Journal of Photonics for Energy

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Piangjai Peerakiatkhajohn, Jung-Ho Yun, Songcan Wang, Lianzhou Wang, "Review of recent progress in unassisted photoelectrochemical water splitting: from material modification to configuration design," *J. Photon. Energy* **7**(1), 012006 (2016), doi: 10.1117/1.JPE.7.012006.

REVIEW

Review of recent progress in unassisted photoelectrochemical water splitting: from material modification to configuration design

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Abstract. Photoelectrochemical (PEC) energy conversion systems have been considered as a highly potential strategy for clean solar fuel production, simultaneously addressing the energy and environment challenges we are facing. Tremendous research efforts have been made to design and develop feasible unassisted PEC systems that can efficiently split water into hydrogen (H_2) and oxygen with only the energy input of sunlight. A fundamental understanding of the concepts involved in PEC water splitting and energy conversion efficiency enhancement for solar fuel production is important for better system design. This review gives a concise overview of the unassisted PEC devices with some state-of-the-art progress toward efficient PEC devices for future sustainable solar energy utilization. © *2016 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JPE.7.012006]

Keywords: unassisted photoelectrochemical water splitting; hydrogen production; semiconductors; nanostructure engineering; surface modification; tandem configuration.

Paper 16064SS received May 31, 2016; accepted for publication Aug. 8, 2016; published online Aug. 24, 2016.

1 Introduction

With the increasing energy consumption and the depletion of fossil fuels, it is urgent to develop clean, earth-abundant, and renewable energy resources to effectively address energy issues. Photoelectrochemical (PEC) water splitting has been found to be a promising approach for directly converting solar energy into sustainable and environmentally friendly hydrogen fuel.[1–5] Over the past four decades, even though great achievements have been obtained, the solar-to-hydrogen (STH) efficiency is still too low for practical applications.[6] The key challenge for efficient solar hydrogen generation is to explore suitable photoelectrode materials that meet the following criteria: (1) broad range of solar spectrum absorption, (2) high photochemical stability, (3) efficient use of photogenerated electrons and holes, (4) suitable band edge positions, (5) low overpotential, and (6) low cost.[7–10] Typically, a single semiconductor is difficult for achieving all of the above requirements. For example, TiO_2 is stable in aqueous electrolytes under light illumination, but its large bandgap (3.0 eV) limits its light utilization to the UV region that accounts for only ~4% of the solar energy on earth, resulting in low STH efficiency.[11,12] On the other hand, although multijunction silicon or heterojunction III–V semiconductors as photoelectrodes considerably increase the visible light conversion efficiency, they increase the cost while shortening the lifetime of the whole devices due to their photocorrosion in aqueous electrolytes.[13–15] Therefore, the number of reliable and reproducible semiconductors for solar water splitting is limited. Combining the advantages of different semiconductors to form heterojunction systems or integrating state-of-the-art semiconductors with photovoltaic (PV) devices to form tandem cells may open up more opportunities, which have been extensively investigated during the past decade.[16–20] Especially, self-driven monolithic and PEC tandem

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systems have attracted great attention due to the low cost when compared to the use of only PV devices for water splitting.[21–26] Nevertheless, the obtained STH and stability for the reported systems are still too low for the 10% target toward practical applications, even though many unique and novel material configurations have been revealed in recent years.[27–33]

In this review, we concisely summarize the recent progress and challenges in the unassisted PEC water splitting system, which has been considered as the ultimate solar water splitting process, compared to many reported PEC systems, which still rely on the applied external bias. We pay particular attention to nanostructure engineering of the photoelectrodes and the concepts of PEC configuration design for efficient water splitting. The review will start with some basic principles of unassisted PEC water splitting, followed by the design of photoelectrode materials based on nanostructure engineering and surface modifications. Then, the recent progress of PEC system configurations will be summarized. Finally, a brief overview including the challenges and perspectives of this research field will be given. We believe that this comprehensive review would not only provide important information about the recent progress of unassisted PEC water splitting systems but also could inspire readers to apply the discussed strategies to further improve the PEC solar fuel production performance.

2 Principles of Unassisted Photoelectrochemical Systems

Figure 1(a) presents the basic principle of a conventional PEC water splitting system. Under light illumination, electrons (e^-) will be excited from the valence band (VB) to the conduction band (CB), where holes (h^+) are left in the VB of the working electrode. Then, the electrons transport to the counter electrode and participate in the hydrogen-evolution half-reaction (HER). Meanwhile the holes transfer to the surface of the working electrode and are involved in the oxygen-evolution half-reaction (OER).[34,35] Typically, overall water splitting can be achieved by applying an external bias if the semiconductor itself in the working electrode is suitable only for OER or HER. For example, some metal oxides, such as Fe_2O_3, WO_3, and $BiVO_4$, can be used as working electrodes for water splitting with a proper bias, even though their CB positions are unable to reduce water themselves.[36–40]

According to the general mechanism in PEC H_2 production, the selection of light absorbers and device configurations is important in driving effective water splitting reactions. A Z-scheme concept has been developed through a two-step excitation mechanism induced by coupling two different light absorbers, which is inspired by natural photosynthesis in green plants.[41–44] The charge transfer in a Z-scheme system is different from that in the general p-n heterojunction configuration. For p-n heterojunctions, photogenerated electrons in photosystem II (PS II) with higher CB are transferred to photosystem I (PS I) with lower CB to be involved in HER, while holes are transferred to the opposite direction for OER due to the built-in electrical potential in the interfaces [Fig. 1(b)]. By contrast, photogenerated holes in the VB of PS I are promoted in OER, while electrons in the CB of PS II are used for HER in the Z-scheme configuration [Fig. 1(c)]. Thus, the Z-scheme system demonstrates the strong oxidized ability of PS I and the strong reduced ability of PS II. The advantage of the Z-scheme water splitting system is to utilize a wider range of visible light because the energy required to activate each photocatalyst can be reduced as compared to the one-step water splitting system.[45–47] Successful overall water

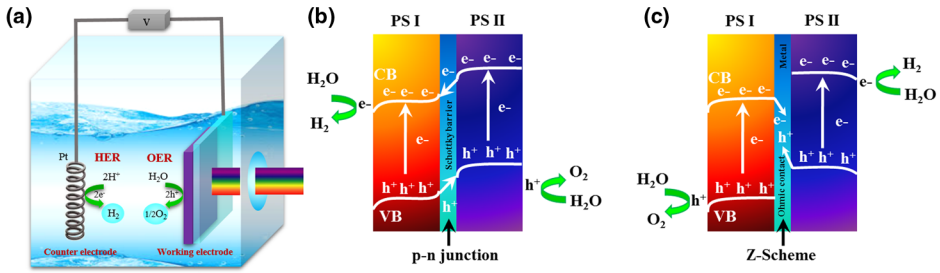


Fig. 1 (a) A schematic illustration of the photoelectrochemical water splitting process, charge transfer in a heterojunction PEC system with (b) p-n junction type, and (c) Z-scheme configuration.

splitting via two-step photoexcitation under visible light illumination has been reported by combining several semiconductors.[48–51] Especially, the artificial photosynthesis (AP) concept has emerged as an attractive approach to mimic the natural photosynthesis process by utilizing suitable semiconductors to efficiently drive the thermodynamically uphill water splitting reaction under sunlight illumination.[52–55]

3 Recent Progress and Challenges of Unassisted Photoelectrochemical Devices

In this section, recent efforts on the development of novel nanostructured design concepts and surface modification strategies for an unassisted PEC water splitting system will be briefly presented and discussed in terms of the improvement of performance.

3.1 *Nanostructured Semiconductor Design*

In general, PEC performance of the devices depends on the efficient light utilization, photogenerated carrier transport/separation, and stability in the PEC system. Nanostructured semiconductors have been revealed to be promising for PEC water splitting due to their large surface area and size-dependent properties (e.g., tuned bandgap energy, shortened carrier collection pathways, and efficient charge transfer).[56] Therefore, the selection of a suitable semiconductor with excellent nanoarchitecture is of importance for PEC system construction. n-type semiconductors (e.g., WO_3, Fe_2O_3, TiO_2, and $BiVO_4$) are commonly developed as photoanodes or top absorbers in tandem devices due to their low VB energy positions with more positive VB potential for water oxidation reaction.[57–61] However, when these semiconductors are used as photoelectrodes, the randomly oriented bulk nanoparticles (NPs) in photoelectrodes might decrease the PEC performance with a high charge recombination rate due to a large number of charge trap sites. To overcome this issue, well oriented one-dimensional (1-D),[62–68] two-dimensional (2-D),[69–73] and three-dimensional (3-D)[74–76] nanostructures have been developed in recent years. The 1-D nanostructures including nanowires,[77–79] nanorods,[80–82] and nanotubes[83–86] provide both efficient light harvesting and superior charge transport for PEC water splitting. Meanwhile, 2-D nanostructures have also shown interesting properties in various photochemical fields.[87–89] In particular, metal oxide and chalcogenide 2-D nanosheets are unique nanostructures with high-specific surface area and excellent crystallinity, which is beneficial for efficient charge separation and migration in water splitting.[90–94] More recently, researchers have integrated different functional materials of 1-D or 2-D structures to construct 3-D hierarchical nanostructures in order to increase large surface areas for light harvesting without inhibiting charge transfer and separation.[95–99] Hence, it is a promising nanostructure model for efficient water splitting due to broader light absorption, rapid charge migration and separation.

On the other hand, p-type semiconductors such as boron-doped Si,[100] Cu_2O,[101] $CuInS_2$,[102] and $GaInP_2$[14] exhibit small bandgaps, thereby a significant proportion of visible light can be harvested. However, when p-type materials are employed to PEC water splitting, severe challenges such as large overpotential, instability, and low absorption coefficient have been observed.[103] Thus, recent strategies have been focused on improving the photostability through loading suitable protective layers or coupling with n-type semiconductors to form heterojunctions.[104] For example, n-TiO_2 has been reported as an effective protective layer for enhancing the photostability and photoactivity of p-type photoelectrodes.[105–107] Such a heterojunction concept by coupling different photoanode and photocathode layers would be a promising approach for unassisted PEC water splitting systems. For designing such systems, the nanostructured morphology and crystallinity of semiconductors with suitable CB and VB positions for water splitting and the interfacial properties in the heterojunction should be carefully considered. Moreover, the fabrication process of the photoelectrodes in a PEC system should be optimized by exploring simple, cost-effective, and environmentally friendly techniques. Figure 2 represents the engineering strategies that are critical to meet all requirements for efficient PEC water splitting. The recent reported PEC systems, which have been developed based on these strategies, will be further presented and discussed in Sec. 3.3.

Fig. 2 The important engineering strategies to achieve efficient PEC water splitting.

3.2 *Surface Modification of Photoelectrodes*

In addition to nanostructure engineering, the surface modification of photoelectrodes is also important for achieving high PEC performance. As the surfaces of the photoelectrode materials are active sites for redox reaction, the surface states are closely related to photon energy absorption properties and surface charge transfer ability of the semiconductors. Doping is one common strategy to improve the conductivity of semiconductors and extend the lifetime of charge carriers by reducing recombination of the photogenerated electron–hole pairs.[108–116] In addition, loading HER or OER cocatalysts on the surface of the semiconductor is also an efficient approach to reduce the charge recombination at a lower applied potential and increase the charge transfer for the water splitting process.[117] Cocatalysts should be optimized to offer highly active sites to separate the photogenerated charges for HER or OER half reactions, avoiding the photogenerated electrons and holes with high redox ability to react with the semiconductor itself, which improves the stability. Noble metals (e.g., Pt) and noble metal oxides (e.g., IrO_2, RuO_2) are usually used as effective HER and OER cocatalysts, respectively.[118,119] Nevertheless, it is not favorable to scale up their utilization in PEC devices due to their cost and rarity. Thus, noble metal-free cocatalysts, such as cobalt compounds,[120–126] nickel-based materials,[127,128] and chalcogenides[129–132] for photoelectrode surface modification, have been developed.

In addition, plasmonic NP coupling is another strategy to utilize the optical properties of nanometals for better light harvesting.[133–135] Typically, plasmonic metal NPs can be employed to capture light and transfer the excitation energy through the localized surface plasmon to a combined semiconductor with large bandgap. In general, when plasmonic metal nanostructures are contacted with semiconductors, they should be able to alleviate charge recombination and enhance light absorption, resulting in higher PEC performance than their pure semiconductor counterparts.[136–146] For instance, Zhang et al.[97] studied PEC performance of Au NPs deposited on the TiO_2 bilayered structure photoanode and reported a STH efficiency of 0.71% achieved, around which is one of the highest values reported in Au/TiO_2-based photoanodes. The excellent PEC water splitting activity in visible light can be ascribed to the generated energetic hot e^-/h^+ of Au NPs that were injected into the CB of TiO_2 through the excitation and decay of surface plasmons. In another study, the utilization of a plasmonic Au nanohole array combined with Fe_2O_3 nanorod array photoanode led to significant enhancement of the photocurrent density[147] and a plasmon-induced resonant energy transfer (PIRET) effect was proposed to explain this phenomenon. In addition to photoanodes, CuO nanowires decorated with Ag NPs as photocathodes were also studied in which the surface plasmon energy transfer from Ag NPs contributed to enhanced photocurrent with a STH efficiency of 2.16% achieved.[148] The use of plasmonic Ag NPs deposited on TiO_2 photoanodes can also further improve the photocurrent density by LSPR property of Ag NPs.[149,150]

Recent works on nanostructure engineering and surface modification for innovative PEC system design are summarized in Table 1. It is apparent that many efforts have focused on

Table 1 PEC devices for solar water splitting.

Photoelectrode system	Cocatalysts	Photocurrent ($mA\,cm^{-2}$)	Light source	STH/IPCE (%)	References
p-$GaInP_2$(Pt)/TJ/GaAs	Pt	120 at ~0.15 V	11 suns, $1.19 \pm 0.05\ W\,cm^{-2}$	STH = 12.4%	Ref. 24
3jn-a-Si	OER: Co–Bi, HER: NiMoZn	~3 at 0 V_{RHE}	1 sun, AM 1.5 G	STH = 2.5% (wireless) and 4.7% (wired)	Ref. 151
Si pillars	Mo_3S_4	~9 at 0 V_{RHE}	$\lambda > 620$ nm, $28.3\ mW\,cm^{-2}$	STH = 10%	Ref. 130
p-Si/SiO_2/Ti	Pt	~20 at 0 V_{RHE}	1 sun, AM 1.5 G	STH = 2.9%	Ref. 152
n + p-Si/TiO_2	Pt	~22 at 0.3 V_{RHE}	$\lambda > 635$ nm, AM 1.5 G	IPCE = ~90%	Ref. 153
AlGaAs/Si	RuO_2/Pt black	20.1, unassisted	$135\ mW\,cm^{-2}$	STH = 18.3%	Ref. 154
W-doped $BiVO_4$/Si	Co-Pi	4 at 1.23 V_{RHE}	1 sun, AM 1.5 G	STH = 4.9%	Ref. 155
$BiVO_4$ on 1D ZnO nanorods	Co-Pi	3 at 1.2 V_{RHE}	$\lambda > 420$ nm, AM 1.5 G	STH = 0.88%	Ref. 68
Ba-Ta_3N_5 nanorod	IrO_2	6.7 at 1.23 V_{RHE}	1 sun, AM 1.5 G	STH = 1.5%	Ref. 156
WSe_2	Pt/Ru	15 at 0 V_{RHE}	$100\ mW\,cm^{-2}$	$\eta_c = 7.0\%$	Ref. 157
Si/TiO_2 nanotree	HER: Pt OER: IrO_x	—	$150\ mW\,cm^{-2}$	STH = 0.12%	Ref. 79
p-Si/Fe_2O_3–AuNPs	Au	2.6 at 0 V_{Pt}	$60\ mW\,cm^{-2}$	STH = 6%	Ref. 158
DSSC/WO_3(n)	Pt	~1.56 at 0 V_{RHE}	$100\ mW\,cm^{-2}$	STH = 1.9%	Ref. 22
WO_3/C_3N_4	CoO_x	5.76 at 2.1 V_{RHE}	AM 1.5 G	IPCE = 37.5% at 400 nm and 1.6 V_{RHE}	Ref. 95
Pt-doped Fe_2O_3	Co-Pi	4.32 at 1.23 V_{RHE}	1 sun, AM 1.5 G	IPCE = 50% at 400 nm and 1.23 V_{RHE}	Ref. 159
$Cu_2O/(ZnO, Al_2O_3)/TiO_2$	Pt	–7.6 at 0 V_{RHE}	AM 1.5 G	IPCE = 40% between 350 and 480 nm, 0 V_{RHE}	Ref. 160
$Cu_2O/(ZnO, Al_2O_3)/TiO_2$	MoS_{2+x}	–5.7 at 0 V_{RHE}	AM 1.5 G	STH = 7%	Ref. 131
$Cu_2O/BiVO_4$	HER: RuO_x OER: Co-Pi	1, unassisted	$100\ mW\,cm^{-2}$	STH = 0.5%	Ref. 161
Au at $TiO_2/Al_2O_3/Cu_2O$	—	–4.34 at 0 V_{RHE}	AM 1.5 G	IPCE = 78% at 340 nm	Ref. 43
C/Cu_2O/Cu	—	–3.95 at 0 V_{RHE}	AM 1.5 G	STH = 0.56% at 0.21 V_{RHE}	Ref. 162
CdS/$CuGaSe_2$	Pt	~19 at 0 V_{RHE}	300 W Xe lamp	STH = 0.83% at 0.2 V_{RHE}	Ref. 163
CdS/$Ag_xCu_{1-x}GaSe_2$	Pt	8.1 at 0 V_{RHE}	AM 1.5 G	IPCE ≈ 50% at 500 nm and 0 V_{RHE}	Ref. 164

Table 1 (*Continued*).

Photoelectrode system	Cocatalysts	Photocurrent ($mA\,cm^{-2}$)	Light source	STH/IPCE (%)	References
$CH_3NH_3PbI_3$ with NiFe DLH/Ni foam	NiFe DLH	10, unassisted	AM 1.5 G	STH = 12.3%	Ref. 165
$CH_3NH_3PbI_3$	Ni	12 at 0 $V_{Ag/AgCl}$	1 sun, AM 1.5 G	—	Ref. 166

controlling nanostructures, doping with suitable elements, and loading cocatalysts in heterojunction photoelectrodes. However, the high photocurrent and STH efficiency achievements in most of the systems are limited and external bias is generally required for overall water splitting. Notably, multilayered PEC devices composed of nanostructured metal oxide semiconductors, perovskite solar cells (PSCs), and Si photoelectrodes can exhibit high STH up to 10%, whereas such PEC devices are expensive, complicated, and unstable in aqueous electrolyte under light illumination. In order to overcome these drawbacks, the selection of excellent crystalline photoelectrode materials and suitable electrolytes is essentially important, and the overall PEC system should be considered by designing the configuration of multilayered photoelectrodes with protective layers. Such conditions would be the key factors in developing unassisted PEC systems for overall water splitting.

3.3 *Artificial Photosynthesis Photoelectrochemical System Design*

3.3.1 *Tandem cell configuration*

Tandem cell configuration is a promising approach to address the issues of single or heterojunction PEC devices for unassisted solar water splitting. In the early stage, tandem PEC devices consisting of a semiconductor and a dye-sensitized solar cell (DSSC) were applied for water splitting. For instance, Kim et al.[167] revealed a tandem cell composed of a WO_3/Pt photoelectrode connected with a DSSC for unassisted water splitting where the maximum STH efficiency of 0.35% was obtained. Subsequently, a Fe_2O_3 and WO_3 photoanode with a DSSC in tandem configuration was developed, as illustrated in Fig. 3.[168] Without external bias, the achieved STH efficiencies were 3.10% and 1.17% for the WO_3/DSSC and Fe_2O_3/DSSC tandem systems,

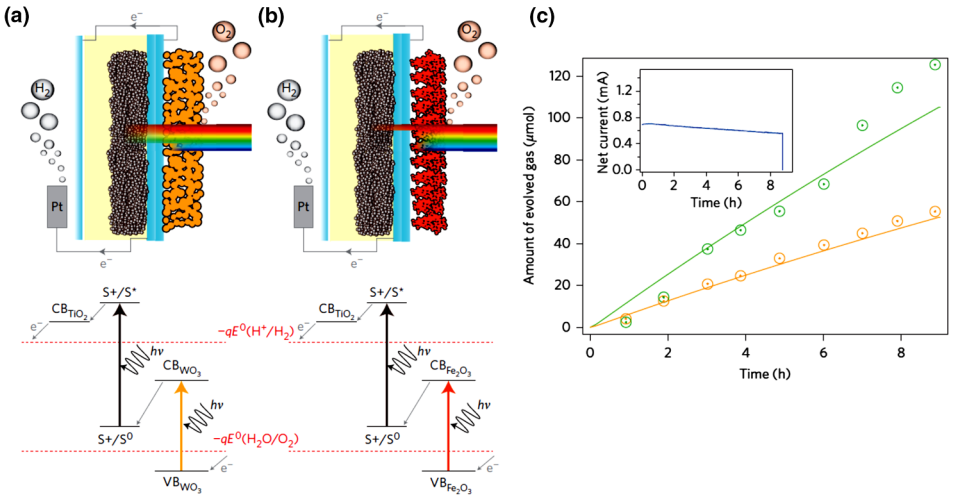


Fig. 3 Schematic and band energy diagrams represent (a) WO_3, (b) Fe_2O_3 photoanodes combined with a DSSC using D4 dye in tandem cell design. Red dotted lines indicate the reduction and oxidation potentials of water and (c) Faradaic efficiency measurement of a tandem cell with inset shows a net measured photocurrent within 9 h. Green and orange circled plots correspond to H_2 and O_2 evolved gases, respectively. Reprinted with permission from Ref. 168. Copyright 2011 Nature Publishing Group.

respectively. The low STH efficiency in this tandem configuration is due to the mismatched band energy configuration and interfacial charge recombination between photoelectrodes and the combined DSSCs. Especially, charge recombination occurred between the injected electrons from the semiconductors and the oxidized dye (I_3^-), inhibiting the efficient redox reaction with water in the system.

More recently, an efficient wireless monolithic tandem device consisting of a bipolar configuration with a highly transparent $BiVO_4$-sensitised mesoporous WO_3/Pt film and a porphyrin-dye-based photoelectrode was reported.[169] An extraordinarily high STH efficiency of 5.7% and H_2/O_2 evolutions were revealed without any applied bias. The porphyrin-dye-sensitized photoanode with a cobalt electrolyte generated sufficient bias to drive the water splitting reaction forward in this monolithic tandem configuration. Although the efficient design for AP is controversial, the combination of abundant metal oxide-based photoelectrodes with DSSCs has been explored as a promising PEC device configuration for unassisted solar water splitting. Nevertheless, the DSSC component generates low voltages that are not sufficient for water splitting, and more attention has been paid to recently developed PSCs due to their much higher V_{oc} (0.9 to 1.5 V).[170] For instance, a dual artificial-leaf-type tandem PEC device composed of a robust cobalt carbonate (Co-Ci)-catalyzed Mo-doped $BiVO_4$ photoanode and a $CH_3NH_3PbI_3$-based PSCs (Fig. 4) can deliver a photocurrent density of 5 mA cm^{-2} at 1.23 V versus RHE for the unique and stable photoanode and a STH efficiency of 3.0% for the wireless device.[171] Gratzel et al. reported a novel PSCs-assisted PEC water splitting system composed of organohalide $CH_3NH_3PbI_3$-based PSCs as the external power supply and NiFe-layered double hydroxides as the catalytic electrodes, which achieved a photocurrent density of ~10 mA cm^{-2} with a STH efficiency of 12.3%.[165] Although this device configuration exhibited a high efficiency for PEC water splitting, the electrodes were not directly settled in photoreactions. Consequently, the hydrogen generation occurred by a water electrolysis process that power was generated through the externally wired two PSCs in series. Meanwhile, a monolithic tandem design with only one $CH_3NH_3PbI_3$ PSC/Ni layer without an external wire connection was developed and a high photocurrent density of 12 mA cm^{-2} was achieved (Fig. 5).[166] Overall, the device complexity and stability issue of the dye and organohalide perovskite materials in the DSSCs and PSCs, and efficient photon utilization should be considered in these design concepts.

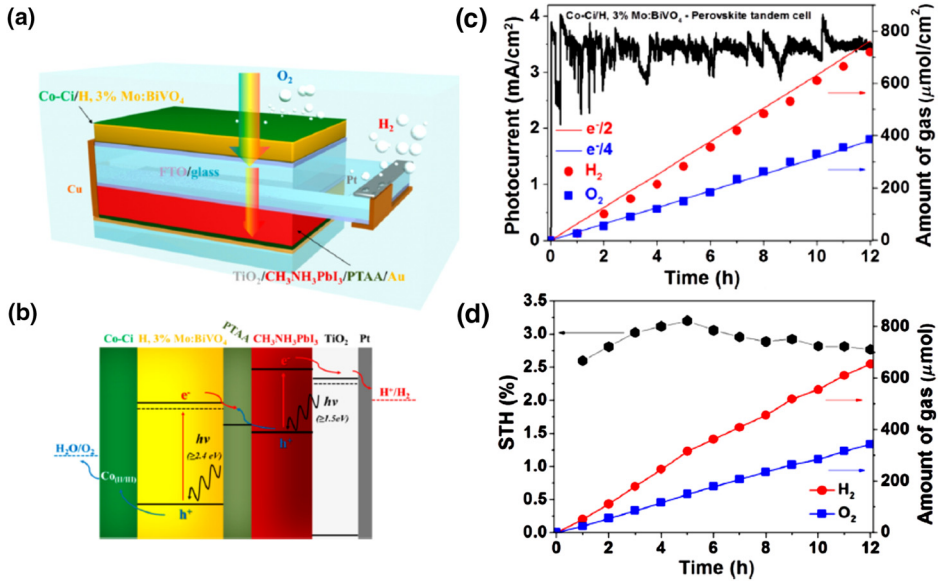


Fig. 4 Schematic diagrams of (a) wireless dual light absorber tandem PEC device, (b) energy band diagram and charge transfer in artificial water splitting, (c) photocurrent density and H_2/O_2 gases evolutions of Co-Ci/H, 3%Mo:$BiVO_4$ PSC tandem device, and (d) evolved H_2/O_2 gases and calculated STH in unassisted solar water splitting. Reprinted with permission from Ref. 171. Copyright 2015 American Chemical Society.

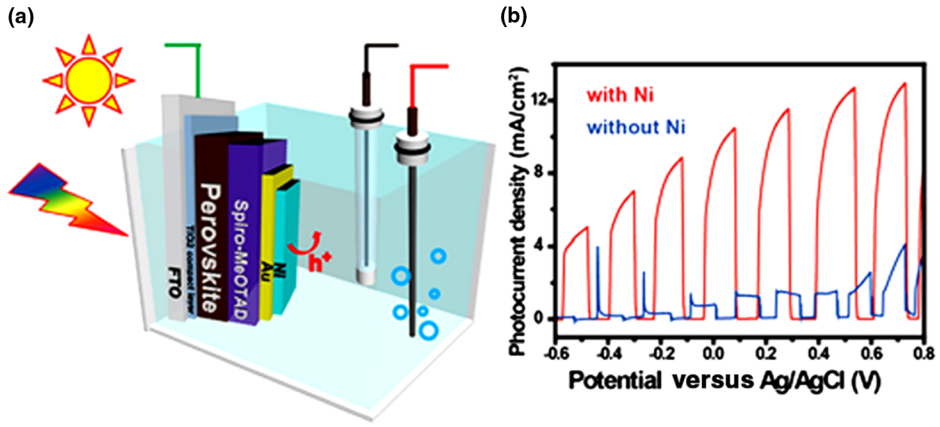
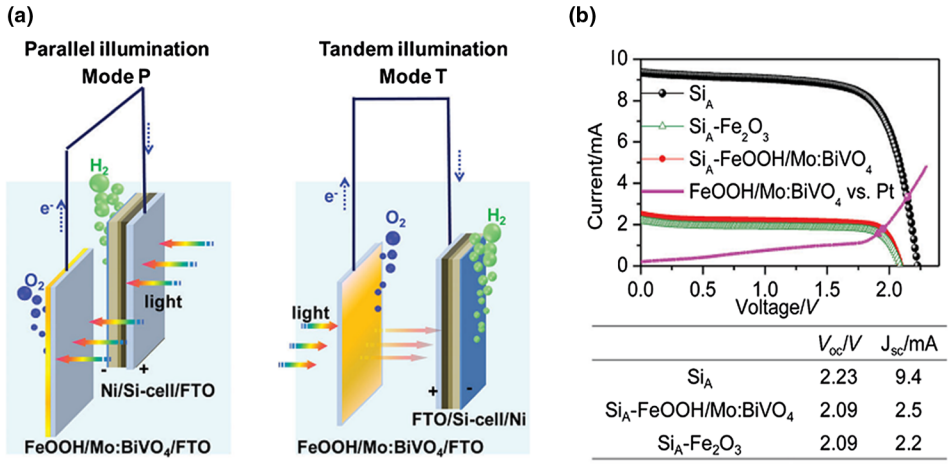


Fig. 5 (a) Schematic diagrams of $CH_3NH_3PbI_3$ with Ni surface layer tandem cell configuration and (b) photocurrent densities in unassisted hydrogen production at 1 sun illumination. Reprinted with permission from Ref. 166. Copyright 2015, American Chemical Society.

On the other hand, coupling a PEC device with a PV cell in tandem was developed to extend the light absorption range and improve the photocurrent density in unassisted solar water splitting. Ding et al.[172] achieved a STH efficiency up to 2.5% in an unassisted water splitting system using an earth-abundant photoanode and a Si-solar-cell-based photocathode (Fig. 6). The parallel irradiation mode exhibited higher efficiency than the tandem illumination one because the former system offered sufficient driving force for water splitting. More recently, an overall STH efficiency of 0.91% was achieved on a system composed of a Fe_2O_3 photoanode and a Si photocathode with $NiFeO_x$ and TiO_2/Pt as cocatalysts (Fig. 7).[173]

3.3.2 *Monolithic design*

Despite continuing efforts on searching various photoanode materials to combine with solar cells, the high current densities are accompanied with the challenges of photocorrosion or chemical instability under oxidative conditions. A stand-alone unassisted PEC device would be an ultimate consideration for H_2/O_2 evolutions in water splitting. Accordingly, simpler concepts using dual-absorber tandem devices have been explored with acceptable STH efficiencies. For



	V_{oc}/V	J_{sc}/mA
Si_A	2.23	9.4
Si_A-FeOOH/Mo:$BiVO_4$	2.09	2.5
Si_A-Fe_2O_3	2.09	2.2

Fig. 6 (a) Schematic diagram of FeOOH/Mo/$BiVO_4$ photoanode with the Ni/Si-solar-cell-based photocathode under parallel and tandem light illumination for direct water splitting and (b) *I*–V curves and obtained values of photoelectrodes measured in 0.5M Na_2SO_4 electrolyte and two electrode configurations under AM 1.5G light illumination. Reprinted with permission from Ref. 172. Copyright 2014, Royal Society of Chemistry.

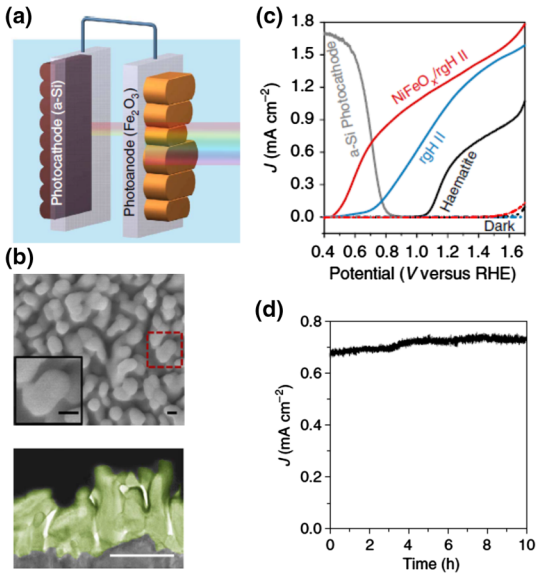


Fig. 7 (a) Schematic diagrams of Fe_2O_3 photoanode and amorphous Si photocathode tandem device for overall unassisted water splitting, (b) SEM image of a tandem photoelectrode, (c) current–potential (J–V) curves of various photoelectrodes, and (d) net photocurrent of $NiFeO_x$-modified second regrowth treatment (rgH II) with TiO_2/Pt loaded amorphous silicon photocathode over 10 h in 0.5M phosphate solution in a unassisted two-electrode system. Reprinted with permission from Ref. 173. Copyright 2015 Nature Publishing Group.

example, a p-n junction photoelectrode comprising p-type Cu-Ti-O and n-type TiO_2 nanotube arrays with efficient spectral photoresponse (380 to 885 nm) and antiphotocorrosion properties can result in a significantly enhanced photocurrent density of ~0.25 mA cm^{-2} and a photoconversion efficiency of 0.30% under global AM 1.5 G illumination (Fig. 8).[174] Similarly, a Mn-oxide–TiO_2 coated triple junction-amorphous-Si (Tj-a-Si) was used for monolithic self-driven water splitting with a high STH efficiency of 3.25% and good long-term stability under solar-simulated light illumination.[175]

In a parallel study, Reece et al.[151] reported a Tj-a-Si system modified with cocatalysts for water splitting. The wireless configuration of a Tj-a-Si with Co-oxygen-evolving complex and

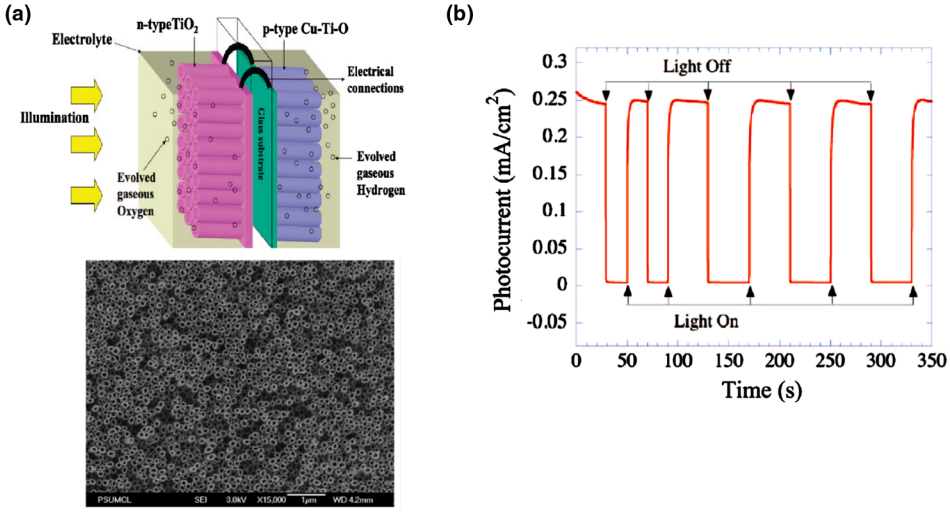


Fig. 8 (a) Schematic illustration of the n-type TiO_2/p-type Cu-Ti-O nanotube arrays in tandem with a salt bridge and immersed in hybrid electrolyte containing 1 M KOH and 0.1 M Na_2HPO_4 and (b) Self-biased photocurrent density of the n-type TiO_2/p-type Cu-Ti-O nanotube arrays in tandem under global AM 1.5 G illumination. Reprinted with permission from Ref. 174. Copyright 2008 American Chemical Society.

NiMoZn as OER and HER cocatalysts presented a high STH efficiency of 4.7% under AM 1.5 G simulated sunlight illumination. It has been confirmed that this design can generate electrons and holes with enough energy to split water ($V_{OC} > 1.23$ V) in a simply engineered configuration. However, the high cost of the photoelectrode materials and the complexity of the fabrication process would be critical limiting factors in commercializing this water splitting system.

3.3.3 *Heterojunction components of photoelectrochemical device design*

Most studies have been focused on improving the performance of individual semiconductors to achieve the targeted STH efficiency. However, the performance of the whole PEC system and the interaction between the individual components for solar energy conversion should also be explored. Liu et al.[79] reported a fully integrated nanotree PEC system consisting of cocatalysts loaded Si and TiO_2 nanowires for direct solar water splitting (Fig. 9). An STH efficiency of 0.12% was achieved in this unassisted PEC water splitting system. However, this nanotree PEC system still needs to improve the current density and maximize the STH efficiency via excellent interfacial engineering and surface modifications. More recently, a tandem PEC system consisting of a n-p homojunction of Si microwire arrays coated with TiO_2 thin films presented a current density of 0.32 mA cm^{-2} and a STH efficiency of 0.6% without external bias (Fig. 10).[176] It is well known that the use of Si photoelectrodes in a PEC water splitting system reduces the cost competitiveness, thus novel systems with low cost materials have continuously been explored.

Another promising concept for unassisted PEC water splitting systems is a standalone Z-scheme configuration. To obtain high performance, we need to consider the main factors, in particular, the design of the fully integrated system, the functions of the individual materials, and the optimization of the interfaces between the individual components.[177] One typical example is the design of W/Mo-doped $BiVO_4$ and $Zn_xCd_{1-x}Se$ dual n-type photoelectrode system with the presence of redox mediators (I^-/IO_3^- or S^{2-}/S_n^{2-}),[178] which highlights the challenging nature of designing redox mediator-free Z-scheme systems via metal doping and surface modification for efficient water splitting. Likewise, Yang et al.[179] studied the surface modification with different catalysts in order to improve the overall water splitting efficiency and stability of the system (Fig. 11). They designed a system comprising a CdS QD/TiO_2 nanorod photoanode and a ZnS/CdSe QD/NiO_x nanosheet photocathode for self-driven PEC water splitting,

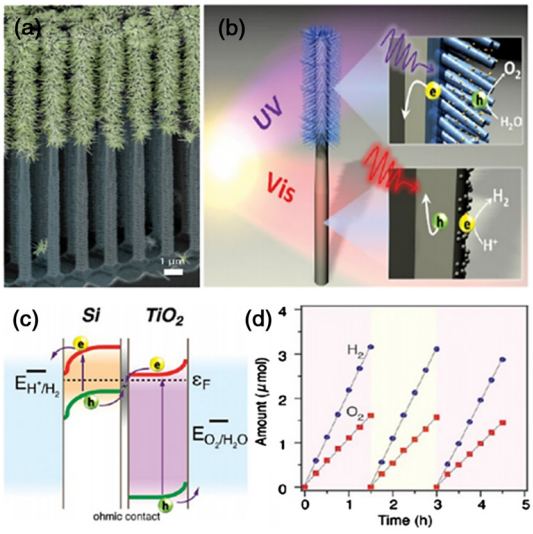


Fig. 9 (a) SEM image of the Si/TiO_2 heterostructure nanotree arrays photoelectrodes, (b, c) Schematic illustrations of the light absorption and charge transfer of Si/TiO_2 photoelectrodes in unassisted water splitting reaction, and (d) the evolution of H_2 and O_2 with 2:1 stoichiometry under simulated sunlight (1.5 suns) Reprinted with permission from Ref. 79. Copyright 2013 American Chemical Society.

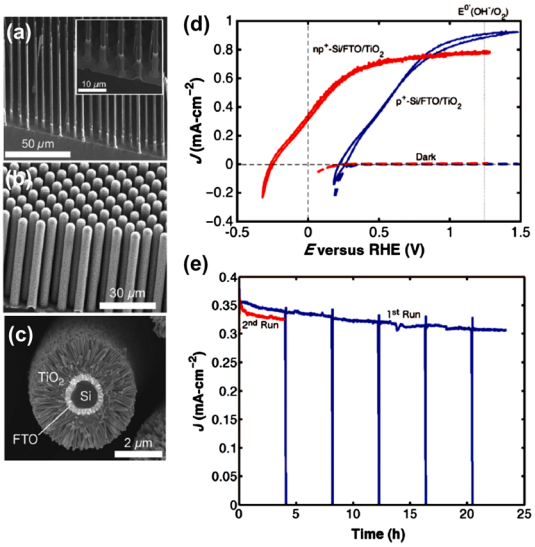


Fig. 10 SEM images of (a) n-p homojunction of Si microwire array (inset shows a zoomed-in image of the SiO_2 microwires), (b) FTO-coated n-p homojunction of Si microwire array, and (c) cross-section of TiO_2-coated n-p Si/FTO microwire array. (d) Current density versus potential curves of $p+$-$Si/FTO/TiO_2$ and n-p $Si/FTO/TiO_2$ microwire array photoelectrodes and (e) amperometric curves of n-p $Si/FTO/TiO_2$ microwire array photoelectrodes at 0 V versus RHE under the dark and 1 sun light illumination conditions. Reprinted with permission from Ref. 176. Copyright 2016, The Electrochemical Society.

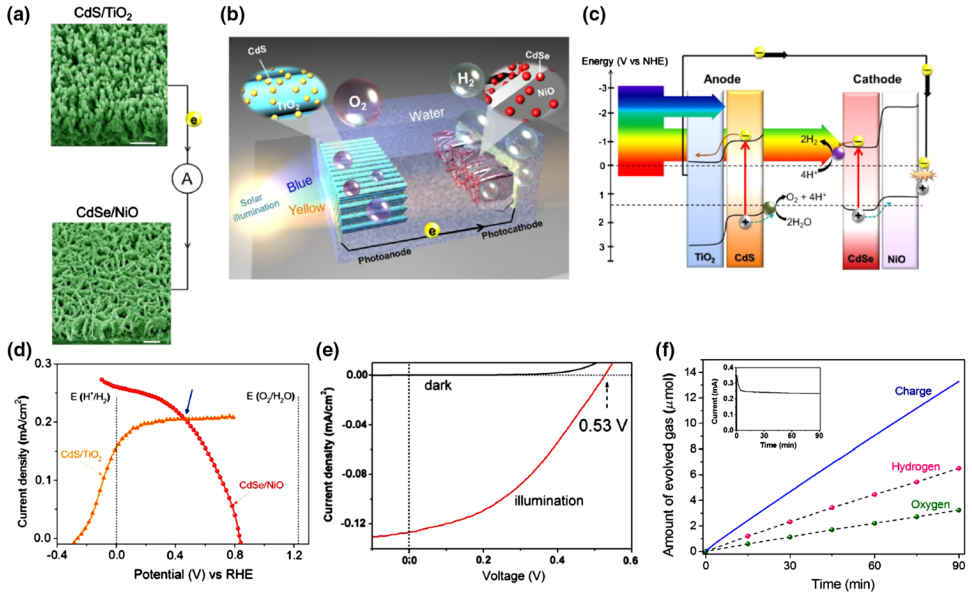


Fig. 11 (a) SEM images of CdS QD/TiO_2 nanorod photoanode (top) and CdSe QD/NiO nanosheet (bottom) photocathode (scale bar: 500 nm), (b) schematic representation of PEC device configuration, (c) band diagram and charge transfer in heterojunction photoelectrodes, (d) amperometric curves of CdS QD/TiO_2 nanorod photoanode and CdSe QD/NiO nanosheet in 0.5 M Na_2SO_4 electrolyte, (e) J–V curve of CdS QD/TiO_2 nanorod photoanode and CdSe QD/NiO nanosheet photocathode in unbiased water splitting, and (f) hydrogen and oxygen gases evolutions and inset presents stability of the photocurrent under 90-min light illuminations. Reprinted with permission from Ref. 179. Copyright 2014 American Chemical Society.

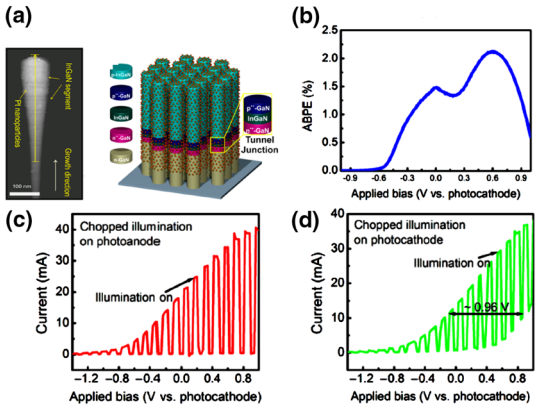


Fig. 12 (a) STEM-HAADF image of a single Pt-InGaN nanowire and schematic of the p-InGaN nanowire photocathode and n-Si substrate, in which connected directly in tunnel junction, (b) the solar conversion efficiency of the dual-photoelectrodes as a function of applied bias under AM1.5G 1 sun illumination, $I-V$ curve of the dual-photoelectrode device with the (c) photoanode and (d) photocathode under chopped illumination. Reprinted with permission from Ref. 180. Copyright 2015 American Chemical Society.

which delivered a maximum STH efficiency of 0.17%, comparable to natural photosynthesis. Later, a system composed of dual nanowire photoelectrodes of p-InGaN/Si-InGaN was developed, where a STH efficiency of 2% at 0.6 V versus RHE and a high open circuit potential were achieved under AM 1.5 G 1 sun illumination (Fig. 12).[180] Nevertheless, this design requires expensive and rare cocatalysts to drive the solar water splitting reaction. Therefore, other active and cheaper semiconductors and cocatalysts for overall water splitting should be explored in future studies.

4 Summary and Perspectives

In this review article, we provided an overview of a library of PEC system designs toward unassisted solar water splitting. It is clear that the design of efficient unassisted PEC devices relies not only on material design but also the integration of PEC configuration. In particular, the development of semiconductors via novel nanostructure engineering, surface modification with exotic element doping or cocatalyst loading, and innovative system design based on heterojunction configurations are important strategies for improving light harvesting, charge separation, and surface reaction kinetics. This brief review would deliver useful information for further construction and development of efficient unassisted PEC water splitting systems with high STH efficiency, long-term stability, and low cost. For example, the stability and poor kinetics of water splitting issues in the wireless integrated tandem system with dual light absorber configuration should be addressed by employing earth abundant materials, protective layers, and morphology engineering techniques. On the other hand, novel strategies to inhibit photocorrosion of the photocathode materials are urgently needed for efficient water splitting in a long-term period. Additionally, the tandem system combining semiconductors with a PV device has a conflict in terms of instability in aqueous electrolyte, high cost and complexity. Using DSSCs or PSCs in tandem systems for unassisted water splitting demonstrates low cost and comparable STH efficiencies, but the efficient light absorption and stable organic dyes for DSSCs and the stability of perovskites should be considered when equipped in a PEC system.

Although numerous achievements have been obtained in recent years, it is still highly challenging to develop an efficient unassisted PEC water splitting system for practical applications. Currently, the tentative STH goal for practical applications of the unassisted PEC water splitting device is 10%. It is expected that some novel concepts of fully integrated PEC devices put forward the breakthrough in solar hydrogen energy conversion and long-term stability. Notably, the Z-scheme concept for unassisted PEC water splitting systems is promising for effective photon utilization and efficient solar water splitting. However, there still remains significant room for the improvement of this system for practical applications. It is also important to explore new active

and low cost cocatalysts that can efficiently promote the forward reactions for water splitting. To this end, in-depth understanding of the mechanisms of unassisted PEC water splitting and the strategies to boost charge transfer and separation for redox reaction is critically important to develop an efficient solar water splitting system for more sustainable solar energy utilization.

Acknowledgments

The authors would like to acknowledge financial support from the Australian Research Council through its DP and FF programs. P.P. acknowledges support from the University of Queensland for International Scholarships (UQI). S.W. acknowledges support from IPRS and UQ Centennial Scholarships.

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