Recent Advances in Visible-Light-Driven Photoelectrochemical Water Splitting: Catalyst Nanostructures and Reaction Systems

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Received: 17 August 2015 / Accepted: 31 August 2015 / Published online: 28 October 2015 © The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract Photoelectrochemical (PEC) water splitting using solar energy has attracted great attention for generation of renewable hydrogen with less carbon footprint, while there are enormous challenges that still remain for improving solar energy water splitting efficiency, due to limited light harvesting, energy loss associated to fast recombination of photo-generated charge carriers, as well as electrode degradation. This overview focuses on the recent development about catalyst nanomaterials and nanostructures in different PEC water splitting systems. As photoanode, Au nanoparticle-decorated TiO₂ nanowire electrodes exhibited enhanced photoactivity in both the UV and the visible regions due to surface plasmon resonance of Au and showed the largest photocurrent generation of up to 710 nm. Pt/CdS/CGSe electrodes were developed as photocathode. With the role of p–n heterojunction, the photoelectrode showed high stability and evolved hydrogen continuously for more than 10 days. Further, in the Z-scheme system (Bi₂S₃/TNA as photoanode and Pt/SiPVC as photocathode at the same time), a self-bias (open-circuit voltage \(V_{oc} = 0.766\) V) was formed between two photoelectrodes, which could facilitate photogenerated charge transfers and enhance the photoelectrochemical performance, and which might provide new hints for PEC water splitting. Meanwhile, the existing problems and prospective solutions have also been reviewed.

Keywords Photoelectrochemical water splitting · Nanostructures · Reaction system · Heterojunction · Hybrid systems

1 Introduction

The energy consumption nowadays to maintain modern lifestyle of mankind mainly relies on primary fossil fuels such as oil, coal, natural gas, etc. However, the fossil fuels are suffering from accelerated depletion and bringing about serious environmental issues and threats to global climate. It is a mission of international scale to explore and utilize alternative energy to compensate for the consumption of fossil fuels and mitigate the corresponding climate changes. Among various alternative energies, hydrogen has been considered as a promising candidate to solve aforementioned problems because it is a source of green and renewable energy. There are a variety of strategies for hydrogen production, such as electrolysis, thermal water splitting, cracking of petroleum, hydrocarbon reforming, etc. However, these techniques are either costly or rely on fossil fuels. In 1972, Fukushima and Honda discovered photoelectrochemical (PEC) water splitting in which hydrogen and oxygen were released, respectively, from titanium dioxide (TiO₂) photoelectrode and Platinum (Pt) counter electrode under ultraviolet (UV) light irradiation [1], revealing the potential of solar energy water splitting to produce...
sustainable hydrogen. This discovery stimulated great
interest to explore effective photoelectrode materials for
solar energy hydrogen generation via solar energy water
splitting which is not only a clean process but also stores
solar energy in hydrogen [2–4]. However, the widespread
application of PEC water splitting still demands great
efforts in the discovery of effective photocatalysts and
coating process.

In comparison with photocatalytic water splitting using
heterogeneous powder semiconductors, PEC water splitting
possesses great advantages in (i) the external or self-bias
voltage can suppress recombination of photogenerated
carriers and thus improve the separation and transfer of excited electron–hole pairs of the photocatalysts; (ii) hydrogen and oxygen can be easily separated via
collection at different photoelectrodes; (iii) semiconductor
films are coated on the conductive substrates, which favors scale up for industrial application in the future; and (iv)
last, but not the least, it does not need stirring, so it con-
sumes less power relative to powder photocatalytic water
splitting systems [2, 5]. In practice, the performance of
PEC water splitting system is dominated by the properties
of the semiconductor photocatalysts that harvest solar
energy for hydrogen generation.

Various effective UV-light-responsive photocatalysts
have been well established [6, 7], although most of them
suffer from photocorrosion and are not active under
visible light which accounts for 45 % energy of solar
spectrum, nearly an order of solar energy in UV region.
In the recent decades, designing visible-light-driven
photocatalysts for water splitting represents a major
mission for photocatalytic water splitting to maximize the
solar energy conversion and storage. For instance, the
metal sulfides have been found as a class of efficient
photocatalysts but require sacrificial agents to reduce
photocorrosion [8–12]. (Oxy) nitride semiconductors
recently emerged as new type of phototcatalysts for
visible-light-responsive photocatalytic water splitting [13–
15], whereas they can respond to short-wavelength visi-
ble light with rather low solar energy conversion effi-
ciency. Fortunately, the hybrid photocatalyst systems
have demonstrated enhanced water splitting efficiency,
which, however, require dedicated design and alignment
of the corresponding photocatalytic materials [6].

In this study, we briefly overviewed the recent
research advances in the field of hydrogen evolution from
PEC water splitting, addressing the different PEC water
splitting systems and corresponding electrode materials.
Key issues and challenges involved in PEC water split-
ing systems and potential solutions were highlighted via
the comparison of various photoelectrode materials and
nanostructures.

### 2 Working Principle of Photoelectrochemical
Water Splitting

Loaded with semiconductor photocatalysts, the conduc-
tive electrode substrates can be metal plates, silicon substrates, or
glass coated with conductive layers, such as fluorine-doped
tin oxide (FTO) and indium tin oxide (ITO) [16–19]. In PEC
water splitting system, the free energy change (ΔG) is
237.2 kJ mol⁻¹ for converting one molecule of H₂O–H₂ and
1/2 O₂ under standard condition. When a photoelectrode is
immersed in an electrolyte solution, electron transfer takes
place between the semiconductor and the electrolyte solution
so that the Fermi level is equilibrated with the redox potential
of electrolyte solution [15]. With n-type semiconductors as
working photoanodes, for example, as shown in Fig. 1,
photoexcited holes on the semiconductors would oxidize
water and produce oxygen, while electrons are transferred to
the counter electrode to generate hydrogen. Sometimes, an
external voltage is needed to compensate for the potential
deficiency, which can also accelerate the separation of
excited charges. The electrolytes are essential in the PEC
system for charge transfers, which usually are NaOH, Na₂,
SO₄, etc. [20, 21]. Some sulfides and organic agents can also
serve as electrolytes [19, 22]; where there is no oxygen
evolution, as water oxidation potential is more positive than
the oxidation potential of these materials.

### 3 Semiconductors Systems for PEC Water
Splitting

Different semiconductor systems for PEC water splitting
and their PEC performance are shown as in Table 1. They
can be classified into three groups: (1) photoanode, (2)
photocathode, and (3) Z-scheme system for PEC water
splitting.

![Fig. 1 The schematic setup of PEC water splitting system](image-url)
3.1 Photoanode and Anodic Semiconductors

In the PEC water splitting setup, photoanode usually comprises n-type semiconductors coated on conductive substrates [15, 19]. Under light illumination, photoexcited holes accumulate on the surface of the photoanode semiconductors and are consumed in oxidation reactions, while electrons are transferred to a counter electrode via an external circuit as shown in Fig. 2 [15]. From the electrochemical potential point of view, the valence band edge of the photocatalysts should be more positive than the oxygen evolution potential enabling the photoanode to generate oxygen. As one of the significant advantages of PEC, external voltage bias may be applied to compensate for the potential deficiency and accelerate the separation of excited charge carriers, although zero bias is desirable once the PEC systems become well aligned with suitable semiconductor materials. Starting with traditional TiO$_2$

### Table 1 Different photoelectrodes and their photoelectrochemical performance

| Photoanode/Photocathode | Photocurrent (mA cm$^{-2}$) | Experimental condition | Reference |
|-------------------------|-----------------------------|------------------------|-----------|
| TiO$_2$-C$_x$ nanotube array | 1.0 | 0 V versus Ag/AgCl, 1 M KOH(aq), 2500 W Xe lamp (100 mw cm$^{-2}$), >420 nm | 35 |
| N-doped TiO$_2$ nanotube arrays | 0.182 | 0 V versus calomel electrode, 0.01 M Na$_2$SO$_4$ (aq), 250 W halogen lamp, >400 nm | 36 |
| S-doped TiO$_2$ nanotube arrays | 0.41 | 0.1 V versus SCE, 0.1 M Na$_2$SO$_4$ (aq), 50 W fiber optic illuminator, >400 nm | 37 |
| Au nanoparticle-decorated TiO$_2$ nanowire electrodes | 1.49 | 0 V versus Ag/AgCl, 1 M NaOH(aq), white-light illumination (100 mW cm$^{-2}$) | 40 |
| Au decorated ZnO nanowire arrays | 1.5 | 1 V versus RHE, 0.5 M Na$_2$SO$_4$ (aq), 300 W Xe lamp (100 mW cm$^{-2}$), >420 nm | 42 |
| CdTe/TiO$_2$ | 0.44 | 0 V versus Ag/AgCl, 0.6 M Na$_2$S (aq), 300 W Xe arc lamp (6.0 W cm$^{-2}$ >400 nm) | 43 |
| CdS/TiO$_2$ | 5.6 | 0 V versus Ag/AgCl, 0.1 M Na$_2$S (aq), 300 W Oriel solar simulator (100 mW cm$^{-2}$) | 46 |
| Bi$_2$WO$_6$/TiO$_2$ | 0.014 | 1 V versus Ag/AgCl, 0.5 M Na$_2$SO$_4$ (aq), 300 W Xe lamp, >420 nm | 47 |
| CdS/TiO$_2$/WO$_3$ | 1.6 | 0 V versus Ag/AgCl, 0.05 M Na$_2$S (aq), 300 W Xe lamp, >495 nm | 50 |
| Hydrogen-treated TiO$_2$ nanowire arrays | 1.97 | −0.6 V versus Ag/AgCl, 1 M NaOH(aq), 150 W Xe lamp (100 mW cm$^{-2}$) | 52 |
| N-doped ZnO nanowire arrays | ~0.15 | 0.5 V versus NHE, 0.5 M NaClO$_4$ (aq), white light source (100 mW cm$^{-2}$) | 56 |
| WO$_3$/BiVO$_4$ | 0.8 | 0.5 V versus NHE, 0.5 M NaClO$_4$ (aq), chopped white light (100 mW cm$^{-2}$) | 58 |
| FeOOH | 10 | 0.55 V versus RHE, 1 M Na$_2$CO$_3$ (aq), 150 W Xe arc lamp (100 mW cm$^{-2}$), >400 nm | 60 |
| IrO$_2$-nH$_2$O/TaON | ~3.75 | 0.6 V versus Ag/AgCl, 0.1 M Na$_2$SO$_4$ (aq), chopped visible light | 65 |
| IrO$_2$-loaded Ta$_5$N$_5$ | 3.6 | 0.6 V versus Ag/AgCl, 0.1 M Na$_2$SO$_4$ (aq), 300 W Xe lamp, >495 nm | 67 |
| TiO$_2$ nanoarrays sensitized with CdS quantum dots | 3.98 | 0 V versus Ag/AgCl, 1.0 M KOH (aq), 300 W Xe lamp (100 mW cm$^{-2}$), >420 nm | 68 |
| Pt-In$_2$S$_3$/CuInS$_2$ | −17.5 to −7.0 | 0 V versus RHE, 0.1 M Na$_2$SO$_4$ (aq), 300 W Xe lamp | 74 |
| Pt-CdS/CuGaSe$_2$ | −3.2 | 0 V versus RHE, 0.05 M Na$_2$HPO$_4$(aq) + 0.05 M NaH$_2$PO$_4$(aq), 150 W Xe lamp | 18 |
| p-n Cu$_2$O homojunction | −0.2 | 0 V versus NHE, 0.5 M Na$_2$SO$_4$ (aq), 500 W Xe lamp | 79 |
| Pt/ZnO, Al$_2$O$_3$, TiO$_2$/Cu$_2$O | −7.6 | 0 V versus RHE, 1 M Na$_2$SO$_4$ (aq), 500 W Xe lamp (100 mW cm$^{-2}$), visible light | 80 |
| Photoanode: TiO$_2$ | 0.2 | 0 V versus Ag/AgCl, 1 M NaOH(aq), 500 W Xe lamp | 83 |
| Photocathode: CaFe$_2$O$_4$ | 0.02 | 3 M H$_2$SO$_4$(aq), 250 W Oriel tungsten–halogen quartz lamp (200 mW cm$^{-2}$) | 84 |
| Photoanode: WO$_3$ | 1.6 | 0 V versus Ag/AgCl, 0.25 M Na$_2$S + 0.125 M Na$_2$SO$_4$, Xe lamp (100 mW cm$^{-2}$), >400 nm | 19 |

Nano-Micro Lett. (2016) 8(1):1–12 3

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photoanode, this section highlights the recent advances in photoanodes composed of one-dimensional (1D) TiO₂ and various hybrid photoanode systems (Fig. 3).

Titanium dioxide (TiO₂) is the most attempted n-type semiconductor for PEC water splitting due to its low cost, and better chemical and optical stability [23–26]. Among various nanostructured TiO₂, 1D titanium dioxide nanotube arrays (TNAs) have gained much attention due to their intrinsic large surface area and unidirectional flow of charges [24, 27]. TNA can be easily fabricated via anodization of metal titanium foil or plate with great potential for large-scale application [24, 27–29]. 1D TiO₂ nanowire arrays were also coated on transparent conducting oxide (TCO)-coated glass through a mild hydrothermal reaction [30]. The photoconversion efficiencies of N719 dye-sensitized solar cells fabricated with the 1D nanowire arrays can be up to 5.02 %, which is much higher than those fabricated with the simple TiO₂ powders. Titanium dioxide itself shows low photoelectrochemical activity since it is not responsive to visible light due to wide bandgap (~3.2 eV). In order to enhance the visible light absorption, researchers have developed various strategies including doping TiO₂ with metal or non-metal, construction of heterojunction, and hydrogenation, or creation of structural vacancies [31–33]. Doping with metal or/and non-metal (C, N, S, B, etc.) was started in the early-twenty-first century as an effective solution to narrow the bandgap of TiO₂ for enhancing PEC efficiency [6, 34–39]. Metal doping and non-metal doping can lead to the conduct band and the valence band increases of acceptor, respectively, which narrowed the bandgap of the photocatalysts and made the photocatalysts respond to visible light. Park et al. prepared carbon-doped TiO₂ nanotube arrays with high aspect ratios. The total photocurrent was more than 20 times higher than that with a P-25 nanoparticulate film under white-light illumination [35]. Recently, surface plasmon resonance has been applied in PEC water splitting with extend light absorbance in the entire UV–Visible region [40–42]. Surface plasmon resonance is an intrinsic property of metal nanoparticles, in which the oscillation frequency is highly sensitive to the metal size and shape as well as the dielectric constant of the surrounding environment. For instance, Au nanoparticle-decorated TiO₂ nanowire electrodes showed the largest photocurrent generation at 710 nm and enhanced photoactivity across the entire UV–Visible region, which is due to the excitation of surface plasmon resonance of Au [40].

Modifying TiO₂ nano-semiconductor with second nano-semiconductor of lower bandgap to form heterojunction represents another promising route to harvest visible light. The second nano-semiconductor serves as a photosensitizer and builder for internal electric field across the interface. The internal potential bias significantly promotes the excited electrons and holes’ separation and transportation across the interface of the dual photocatalysts, leading to reducing recombination. For instance, TiO₂ nanotube arrays (TNAs) were always modified with p-type CdTe and Cu₂O semiconductors [43–45]. TiO₂ is n-type semiconductor. CdTe and Cu₂O are p-type semiconductors. Thus, p–n junctions can be formed between them, respectively, which facilitate the separation of the excited electrons and holes. Some heterojunctions can enhance the...
photoelectrochemical properties because of the overlapping in band gaps between two different photocatalysts, which could favor the charge carrier transfer and separation. Typical examples are the ones illustrated in Figs. 4, 5. The conduction band (CB) of catalyst A (Bi$_2$WO$_6$) is more negative than the one of catalyst B (TiO$_2$); therefore, the excited electrons from catalyst B (TiO$_2$) can be quickly transferred to catalyst A (Bi$_2$WO$_6$). The valance band (VB) of catalyst A (Bi$_2$WO$_6$) is more positive than the one of catalyst B (TiO$_2$), and the excited holes from catalyst A (Bi$_2$WO$_6$) can be quickly transferred to catalyst B (TiO$_2$). As a result, the excited electrons and holes can be separated and transferred quickly for efficient water splitting. This technique has been extensively applied in enhancing the photoelectrochemical performance of TiO$_2$ for PEC water splitting in recent years [51]. Oxygen vacancies can be produced through hydrogen treatment [51, 52]. It can also be generated by annealing metal oxide under oxygen-deficient conditions [53]. In comparison with the hydrogen treatment method, this approach eliminates the potential influence of hydrogen impurities. The PEC performance of TiO$_2$ electrodes can be enhanced by controlling the introduction of oxygen vacancies, which as shallow donors can significantly improve electrical conductivities of TiO$_2$ nanosemiconductors.

Besides TiO$_2$, many other metal-oxide photocatalysts such as BiVO$_4$, WO$_3$, ZnO, etc. have invariably been attempted to be coated on substrate as photoanodes for PEC water splitting [17, 54–57]. External voltage is needed when BiVO$_4$ or/and WO$_3$ photoanodes are applied for PEC water splitting. This is because their conduct bands are more positive than the potential of hydrogen evolution. Heterojunction can be applied to improve their photoelectrochemical performance. For example, nanostructured WO$_3$/BiVO$_4$ heterojunction is prepared for PEC water splitting as shown in Fig. 6 [58]. BiVO$_4$ layer was coated on WO$_3$ nanorod array by spin coating. The charges can be quickly separated and transferred due to the energy diagram of WO$_3$/BiVO$_4$ heterojunction. Because of excellent properties of graphene oxides for electron transfer, they have often been used to improve the photoelectrochemical properties of semiconductors in recent years [59]. And some metal hydroxides such as FeOOH (Fig. 7), NiOOH, and layered double hydroxide (LDH) have been reported as effective photoanode materials for PEC water splitting because the alignment reduced interface recombination at the junction between them and semiconductors, and created a more favorable Helmholtz layer potential drop at the semiconductor/electrolyte junction [16, 60, 61], which provides a hint for searching new materials in the field of PEC water splitting.

Owing to their narrow bandgap, some n-type metal sulfide [62–64] and oxynitride [65–67] photocatalysts can respond to visible light with long wavelength and appropriate band levels for water splitting, and therefore are chosen as photoanode materials for PEC water splitting in order to make better use of solar energy. CdS (Fig. 8) and other sulfides are often used in photoanodes as sensitizer for PEC water splitting [68]. However, the sulfides are not stable because of photocorrosion, which can be reduced by adding sacrificial agents [69]. Tantalum oxynitriles also show visible light absorption with long wavelength—yet they are not
stable and the intensity of absorption is low. Therefore, different techniques such as modification with cocatalysts, heterojunction, etc., have been developed to reduce the photocorrosion and enhance the PEC properties [66–68].

3.2 Photocathode and Cathodic Semiconductors

Photocathode usually comprises p-type semiconductor coated on conductive substrates in the PEC water splitting system. As shown in Fig. 9, under light illumination, water is reduced on the surface of semiconductor, while water is oxidized on the counter photoelectrode. From the electrochemical potential point of view, the conduction band edge of the photocatalysts should be more negative than the hydrogen evolution potential enabling the photocathode to generate hydrogen. Compared with the reports of n-type semiconductor photoanodes, there are fewer reports based on p-type semiconductor as photocathodes for PEC water splitting [70–77].
Cu$_2$O is a typical p-type semiconductor used as photoanode for PEC water splitting, while it readily gets degraded due to self-reduction by photogenerated electrons. WO$_3$/Cu$_2$O p–n junctions have been synthesized to reduce the self-reduction of Cu$_2$O and enhance the PEC properties [77]. In addition, p–n homojunctions have also been prepared to improve their PEC performance [78, 79]. Colleen et al. [78] fabricated p–n Cu$_2$O homojunction solar cells by electrochemically depositing an n-Cu$_2$O layer on a p-Cu$_2$O layer as shown in Fig. 10. The intrinsic doping levels of the prepared p-Cu$_2$O and n-Cu$_2$O layers were very low, and they made Ohmic junctions with Cu metal. The best cell performance (an $\eta$ of 1.06 %, a $V_{OC}$ of 0.621 V, an $I_{SC}$ of 4.07 mA cm$^{-2}$, and a fill factor of 42 %) was obtained, which was better than other p–n Cu$_2$O homojunctions. Paracchino et al. reported Cu$_2$O photocathode, as shown in Fig. 11, which was protected against photocorrosion. Moriy et al. deposited CdS on Cu(In, Ga)Se$_2$ through chemical bath deposition (CBD) as shown in Fig. 12 [18]. The photocurrent increased due to the p–n junctions formed between them, which accelerated the charge separation. Further, the Pt/CdS/CuGaSe$_2$ electrode showed a stable photocurrent (about 4 mA cm$^{-2}$, 0.05 M Na$_2$HPO$_4$(aq) + 0.05 M NaH$_2$PO$_4$(aq), pH 7, 150 W Xe lamp, 0 V vs RHE) under reductive conditions for more than 10 days under visible-light irradiation.

3.3 Z-scheme System for PEC Water Splitting

With suitable band structure, n-type semiconductors are usually used as photoanode and p-type semiconductors as photocathode for PEC water splitting. It is known that n-type semiconductor has a Fermi level near the conductor band (CB) edge and p-type semiconductor has a Fermi level near the valance band (VB) edge [19]. When n-type and p-type semiconductors are simultaneously used as photoanode and photocathode, respectively, (Z-scheme) as shown in Fig. 13, the mismatching Fermi levels could produce self-bias which can drive the excited electrons from photoanode to combine with the excited holes from photocathode. Meanwhile, water oxidation and reduction take place over the photoanode and photocathode, respectively. In the Z-scheme systems, the self-bias would act as an extra driving force for carriers’ charge transfers and transportation while their performance is still governed by the materials and the competition between chemical reaction and recombination.

Ida et al. constructed a PEC water splitting using p-type CaFe$_2$O$_4$ as photocathode and n-type TiO$_2$ as photoanode...
As shown in Fig. 14, under illumination without external voltage, hydrogen and oxygen were produced from photocathode and photoanode, respectively, with a short-circuit current of about 200 μA cm⁻². However, this system is not responsive to visible light because TiO₂ only responds to ultraviolet light. A PEC cell [84] made up of WO₃ photoanode and p-GaInP₂ photocathode has been reported, both of which are responsive to visible light. However, the conduct band edge of WO₃ (about 0.25 V vs. NHE) is more positive than the valance band of p-GaInP₂ (about 0 V vs. NHE), which restricts the charge transfer from photoanode to photocathode via external circuit. Furthermore, the WO₃ films show relatively poor charge separation properties and weak visible-light absorbance. Thus, this PEC cell cannot split water till enough light intensity is applied. TiO₂ itself could not respond to visible light. Zeng et al. used Bi₂S₃-decorated TiO₂ nanotube arrays as photoanode and Pt-modified Si photovoltaic cell (Pt/SiPVC) as photocathode [19]. Both of them could respond to visible light. As shown in Fig. 15, the conduct band edge of TiO₂ (about −0.05 V vs. NHE) is more negative than the valance band edge of p-GaInP₂ (about 0.8 V vs. NHE). A self-bias of about 0.85 V is formed between two photodevices for efficient spontaneous hydrogen evolution and electricity generation under visible light irradiation. However, this system for PEC water splitting needs to be added with sacrificial agents. Thus, an efficient Z-scheme system consisting visible-light responsive photocatalysts for PEC water splitting without addition of sacrificial agents needs to be developed.

4 Conclusions and Future Perspective

Photoelectrochemical devices comprising of visible-light-responsive semiconductors have attracted great efforts in water splitting processes to obtain sustainable hydrogen, in search of a promising technique to combat the challenges from global climate change. The prospect of the PEC water splitting systems were highly limited by the nanostructured
photocatalysts and their device configurations. The most important issues associated with the PEC devices lay on the sunlight absorbance, energy loss due to undesirable charge carrier recombination and photodegradation of the photoelectrodes. Along with the rapid and great development of nanomaterial science and semiconductor engineering, significant advances have been observed, which shed light on resolving the aforementioned challenges in the PEC water splitting in the recent decades, since the discovery of PEC water splitting by Honda and Fujisma in the 1970s.

Starting from brief introduction of the working mechanism and history of PEC system, this article overviewed the greatest progress in PEC water splitting systems comprising visible-light-responsive photocatalysts. The advantages and disadvantages of the emerging photoanodes and photocathodes were assessed with typical examples, to disclose the potentially effective strategies to promote the efficiency and stability of various PEC systems. Special attention was paid to the TiO$_2$ nanotube arrays and modified TiO$_2$ photoelectrodes, which can be responsive to visible light via doping with metal and/or nonmetal elements, creating lattice vacancies, and designing heterojunction or Schottky junctions by means of combining other semiconductors or nanoscaled metal particles. Such modifications would not only revise the band structures and energy alignment of TiO$_2$ photoelectrodes in the PEC electrolyte solution but also introduce additional drivers that influence photogenerated charge carrier’s separation and transfer. On the basis of advances in TiO$_2$ photoelectrodes and PEC systems, other visible-light-responsive semiconductor photoelectrodes and Z-scheme systems were addressed. Among those strategies, heterojunctions and homojunctions were found to be more attractive for single photoelectrode due to the low cost and broad room to align the energy gradient across the semiconductor interface.

The recent advances in the photoelectrodes and their configurations have shed light on resolving the great challenges in PEC water splitting systems, in which one of the very promising solutions could be constructing Z-scheme PEC system involving suitable semiconductor photoanode and photocathode. With reasonable design, the photoexcited charge carriers may be quickly separated and transferred as a result of driven force generated from the self-bias among the separated photoelectrodes. More importantly, semiconductor with small bandgap even responsive to infrared light (heat) could be combined with the Z-scheme systems to harvest full spectrum sunlight. However, the Z-scheme PEC system is still in its early stage and demand further research input due to only limited report on this thriving configuration. The major obstacles in the Z-scheme systems are, similar to the normal PEC system, the efficient (deficient) light harvesting and (in)stability (due to photodegradation) of the semiconductors employed in the photoelectrodes.

Resistance photocorrosion is pivotal to realizing long-term application of PEC water splitting. Although introduction of sacrificial agents may somehow resist photocorrosion of the photoelectrodes, configurations of semiconductor heterojunctions have proven to be more promising because of their broader manufacturing possibility and low cost. In terms of the heterojunction principle, the Z-scheme systems may be stable due to the closed electric circuit involved; however, limited information can be found from the literature regarding their stability, suggesting greater efforts are still required in this area. Apparently, there is a significant step to apply PEC water splitting in hydrogen generation on industrial scale in the near future. However, spurred by global energy and environmental challenge, PEC water splitting is an ideal route to generate hydrogen with less-adverse impact on climate change, and hence, industrial-scale application of PEC water splitting would be the next-door event once the highly efficient and stable photoelectrodes with visible-light-response could be developed, where the most promising PEC system might emerge from the breakthrough on Z-scheme system.

Acknowledgments This work was supported by the EU-China Eco-Fuel project (FP7, 246772) from the European Commission.

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