fi modules; G2E's (now HGlass) first energy noise barrier panels that yield energy of 10125 KWh/year; Graz Science tower of 1000 m² DSSC panels from HGlass inaugurated in September 2017, etc.

10.8 Academic

The highest uncertified record PCE is by the Japanese group of Kariage *et al.* of 14.3 % using organic dyes (ADEKA 1 and LEG 4) with Co-complex electrolytes [17]. It is known that DSSC is a complex interacting system and no one material component can be considered the ideal, but the optimization of selected component materials with the rest of the components was very critical to obtaining high performance DSSCs. Nevertheless, for n-type ETMs, TiO₂ is still the best material.

With regard to HCM/electrolytes, it has shifted from I⁻/I₃⁻ to Co-complexes, and now Cu-complexes, with the reminder that

optimization of selected material components is critical. The Co-complex HCMs, compared to the I^-/I_3^- , have a one-electron reduction process, are colorless, and are noncorrosive. The Cu-complex HCMs on the other hand improve upon the Co-complexes by being of lower cost, low dye regeneration potential of only ~ 0.1 V, efficient diffusion rate (about 3.4 times faster than the Co-based HTMs) due to their smaller size, slower recombination rate, and also noncorrosive. They also increase V_{oc} beyond 1 V. Thus with these new noncorrosive HTMs, low-cost C-based CE (graphite, graphene, graphene oxide, etc.), DSSCs have been reported with higher performances over the traditional Pt CE.

Studies on dye/sensitizers with fundamental and in-depth engineering of the various functional groups, ligands, and anchorage have been carried out, to achieve high-performance DSSCs. Nevertheless, some say that research on light harvesting has almost been neglected in the DSSC performance optimization efforts, which opinion is partially supported by the fact that the current DSSCs are not harvesting up to one-third of the light spectrum.

References

1. IEA, Key world energy statistics, 2017.
2. Lewis, N., Toward cost-effective solar energy use, *Science*, 315, 798–801, 2007.
3. International renewable energy agency, 1, 2012.
4. Becquerel, A.-E., Memory of the electrical effects produced under the influence of solar rays, *C. R. Acad. Sci. Paris*, 9, 561–567, 1839.
5. Moser, J. Notiz fiber verstärkung photoelektrischer ströme durch optische sensibilisierung, *Mh. Chem.*, 8, 373, 1887.
6. Rigollot, H. Memoirs and Communications, *C.R. Acad. Sci. Paris*, 116, 878, 1893.
7. Copeland, A.W., Black, O.D., Garrett, A.B. The photovoltaic effect, *Chem. Rev.*, 31, 177–226, 1942.
8. Kuwana, T., In *electroanalytical chemistry*, A.J. Bard (ed.), Marcel Dekker, New York, Vol. 1, 197, 1966.
9. Archer, M.D. Electrochemical aspects of solar energy conversion, *J. Appl. Electrochem.*, 5, 17–38, 1975.
10. Jana, A.K. Solar cells based on dyes, *J. Photochem. Photobiol. A: Chem.*, 132, 1–17, 2000.
11. Gerischer, H., Michel-Beyerle, M.E., Rebentrost, F., Tributsch, H. Sensitization of charge injection into semiconductors with large band gap, *Electrochim. Acta.*, 13, 1509–1515, 1968.
12. Tributsch, H., Calvin, M. Electrochemistry of excited molecules: photo-electrochemical reactions of chlorophylls, *Photochem. Photobiol.*, 14, 95–112, 1971.

13. Fujishima, A., Honda, K., Electrochemical photolysis of water at a semiconductor electrode, *Nature*, 238, 37–38, 1972.
14. Matsumura, M.S., Matsudaira, S., Tsubomura, H., Takata, M., Yanagida, H. Dye-sensitization and surface structures of semiconductor electrodes, *Ind. Eng. Chem. Prod. Res. Dev.*, 19, 415–421, 1980.
15. O'Regan, B., Gratzel, M. A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO_2 films, *Nature*, 353, 737–740, 1991.
16. Best research-cell efficiencies. NREL <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>, 2017.
17. Kakiage, K., Aoyama, Y., Yano, T., Oya, K., Fujisawa, J., Hanaya, M. Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes, *Chem. Commun.*, 51, 15894–15897, 2015.
18. Nbelayim, P., Kawamura, G., Tan, W.K., Muto, H., Matsuda, A. Systematic characterization of the effect of Ag@TiO_2 nanoparticles on the performance of plasmonic dye-sensitized solar cells, *Sci. Rep.*, 7, 15690, 2017.
19. Vivo, P., Ojanper, A., Smått, J.-H., Sand, S., Hashmi, S.G., Kaunisto, K., Ihalainen, P., Masood, M.T., Osterbacka, R., Lund, P.D., Lemmetyinen, H. Influence of TiO_2 compact layer precursor on the performance of perovskite solar cells, *Organic Electronics*, 41, 287–293, 2017.
20. Xiaoyan, D., Chengwu, S., Yanru, Z., Ni, W. Hydrolysis preparation of the compact TiO_2 layer using metastable TiCl_4 isopropanol/water solution for inorganic-organic hybrid heterojunction perovskite solar cells, *J. Semicond.*, 36, 074003, 1–4, 2015.
21. Kavan, L., Te'reault, N., Moehl, T., Grätzel, M. Electrochemical characterization of TiO_2 blocking layers for dye-sensitized solar cells, *J. Phys. Chem. C*, 118, 16408–16418, 2014.
22. Wu, Y., Yang, X., Chen, H., Zhang, K., Qin, C., Liu, J., Peng, W., Islam, A., Bi, E., Ye, F., Yin, M., Zhang, P., Han, L. Highly compact TiO_2 layer for efficient hole-blocking in perovskite solar cells, *Appl. Phys. Express*, 7, 052301–1–052301–4, 2014.
23. Kavan, L., O'Regan, B., Kay, A., Grätzel, M. Preparation of TiO_2 (anatase) films on electrodes by anodic oxidative hydrolysis of TiCl_3 , *J. Electroanal. Chem.*, 346, 291–307, 1993.
24. Ke, W., Fang, G., Wang, J., Qin, P., Tao, H., Lei, H., Liu, Q., Dai, X., Zhao, X. Perovskite solar cell with an efficient TiO_2 compact film, *ACS Appl. Mater. Interfaces*, 6, 15959–15965, 2014.
25. Tan, W.K., Lockman, Z., Abdul Razak, K., Kawamura, G., Muto, H., Matsuda, A. Enhanced dye-sensitized solar cells performance of ZnO nanorod arrays grown by low-temperature hydrothermal reaction, *Int. J. Energy Res.*, 37, 1992–2000, 2013.
26. Lee, S., Noh, J.H., Han, H.S., Yim, D.K., Kim, D.H., Lee, J.-K., Kim, J.Y., Jung, H.S., Hong, K.S. Nb-doped TiO_2 : a new compact layer material for TiO_2 dye-sensitized solar cells, *J. Phys. Chem. C*, 113, 6878–6882, 2009.

27. Tan, W.K., Lockman, Z., Abdul Razak, K., Kawamura, G., Muto, H., Matsuda, A. Enhanced dye-sensitized solar cells performance of ZnO nanorod arrays grown by low-temperature hydrothermal reaction, *Int. J. Energy Res.*, 37, 1992–2000, 2013.
28. Qiu, Y., Chen, W., Yang, S. Facile hydrothermal preparation of hierarchically assembled, porous single-crystalline ZnO nanoplates and their application in dye-sensitized solar cells, *J. Mater. Chem.*, 20, 1001–1006, 2010.
29. Ko, S.H., Lee, D., Kang, H.W., Nam, K.H., Yeo, J.Y., Hong, S.J., Grigoropoulos, C., P. Sung, H.J. Nanoforest of Hydrothermally Grown Hierarchical ZnO Nanowires for a High Efficiency Dye-Sensitized Solar Cell, *Nano Lett.*, 11, 666–671, 2011.
30. Kay, A., Grätzel, M. Dye-sensitized core-shell nanocrystals: improved efficiency of mesoporous tin oxide electrodes coated with a thin layer of an insulating oxide, *Chem. Mater.*, 14, 2930–2935, 2002.
31. O'Regan, B., Schwartz, D.T. Efficient dye-sensitized charge separation in a wide-band-gap *p-n* heterojunction, *J. Appl. Phys.*, 80, 4749–4754, 1996.
32. Hamann, W.T., Jensen, R.A., Martinson, A.B.F., Van Ryswyk, H., Hupp, J.T. Advancing beyond current generation dye-sensitized solar cells, *Energy Environ. Sci.*, 1, 66–78, 2008.
33. Pagliaro, M., Palmisano, G., Ciriminna, R., Loddo, V. Nanochemistry aspects of titania in dye-sensitized solar cells, *Energy Environ. Sci.*, 2, 838–844, 2009.
34. Farré, Y., Raissi, M., Fihey, A., Pellegrin, Y., Blart, E., Jacquemin, D., Odobel, F. A Blue diketopyrrolopyrrole sensitizer with high efficiency in nickel-oxide-based dye-sensitized Solar Cells, *ChemSusChem*, 10, 2618–2625, 2017.
35. Marinakis, N., Willgert, M., Constable, E.C., Housecroft, C.E. Optimization of performance and long-term stability of p-type dye-sensitized solar cells with a cycloruthenated dye through electrolyte solvent tuning, *Sustainable Energy Fuels*, 1, 626–635, 2017.
36. Brisse, R., Faddoul, R., Bourgeteau, T., Tondelier, D., Leroy, J., Campidelli, S., Berthelot, T., Geffroy, B., Jusselme, B. Inkjet printing NiO-Based p-type dye-sensitized solar cells, *ACS Appl. Mater. Interfaces*, 9, 2369–2377, 2017.
37. Jose, R., Thavasi, V., Ramakrishna, S. Metal oxides for dye-sensitized solar cells, *J. Am. Ceram. Soc.*, 92, 289–301, 2009.
38. Leung, D., Fu, X., Wang, C., Ni, M., Leung, M., Wang, X., Fu, X. Hydrogen production over titania-based photocatalysts, *ChemSusChem*, 3, 681–694, 2010.
39. Rauf, M., Meetani, M., Hisaindee, S. An overview on the photocatalytic degradation of azo dyes in the presence of TiO₂ doped with selective transition metals, *Desalination*, 276, 13–27, 2011.
40. Ahmada, M.S., Pandeya, A.K., Abd Rahima, N. Advancements in the development of TiO₂ photoanodes and its fabrication methods for dye sensitized solar cell (DSSC) applications. A review, *Renew. Sustain. Energy Rev.*, 77, 89–108, 2017.

41. Park, H., Park, Y., Kim, W., Choi, W. Surface modification of TiO_2 photocatalyst for environmental applications, *J. Photochem. Photobiol. C*, 15, 1–20, 2013.
42. Li, G., Richter, C.P., Milot, R.L., Cai, L., Schmuttenmaer, C.A., Crabtree, R.H., Brudvig, G.W., Batista, V.S. Synergistic effect between anatase and rutile TiO_2 nanoparticles in dye-sensitized solar cells, *Dalton Trans.*, 45, 10078–10085, 2009.
43. Kim, B.-M., Rho, S.-G., Kang, C.-H. Effects of TiO_2 structures in dye-sensitized solar cell, *J. Nanosci. Nanotechnol.*, 11, 1515–1517, 2011.
44. Scanlon, D.O., Dunnill, C.W., Buckeridge, J., Shevlin, S.A., Logsdail, A.J., Woodley, S.M., Catlow, C.R.A., Powell, M.J., Palgrave, R.G., Parkin, I.P., Watson, G.W., Keal, T.W., Sherwood, P. Band alignment of rutile and anatase TiO_2 , *Nat. Mater.*, 12, 798–801, 2013.
45. Ardakani, H. Electrical and optical properties of *in situ* “hydrogen-reduced” titanium dioxide thin films deposited by pulsed excimer laser ablation, *Thin Solid Films*, 248, 234–239, 1994.
46. Asahi, R., Taga, Y., Mannstadt, W., Freeman, A. Electronic and optical properties of anatase TiO_2 , *Phys. Rev. B Condens. Matter Mater. Phys.*, 61, 7459–7465, 2000.
47. Paxton, A., Thien-Nga, L. Electronic structure of reduced titanium dioxide, *Phys. Rev. B Condens. Matter Mater. Phys.*, 57, 1579–1584, 1998.
48. Nelson, J. Continuous-time random-walk model of electron transport in nanocrystalline TiO_2 electrodes, *Phys. Rev. B*, 59, 15374–15380.
49. Bisquert, J. Chemical diffusion coefficient of electrons in nanostructured semiconductor electrodes and dye-sensitized solar cells, *J. Phys. Chem. B*, 108, 2323–2332, 2004.
50. Dloczik, L., Ileperume, O., Lauermann, I., Peter, L.M., Ponomarev, E.A., Redmond, G., Shaw, N.J., Uhlendorf, I. Dynamic response of dye-sensitized nanocrystalline solar cells: characterization by intensity-modulated photocurrent spectroscopy, *J. Phys. Chem. B*, 101, 10281–10289, 1997.
51. Orenstein, J., Kastner, M. Photocurrent Transient Spectroscopy: Measurement of the Density of Localized States in $a\text{-As}_2\text{Se}_3$, *Phys. Rev. Lett.*, 46, 1421–1424, 1981.
52. Tiedje, T., Rose, A. A physical interpretation of dispersive transport in disordered semiconductors, *Solid State Commun.*, 37, 49–52, 1981.
53. Adachi, M., Murata, Y., Takao, J., Jiu, J., Sakamoto, M., Wang, F. Highly efficient dye-sensitized solar cells with a titania thin-film electrode composed of a network structure of single-crystal-like TiO_2 nanowires made by the “oriented attachment” mechanism, *J. Am. Chem. Soc.*, 126, 14943–14949, 2004.
54. Schlichthörl, G., Park, N.G., Frank, A.J. Evaluation of the charge-collection efficiency of dye-sensitized nanocrystalline TiO_2 solar cells, *J. Phys. Chem. B*, 103, (1999) 782–791.
55. Franco, G., Gehring, J., Peter, L.M., Ponomarev, E.A., Uhlendorf, I. Frequency-resolved optical detection of photoinjected electrons in dye-sensitized nanocrystalline photovoltaic cells, *J. Phys. Chem. B*, 103, 692–698, 1999.

56. Bisquert, J., Vikhrenko, V.S. Interpretation of the time constants measured by kinetic techniques in nanostructured semiconductor electrodes and dye-sensitized solar cells, *J. Phys. Chem. B*, 108, 2313–2322, 2004.
57. Kopidakis, N., Neale, N.R., Zhu, K., van de Lagemaat, J., Frank, A. J. Spatial location of transport-limiting traps in TiO_2 nanoparticle films in dye-sensitized solar cells, *Appl. Phys. Lett.*, 87, 202106.
58. Chen, X., Mao, S.S. Titanium dioxide nanomaterials: synthesis, properties, modifications and applications, *Chem. Rev.*, 107, 2891–2959.
59. Roose, B., Pathak, S., Steiner, U. Doping of TiO_2 for sensitized solar cells, *Chem. Soc. Rev.*, 44, 8326–8349.
60. Gratzel, M., Photoelectrochemical cells, *Nature*, 414, 338–344, 2001.
61. Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., Pettersson, H. Dye-sensitized solar cells, *Chem. Rev.*, 110, 6595–6663.
62. Qin, P., Zhu, H., Edvinsson, T., Boschloo, G., Hagfeldt, A., Sun, L. Design of an organic chromophore for p-type dye-sensitized solar cells, *J. Am. Chem. Soc.* 2008, 130, 8570.
63. Qin, P., Linder, M., Brinck, T., Boschloo, G., Hagfeldt, A., Sun, L. High Incident Photon-to-Current Conversion Efficiency of p-Type Dye-Sensitized Solar Cells Based on NiO and Organic Chromophores, *Adv. Mater.*, 2009, 21, 2993–2996.
64. Kumara, N.T.R.N., Limb, A., Lim, C.M., Petra, M.I. Ekanayake, P. Recent progress and utilization of natural pigments in dye sensitized solar cells: A review, *Renew. Sustainable Energy Rev.*, 78, 301–317, 2017.
65. Santhanamoorthi, N., Lo, C.-M., Jiang, J.-C. Molecular Design of Porphyrins for Dye-Sensitized Solar Cells: A DFT/TDDFT Study, *J. Phys. Chem. Lett.*, 4, 524–530, 2013.
66. Freitag, M., Teuscher, J., Saygili, Y., Zhang, X., Giordano, F. Liska, P., Hua, J., Zakeeruddin, S.M., Moser, J.E., Grätzel, M., Hagfeldt, A. Dye-sensitized solar cells for efficient power generation under ambient lighting, *Nature Photonics*. 11 (2017) 372–378.
67. Hua, J., Zakeeruddin, S.M., Moser, J.-E., Grätzel, M., Hagfeldt, A. Dye-sensitized solar cells for efficient power generation under ambient lighting, *Nat. Photonics*, 11, 372–379, 2017.
68. Fedlt, S.M., Gibson, E.A., Gabrielsson, E., Sun, L., Boschloo, G., Hagfeldt, A. Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells, *J. Am. Chem. Soc.*, 132, 16714–16724, 2010.
69. Yanagida, S., Yu, Y., Manseki, K. Iodine/Iodide-free dye-sensitized solar cells, *Acc. Chem. Res.*, 42, 1827–1838.
70. Boschloo, G., Hagfeldt, A. Characteristics of the Iodide/triiodide redox mediator in dye-sensitized solar cells, *Acc. Chem. Res.*, 42, 1819–1826, 2009.
71. Hattori, S., Wada, Y., Yanagida, S., Fukuzumi, S. Blue copper model complexes with distorted tetragonal geometry acting as effective electron-transfer mediators in dye-sensitized solar cells, *J. Am. Chem. Soc.*, 127, 9648–9654, 2005.

72. Bai, Y., Yu, Q., Cai, N., Wang, Y., Zhang, M., Wang, P. High-efficiency organic dye-sensitized mesoscopic solar cells with a copper redox shuttle, *Chem. Commun.*, 47, 4376–4378, 2011.
73. Cong, J., Kinschel, D., Daniel, Q., Safdari, M., Gabrielsson, E., Chen, H., Svensson, P.H., Sun, L., Kloo, L. Bis(1,1-bis(2-pyridyl)ethane) copper(I/II) as an efficient redox couple for liquid dye-sensitized solar cells, *J. Mater. Chem. A*, 4, 14550–14554, 2016.
74. Frietag, M., Daniel, Q., Pazoki, M., Sveinbjornsson, K., Zhang, J., Sun, L., Hagfeldt, A., Boschloo, B. High-efficiency dye-sensitized solar cells with molecular copper phenanthroline as a solid hole conductor, *Energy Environ. Sci.*, 8, 2634–2637, 2015.
75. Li, J., Yang, X., Yu, Z., Gurzadyan, G.G., Cheng, M., Zhang, F., Cong, J., Wang, W., Wang, H., Li, X., Kloo, L., Wang, M., Sun, L. Efficient dye-sensitized solar cells with [copper(6,6'-dimethyl-2,2'-bipyridine)₂]^{2+/1+} redox shuttle, *RSC Adv.*, 7, 4611–4615.
76. Ju, M.J., Kim, J.C., Choi, H.J., Kim, S.G., Lim, K., Ko, J., Lee, J.J., Jeon, I.Y., Baek, J.B., Kim, H.K. N-doped graphene nanoplatelets as superior metal-free counter electrodes for organic dye-sensitized solar cells, *ACS Nano*, 7, 5243–5250, 2013.
77. Ju, M.J., Jeon, I.J., Kim, J.C., Lim, K., Choi, H.J., Jung, S.M., Choi, I.T., Eom, Y.K., Kwon, Y.J., Ko, J., Lee, J.J., Kim, H.K., Baek, J.B. Graphene nanoplatelets doped with N at its edges as metal-free cathodes for organic dye-sensitized solar cells, *Adv. Mater.*, 26, 3055–3062, 2014.
78. Takagi, K., Magaino, S., Saito, H., Aoki, T., Aoki, D. Measurements and evaluation of dye-sensitized solar cell performance, *J. Photochem. Photobiol. C: Photochem. Rev.*, 14, 1–12, 2013.
79. Pazoki, M., Cappel, U.B., Johansson, E.M.J., Hagfeldt, A., Boschloo, G. Characterization techniques for dye-sensitized solar cells, *Energy Environ. Sci.*, 10, 672–709, 2017.
80. Ye, M., Wen, X., Wang, M., Iocozzia, J., Zhang, N., Lin, C., Lin, Z. Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes, *Mater. Today*, 18, 155–162, 2015.
81. Jang, Y.H., Jang, Y.J., Kim, S., Quan, L.N., Chung, K., Kim, D.H. Plasmonic solar cells: from rational design to mechanism overview, *Chem. Rev.*, 116, 14982–15034, 2016.
82. Gao, X.-D., Li, X.-M., Gan, X.-Y. Enhancing the light harvesting capacity of the photoanode films in dye-sensitized solar cells, *InTech*, 169–202, 2013.
83. Erwin, W.R., Zaricka, H.F., Talbert, E.M., Bardhan, R. Light trapping in mesoporous solar cells with plasmonic nanostructures, *Energy Environ. Sci.*, 9, 1577–1601, 2016.
84. Boriskina, S.V., Ghasemi, H., Chen, G. Plasmonic materials for energy: From physics to applications, *Mater. Today*, 16, 375–386, 2013.
85. Ueno, K., Oshikiri, T., Sun, Q., Shi, X., Misawa, H. Solid-state plasmonic solar cells, *Chem. Rev.* 118 (6), pp 2955–2993, 2017.

86. Ma, X.-C., Dai, Y., Yu, L., Huang, B.-B. Energy transfer in plasmonic photocatalytic composites, *Light Sci. Appl.*, 5, 1–13, 2016.
87. Ferry, V.E., Sweatlock, L.A., Pacifici, D., Atwater, H.A. Plasmonic nanostructure design for efficient light coupling into solar cells, *Nano Lett.*, 8, 43914397, 2008.
88. Ding, I.K., Zhu, J., Cai, W., Moon, S.-J., Cai, N., Wang, P., Zakeeruddin, S.M., Gratzel, M., Brongersma, M.L., Cui, Y., McGehee, M.D. Plasmonic dye-sensitized solar cells, *Adv. Energy Mater.*, 1, 52–57, 2011.
89. Kawamura, G., Ohmi, H., Tan, W.K., Lockman, Z., Muto, H., Matsuda, A. Ag nanoparticle-deposited TiO₂ nanotube arrays for electrodes of dye-sensitized solar cells. *Nanoscale Res. Lett.*, 10, 10:219, 2015.
90. Nyein, N., Tan, W.K., Kawaura, G., Matsuda, A., Lockman, Z. Anodic Ag/TiO₂ nanotube array formation in NaOH/fluoride/ethylene glycol electrolyte as a photoanode for dye-sensitized solar cells, *Nanotechnology*, 27, 355605–355616, 2016.
91. Wei, X., Nbelayim, P.S., Kwamura, G., Muto, H., Matsuda, A. Ag nanoparticle-filled TiO₂ nanotube arrays prepared by anodization and electrophoretic deposition for dye-sensitized solar cell, *Nanotechnology*, 28, 135207–135214, 2017.
92. Villanueva-Cab, J., Montañó-Priede, J.L., Pal, U. Effects of Plasmonic nanoparticle incorporation on electrodynamics and photovoltaic performance of dye sensitized solar cells, *J. Phys. Chem. C*, 120, 10129–10136, 2016.
93. Choi, H., Chen, W.T., Kamat, P.V. Know thy nano neighbor. plasmonic versus electron charging effects of metal nanoparticles in dye-sensitized solar cells, *ACS Nano*, 6, 4418–4427, 2012.
94. Qi, J., Dang, X., Hammond, P.T., Belcher, A.M. Highly efficient plasmon-enhanced dye-sensitized solar cells through metal@oxide core-shell nanostructure, *ACS Nano*, 5, 7108–7116.
95. Xu, Q., Liu, F., Liu, Y., Cui, K., Feng, X., Zhang, W., Huang, Y. Broadband light absorption enhancement in dye-sensitized solar cells with Au-Ag alloy popcorn nanoparticles, *Sci. Rep.*, 3, 2112, 2013.
96. Guo, L., Jackman, J.A., Yang, H.-H., Chen, P., Cho, N.-J., Kim, D.-H. Strategies for enhancing the sensitivity of plasmonic nanosensors, *Nano Today*, 10, 213–239, 2015.
97. Wen, W., Ishikawa, K., Kishima, M., Yamada, K., Effects of silver particles on the photovoltaic properties of dye-sensitized TiO₂ thin films, *Sol. Energy Mater. Sol. Cells*, 61, 339–351, 2000.
98. Lim, S.P., Pandikumar, A., Lim, H.N., Ramaraj, R., Huang, N.M. Boosting Photovoltaic Performance of Dye-Sensitized Solar Cells Using Silver Nanoparticle-Decorated N,S-Co-Doped-TiO₂ Photoanode, *Sci. Rep.*, 5, 11922, 2015.
99. Nbelayim, P., Kawamura, G., Abdel-Galeil, M.M., Tan, W.K., Wei, X., Muto, H., Matsuda, Effects of multi-sized and -shaped Ag@TiO₂ nanoparticles on the performance of plasmonic dye-sensitized solar cells, *X. J. Ceram. Soc. Jpn.*, 126, 139–151, 2018.

100. Fritts, C.E. On a New Form of Selenium Photocell, *Am. J. Sci.*, 26, 465, 1883.
101. Hagberg, D.P., Edvinsson, T., Marinado, T., Boschloo, G., Hagfeldt, A., Sun, L. A novel organic chromophore for dye-sensitized nanostructured solar cells, *Chem. Commun.*, 0, 2245–2247, 2006.
102. Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells solar, *J. Am. Chem. Soc.*, 131, 6050–6051, 2009.
103. Nusbaumer, H., Moser, J.-E., Zakeeruddin, S.M., Nazeeruddin, M.K., Gratzel, M. CoII(dbbip)2²⁺ Complex Rivals Tri-iodide/Iodide Redox Mediator in Dye-Sensitized Photovoltaic Cells, *J. Phys. Chem. B*, 105, 10461–10464, 2001.
104. Hattori, S., Wada, Y., Yanagida, S., Fukuzumi, S. Blue copper model complexes with distorted tetragonal geometry acting as effective electron-transfer mediators in dye- sensitized solar cells, *J. Am. Chem. Soc.*, 127, 9648–9654, 2005.
105. Wen, C., Ishikawa, K., Kishima, M., Yamada, K. Effects of Silver Particles on the Photovoltaic Properties of Dye-sensitized TiO₂ Thin Films, *Sol. Energy Mater. Sol. Cells*, 61, 339–351, 2000.
106. Su, Y.H., Lai, W.H., Teoh, L.G., Hon, M.H., Huang, J.L., Layer-by-layer Au nanoparticles as a Schottky barrier in a water-based dye-sensitized solar cell, *Appl. Phys. A: Mater. Sci. Process.*, 88, 173–178.
107. Hägglund, C., Zäch, M., Kasemo, B., Enhanced charge carrier generation in dye sensitized solar cells by nanoparticle plasmons, *Appl. Phys. Lett.*, 92, 013113, 2008.
108. Chen, Z., Tang, Y., Liu, C., Leung, Y., Yuan, G., Chen, L., Wang, Y., Bello, I., Zapien, J., Zhang, W., Lee, C.S., Lee, S.T., Vertically aligned ZnO Nanorod arrays sensitized with gold nanoparticles for Schottky barrier photovoltaic cells, *J. Phys. Chem. C*, 113, 13433–13437, 2009.
109. Standridge, S.D., Schatz, G.C., Hupp, J.T. Toward plasmonic solar cells: protection of silver nanoparticles via atomic layer deposition of TiO₂, *Langmuir*, 25, 2596–2600, 2009.
110. Qi, J., Dang, X., Hammond, P.T., Belcher, A.M. Highly efficient Plasmon-enhanced Dye-sensitized Solar Cells through metal@oxide core-shell nanostructure, *ACS Nano*, 5, 7108–7116, 2011.
111. Deepa, K., Lekha, P., Sindhu, S. Efficiency enhancement in DSSC using metal nanoparticles: a size dependent study, *Sol. Energy*, 86, 326–330, 2012.
112. Chang, S., Li, Q., Xiao, X., Wong, K.Y., Chen, T. Enhancement of low energy sunlight harvesting in dye-sensitized solar cells using plasmonic gold nanorods, *Energy Environ. Sci.*, 5, 9444–9448, 2012.
113. Sahu, G., Gordon, S.W., Tarr, M.A. Synthesis and application of core-shell Au–TiO₂ nanowire photoanode materials for dye sensitized solar cells, *RSC Adv.*, 2, 573–582, 2012.
114. Dang, X., Qi, J., Klug, M.T., Chen, P.-Y., Yun, D.S., Fang, N.X., Hammond, P.T. Belcher, A.M. Tunable localized surface plasmon-enabled broadband light-harvesting enhancement for high efficiency panchromatic dye-sensitized solar cells, *Nano Lett.*, 13, 637–642, 2013.

115. Gangishetty, M.K., Scott, R.W.J., Kelly, T.L. Panchromatic enhancement of light-harvesting efficiency in dye-sensitized solar cells using thermally annealed Au@SiO₂ triangular nanoprisms, *Langmuir*, 30, 14352–14359, 2014.
116. Huang, P.-C., Chen, T.-Y., Wang, Y.-L., Wu, C.-Y., Lin, T.-L. Improving interfacial electron transfer and light harvesting in dye-sensitized solar cells by using Ag nanowire/TiO₂ nanoparticle composite films, *RSC Adv.*, 5, 70172–70177, 2015.
117. Zhang, Y., Sun, Z., Cheng, S., Yan, F. Plasmon-Induced Broadband Light-Harvesting for Dye-Sensitized Solar Cells Using a Mixture of Gold Nanocrystals, *ChemSusChem*, 9, 813–819, 2016.
118. Dhondea, M., Sahu, K., Murtya, V.V.V., Nimalab, S.S., Bhargava, P. Surface plasmon resonance effect of Cu nanoparticles in a dye sensitized solar cell, *Electrochim. Acta*, 249, 89–95, 2017.
119. Cecconi, B., Manfredi, N., Montini, T., Fornasiero, P., Abboto, A. Dye-sensitized solar hydrogen production: the emerging role of metal-free organic sensitizers, *Eur. J. Org. Chem.*, 31, 5194–5215, 2016.
120. Chowdhury, P., Malekshoar, G., Ray, A.K. Dye-sensitized photocatalytic water splitting and sacrificial hydrogen generation: current status and future prospects, *Inorganics*, 5, 34, 2017.
121. Armaroli, N., Balzani, V. Solar electricity and solar fuels: status and perspectives in the context of the energy transition, *Chem. Eur. J.*, 22, 32–57, 2016.

Photocatalytic Formation of Composite Electrodes for Semiconductor-Sensitized Solar Cells

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Abstract

The chapter presents a review of recent reports on the photocatalytic formation of metal chalcogenide/metal oxide nanoheterostructures—perspective components of solar cells and other light-harvesting systems. We present recent results on the photocatalytic deposition of metal sulfide (CdS, PbS, MoS₂, Cu_xS, etc.) and metal selenide (CdSe, PbSe) nanoparticles on the surface of nanocrystalline oxides (TiO₂, ZnO) and highlight the mechanisms of these reactions and special features of the photodeposited metal chalcogenide nanoparticles differing them from the counterparts prepared by other conventional techniques. The photocatalytically formed heterostructures typically serve as much more efficient photoanodes of solar cells and photocatalysts as compared to similar composites synthesized in “dark” regimes. This advantage stems from a “memory” effect when the chalcogenide nanoparticles photodeposited on the most active sites of the oxide photocatalyst surface provide an efficient interfacial transfer of the charge carriers photogenerated in the chalcogenide/oxide composites. The photocatalytic deposition method is very versatile and can potentially be extended to new emerging photosensitive materials such as layered and organic semiconductors and metal-organic frameworks. Of special interest is also a further search for reliable methods of variation of the morphology (size, shape, aggregation mode, etc.) of the photodeposited metal chalcogenides.

Keywords: Charge separation, charge transfer, metal chalcogenide, nanocrystals, photodeposition

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11.1 Introduction

The semiconductor nanocrystal-based solar cells emerged in recent years as an alternative to the well-established dye-sensitized solar cells reaching a solar light conversion of $\sim 12\%$ [1–6]. The semiconductor nanoparticles (NPs) can be used as efficient and stable broadband light absorbers both in bulk heterojunction and in liquid-junction solar cells. In the latter cell type, a liquid electrolyte separates spatially a light-sensitive photoanode/photocathode and a counterelectrode allowing for an independent design of these components. Simultaneously, the electrolyte connects both electrodes by a dissolved charge-shuttling redox couple.

Typically, the light-sensitive electrodes of a semiconductor-sensitized solar cell (SSSC) are built on a composite of a wide-bandgap oxide (TiO_2 , ZnO , NiO) with narrower-bandgap NPs (chalcogenides of cadmium, lead, indium, and other metals) [3, 4, 7]. The photoelectrode contacts with an aqueous electrolyte containing a sulfide/polysulfide redox shuttle, and in this way, it is electrically connected to the counterelectrode based on chalcogenides of Cu, Ni, Co, etc.

The choice of methods used for the preparation of both the photoanodes and counterelectrodes plays a crucial role in the SSSC performance and, therefore, new emerging methods are constantly probed while the well-known ones modified and perfected to achieve an enhanced efficiency of the light conversion. One of such methods exploits an inherent photocatalytic activity of wide-bandgap metal oxides, such as TiO_2 and ZnO to decorate the oxide surface with narrower-bandgap metal chalcogenide NPs [6, 8, 9] or with metal NPs [6, 9, 10] by a novel approach of the *in situ* photocatalytic deposition.

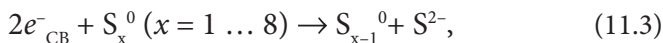
In this chapter, we focus on a review of our recent studies on the *photocatalytic formation* of NP-based composite electrodes for the SSSCs. We aim to show that the deposition of metal sulfide NPs on the surface of nanocrystalline titania and zinc oxide via the photocatalytic reduction of sulfur allows producing a variety of photoanodes (ZnO/CdS , TiO_2/CdS , $\text{TiO}_2/\text{Sb}_2\text{S}_3$) and counterelectrodes ($\text{ZnO}/\text{Cu}_x\text{S}$, $\text{TiO}_2/\text{Cu}_x\text{S}$) for SSSCs based on aqueous polysulfide electrolytes. These approaches can be extended also to synthesize metal selenide/metal oxide composites.

The photocatalytic deposition of metal sulfide NPs can occur via a so-called “metallic” way when the primarily photodeposited metal (Cd, Cu, etc.) NPs react with elemental sulfur and, alternatively or simultaneously, via an “ionic” route when sulfur is photocatalytically reduced to sulfide ions reacting with metal ions to produce metal chalcogenide NPs [8]. In both cases, the photodeposition involves the most active sites on the

wide-bandgap oxide surface and, therefore, the final oxide/NP heterostructures retain favorable conditions for the photoinduced (in the photoanodes) and “dark” (in the counterelectrodes) charge separations when used as SSSC electrodes, thus resulting in an unrivaled light conversion efficiency.

11.2 Photocatalytic Deposition of Metal Sulfide Nanoparticles on the Surface of Wide-Bandgap Semiconductors

As mentioned in the introduction, the photocatalytic deposition (PD) of metal sulfide NPs on the surface of the wide-bandgap metal-oxide semiconductors (TiO_2 , ZnO , SnO_2) can occur in three different ways, including (i) the photocatalytic reduction of elemental sulfur S_8 to sulfide anions followed by their reaction with metal cations and the formation of nanoparticulate deposits (an “ionic” PD mechanism); (ii) the photocatalytic reduction of metal ions to M^0 NPs followed by their sulfidation by the elemental sulfur (an “atomic” mechanism), and (iii) by the photocatalytic reduction of water-soluble sulfide complexes of transition metals resulting in their decomposition and the formation of corresponding insoluble metal sulfides on the surface of a wide-bandgap photocatalyst supplying the photoelectrons for the reduction of the central metal ion. In general terms, the PD mechanism can be described by the following combination of processes:



where $h\nu$ is a light quantum with the energy higher than the bandgap (E_g) of the semiconductor photocatalyst, e_{CB}^- and h_{VB}^+ are a conduction band

(CB) electron and a valence band (VB) hole. In the following discussion, we focus on each of the above processes (11.1–11.6) in detail.

The absorption of a light quantum with the energy $h\nu > E_g$ by a wide-bandgap semiconductor results in the generation of an exciton—a pair of an electron and a hole bound by the electrostatic interaction (process (11.1)). Typically, the exciton dissociates very rapidly (hundreds of fs to several ps) to free e^-_{CB} and h^+_{VB} , which can then be “trapped” by localized states associated with the lattice defects (vacancies and dislocations, adatoms, surface undercoordinated atoms, and adsorbates). Alternatively, the electron and hole can recombine resulting in the emission of photoluminescence or the nonradiative vibrational dissipation of the photoexcitation energy.

As the CB electron is a major factor in the PD of metal sulfides, the presence of an efficient hole scavenger (a substance that can efficiently donate an electron filling the VB/trapped hole) is a prerequisite for the efficient photocatalytic process. The function of a hole scavenger is often delegated to ethanol that simultaneously acts as a perfect solvent for both the elemental sulfur and the precursor metal salts (Figure 11.1). Ethanol reacts with h^+_{VB} transforming into ethoxy radical that can inject an additional electron into the wide-bandgap photocatalyst CB (a well-known “current doubling” effect [11]) transforming finally into acetaldehyde. Thus, each scavenger molecule provides two electrons for the PD of a metal sulfide NPs.

The CB/trapped electrons collected by the photocatalyst are spent in the reduction of the elemental sulfur to sulfide ions (the ionic pathway (3)) or

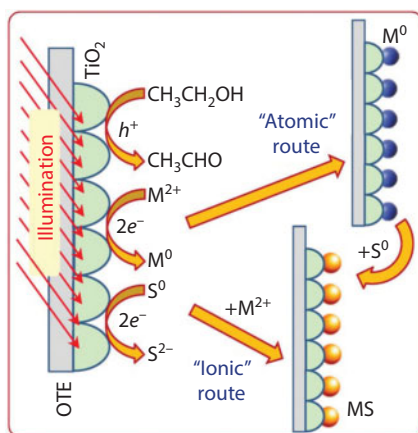


Figure 11.1 A schematic of the photocatalytic deposition of metal sulfide (MS) NPs via the “atomic” and “ionic” routes. OTE is an optically transparent electrode.

metal ions to the corresponding metals depositing in the form of NPs on the photocatalyst surface (the atomic pathway (4), Figure 11.1). Finally, S^{2-} species produced by the ionic pathway react with available metal ions (reaction (11.5)), while the metal NPs are sulfidized by the elemental sulfur (reaction (11.6)), both pathways resulting in the same products—metal sulfide NPs. The third possible pathway of metal sulfide formation via the reduction of the central ions of the sulfide complexes may be attributed to the ionic pathway because it avoids a step of the metal NP deposition.

The above general mechanism implies a number of requirements to the components of the photocatalytic systems and defines natural limitations of the PD method. In particular, the method requires the CB potential of the wide-bandgap semiconductor photocatalyst to be more negative than the potential of the M^{n+}/M^0 reduction in the atomic route or the two-electron S^0/S^{2-} reduction in the ionic route. A survey of the reported results on the PD of metal sulfide NPs shows that in most cases the reaction comes simultaneously by the atomic and ionic routes, the relative contribution of each channel depending on the reaction conditions and the precursor concentrations. Besides, in some cases, the intermediate composites of the photocatalyst with metal NPs or emerging oxide/sulfide heterostructures possess a much higher photocatalytic activity as compared to the starting photocatalyst as a result of a more efficient spatial separation of the photo-generated electrons and holes between the components of such composites.

The morphology of the PD-formed sulfide/oxide composites depends on the composition of the metal sulfide component. Typically the metal sulfide is deposited in the form of NPs with the shape tending to the spherical one (Figure 11.2). In the case of metal sulfide deposition onto preformed photocatalyst/metal composites, the photodeposit can form a thin layer on the surface of metal NPs, as in the case of the ternary $TiO_2/Au/CdS$ heterostructure [12, 13]. Layered metal sulfides produced by the photocatalytic deposition retain their lamellar morphology similar to the products of other deposition techniques (see for MoS_2 in Figure 11.2a).

The PD approach for the deposition of sulfide and selenide NPs on the surface of oxide supports was recently probed to produce new complex photocatalysts and components of the photoelectrochemical/photovoltaic systems. Table 11.1 summarizes some recently reported examples of liquid-junction NP-sensitized solar cells with the photoanodes produced by the PD. However, the scope of the metal chalcogenide produced by the PD still remains quite narrow, while the possible applications depend considerably on the nature of the photodeposited NPs. In this view, we structurize the present chapter by discussing separately and consecutively each reported metal chalcogenide produced by the photocatalytic deposition.

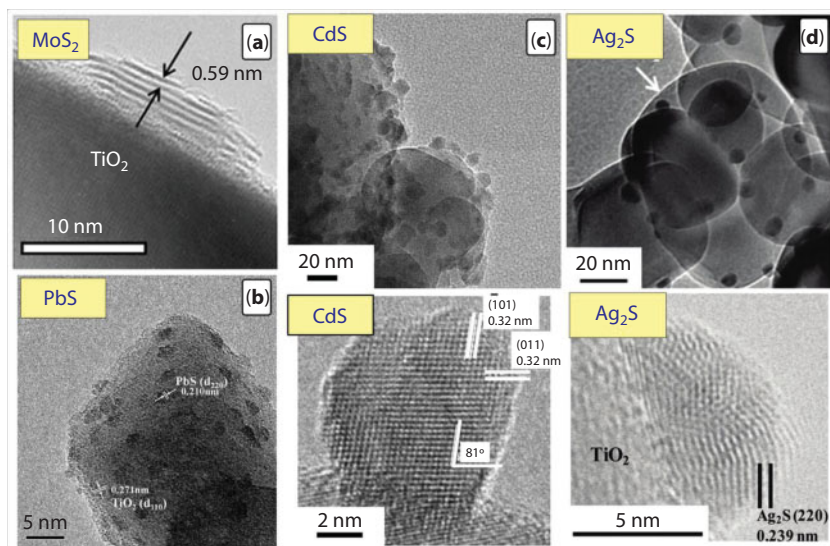


Figure 11.2 TEM/HRTEM images of photocatalytically deposited MoS₂ NPs (a), PbS NPs (b), CdS NPs (c), and Ag₂S NPs (d) on the nanocrystalline titania surface. Reprinted with permissions from [14] (a), [15] (b), [12] (c), and [16] (d). Copyright (2011 (a, b, d) and 2009 (c)) Elsevier (a), The Royal Society of Chemistry (b), and American Chemical Society (c, d).

Table 11.1 Some examples of SSSCs produced by the photodeposition of sensitizer NPs.

Light-sensitive photoanode	Counterelectrode	Redox species in electrolyte	η , %	Ref.
TiO ₂ /PbS	Pt	Na ₂ S/Na ₂ SO ₃	0.16	[15]
TiO ₂ /CdS	Pt	I ⁻ /I ₂	2.51	[17]
TiO ₂ /Ag ₂ S	Pt	Na ₂ S/Na ₂ SO ₃	0.29	[16]
TiO ₂ NR/Ag ₂ S	Pt	S ²⁻ /S _x ²⁻	0.19	[18]
ZnO NR/CdS/CdSe	Cu _x S	S ²⁻ /S _x ²⁻	2.03	[19]

Note: NR is a nanorod; light intensity is 100 mW/cm².

11.2.1 Photodeposition of Cadmium Sulfide NPs

The photodeposition of CdS NPs on the surface of mesoporous titania films was first reported by Tada *et al.* in 2008 [20]. We reported the PD of cadmium sulfide on the mesoporous TiO₂ films comprised of loosely

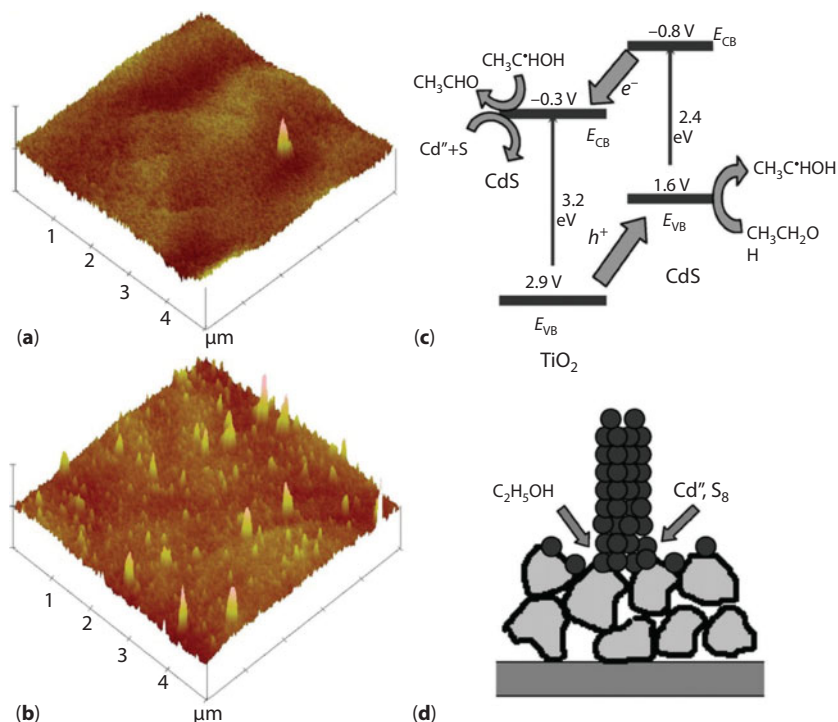


Figure 11.3 Atomic force microscopic images of TiO₂/CdS composites produced by CBD (a) and photodeposition (b) as well as schemes of charge separation in TiO₂/CdS heterojunctions (c) and the growth of columnar CdS NP aggregates by the PD (d). Reprinted with permissions from (21). Copyright (2009) Elsevier.

aggregated 10-nm titania NPs [21, 22]. The PD deposition was found to result in much smaller CdS NPs (~6 nm) as compared to the chemical bath deposition (CBD, 15–20 nm). Besides, the PD was found to yield rod-like CdS NP aggregates as high as ~80 nm not observed in the CBD approach (Figure 11.3a,b). The peculiar morphology of the PD products was interpreted in terms of an active involvement of the forming TiO₂/CdS composites in the photodeposition of following portions of cadmium sulfide. The composite enables the spatial separation of the photogenerated charge carriers (electrons—on titania NPs, holes—on CdS NPs), resulting in a higher photocatalytic activity of TiO₂/CdS films as compared with the native TiO₂ (Figure 11.3c). As a result, cadmium sulfide is deposited exclusively on preformed TiO₂/CdS “seeds” resulting in the vertical column-like aggregates of CdS NPs (Figure 11.3c) in contrast to the uniform surface coverage achieved typically by the CBD.

A combination of kinetic and chronopotentiometric measurements [12, 13] showed that the PD of CdS NPs on titania occurs predominantly via the atomic pathway through a step of Cd NP deposition. However, in the case of titania electrodes decorated with ~ 3.2 -nm gold NPs, the PD of CdS NPs switches almost exclusively to the ionic pathway going via the S_8 reduction to S^{2-} . The difference between the bare and Au-decorated titania photocatalysts was attributed [12, 13] to the very efficient S_8 adsorption on the surface of gold NPs favoring to the preferential reduction of sulfur by the electrons photogenerated in the TiO_2 /Au composites.

The morphology of the photodeposited cadmium sulfide depends considerably on the nature and morphology of the wide-bandgap photocatalytic support [9]. In particular, we found [23] that the illumination of ethanol solutions containing colloidal ~ 5 -nm ZnO NPs, sulfur, and Cd(II) acetate yields porous ZnO/CdS spheres with an average size of 150–170 nm (Figure 11.4a). At the same time, the PD of CdS NPs on the zinc oxide nanorods in similar conditions results in the formation of CdS nanotubes with a length of 0.5–0.8 μm and an inner diameter of 15–110 nm (Figure 11.4b).

Similar to the case of PD-formed TiO_2 /CdS composites, this phenomenon was interpreted in terms of a directed growth of the CdS NPs on

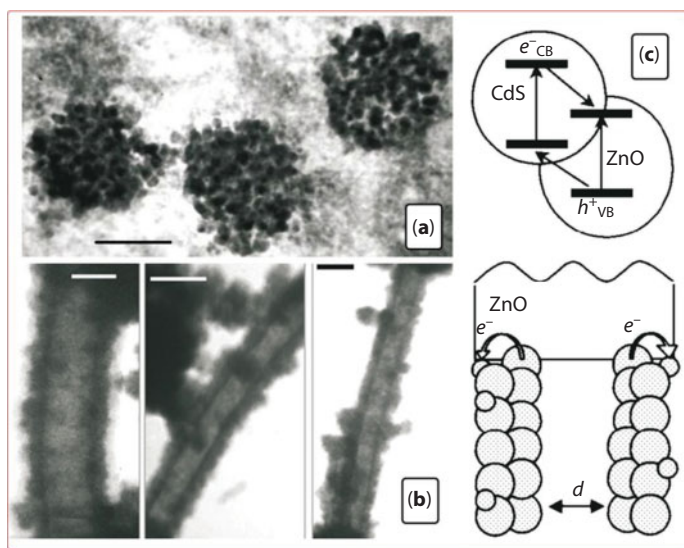


Figure 11.4 (a, b) ZnO/CdS composites formed from ZnO NPs (a) and ZnO nanorods (b). Scale bars in (a, b) are 100 nm. (c) A scheme of the charge separation in ZnO/CdS heterostructures and the formation of CdS nanotubes on the rims of ZnO nanorods. Reprinted with permission from [23]. Copyright (2007) Springer.

the rims of ZnO nanorods decorated with primary CdS deposits similar to the above-discussed case of column-like TiO_2/CdS nanocomposites (Figure 11.4c). When cadmium sulfide starts to deposit on the oxide surface, a ZnO–CdS (TiO_2 –CdS) heterojunction forms where the photogenerated electrons and holes can be spatially separated. As the oppositely charged carriers are attracted to each other, the photoinduced redox reactions occur predominantly at the oxide–CdS interface resulting in the growth of new CdS NPs at the same place and geometrical environment yielding ordered nanotubes and nanorods. As a result, the morphology of photocatalytically produced TiO_2/CdS composites differs drastically from the morphology of similar heterostructures synthesized by the CBD procedure. Also, no effects of spatial organization of the photodeposited NPs were observed when the deposited metal sulfide is photochemically passive and cannot supply the photogenerated charge carriers to the oxide–sulfide heterojunction as, for example, in the case of the photodeposited $\text{TiO}_2/\text{Cu}_x\text{S}$ heterostructures.

The PD approach for the production of components of the photoelectrochemical solar cells was first introduced for FTO/ TiO_2 /CdS heterostructures [17] (FTO—transparent conductive fluorine-doped tin oxide films on glass). It was found that the PD allows to fill more efficiently the inner volume of the mesoporous titania with CdS NPs as compared to the popular methods of the successive ionic layer adsorption and reaction (SILAR) and the adsorption of *ex situ*-synthesized colloidal CdS NPs. The filling with sensitizer NPs played a decisive effect on the activity of the FTO/ TiO_2 /CdS photoanodes in SSSCs with a Pt counterelectrode and aqueous polysulfide electrolyte [17, 24]. Table 11.2 illustrates this effect showing that the cells with PD-deposited sensitizer NPs demonstrated more than twice higher short-circuit photocurrent density J_{sc} than similar systems based on the SILAR-deposited and *ex situ*-produced CdS NPs. Other two vital photovoltaic parameters—the open-circuit voltage V_{oc} and fill factor of the J – V curve (FF)—were similar for all studied cells, resulting in the total light conversion efficiency η of $\sim 2.5\%$ for PD-deposited CdS NPs as compared to $\sim 1.2\%$ and less than 0.2% for SILAR- and *ex situ*-deposited cadmium sulfide NPs.

We introduced a similar PD approach for the formation of visible-light-sensitive photoanodes based on zinc oxide [25]. ZnO/CdS heterostructures prepared by the PD demonstrated twice as superior light conversion efficiency at $\lambda \geq 400$ nm (cells with the polysulfide electrolyte) as the photoanodes produced by the SILAR with the same amount of the loaded CdS NPs.

Figure 11.5 shows some time-resolved photoelectrochemical responses from the TiO_2/CdS and ZnO/CdS heterostructures produced by the SILAR

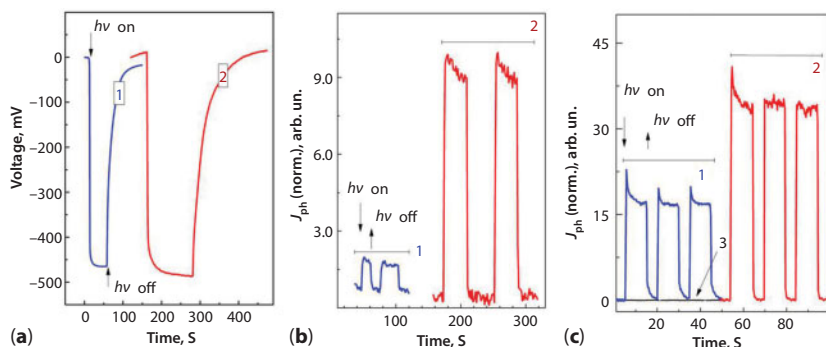


Figure 11.5 Temporal changes of voltage (a) and current (b,c) induced by the illumination (“ $h\nu$ on” moments)/extinction (“ $h\nu$ off” moments) registered for ITO/TiO₂/CdS (a, b) and ITO/ZnO/CdS (c) photoanodes produced by the SILAR (curves 1) and the photocatalytic deposition (curves 2). Curve 3 (c) corresponds to the bare ITO/ZnO film.

Table 11.2 Photoelectrochemical characteristics of the SSSCs based on FTO/TiO₂/CdS photoanodes produced by different methods [17].

CdS NP deposition method	J_{sc} , mA/cm ²	V_{oc} , V	FF	η , %
Photocatalytic deposition	6.5	0.7	0.7	2.51
SILAR	2.7	0.7	0.7	1.21
Adsorption of NPs	0.5	0.6	0.6	0.14

and by the photocatalytic deposition and having similar composition and optical properties [25, 26]. Illumination of ITO/TiO₂/CdS or ITO/ZnO/CdS photoanodes (ITO is an indium-tin oxide film on glass) immersed into aqueous 0.01 M Na₂S electrolyte by the “white” light with $\lambda > 400$ nm results in a rise of photovoltage and photoinduced current between the photoanode and a Pt counterelectrode. The photovoltage is roughly the same for the ITO/TiO₂/CdS films produced by both methods (Figure 11.5a) which is expected for the systems with similar chemical composition.

At the same time, the sensitization of both TiO₂ and ZnO via the photocatalytic deposition of CdS NPs results in much higher photocurrent densities as compared to the SILAR-produced analogs (Figure 11.5b,c). In the case of ITO/TiO₂/CdS, the absorption-normalized photocurrent density generated by the PD-formed anode is five times higher than for the SILAR-produced heterostructure (Figure 11.5b), while in the case of ITO/ZnO/CdS, the photodeposited cadmium sulfide NPs reveal twice as high efficiency as CdS NPs formed by the SILAR (Figure 11.5c). The

photoexcitation of nonsensitized ZnO films does not produce any appreciable photoresponse (Figure 11.5c, curve 3).

The photocurrent density generated by the illuminated ZnO/CdS heterostructures increases in a direct proportion to the amount of sensitizer NPs, which, in turn, depends on the SILAR cycle number and the photodeposition duration. However, after the normalization to the light absorbance, the photoanodes differing in CdS NP content show more or less the same efficiency of light conversion. Therefore, the size factor is of low importance for the ZnO/CdS heterostructures and the overall light conversion efficiency is affected rather by the sensitizer content than by the NP dimensions. The reason for the lack of size dependence can be in very favorable conditions for the spatial charge separation that exist in the ZnO–CdS and TiO_2 –CdS heterojunctions.

We suggested [27] an indication on the origins of advanced photoelectrochemical activity of the PD-produced ZnO/CdS heterostructures on the basis of a comparative study of a series of photoanodes with the same composition but differing in a mode of the formation of a CdS NP layer. In particular, we studied a photoanode produced entirely by the SILAR (FTO/ZnO/CdS-S), a photoanode formed only by the PD (FTO/ZnO/CdS-P) and two electrodes prepared with two-step procedures “first SILAR—then PD” (FTO/ZnO/CdS-SP) and “first PD—then SILAR” (FTO/ZnO/CdS-PS). The feasibility of the formation of FTO/ZnO/CdS-SP films originates from the fact that CdS NPs, like the ZnO substrate, reveal photocatalytic properties in the photodeposition of an additional amount of cadmium sulfide [28, 29].

Figure 11.6 presents the current–voltage curves registered at the illumination of the above-described photoanodes in a three-electrode scheme with a Pt counterelectrode. The cell with PD-formed FTO/ZnO/CdS-P photoanode showed a much higher photocurrent density (curve 2) as compared with the FTO/ZnO/CdS-S analog (curve 1).

The FTO/ZnO/CdS-SP photoanode where only a small initial portion of CdS NPs was deposited by the SILAR, while the major part of sensitizer was formed by the PD, showed a surprisingly low activity (curve 3) comparable to that of the pure SILAR-deposited photoanode indicating that the introduction of even a thin SILAR-formed layer between ZnO and CdS annihilates all the benefits of the photocatalytic deposition of the rest of sensitizer NPs. Oppositely, if an initial layer of CdS NPs was deposited by the PD and the rest—with the SILAR (FTO/ZnO/CdS-PS structure, curve 4), the photoanode reveals almost the same activity as the purely photodeposited composite, again indicating a crucial role of the primary CdS layer on the interface between zinc oxide and cadmium sulfide.

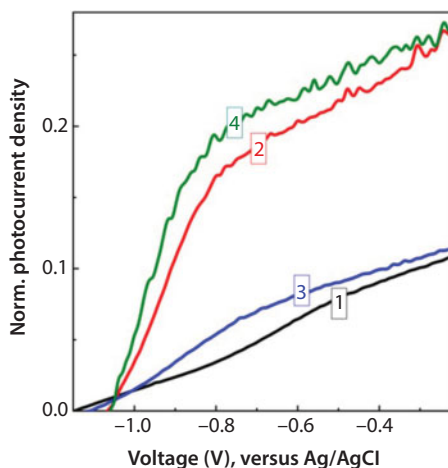


Figure 11.6 Current–voltage dependences registered for FTO/ZnO/CdS-S (curve 1), FTO/ZnO/CdS-P (2), FTO/ZnO/CdS-SP (3), and FTO/ZnO/CdS-PS (4). The curves are normalized to the integral absorbances at $\lambda > 350$ nm.

These results show unambiguously that the structure of the interface between ZnO and CdS is a major factor determining the advanced efficiency of the PD-formed ZnO/CdS photoanodes distinguishing them from analogs produced by the conventional methods. At that, other possible contributions arising from differences in the structure, shape, and size of CdS NPs formed by the SILAR and PD, a character of the CdS NP surface, and their aggregation on the ZnO scaffold are obviously of a minor importance for the solar cell applications.

Similar conclusions were drawn from comparative studies of TiO_2/CdS composites produced by the PD and the CBD [27] by the laser flash photolysis. We found that the formation of trapped electrons and holes (in the form of Ti^{3+} in TiO_2 and $\text{S}^{\cdot-}$ in CdS) occurs by an order of magnitude faster for the TiO_2/CdS -PD films as compared with the TiO_2/CdS -CBD analogs.

The fundamental band edge of nanocrystalline titania deposited on glass [11] is around 360–370 nm (Figure 11.7a, curve 1) and, therefore, the laser pulses with $\lambda = 355$ nm (3.5 eV) can excite interband electron transition from the valence band into the conduction band. A differential absorption spectrum of the TiO_2 films reveals a broad band in the range of 670–710 nm with a peak at $\lambda = 680$ –690 nm (Figure 11.7a, insert) [27]. The band can be assigned to a long-lived intermediate as the transient signal shows no signs of decay during hundreds of μs after the pulse extinction (Figure 11.7b). Similar bands are typically observed [30, 31] in the case of the CB electron capture by deep traps (Ti^{4+} ions) resulting in Ti^{3+}

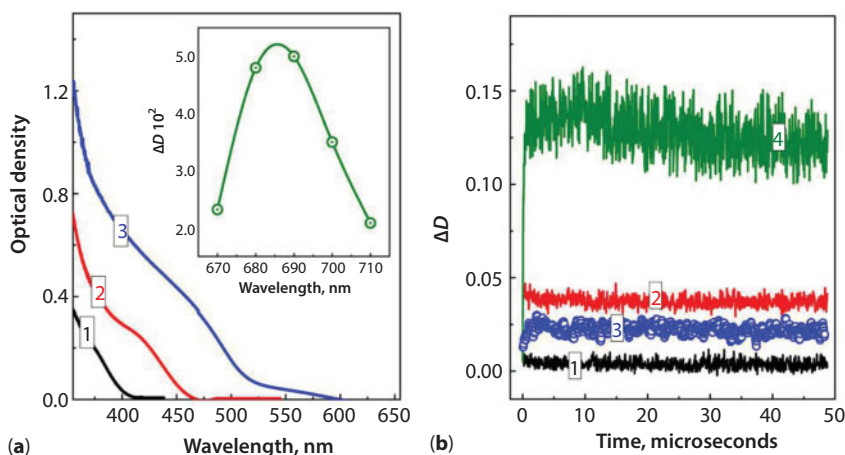


Figure 11.7 (a) Absorption spectra of the nanocrystalline TiO₂ film (curve 1) and TiO₂/CdS nanoheterostructures (curves 2,3) produced by the photocatalytic CdS deposition (2) and CBD (3) [11]. Insert in (a): transient absorption spectrum of TiO₂ film excited by the laser pulses with $\lambda = 355$ nm. (b) Kinetic curves of transient signal decay at $\lambda = 680$ nm registered for the CBD-deposited TiO₂/CdS films (curves 1,2) and the photodeposited TiO₂/CdS films (curves 3,4). Curves 2 and 4 registered after the deposition of a sucrose layer. Adapted and reprinted from [27]. Copyright (2009) Springer.

generation ($\text{Ti}^{4+} + e^-_{\text{CB}} \rightarrow \text{Ti}^{3+}$). The VB holes are also rapidly captured by hole traps—typically surface hydroxide anions ($h^+_{\text{VB}} + \text{OH}^- \rightarrow \text{OH}^\bullet$) [11, 30]—or interact with donor compounds adsorbed on the TiO₂ NP surface. A large portion of the photogenerated charge carriers decays in the recombination processes, which have a predominantly nonradiative character for the nanocrystalline titania [11, 30].

To increase the transient Ti³⁺-related band intensity, a thin transparent layer of sucrose was applied on top of the TiO₂ films that do not interfere with the light absorption but supplies additional electrons as a sacrificial donor [32].

When the nanocrystalline cadmium sulfide is deposited on the titania surface by the CBD, a new absorption band appears with an edge at 510–520 nm (Figure 11.7a, curve 3) while the optical density of the TiO₂/CdS film at the laser wavelength (355 nm) increases to 1.75 indicating a complete light absorption by cadmium sulfide.

Such TiO₂/CdS nanoheterostructure showed almost zero intensity of the transient signal at 670–710 nm (Figure 11.7b, curve 1). The fact indicates that the efficiency of interfacial electron transfer from the photoexcited CdS to TiO₂ followed by the electron capture and formation of Ti³⁺ is very low for this TiO₂/CdS composite, despite favorable thermodynamic

conditions ($E_{\text{CB}}(\text{CdS}) = -0.8$ V versus normal hydrogen electrode (NHE) [11, 33], $E_{\text{CB}}(\text{TiO}_2) = -0.3$ V at pH 7 [11, 33]).

The electron transfer can be hindered by an interfacial barrier between titania and CdS, because the CBD of cadmium sulfide typically yields hexagonal CdS NPs [34], while TiO_2 is crystallized in a cubic anatase modification [35]. Also, the CBD-deposited CdS NPs show drastic recombinational losses of the photogenerated charge carriers as evidenced by a large increase of the transient signal intensity in the presence of sucrose capable of capturing of the photogenerated holes (Figure 11.7b, curves 1,2) and interfering with the recombinative processes.

The flash photolysis of similar TiO_2/CdS nanoheterostructures produced by the PD results in the same transients; however, the signal intensity is much higher in the presence of sucrose in this case (Figure 11.7b, curves 2,4). After a correction on the light absorbance, the difference in the transient signal intensity between both nanoheterostructures increases additionally by a factor of 3. The observations indicate that the efficiency of photoinduced interfacial electron transfer from CdS to TiO_2 and the formation of Ti^{3+} species is by an order of magnitude higher for the photocatalytically produced TiO_2/CdS nanoheterostructure as compared with the analog synthesized by the conventional CBD [21].

As opposed to the bare titania films, the TiO_2/CdS nanocomposites revealed a second quite intense transient signal in the range of 420–570 nm peaked at 470–500 nm (Figure 11.8a). This band can be assigned to surface-adsorbed $\text{S}^{\cdot-}$ radicals formed via the capture of photogenerated VB holes by deep traps (lattice S^{2-} anions).

The transient band observed for the CBD-deposited TiO_2/CdS nanocomposite seems to be composed of two spectral components. However, the kinetic decay curves registered for this band on different wavelengths (460, 490, and 520 nm) are the same and, therefore, describe the decay of a single short-lived intermediate. The band distortion can be caused by an overlap of the positive transient signal with a nonstationary bleaching band of CdS NPs bearing excessive negative charge. The bleaching band maximum for the given TiO_2/CdS nanoheterostructure is expected to be at 480–500 nm, thus indeed overlapping with the absorption band of $\text{S}^{\cdot-}$ anion-radical. The presence of a nonstationary bleaching band indicates that the photogenerated CdS conduction band electrons accumulate on CdS NPs as a result of a low efficiency of the interfacial transfer to TiO_2 NPs [37]. A reconstruction of the $\text{S}^{\cdot-}$ absorption band (Figure 11.8a, dashed line) shows that the band maximum should be observed at 485–490 nm.

The intensity of $\text{S}^{\cdot-}$ -related band of the PD-produced TiO_2/CdS nanocomposites is twice as high as for the CBD-produced analog, its peak

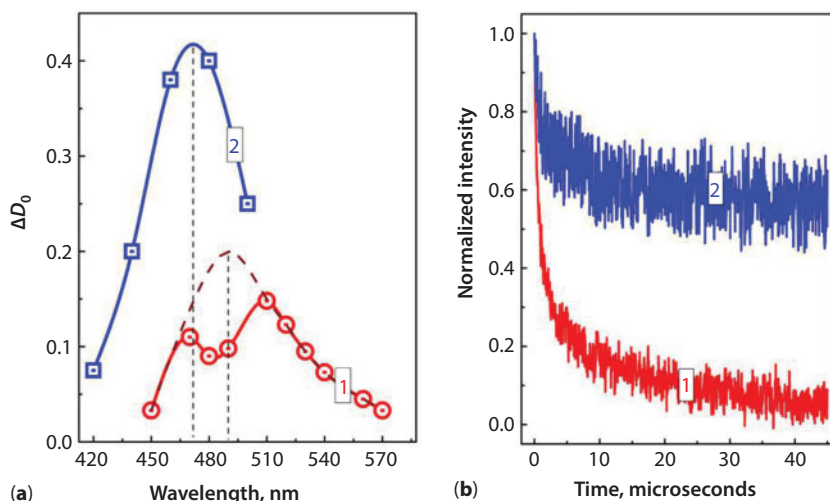


Figure 11.8 (a) Transient differential absorption spectra of TiO_2/CdS nanoheterostructures produced by the CBD (curve 1) and the photocatalytic CdS deposition (curve 2); (b) normalized kinetic curves of transient signal decay for the CBD-produced TiO_2/CdS registered at 500 nm (curve 1) and for the photodeposited composite registered at 470 nm (curve 2). Adapted and reprinted from [27]. Copyright (2009) Springer.

blueshifting to 465 nm. The first observation is in accordance with an increase in the Ti^{3+} signal intensity at 670–710 nm, while the second one illustrates a well-reported shift of the NP-adsorbed $\text{S}^{\cdot-}$ band maximum to shorter wavelengths with a decrease of the size of CdS NPs [38, 39].

The decay dynamics of the sulfur anion-radical is also different for the CBD-deposited and photodeposited TiO_2/CdS nanoheterostructures (Figure 11.8b). The kinetic curves have a complex shape that cannot be fitted with a simple first-order or second-order kinetic model. The complexity attests to several simultaneous reactions with the participation of $\text{S}^{\cdot-}$. Also, it can arise from a size distribution of CdS NPs. Figure 11.8b shows that the CBD-deposited CdS NPs show a sharp decrease of the transient signal intensity in the first 3–5 μs after the laser pulse followed by a slower signal relaxation till the zero level (at $t > 50 \mu\text{s}$). At the same time, no fast component can be observed in the decay curves of the photodeposited TiO_2/CdS nanocomposites (Figure 11.8b, curve 2). The decay is generally slower and more than a half of the photogenerated $\text{S}^{\cdot-}$ anion-radical survives as long as 50–100 μs after the exciting pulse. The differences in the decay curve shape cannot be explained solely by possible differences in the rate of radical recombination ($\text{S}^{\cdot-} + \text{S}^{\cdot-} \rightarrow \text{S}_2^{2-}$) or interaction with oxygen ($\text{S}^{\cdot-} + \text{O}_2 \rightarrow \text{S}^0 + \text{O}_2^{\cdot-}$).

Taking into account the presence of excessive electrons on CdS NPs in the CBD-deposited TiO_2/CdS nanoheterostructure, the different decay dynamics can be assigned to the recombination of the excessive electrons and $\text{S}^{\cdot-}$ anion-radicals ($\text{Cd(II)S}^{\cdot-} + e^-_{\text{tr}} \rightarrow \text{CdS}$). In the case of photoproduced TiO_2/CdS nanocomposites, this process is blocked by an efficient electron transfer from CdS NPs to the titania scaffold. Formally, the latter reaction corresponds to the electron recombination with a deeply trapped hole. The recombination of free charge carriers in CdS NPs is typically over in 1–10 ns after the photoexcitation [38], but the process can be extended to 200–300 ns if one of the carriers gets captured by a deep trap [38, 40]. It may be safely assumed that the recombination between an electron and a hole both deeply trapped will occur by one to two orders of magnitude slower, thus corresponding to the discussed time scale.

11.2.2 Photocatalytic Deposition of Lead Sulfide

We were among the first groups to report the feasibility of the photocatalytic deposition of PbS NPs on the surface of mesoporous titania [21]. The lead sulfide NPs form in the photocatalytic reduction of S_8 with ethanol containing lead(II) acetate as aggregated 20–30-nm particles covering uniformly the TiO_2 surface.

The photocatalytic deposition starting from lead perchlorate [15] yields photoelectrochemically active TiO_2/PbS heterostructures comprising ~3-nm PbS particles (Figure 11.2b). A much smaller size of lead sulfide NPs in such system, most probably, originates from a higher stability of $\text{Pb}(\text{ClO}_4)_2$ to hydrolytic reactions resulting in a relatively higher stationary concentration of free Pb^{2+} ions in the illuminated solution. The studies of the internal photon-to-current efficiency spectra of the TiO_2/PbS -PD photoanodes revealed small light conversion quantum yields in the entire spectral sensitivity range of lead sulfide NPs [15]. It should be noted that the values of J_{sc} , V_{oc} , and η reported in this paper were measured in a three-electrode scheme, where possible deficiencies of a counterelectrode were compensated by a polarization and, therefore, cannot be compared directly with other reports.

The lead sulfide NPs were formed on the titania surface by a so-called surface-assisted photodeposition in the presence of thioglycolic acid (TGA) as a NP growth-regulating and a surface-binding agent [41]. It was found that an increase of the TGA concentration from 0 to 0.04 M results in a reduction of the PbS NP size from around 65 to ~5 nm, other conditions kept constant. The bifunctional TGA molecules also act as a bridge binding simultaneously to PbS NPs via the mercapto-groups and to the titania surface—via the carboxylate functionality [41]. As a stronger reductant than ethanol, the TGA

molecules can also capture the photogenerated TiO_2 VB holes, thus contributing additionally to the overall efficiency of the photocatalytic deposition. A chronopotentiometric study of the reaction showed it to occur predominantly by the atomic route via the primary deposition of Pb NPs.

Sometime later the same authors reported the TiO_2/PbS -PD composite as an efficient photocatalyst of the hydrogen evolution from aqueous sulfide/sulfite solutions under the simulated solar light [42]. The highest photocatalytic activity was reported for an intermediate size of PbS NPs, ~ 7 nm, being lower both for smaller and larger lead sulfide NPs. This effect was interpreted [42] in terms of a balance between the efficiency of the photoinduced electron transport from PbS NPs to TiO_2 (increasing with a PbS NP size decrease as a result of the bandgap expansion) and the light-harvesting efficiency (lowering with the NP size decrease as the smaller PbS NPs with a larger E_g absorb a smaller portion of the solar light).

11.2.3 Photocatalytic Deposition of Silver Sulfide

The illumination of titania films in alcohol solutions of S_8 and silver(I) nitrate was reported [16] to yield polydispersed Ag_2S NPs ranging in size from 3 to 10 nm (Figure 11.2d). The atomic pathway dominates in this reaction and the photoexcitation in the absence (or a deficiency) of the elemental sulfur results in the deposition of plasmonic Ag NPs. The FTO/ $\text{TiO}_2/\text{Ag}_2\text{S}$ composites revealed a high photocatalytic activity in the hydrogen evolution from aqueous sulfide/sulfite solutions with a total efficiency reaching 0.29 %, while no photoproducts were detected after the illumination of FTO/ TiO_2/Ag heterostructures in the same conditions [16].

A two-stage approach for the PD of silver sulfide on the surface of TiO_2 nanorods was suggested [18] using the sulfidation of the photodeposited Ag NPs in aqueous solutions of sodium polysulfide. At that, an increase in the illumination duration on the first stage of Ag NPs deposition results in an increase of the size and amount of final Ag_2S NPs. It was found that there exists an optimal photodeposition duration providing the highest light conversion efficiency of $\sim 1\%$ under the simulated solar illumination [18].

11.2.4 Photodeposition of Antimony Sulfide

We introduced a photocatalytic method for the formation of binary $\text{TiO}_2/\text{Sb}_2\text{S}_3$ heterostructures on the surface of optically transparent electrodes [43]. The illumination of FTO/ TiO_2 films (Figure 11.9a) in degassed ethanol solutions of SbCl_3 and sulfur results in the deposition of amorphous Sb_2S_3 on the titania surface. As shown by Raman spectroscopy and X-ray

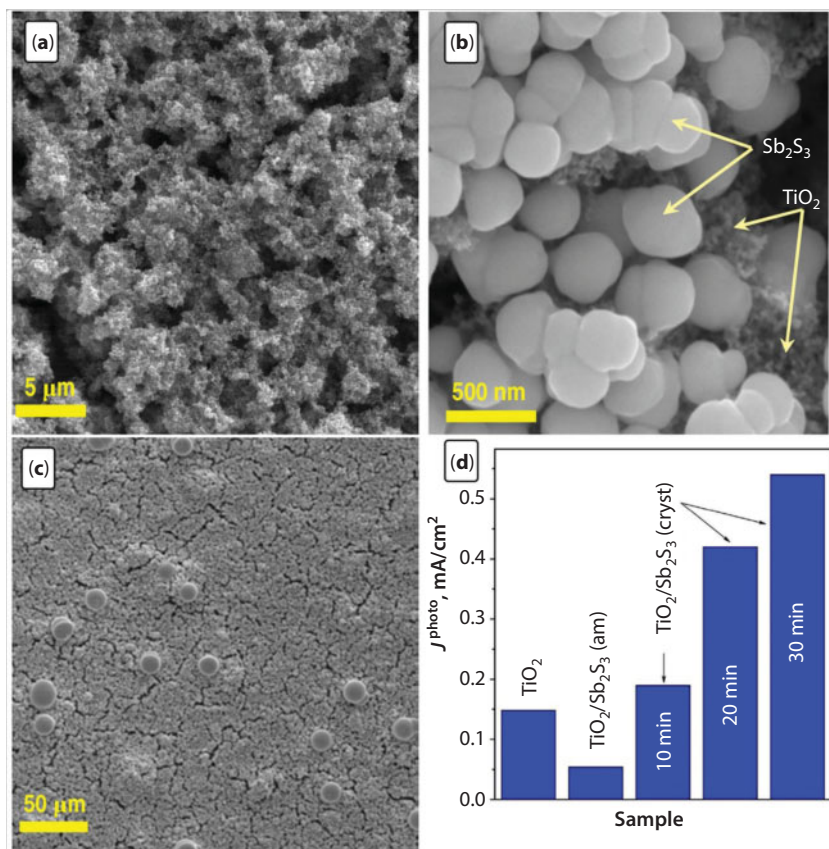


Figure 11.9 SEM images of starting nanocrystalline TiO₂ film (a) and TiO₂/Sb₂S₃ (b, c) films; (d) photocurrent density J_{photo} at 0.1 V vs. Ag/AgCl for FTO/TiO₂ and FTO/Sb₂S₃ electrodes. The PD duration is marked on bars. Reprinted with permissions from [43]. Copyright (2015) Elsevier.

diffraction, the annealing of such films at around 350 °C in a stream of argon yields the crystalline stibnite Sb₂S₃ modification in the form of aggregates of spherical nearly stoichiometric 150–300 nm particles distributed uniformly on the surface of TiO₂ (Figure 11.9a).

The simultaneous deposition of micron particles was also observed (Figure 11.9c) strongly enriched with Sb (with an atomic Sb:S ratio reaching ~13:1) along with Sb₂S₃ NPs. The fact indicates that the PD of antimony sulfide occurs predominantly via the atomic route of Sb³⁺ reduction to metallic antimony which afterward reacts with the elemental sulfur.

The composite FTO/TiO₂/Sb₂S₃ films cannot be directly applied as photoanodes of polysulfide-based solar cells because of fast dissolution of Sb₂S₃

NPs in such electrolytes down to molecular Sb-sulfide complexes. However, in the presence of a sacrificial donor—ascorbic acid, FTO/TiO₂/Sb₂S₃ demonstrated a much higher photoelectrochemical activity when illuminated with the visible light as compared to the bare titania films clearly showing a sensitizing effect of antimony sulfide NPs (Figure 11.9d).

The electron–hole recombination on the TiO₂–Sb₂S₃ interface can be efficiently suppressed by the modification of the FTO/TiO₂ film with a layer of In_x(OH)_yS_z prior to the photodeposition of antimony sulfide. Additionally, the possibility of reverse electron transfer from Sb₂S₃ NPs to the electrolyte can be reduced by depositing a layer of wider-bandgap SbO(OH) on the surface of sensitizer NPs. The combination of these approaches results in an appreciable increase of the photoelectrochemical activity of TiO₂/Sb₂S₃ heterostructures [43].

11.2.5 Photocatalytic Deposition of Molybdenum and Tungsten Sulfides

The photocatalytic deposition of MoS₂ and WS₂ NPs on the titania was realized via the reduction of central metal ions of the corresponding sulfide (NH₄)₂MS₄ (M = Mo, W) complexes with the photogenerated TiO₂ CB electrons [44]. The VB holes were simultaneously captured by an efficient sacrificial electron donor—hydrazine. The PD procedure yielded nanocrystals with strong quantum size effects. In particular, the absorption band edge of the photodeposited MoS₂ and WS₂ NPs was found at 700 nm and 620 nm, while the bulk molybdenum and tungsten sulfides show the band edges at 1040 nm ($E_g = 1.23$ eV) and 920 nm ($E_g = 1.35$ eV). The PD-formed TiO₂/MoS₂ and TiO₂/WS₂ nanocomposites demonstrated a much higher photocatalytic activity in the oxidation of methylene blue and 4-chlorophenol, as compared to the bare titania [44]. The photocatalytic decomposition of (NH₄)₂MoS₄ complex precursor on the surface of CdS nanorods was found to result in the formation of MoS₂ NPs acting as an efficient cocatalyst of the photocatalytic water reduction to H₂ [45].

Later, the PD-formed TiO₂/MoS₂ composites were used as a precursor for the preparation of TiO₂/MoO₃ composites through the thermal oxidation of molybdenum sulfide [14]. MoS₂ is photodeposited on titania in a form of layered NPs with a characteristic interlayer periodicity of 0.59 nm (Figure 11.2a). Such TiO₂/MoS₂ composites revealed a high photocatalytic activity in the hydrogen evolution from aqueous solutions of formic acid. At the same time, the derived TiO₂/MoO₃ heterostructures demonstrated a unique photochromism originating from a partial reduction of Mo(VI) by the TiO₂ CB electrons followed by the dark oxidation of Mo(V) by the molecular oxygen.

The molybdenum sulfide NPs were deposited photocatalytically onto the composites of reduced graphene oxide sheets with CdS NPs [46]. Depending on the pH of precursor solution used for the photoreaction, the MoS₂ NPs are deposited either on the surface of CdS NPs (at pH 7) or separately on the reduced graphene oxide sheets (at pH 11).

11.2.6 Photocatalytic Deposition of Copper Sulfide

We reported that the illumination of mesoporous titania films immersed in ethanol solutions of S₈ and copper(II) acetate results in the formation of nonstoichiometric Cu_xS on the TiO₂ surface [21]. Copper sulfide is deposited as largely agglomerated NPs with a size of up to 250 nm.

Later, a similar approach was applied for the PD of copper sulfide on the surface of titania nanorods [47]. It was found that the size of photodeposited Cu_xS NPs strongly depends on the morphology of the titania support. In the case of commercial rutile powders, copper sulfide is photodeposited in the form of NPs with an average size of ~25 nm. At the same time, the PD on the titania nanorods with a size of 6 per 35 nm yields ~2.5-nm Cu_xS NPs. The primary PD stage on rutile produces the stoichiometric CuS demonstrating a characteristic X-ray diffraction {130} peak. As the illumination is continued, this peak gradually disappears with a simultaneous rise of the characteristic Cu₂S {110} peak. At the same time, the PD on titania nanorods produces directly copper sulfide with the composition close to Cu₂S. A chronopotentiometric study [47] showed the photoreaction going by the atomic pathway in both cases despite the large differences in the morphology and composition of the PD products.

We introduced a photocatalytic approach for the deposition of Cu NPs on the surface of nanostructured zinc oxide microplatelets on FTO [48] with the following sulfidation of FTO/ZnO/Cu films to FTO/ZnO/Cu_xS. The primary step of the illumination of FTO/ZnO films in ethanol solution of copper(II) acetate yields deposits of Cu NPs with a broad size distribution up to 500 nm (Figure 11.10a, b). The sulfidation of such films in aqueous polysulfide solutions results in the oxidation of copper metal and the conversion of Cu NPs into the aggregates of Cu_xS nanoplatelets with $x \approx 1.3$ –1.4 (Figure 11.10c, d).

An energy-dispersive X-ray spectroscopic analysis of the film surface showed copper sulfide to be uniformly distributed in the volume of porous ZnS film (the film thickness is around 5 μm) and, therefore, Cu_xS aggregates have an electric contact with the conductive FTO layer. As a result, the FTO/ZnO/Cu_xS films can be used as catalytically active counterelectrodes with aqueous polysulfide electrolyte and FTO/ZnO/CdS photoanodes. In

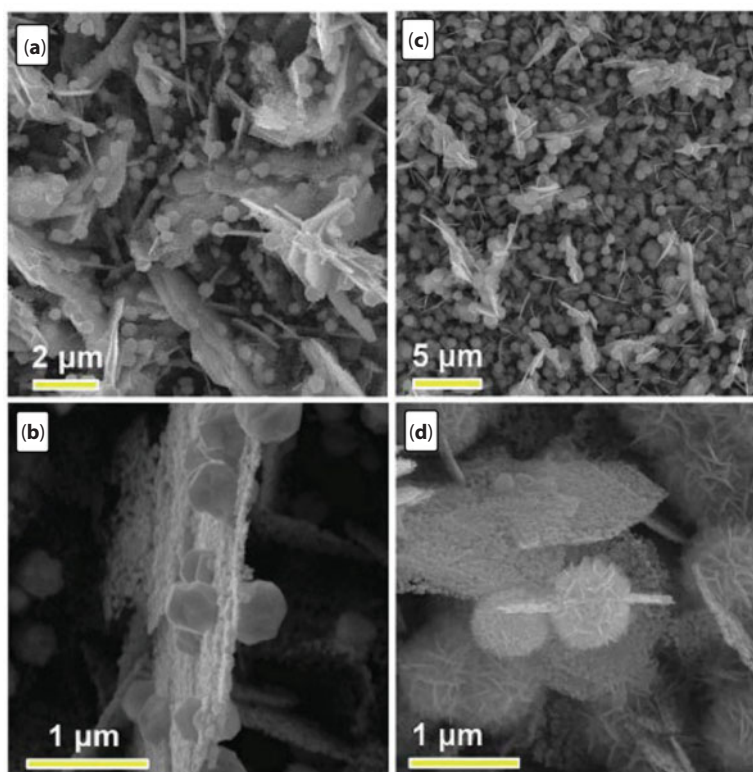


Figure 11.10 SEM images of the photodeposited FTO/ZnO/Cu films (a, b) and FTO/ZnO/Cu_xS (c, d) films. Reprinted with permissions from [48]. Copyright (2015) The Royal Society of Chemistry.

a similar way, the FTO/TiO₂/Cu_xS composites were produced [49]. We found that the solar cells based on FTO/ZnO/CdS photoanodes and FTO/ZnO/Cu_xS cathodes produced by the photoassisted approach revealed a much higher light conversion efficiency ($\eta = 3.5\%$) than in a similar system comprising a FTO/ZnO/Cu_xS counterelectrode synthesized by the conventional ions exchange method ($\eta = 1.5\%$) [26].

11.3 Photocatalytic Deposition of Metal Selenides

The photocatalytic deposition of metal selenides is reported mostly for the deposition of CdSe on the surface of wide-bandgap metal oxides. Probably, the pioneer place in this direction belongs to the report of Rajeshwar *et al.*

[50] on the photocatalytic synthesis of CdSe and PbSe NPs via the reduction of Se(IV) by the photogenerated titania CB electrons. The first stage of the process resulted in the deposition of elemental selenium. On the second stage the TiO_2/Se was illuminated in the presence of Cd(II) or Pb(II) salts resulting in TiO_2/CdSe or TiO_2/PbSe composites:



This work illustrates an example of the underpotential photocatalytic deposition when the metal selenide requires the presence of metal ions for the selenium to be reduced. The redox potential of the CB electron of TiO_2 is not high enough either for the reduction of Se^0 to Se^{2-} or M^{2+} to M^0 . However, in the presence of both Se and M^{2+} , the redox potential of Se^0 reduction decreases as a result of the formation of nonsoluble metal selenide.

Selenium(IV) species (selenite ions) were reported to be photocatalytically reduced to Se^0 on the titania surface in the presence of formic acid [51]. It was found that the size of photodeposited Se NPs is much larger than the size of TiO_2 grains and reaches ~ 150 nm. However, a similar reaction starting from selenate ions SeO_4^{2-} yields much smaller Se NPs with a size lower than 25 nm. In our opinion, such variations in the morphology of the photodeposited selenium NPs can be attributed to the difference between the redox-potentials of $\text{Se}^0/\text{Se}^{4+}$ and $\text{Se}^0/\text{Se}^{6+}$ pairs. The selenite ion is a weaker reducing agent as compared to the selenate ion. This fact favors to the preferential reduction of fresh portions of Se(IV) on the surface of preformed Se NPs as a result of the possibility of the spatial charge separation between TiO_2 and Se and enrichment of selenium NPs with excessive electrons (Figure 11.11a). The selenate ion is a more efficient oxidant and, therefore, a better electron scavenger that can be reduced much efficiently on the surface of both primary Se nuclei and titania photocatalyst resulting in a more uniform distribution of the photoproduct and formation of smaller Se NPs.

The mechanism of photocatalytic reduction of Se^0 on the titania surface in the presence of metal ions (Cd^{2+} and Pb^{2+}) was studied in detail [52, 53]. It was found that the photocatalytic formation of TiO_2/CdSe composites occurs predominantly by the ionic pathway, that is, via the reduction of elemental selenium to Se^{2-} . At the same time, the TiO_2/PbSe heterostructures can be formed both via the reduction of Pb^{2+} ions to metal NPs and by the reduction of Se^0 to selenide anions. The difference was attributed to a higher redox-potential of $\text{Pb}^{2+}/\text{PbSe}$ couple (1.37 V, NHE, pH 7) as compared to the potential of the $\text{Cd}^{2+}/\text{CdSe}$ couple (0.71 V, NHE, pH 7). As a

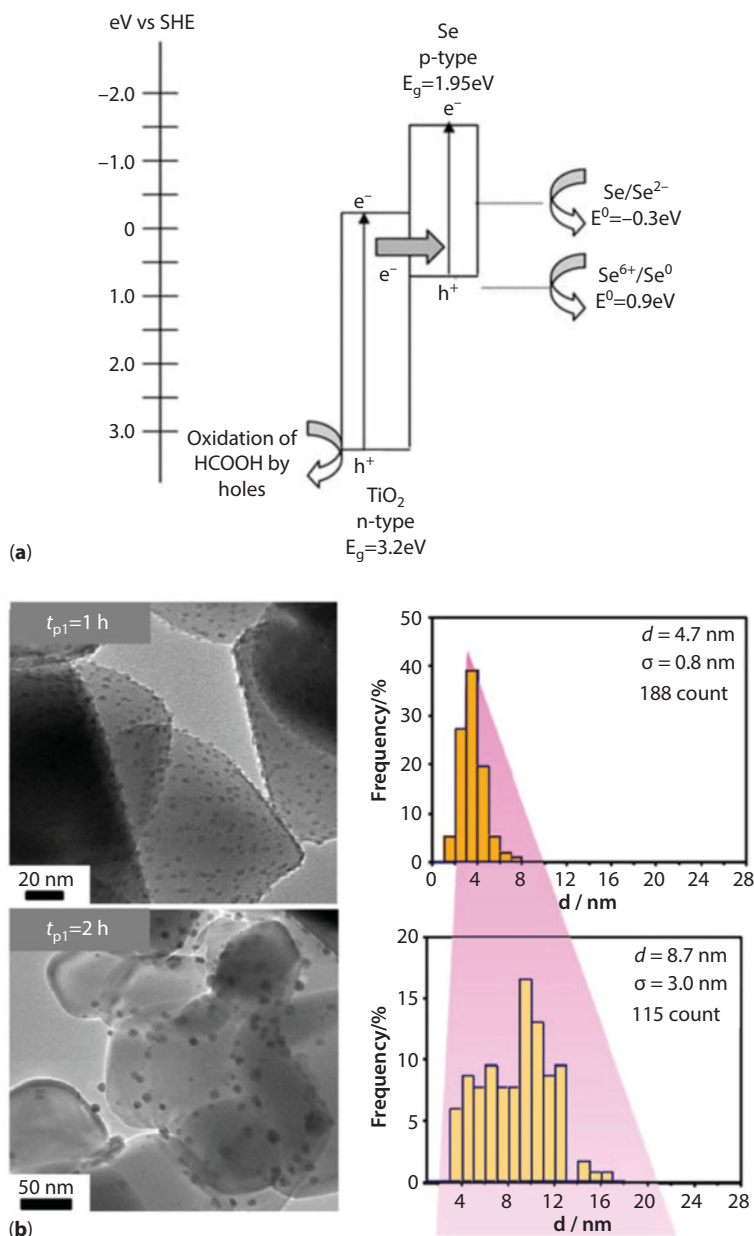


Figure 11.11 (a) Energy diagram of TiO_2/Se composite showing the position of the flat-band potentials and the bandgap energy of TiO_2 (*n*-type) and Se (*p*-type) upon UV illumination. (b) TEM images (left side) and Se NP size distributions on titania prepared at a varied PD duration t_p . Reprinted with permissions from [51] (a) and [55] (b). Copyright (2002) Springer (a) and (2014) American Chemical Society (b).

result, the Pb^{2+} ions can be more efficiently reduced by the photogenerated titania CB electrons [52].

The photodeposited TiO_2/Se composites revealed a photoelectrochemical activity when illuminated with the visible light in aqueous H_2SO_4 solutions, demonstrating the behavior of a photocathode as a result of *p*-type conductivity of the elemental selenium. At the same time, the $\text{TiO}_2/\text{Se}/\text{CdSe}$ heterostructures showed a considerable photocurrent increase both in cathodic and in anodic areas as a result of the *n*-type conductivity of the outer cadmium selenide layer.

It was also found that the PD using Se(IV) as a precursor for the generation of selenide ions results in the formation of a considerable amount of CdSe nanorods, while a similar procedure performed with the Se(VI) precursors yields mostly spherical CdSe NPs [54].

The titania/Se heterostructures were used as a starting material for the photocatalytic formation of CdSe in the systems comprising Cd(II) perchlorate and various hole scavengers, such as water, 2-propanol, ethanol, or methanol [55]. The current doubling effect possible for the alcohols favors the formation of small, around 2–6 nm, CdSe particles on the titania surface.

It was assumed [55] that the CdSe NPs are formed by a “deposition–dissolution–redeposition” mechanism including the formation of relatively small NPs (4–6 nm) selenium NPs on the primary PD stage, their growth to ~16 nm, followed by a partial photocorrosion and redeposition in the form of much larger NPs with a broad size distribution from 4 to 30 nm (Figure 11.11b). This procedure allows for a precise control of the optical properties of Se NPs by varying the exposure to light. In this way, an average E_g of Se NPs can be varied from 2.3 eV to 1.95 eV.

The addition of a ligand capable of the surface passivation of growing CdSe NPs allows to decrease the average size of the photodeposited cadmium selenide NPs as well as to focus the size distribution considerably. For example, the two-stage photodeposition of CdSe NPs onto titania produces typically a broad distribution of the CdSe NP sizes ranging from ~5 to 25 nm (Figure 11.12a) [56], while an ensemble of CdSe NPs with a much lower size and narrower size distribution can be deposited in the presence of mercaptoacetic acid (Figure 11.12b).

From TEM results, the authors calculated the contact angle between the photodeposited CdSe NPs and the titania surface and found that it decreases from around 80–100° to 50–60° after the introduction of TGA [56]. Basing on these observations, they proposed a mechanism of the ligand effect assuming that the mercaptoacid is adsorbed on the surface of growing CdSe NPs blocking the frontal NP growth and favoring to the lateral expansion of the growing NPs (Figure 11.12c).

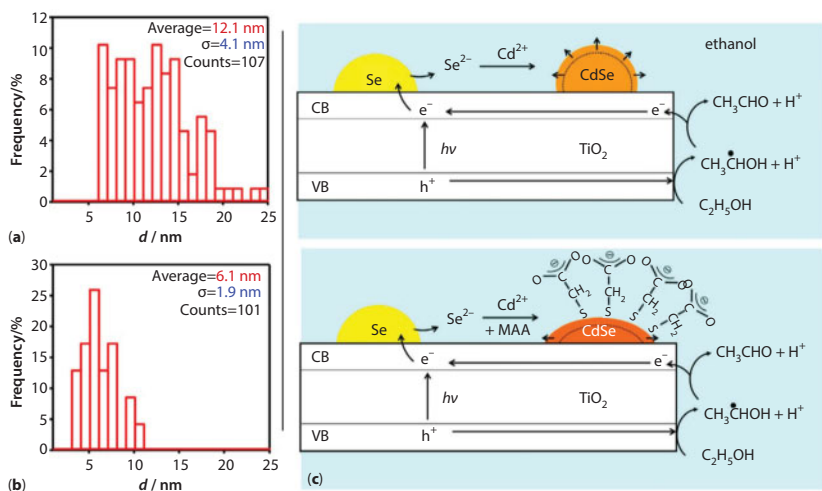


Figure 11.12 Size distributions of CdSe NPs photodeposited on the titania surface without additives (a) and in the presence of TGA (b). (c) A schematic of the TGA effect on the photoinduced growth of CdSe NPs. Reprinted with permissions from [56]. Copyright (2016) Elsevier.

The FTO/TiO₂/CdSe produced on the second stage of the photocatalytic process were then tested as photoanodes of solar cells with the polysulfide electrolyte and a Cu_xS-based counterelectrode demonstrating a light conversion efficiency of 1.76 %.

Antimony selenide NPs can be deposited in a photoelectrochemical regime on the FTO substrates from aqueous solutions of sodium-antimony tartrate and selenic acid [57]. The illumination of electrodes during the Sb₂Se₃ layer deposition accelerates this process and allows for the formation of a more uniform and crystalline deposit. This effect was attributed to the photoexcitation of just-deposited antimony selenide resulting in an increase of its electric conductivity and an acceleration of the Sb₂Se₃ deposition on the spots where the photogenerated charges reach the electrode surface [57]. The films produced by the photoassisted electrodeposition revealed a higher photoelectrochemical response as compared to the analogs prepared by the conventional “dark” electrodeposition.

The photodeposition can also be adapted to the formation of ternary composites. For example, the TiO₂/CdS heterostructures produced by the PD from ethanol solutions of Cd(II) perchlorate and S₈ were then used as a photocatalyst for the photodeposition of Se NPs and their subsequent conversion into cadmium selenide [58]. An X-ray photoelectron spectroscopic (XPS) study showed that CdSe is predominantly deposited as a shell on the surface of CdS

NPs. In an alternative case of the SILAR deposition of cadmium selenide on titania using the SILAR approach the XPS shows the extinction of the signal of Ti 2p electrons indicating a tight coverage of the TiO_2 surface by a layer of CdSe. At the same time, for the doubly photodeposited $\text{TiO}_2/\text{CdS}/\text{CdSe}$ heterostructure, the Ti-related XPS features are still present after the formation of CdS/CdSe core/shell NPs, thus indicating that a portion of the titania surface remains free from the metal chalcogenide deposits and, therefore, attesting to the fact that CdSe is selectively deposited on the preformed CdS NPs. The optical characteristics of the ternary composites can be tailored by varying the PD duration at the stages of both Se photodeposition and the subsequent photocatalytic conversion of selenium into CdSe shell. The PD-formed $\text{TiO}_2/\text{CdS}/\text{CdSe}$ composites were found to be more efficient photocatalysts of the hydrogen evolution from aqueous $\text{Na}_2\text{SO}_3/\text{Na}_2\text{S}$ solutions as compared to TiO_2/CdS showing a light-to-hydrogen conversion efficiency of 0.042%.

A layer of CdSe NPs was grown by the photoassisted deposition on the surface of compound ZnO/CdS nanorod arrays [59]. Both the amount of photodeposited cadmium selenide and the average size of CdSe NPs were found to grow as the illumination duration was increased. The ternary ZnO/CdS/CdSe heterostructures were tested as photoanodes of a liquid-junction solar cell with the polysulfide electrolyte and a Cu_xS -based counterelectrode, demonstrating a light conversion efficiency of 3.59% as compared to 2.88% in the case of a similar composite produced by the CBD of the cadmium selenide layer [59].

We studied the structure of nanoparticulate cadmium selenide photo-deposits on CdS NPs by using the resonant Raman spectroscopy [60]. The binary CdS/CdSe nanoheterostructures were synthesized by the photocatalytic reduction of Na_2SeSO_3 on the surface of colloidal cadmium sulfide NPs [61]. The resonant Raman spectra of CdS/CdSe showed longitudinal optical (LO) phonon peaks of both components with the CdSe LO peak growing with an increase in the content of the photodeposited cadmium selenide (Figure 11.13a,b). The main phonon peak of 6–7-nm CdS NPs used as a photocatalyst can be found at 302 cm^{-1} shifting slightly to lower frequencies as compared to the bulk cadmium selenide (305 cm^{-1} [62]). The small shift magnitude attests to a weak phonon confinement in such NPs. However, the CdS NPs revealed a much higher spectral width of the LO band ($70\text{--}80\text{ cm}^{-1}$) as compared to both the photodeposited CdSe (40 cm^{-1}) and the CdSe NPs prepared in “dark” conditions via the interaction between Na_2SeSO_3 and CdCl_2 ($10\text{--}20\text{ cm}^{-1}$) [61, 63–65]. Most probably, the fact is associated with a high density of bulk and surface lattice defects in CdS NPs that form with a much higher rate than CdSe NPs as well as with an interdiffusion on the CdS–CdSe interface.

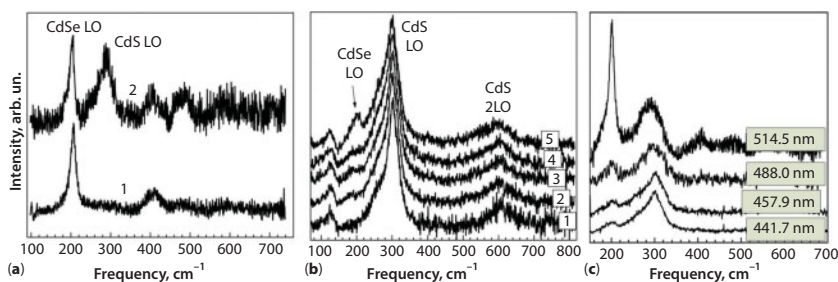


Figure 11.13 Resonance Raman spectra of (a) CdSe NPs (curve 1) and core-shell CdSe/ZnS NPs (curve 2) incorporated into the gelatin films ($\lambda_{\text{exc}} = 457.9$ nm) [63,66]; (b) CdS NPs (curve 1) and photocatalytically formed CdS/CdSe nanoheterostructures (curves 2–5) in the gelatin films (excitation at 441.7 nm, CdSe content is 4 mol.% (curve 2), 7 mol.% (curve 3), 10 mol.% (curve 4), and 13 mol.% (curve 6)) [60]; (c) CdS/CdSe nanoheterostructure with 13 mol.% CdSe (relative to CdS content) registered at a different excitation wavelength [60].

The interdiffusion produces a weak signal at 500 cm^{-1} which is a combination of the second-order vibrations $\text{LO}_{\text{CdS}} + \text{LO}_{\text{CdSe}}$ [63] (Figure 11.13b). A strong interdiffusion is also typical for the core-shell CdSe/CdS NPs produced in a noncatalytic way [63, 64]. As the lattice constants of CdSe and CdS are slightly different, the contact between the two semiconductors results in the diffusion of sulfur atoms into the bulk of cadmium selenide and in the formation of a mixed $\text{CdS}_x\text{Se}_{1-x}$ layer.

The LO phonon peak of CdSe can be observed as a low-intensity shoulder at 185 cm^{-1} for low CdSe contents but appears as a well-resolved peak at 200 cm^{-1} for the highest cadmium selenide content (13 mol.%). The peak is shifted by around 10 cm^{-1} to lower frequencies as compared to bulk CdSe (210 cm^{-1} [62, 63]) indicating a considerable phonon confinement, that is, a small size of the photodeposited CdSe NPs.

The spectral width and position of the LO bands do not reflect directly the size and size distribution of CdSe NPs because the spectra were registered under resonant conditions ($\lambda_{\text{exc}} = 441.7\text{ nm}$) when a spectral contribution of the NPs with the bandgap energy closest to the excitation energy is the highest in the ensemble. At the same time, an increase in the phonon peak intensity with a growing CdSe content indicates that a fraction of resonantly excited CdSe NPs becomes larger. As the excitation wavelength is increased, the resonance conditions for the selective excitation of CdSe NPs become more and more favorable. As a result, the ratio of LO_{CdSe} and LO_{CdS} peaks distinctly grows as λ_{exc} is increased from 441.7 nm to 514.5 nm (Figure 11.13c) indicating that the laser energy (2.41 eV) is close to the bandgap of the photodeposited CdSe NPs. The fact can be taken as an

indication that cadmium selenide is indeed deposited as separate NPs, not as subnanometer 2D islands, for which the resonance energy is expected to be much higher. A driving force for the formation of 3D NPs can be supplied by the lattice constant mismatch of CdS and CdSe resulting in a compressive stress that can be relaxed via the transformation of primary 2D CdSe islands into the 3D NPs similarly to the well-reported Stransky–Krastanov transformation of epitaxial $A^{III}B^V$ semiconductor nanoislands [67].

The ratio of the main phonon mode and its overtone 2LO depends on the electron–phonon interaction in the semiconductor lattice amounting to $I_{2LO}/I_{LO} = 0.3\text{--}0.4$ similar to 2–5 nm CdSe NPs produced by a noncatalytic method [68], the fact additionally proving the formation of separate 3D CdSe NPs as a product of the photocatalytic deposition.

11.4 Conclusion and Outlook

The experimental findings on the photocatalytic formation of various chalcogenide/oxide nanoheterostructures collected and analyzed in the present chapter show quite convincingly a great potential and a large applicability scope of the photodeposition approach.

One of the PD merits is a broad variety of compositions that can be produced, including a number of binary sulfide/oxide and selenide/oxide compositions as well as ternary selenide/sulfide/oxide and sulfide/metal/oxide heterostructures. We expect a further progress in the photodeposition approach involving new emerging photoactive materials such as single/a-few-layer materials (reduced graphene oxide, graphitic carbon nitride, layered metal dichalcogenides, etc.), semiconducting organic polymers, and metal–organic frameworks working as photocatalysts for the deposition of composition- and size-tuned metal chalcogenide NPs for various light-harvesting applications.

Another promising feature of the photodeposition is a broad range of techniques aimed at the control of the size and size distribution of photodeposited chalcogenide NPs, including the tailoring of the photodeposition conditions (precursor concentration, exposure to light, spectral composition of the light flux, etc.), introducing various “seeds” (fine metal NPs or primary metal chalcogenide islands deposited by a conventional method like SILAR) or surface-passivating ligands. Taking into account the importance of the duration and spectral composition of the irradiation during the photodeposition, we can expect that a switch from the stationary to flash photoexcitation can open new ways of controlling the size and shape of the photodeposited chalcogenide NPs as it happened, for

example, in the well-reported case of pulsed electrodeposition used instead of the stationary version.

Finally, the photodeposition typically produces the heterostructures exhibiting a higher efficiency in various light-harvesting processes, including photocatalysis and photovoltaics, as compared to the counterparts prepared by more conventional techniques. This advantage stems from a unique effect of “memory” when the metal chalcogenide NPs (or intermediate metal NPs) are deposited photocatalytically on the spots of metal-oxide photocatalyst, where the interfacial transfers of the photogenerated charge carriers are the most efficient. As a result, the subsequent charge transfers in a heterostructure composed of metal oxide substrate and the photodeposited chalcogenide NPs occur with a much higher efficiency as compared to similar composites produced by the methods with indiscriminate deposition of the chalcogenide layer (such as SILAR or CBD). We expect that the most prominent role of such memory effect can be achieved for the case of anisotropic metal oxide photocatalysts, such as single-crystalline nanorods and nanowires or polycrystalline nanotubes, where the effect of advanced efficiency of the interfacial charge transfer from the photodeposited visible-light-sensitive chalcogenide NPs to the metal-oxide substrate can be coupled to and enhanced by the directional charge migration in the metal oxide component resulting in an unprecedented charge collection efficiency.

References

1. Hodes, G., Comparison of dye- and semiconductor-sensitized porous nanocrystalline liquid junction solar cells. *J. Phys. Chem. C*, 112, 17778, 2008.
2. Sharma, D., Jha, R., Kumar, S., Quantum dot sensitized solar cells: recent advances and future perspectives in photoanode. *Sol. Energy. Mater. Sol. Cells*, 155, 294, 2016.
3. Kamat, P.V., Quantum dot solar cells. Semiconductor nanocrystals as light harvesters. *J. Phys. Chem. C*, 112, 18737, 2008.
4. Rühle, S., Shalom, M., Zaban, A., Quantum dot sensitized solar cells. *ChemPhysChem*, 11, 2290, 2010.
5. Kamat, P.V., Tvrđy, K., Baker, D.R., Radich, J.G., Beyond photovoltaics: semiconductor nanoarchitectures for liquid-junction solar cells. *Chem. Rev.*, 110, 6664, 2010.
6. Stroyuk, O., *Solar Light Harvesting with Nanocrystalline Semiconductors*, pp. 161–240, Springer Cham, 2017.
7. Kozyskiy, A.V., Stroyuk, O.L., Raevskaya, A.E, Kuchmiy, Ya., S., Photoelectrochemical solar cells with semiconductor nanoparticles and liquid electrolytes: A review. *Theor. Exp. Chem.*, 53, 145, 2017.

8. Tada, H., Fujishima, M., Kobayashi, H., Photodeposition of metal sulfide quantum dots on titanium(IV) dioxide and the applications to solar energy conversion. *Chem. Soc. Rev.*, 40, 4232, 2011.
9. Stroyuk, O.L., Shvalagin, V.V., Raevskaya, A.E., Kryukov, A.I., Kuchmiy, Ya., S., Photochemical formation of semiconducting nanostructures. *Theor. Experim. Chem.*, 44, 205, 2008.
10. Wenderich, K., Mul, G., Methods, mechanism, and applications of photodeposition in photocatalysis: A review. *Chem. Rev.* 116, 14587, 2016.
11. Schneider, J., Bahnemann, D., Ye, Y., Puma, G.L., Dionysiou, D.D. (Eds.), *Photocatalysis. Fundamentals and Perspectives*. The Royal Society of Chemistry, 2016.
12. Fujii, M., Nagasuna, K., Fujishima, M., Akita, T., Tada, H., Photodeposition of CdS quantum dots on TiO₂: Preparation, characterization, and reaction mechanism. *J. Phys. Chem. C*, 113, 16711, 2009.
13. Tada, H., Mitsui, T., Kiyonaga, T., Akita, T., Tanaka, K., All-solid-state Z-scheme in CdS-Au-TiO₂ three-component nanojunction system. *Nat. Mater.*, 5, 782, 2006.
14. Kanda, S., Akita, T., Fujishima, M., Tada, H., Facile synthesis and catalytic activity of MoS₂/TiO₂ by a photodeposition-based technique and its oxidized derivative MoO₃/TiO₂ with a unique photochromism. *J. Colloid Interface Sci.*, 354, 607, 2011.
15. Ma, B., Wang, L., Dong, H., Gao, R., Geng, Y., Zhu, Y., Qiu, Y., Photocatalysis of PbS quantum dots in a quantum dot-sensitized solar cell: photovoltaic performance and characteristics. *Phys. Chem. Chem. Phys.*, 13, 2656, 2011.
16. Nagasuna, K., Akita, T., Fujishima, M., Tada, H., Photodeposition of Ag₂S quantum dots and application to photoelectrochemical cells for hydrogen production under simulated sunlight. *Langmuir*, 27, 7294, 2011.
17. Jin-nouchi, Y., Naya, S.I., Tada, H., Quantum-dot-sensitized solar cell using a photoanode prepared by *in situ* photodeposition of CdS on nanocrystalline TiO₂ films. *J. Phys. Chem. C*, 114, 16837, 2010.
18. Hu, H., Ding, J., Zhang, S., Li, Y., Bai, L., Yuan, N., Photodeposition of Ag₂S on TiO₂ nanorod arrays for quantum dot-sensitized solar cells. *Nanoscale Res. Lett.*, 8, 10, 2013.
19. Wang, X., Liu, H., Shen, W., Controllable *in situ* photo-assisted chemical deposition of CdSe quantum dots on ZnO/CdS nanorod arrays and its photovoltaic application. *Nanotechnology*, 27, 085605, 2016.
20. Tada, H., Tanikawa, J., Akita, T., Kobayashi, H., *Abstracts of 17th International Conference on Photochemical Conversion and Storage of Solar Energy*, 756, 114, 2008.
21. Zhukowsky, M.A., Stroyuk, O.L., Shvalagin, V.V., Smirnova, N.P., Lytvyn, O.T., Eremenko, O.T., Photocatalytic growth of CdS, PbS, and Cu_xS nanoparticles on the nanocrystalline TiO₂ films. *J. Photochem. Photobiol. A*, 203, 137, 2009.
22. Stroyuk, O.L., Raevskaya, A.E., Shvalagin, V.V., Kuchmiy, Ya, S., Bavykin, D.V., Streltsov, E.A., Poznyak, S.K., Gelatin-templated mesoporous titania for

- photocatalytic air treatment and application in metal chalcogenide nanoparticle-sensitized solar cells. *Photochem. Photobiol. Sci.*, 12, 621, 2013.
23. Shvalagin, V.V., Stroyuk, O.L., Kuchmiy, Ya, S., Photocatalytic formation of porous CdS/ZnO nanospheres and CdS nanotubes. *Theor. Experim. Chem.* 43, 229, 2007.
 24. Kang, U., Park, K.J., Han, D.S., Kim, Y.M., Kim, S., Park, H., Photoelectrochemical hydrogen production using CdS nanoparticles photodeposited onto Li-ion-inserted titania nanotube arrays. *Catal. Today*, in press, 303, 2017.
 25. Kozyt'skiy, A.V., Stroyuk, O.L., Kuchmiy, Ya, S., Streltsov, E.A., Skoryk, N.A., Moskalyuk, V.O., Effect of the method of preparation of ZnO/CdS and TiO₂/CdS film nanoheterostructures on their photoelectrochemical properties. *Theor. Exp. Chem.*, 49, 165, 2013.
 26. Kozyt'skiy, A.V., Stroyuk, O.L., Kuchmiy, Ya, S., Photoelectrochemical properties of a solar cell based on FTO/ZnO/CdS (photoanode) and FTO/ZnO/Cu_xS (counter-electrode) heterostructures. *Theor. Exp. Chem.*, 51, 203, 2015.
 27. Stroyuk O.L., Kuchmiy, Ya, S., Zhukovskiy, M.A., Smirnova, N.P., Glebov, E.M., Grivin, V.P., Plyusnin, V.F., Effect of the method of production of TiO₂/CdS film nanoheterostructures on the effectiveness of photoinduced charge separation. *Theor. Exp. Chem.*, 45, 302, 2009.
 28. Shvalagin, V.V., Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, S.Ya., Photoinduced variation of CdS nanoparticle size in colloidal solutions. *Theor. Exp. Chem.*, 43, 2007, 170.
 29. Fujishima, M., Nakabayashi, Y., Takayama, K., Kobayashi, H., Tada, H., High coverage formation of CdS quantum dots on TiO₂ by the photocatalytic growth of preformed seeds. *J. Phys. Chem. C*, 120, 17365, 2016.
 30. Serpone, N., Lawless, D., Khairutdinov, R., Pelizzetti, E., Subnanosecond relaxation dynamics in TiO₂ colloidal sols (particle sizes $R_p = 1.0\text{--}13.4$ nm). Relevance to heterogeneous photocatalysis. *J. Phys. Chem.*, 99, 16655, 1995.
 31. Bahnemann, D., Henglein, A., Lilie, J., Spanhel, L., Flash photolysis observation of the absorption spectra of trapped positive holes and electrons in colloidal TiO₂. *J. Phys. Chem.*, 88, 709, 1984.
 32. Teoh, W.Y., Mädler, L., Beydoun, D., Pratsinis, S.E., Amal, R., Direct (one-step) synthesis of TiO₂ and Pt/TiO₂ nanoparticles for photocatalytic mineralisation of sucrose. *Chem. Eng. Sci.*, 60, 5852, 2005.
 33. Duonghong, D., Ramsden, J., Grätzel, M., Dynamics of interfacial electron transfer processes in colloidal semiconductor systems. *J. Am. Chem. Soc.*, 104, 2977, 1982.
 34. Bessekhouad, Y., Chaoui, N., Trzpit, M., Ghazzal, N., Robert, D., Weber, J.V., UV-vis versus visible degradation of Acid Red II in a coupled CdS/TiO₂ semiconductors suspension. *J. Photochem. Photobiol. A*, 183, 218, 2006.
 35. Liu, Y., Wang, X., Yang, F., Yang, X., Excellent antimicrobial properties of mesoporous anatase TiO₂ and Ag/TiO₂ composite films. *Micropor. Mesopor. Mater.*, 114, 431, 2008.

36. Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, S.Ya., Photocatalytic oxidation of hydrosulfide-ions by molecular oxygen over cadmium sulfide nanoparticles. *J. Nanopart. Res.*, 6, 149, 2004.
37. Stroyuk, O.L., Dzhagan, V.M., Kuchmiy, Ya, S., Valakh, Ya, M., Zahn, D.R.T., von Borczyskowski, C., Nanosecond and microsecond decay of photogenerated charges in $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles. *Theor. Exp. Chem.*, 43, 297, 2007.
38. Rajh, T., Micić, O.I., Lawless, D., Serpone, N., Semiconductor photophysics. 7. Photoluminescence and picosecond charge carrier dynamics in cadmium sulfide quantum dots confined in a silicate glass. *J. Phys. Chem.* 96, 4633, 1992.
39. Kamat, P.V., Dimitrijević, N.M., Fessenden, R.W., Photoelectrochemistry in particulate systems. 6. Electron-transfer reactions of small CdS colloids in acetonitrile. *J. Phys. Chem.*, 91, 396, 1987.
40. Stroyuk, O.L., Raevskaya, A.E., Korzhak, A.V., Kotenko, I.E., Glebov, E.M., Plyusnin, V.F., Kuchmiy, S.Ya., Photocatalytic production of hydrogen in systems based on $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{Ni}^0$ nanostructures. *Theor. Experim. Chem.*, 45, 12, 2009.
41. Jin-nouchi, Y., Akita, T., Tada, H., Ultrafast photodeposition of size-controlled PbS quantum dots on TiO_2 . *ChemPhysChem*, 11, 2349, 2010.
42. Jin-nouchi, Y., Hattori, T., Sumida, Y., Fujishima, M., Tada, H., PbS quantum dot-sensitized photoelectrochemical cell for hydrogen production from water under illumination of simulated sunlight. *ChemPhysChem*, 11, 3592, 2010.
43. Kozyskiy, A.V., Stroyuk, O.L., Skoryk, M.A., Dzhagan, V.M., Kuchmiy, Ya, S., Zahn, D.R.T., Photochemical formation and photoelectrochemical properties of $\text{TiO}_2/\text{Sb}_2\text{S}_3$ heterostructures. *J. Photochem. Photobiol. A*, 303–304, 8, 2015.
44. Ho, W., Yu, J.C., Lin, J., Yu, J., Li, P., Preparation and photocatalytic behavior of MoS_2 and WS_2 nanocluster sensitized TiO_2 . *Langmuir*, 20, 5865, 2004.
45. Fu, X., Zhang, L., Liu, L., Li, H., Meng, S., Ye, X., Chen, S., *In situ* photodeposition of MoS_x on CdS nanorods as a highly efficient cocatalyst for photocatalytic hydrogen production. *J. Mater. Chem. A*, 5, 15287, 2017.
46. Li, Y., Wang, H., Peng, S., Tunable photodeposition of MoS_2 onto a composite of reduced graphene oxide and CdS for synergic photocatalytic hydrogen generation. *J. Phys. Chem. C*, 118, 19842, 2014.
47. Eda, S., Moriyasu, K., Fujishima, M., Numura, S., Tada, H., Photodeposition of copper sulphide nanocrystals on titanium(IV) oxide nanorods and their application in smart windows. *RSC Adv.*, 3, 10414, 2013.
48. Kozyskiy, A.V., Stroyuk, O.L., Skoryk, M., Kuchmiy, Ya, S. Photoassisted formation of Cu_xS -based cathodes for CdS-sensitized solar cells with $\text{S}^{2-}/\text{S}_x^{2-}$ electrolyte. *Photochem. Photobiol. Sci.*, 14, 942, 2015.
49. Kozyskiy, A.V., Stroyuk, O.L., Kuchmiy, S.Ya., Method of photocatalytic preparation of $\text{FTO}/\text{TiO}_2/\text{Cu}_x\text{S}$ film material. Patent of Ukraine, No. u 201413018, 2015.
50. Chenthamarakshan, C.R., Ming, Y., Rajeshwar, K., Underpotential photocatalytic deposition: A new preparative route to composite semiconductors. *Chem. Mater.*, 12, 3538, 2000.

51. Tan, T.T.Y., Zaw, M., Beydoun, D., Amal, R., The formation of nano-sized selenium–titanium dioxide composite semiconductors by photocatalysis. *J. Nanopart. Res.*, 4, 541, 2002.
52. Somasundaram, S., Chenthamarakshan, C.R., de Tacconi, N.R., Ming, Y., Rajeshwar, K., Photoassisted deposition of chalcogenide semiconductors on the titanium dioxide surface: mechanistic and other aspects. *Chem. Mater.*, 16, 3846, 2004.
53. Tanaka, K., Jin-nouchi, Y., Fujishima, M., Tada, H., Lead selenide–titanium dioxide heteronanojunction formation by photocatalytic current doubling-induced two-step photodeposition technique. *J. Colloid Interface Sci.*, 457, 248, 2015.
54. Nguyen, V.N.H., Amal, R., Beydoun, D., Photodeposition of CdSe using Se-TiO₂ suspensions as photocatalysts. *J. Photochem. Photobiol. A*, 179, 57, 2006.
55. Fujishima, M., Tanaka, K., Sakami, N., Wada, M., Morii, K., Hattori, T., Sumida, Y., Tada, H., Photocatalytic current doubling-induced generation of uniform selenium and cadmium selenide quantum dots on titanium(IV) oxide. *J. Phys. Chem. C*, 118, 8917, 2014.
56. Yoshii, M., Murata, Y., Nakabayashi, Y., Ikeda, T., Fujishima, M., Tada, H., Coverage control of CdSe quantum dots in the photodeposition on TiO₂ for the photoelectrochemical solar hydrogen generation. *J. Colloid Interface Sci.*, 474, 34, 2016.
57. Yang, J., Lai, Y., Fan, Y., Jiang, Y., Tang, D., Jiang, L., Liu, F., Li, J., Photoelectrochemically deposited Sb₂Se₃ thin films: deposition mechanism and characterization. *RSC Adv.*, 5, 85592, 2015.
58. Kitazono, K., Akashi, R., Fujiwara, K., Akita, A., Naya, S., Fujishima, M., Tada, H., Photocatalytic synthesis of CdS(core)–CdSe(shell) quantum dots with a heteroepitaxial junction on TiO₂: Photoelectrochemical hydrogen generation from water. *ChemPhysChem*, 18, 2840, 2017.
59. Wang, X., Liu, H., Shen, W., Controllable *in situ* photo-assisted chemical deposition of CdSe quantum dots on ZnO/CdS nanorod arrays and its photo-voltaic application. *Nanotechnology*, 27, 085605, 2016.
60. Dzhan, V.M., Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, S., Zahn, D.R.T., Resonant Raman spectroscopy of confined and surface phonons in CdSe-capped CdS nanoparticles. *Phys. Stat. Sol. C*, 6, 2043, 2009.
61. Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, S., Preparation of colloidal CdSe and CdS/CdSe nanoparticles from sodium selenosulfate in aqueous polymers solutions. *J. Colloid Interface Sci.*, 302, 133, 2006.
62. Landolt-Börnstein (Eds.) Numerical data and functional relationships in science and technology. Group III, Vol. 17b – *Semiconductors*, Springer, Berlin, 1982.
63. Dzhan, V.M., Valakh, Ya, M., Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, S., Zahn, D.R.T., Resonant Raman scattering study of CdSe nanocrystals passivated with CdS and ZnS. *Nanotechnology*, 18, 285701, 2007.

64. Dzhagan, V.M., Valakh, M.Ya., Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, S., Zahn, D.R.T., Temperature-dependent resonant Raman scattering study of core/shell nanocrystals. *J. Phys. Conf. Series*, 92, 012045, 2007.
65. Dzhagan, V.M., Valakh, Ya, M., Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, S., Zahn, D.R.T., Characterization of semiconductor core-shell nanoparticles by resonant Raman scattering and photoluminescence spectroscopy. *Appl. Surf. Sci.*, 255, 725, 2008.
66. Dzhagan, V.M., Valakh, M.Y., Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, S., Zahn, D.R.T., The influence of shell parameters on phonons in core-shell nanoparticles: a resonant Raman study. *Nanotechnology*, 20, 365704, 2009.
67. Krasil'nik, Z.K., Lytvyn, P., Lobanov, D.N., Nestres, N., Novikov, A.V., Pascual, J., Valakh, Ya, M., Yukhimchuk, V.A., Microscopic and optical investigation of Ge nanoislands on silicon substrates. *Nanotechnology*, 13, 81, 2002.
68. Raevskaya, A.E., Stroyuk, O.L., Kuchmiy, Ya, M., Azhniuk, Yu, M., Dzhagan, V.M., Yukhymchuk, V.O., Valakh, Ya, M., Growth and spectroscopic characterization of CdSe nanoparticles synthesized from CdCl_2 and Na_2SeSO_3 in aqueous gelatine solutions. *Colloids Surf. A*, 290, 304, 2006.

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