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Photoelectrode for water splitting: Materials, fabrication and characterization

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ABSTRACT Photoelectrochemical (PEC) water splitting is an attractive approach for producing sustainable and environment-friendly hydrogen. An efficient PEC process is rooted in appropriate semiconductor materials, which should possess small bandgap to ensure wide light harvest, facile charge separation to allow the generated photocharges migrating to the reactive sites and highly catalytic capability to fully utilize the separated photocharges. Proper electrode fabrication method is of equal importance for promoting charge transfer and accelerating surface reactions in the electrodes. Moreover, powerful characterization method can shed light on the complex PEC process and provide deep understanding of the rate-determining step for us to improve the PEC systems further. Targeting on high solar conversion efficiency, here we provide a review on the development of PEC water splitting in the aspect of materials exploring, fabrication method and characterization. It is expected to provide some fundamental insight of PEC and inspire the design of more effective PEC systems.

Keywords: photoelectrode, water splitting, semiconductor material, electrode fabrication, characterization

INTRODUCTION

Solar energy is a dreaming source because it is abundant and environmentally benign. The sunlight irradiation received by earth is 1.7×10^{14} J in one second, which is far more than the total energy consumption by human in one year [1,2]. Therefore, converting the solar energy into valuable fuels or electricity will be very appealing and important for decreasing the dependence on fossil fuel. Photoelectrochemistry (PEC) represents a promising method for solar energy conversion.

PEC process has many advantages over other solar

conversion methods (e.g., solar-thermal conversion, solar cell), such as high solar conversion efficiency due to the application of external bias, portable product for the stored energy [3–5]. The fundamentals and concept of PEC have been well developed in 1970s, based on which the dye-sensitized solar cell (DSSC) and PEC water splitting are stimulated by the energy crisis during the 1970–1980s [6–11]. Ever since, many researchers have made great efforts to promote the PEC solar production, especially the PEC water splitting for H₂ production, targeting a solar-to-hydrogen (STH) efficiency of 10 % for commercial application [12–14].

The development of PEC water splitting relies on the progress of advanced materials exploring. The ideal candidate should have a wide range of light absorption, facile surface reaction kinetics and high stability under operating condition [15–17]. Unfortunately, there is no single semiconductor meeting all the requirements until now. On the other hand, suitable electrode fabrication method is of equal importance for PEC because it may determine the charge transfer through the whole photoelectrode [18]. And the electrode fabrication method depends on the property and preparation of the semiconductor itself. Moreover, advanced characterization method can help us deeply understand the PEC water splitting system and figure out the rate-determining steps, which can inspire researchers to explore more effective PEC system. There have been many excellent researches focusing on each of the topics [15–18], but a timely review to take all the aspects about PEC process into consideration is still lacking. Herein, we focus on the materials exploring, electrode fabrication method and characterization method to summarize the development of PEC water splitting progress which have not been

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addressed in much details in literature. It is expected that this review may provide some guidance and inspiration on designing and characterizing new and efficient PEC water splitting system.

FUNDAMENTALS OF PEC PROCESS

The PEC process occurred at the interface of semiconductor/electrolyte composed of a space charge layer of the semiconductor and the adjacent Helmholtz layer of the electrolyte [7,10]. For the semiconductor, the Fermi level (E_F) and band gap (E_g) are determined by the conduction band (CB) and valence band (VB). As photoelectrode, either holes or electrons will be drifted *via* the conductive substrate, leaving only one kind of charge carrier for surface PEC reaction [8]. Especially, for n-type semiconductor, the holes are left and accumulated on the surface space charge layer, leading to a possible oxidative reaction. And for the p-type semiconductor, the reductive reaction is expected. Since the driving force of the reaction is provided by the band bending (originating from the E_F difference between semiconductor and electrolyte) [8,19], the flatted band of CB and VB will thermodynamically determine the reductive and oxidative reaction happening on the surface, respectively [7]. The band structure of some commonly used PEC semiconductors are summarized in Fig. 1 in comparison with the standard redox potential of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Taking the TiO_2 for example, its CB and VB lay at -0.2 and 3 V *vs.* RHE respectively, which straddle the oxidative potential of H^+/H_2 and the reductive potential of $\text{H}_2\text{O}/\text{O}_2$, as confirmed in literature [6,20,21].

Besides the thermodynamic requirement, the PEC reaction also needs to fulfill some kinetic criteria. It has reached a consensus that the PEC process has at least three key steps to utilize the solar energy, which are light harvest, charge separation and surface reaction as shown in Fig. 2, determined by the bulk and surface properties of the semiconductor [22,23]. For the light harvest of an electrode, the efficiency (η_{LH}) depends on the absorbance of the semiconductor which usually has close relationship with the bandgap of the semiconductor, transition model (direct or indirect transition), film thickness, etc. [24]. Based on η_{LH} , the utmost photocurrent (j_{abs}) that one photoelectrode can achieve can be calculated by integrating the light harvest efficiency and flux of sunlight (I , Equation (1)). Especially, with the assumption that the η_{LH} of photons with energy higher than E_g is unit and photons with energy lower than E_g is null, the theoretical photoresponse (j_{ph}) of a semiconductor can be evaluated

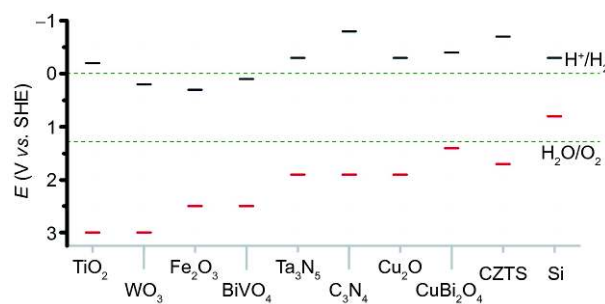


Figure 1 The band structure of selected semiconductors, CZTS: CuZnSnS_4 .

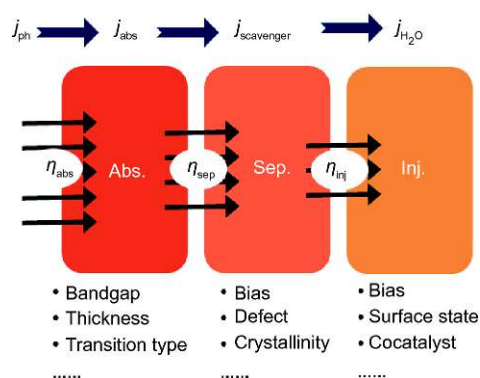


Figure 2 The schematic illustration of the PEC processes and the related influence factor of each step.

according to the E_g of the semiconductor [7,24]. However, the practical photoresponse (j) is often lower than the j_{abs} and j_{ph} due to the recombination of the photon-generated electrons and holes *via* the recombination centres. The charge separation efficiency (η_{sep}) can be used to evaluate the survived photocharges for further surface reaction. It is determined by the built-in field potential (E_{bi}) in the semiconductor principally, so the criteria influencing the magnitude of E_{bi} , such as intermediate energy level (E_i), defect state, applied bias, crystallinity, will largely affect the η_{sep} [25]. Despite of the simple understanding of charge separation, the η_{sep} indeed varies at different moment during the PEC process, especially when considering the recombination process during the charge exchange between semiconductor and electrolyte. In order to make the η_{sep} a measurable parameter, it is specially referred to the process before the semiconductor-electrolyte charge transfer occurs. In this consideration, the η_{sep} can be evaluated with the j_{abs} and the photocurrent ($j_{\text{scavenger}}$) measured with the existence of hole or electron scavenger (e.g., H_2O_2 , $\text{Fe}(\text{CN})_6^{4-/3-}$) to remove the surface reaction barrier and suppress the surface charge re-

combination according to Equation (2) [22]. While for the continuous step of surface reaction, due to the limited reaction kinetics, many separated charges cannot be effectively used for water splitting and the ratio of consumed charges ($j_{\text{H}_2\text{O}}$) over the whole survived ones transferring to the surface ($j_{\text{scavenger}}$) is defined as charge injection efficiency (η_{inj} , Equation (3)). The η_{inj} is usually impacted by factors such as surface states and compositions.

$$j_{\text{abs}} = \int \eta_{\text{LH}}(\lambda) I(\lambda) d\lambda = j_{\text{ph}} \eta_{\text{LH}}, \quad (1)$$

$$j_{\text{scavenger}} = j_{\text{abs}} \eta_{\text{sep}}, \quad (2)$$

$$j_{\text{H}_2\text{O}} = j_{\text{scavenger}} \eta_{\text{inj}}. \quad (3)$$

According to the above discussion, the practical photoresponse (j) is the production of the theoretical photocurrent (j_{ph}), light harvest efficiency (η_{LH}), charge separation efficiency (η_{sep}) and surface charge injection efficiency (η_{inj}) (Equation (4)). And all the efforts are aiming at addressing the limitation of these factors for achieving high photocurrent. However, it is not an easy task because these steps interact with each other and we have to balance every step when we try an optimization. For example, in WO_3 photoanode, the light absorption efficiency can be improved *via* a reductive treatment [26–28]. But as a trade-off, the charge separation efficiency is greatly deteriorated due to the presence of W^{5+} intermediate.

$$j = j_{\text{ph}} \eta_{\text{LH}} \eta_{\text{sep}} \eta_{\text{inj}}. \quad (4)$$

As the most important application of PEC, solar water splitting for hydrogen production has aroused worldwide attention for over four decades since the first report by Fujishima and Honda [6]. Many exciting progresses have achieved in the aspect of materials development, electrode fabrication methods, characterization and the solar conversion efficiency. Herein we will give a brief introduction according to some typical examples.

MATERIALS FOR PEC WATER SPLITTING

Semiconductor materials are the indispensable foundations of the PEC water splitting and the breakthrough in materials always stimulates the progress of PEC research because it may open a new possibility for achieving higher solar conversion efficiency. Many kinds of semiconductors have been reported in literature and based on the cations in the crystal, they can be categorized into metal oxide, nitride, chalcogenide, etc. In the following parts, they will be critically summarized according to some typical semiconductors.

Metal oxides

At the early stage of PEC research, the materials are just limited to some metal oxides, such as TiO_2 [6,29], Fe_2O_3 [30], ZnO [31], WO_3 [32], etc. due to the issue of stability of other semiconductors [33]. Among various metal oxides, BiVO_4 has appealed most of the attention ever since it was first reported by Kudo's group [34]. It has a bandgap of 2.4 eV with a promising photocurrent over 7.4 mA cm^{-2} under 100 mW cm^{-2} sunlight (AM 1.5G) [5]. Wang's group reported that the electrochemical reductive treatment can profoundly improve the photocurrent to 2.5 mA cm^{-2} , [35] which is almost 10 times higher than the pristine one. Another breakthrough from Domen's group demonstrated that the stability of BiVO_4 can exceed 1,000 h under operation with the presence of *in-situ* generated nickel based oxygen-evolution cocatalyst [36]. However, the BiVO_4 based PEC still faces the limitation of relatively large bandgap for the further practical application, which requires a solar conversion efficiency over 10%.

Alternatively, Fe_2O_3 is regard as an attractive candidate for solar fuel production considering that it is very cheap, robust and the light absorption threshold of 600 nm promising over 10% solar conversion efficiency [37,38]. But this tough metal oxide has many limitations in terms of carrier diffusion, surface reaction, and so on. Research from Grätzel's group [39,40] claimed that the cauliflower like hematite electrode with many small crystals aligned was the champion structure for charge transfer, leading to a photocurrent over 3 mA cm^{-2} . Furthermore, Peerakiatkhajohn *et al.* [41] reported a nanosheet structured hematite could reach a photocurrent of 4.68 mA cm^{-2} after modifying with Ag nanoparticles to facilitate the charge separation and CoPi to release the surface reaction (Fig. 3). From these efforts, it is believed that the hematite based PEC could obtain higher and higher solar conversion efficiency if suitable strategies can be applied to addressing the sluggish charge separation and transfer in the bulk and charge injection on the surface.

Most metal oxides are n-type semiconductors due to the presence of oxygen vacancy except the Cu_2O which is a p-type semiconductor that can be used as the photocathode for water reduction. Its small bandgap (about 2 eV) promises an efficiency similar to hematite, but the redox potential of Cu_2O makes it unstable with the presence of electrons or holes [42]. Paracchino *et al.* [43] found that the Cu_2O photocathode can be stabilized after coating with monolayer Al-doped ZnO and TiO_2 . But this relies on expensive equipment (atomic layer deposition) which limits its application in practice. And some other

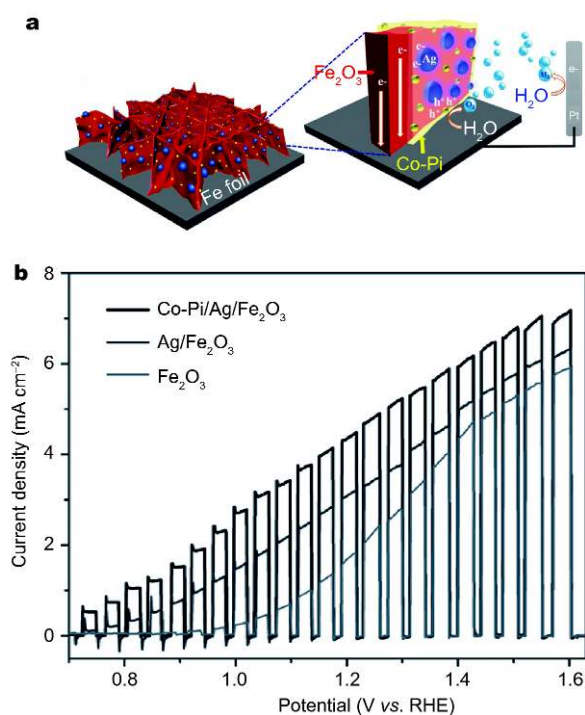


Figure 3 (a) The schematic illustration of Ag decorated Fe₂O₃ nano-flakes with CoPi as cocatalyst. (b) The photocurrent of different Fe₂O₃ electrode measured under 100 W cm⁻² simulated sunlight (AM 1.5G). Reprinted with permission from Ref. [41]. Copyright 2016, John Wiley & Sons, Inc.

Cu based semiconductors, such as CuRuO₂ [44], CuBi₂O₄ [45,46], are found to give a photocathodic response with higher stability. However, the magnitude of photocurrent cannot be comparable with that of Cu₂O which still needs more efforts to broaden light absorption.

Based on the above discussion, it indicates that the metal oxide based semiconductors possess the advantage of relatively facile and economic materials preparation methods. But their performance is still a challenge when aiming at the potential commercial utilization.

Nitride and chalcogenides

There are only limited kinds of visible light responsive metal oxide semiconductors that can be used for PEC research. The appearance of nitride (including oxynitride) and chalcogenide semiconductors greatly enlarges the available candidate for solar water splitting [47,48]. Due to the relatively smaller electronic negativity and lower orbital level, when N or S replaces the O during the nitridization or sulfurization, the VB will move upwards owing to the contribution of N 2p or S 2p orbital to the VB, while CB that is composed of metal atomic orbital has little change, as a result of which the E_g decreases

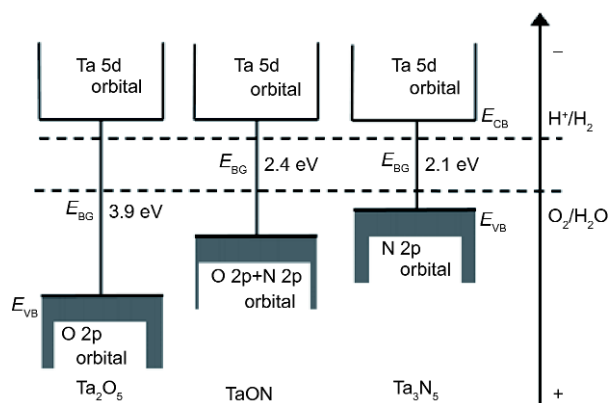


Figure 4 The band structure change when N 2p replaces O 2p orbital step by step. Reprinted with permission from Ref. [49]. Copyright 2003, American Chemical Society.

profoundly. For example, Fig. 4 indicates that when partially replacing the oxygen with N in Ta₂O₅ to form TaON, the bandgap decreases to 2.4 eV from 3.9 eV. If the O is totally replaced by N, it will produce Ta₃N₅ with a bandgap of 2.1 eV [49], which is highly desired for PEC conversion considering the corresponding solar conversion efficiency of 16% [12].

The state-of-the-art photocurrent of Ta₃N₅ has been reported to be 12 mA cm⁻², suggesting the outstanding optoelectronic property of Ta₃N₅ semiconductor [50]. In the Ta₃N₅ electrode, TiO₂ was deposited to block back electron-hole recombination, while ferrihydrite was used to capture holes for the further catalytic reaction on the molecular catalyst (Fig. 5). The near theoretical photocurrent suggests that artificial photosynthesis system has the possibility to approach high efficiency in the simulation. Other examples such as CsTaWO₆, Ba₂Ta₂O₇, ZnGa₂O₄, all have red-shift of their band edge upon nitridizing treatment, giving rise to BaTaO₂N, ZnGaON, etc. [51–54] with enhanced photocurrent. However, narrowing the bandgap is at the cost of weakening the oxidation potential because the potential difference between VB and E_{redox} is decreased. Therefore, these nitride photoelectrodes usually have sluggish surface reaction and suitable cocatalyst is necessary for achieving high photoresponse.

Besides the nitride, chalcogenide is also a kind of good candidates for PEC considering that many of them have been applied in heterojunction solar cells, such as CuInGaSe₂ [55], CuZnSnS₄ [56], CdSe [57], etc. For example, CuZnSnS₄ has been demonstrated to possess a photocurrent over 8 mA cm⁻² at 0 V vs. RHE upon modifying with CdS/In₂S₃/Pt [56]. But the stability of chalcogenide is

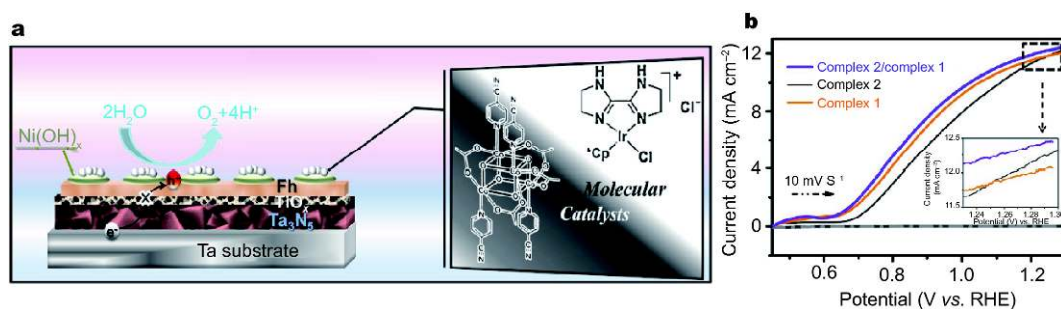


Figure 5 (a) The schematic illustration of $\text{Ta}_3\text{N}_5/\text{TiO}_2/\text{ferrihydrite}/\text{molecular catalyst}$ photoelectrode. (b) The photocurrent of different Ta_3N_5 photoelectrode measured under 100 mW cm^{-2} simulated sunlight (AM 1.5G). Reprinted with permission from Ref. [50]. Copyright 2016, the Royal Society of Chemistry.

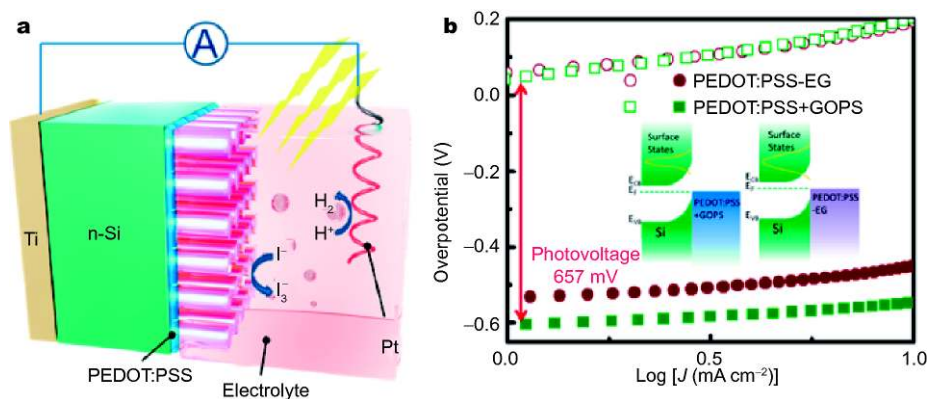


Figure 6 The schematic illustration of PEDOT:PSS modified Si photoelectrode and the corresponding Tafel plot for H_2 splitting. Reprinted with permission from Ref. [62]. Copyright 2016, American Chemical Society.

still a problem since they are easy to be oxidized by the photogenerated holes due to the thermodynamical instability. More efforts are needed to address this issue before these materials can come into practical use.

Other PEC candidates

Some other materials such as perovskite and conductive organic polymers also deserve our attention. Their impressive role in solar cell suggests that they have excellent optoelectric properties including light harvest, charge separation and transfer. Taking perovskite as an example, it can harvest light up to 900 nm and the charge diffusion length can be $\sim 1,000 \text{ nm}$, [58] which endows the perovskite based solar cell a solar conversion efficiency as high as 22.7% [59,60]. But it is so sensitive to water that until now there is no report of using photovoltaic perovskite directing for PEC water splitting. It is believed that a potential way to apply it in PEC is to block perovskite from the direct contact with electrolyte. As for the conductive polymers, such as P3HT and PEDOT, their

band structure is suitable to integrate with some typical semiconductors to realize an organic-inorganic hybrid PEC system [61,62]. Li and coworkers [61] reported that the PEDOT can be coated on the surface of Si arrays for achieving more efficient and stable water oxidation process (Fig. 6). Fumagalli *et al.* [63] reported another structure based on P3HT and PCBM bulk junction for efficient proton reduction after coating TiO_2 on the surface. Despite the success of these examples, the match between inorganic semiconductor and organic polymer remains a great challenge for efficient charge transfer. If the all-organic photoelectrode based on the donor-acceptor bulk junction can be fabricated, it will obtain much more efficient PEC water splitting process.

PHOTOELECTRODE FABRICATION METHODS

Effective PEC depends not only on elaborate choice of semiconductor but also the suitable route of photoelectrode fabrication. Efficient charge transfer relies on well

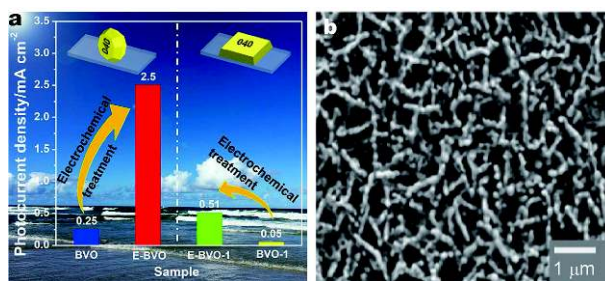


Figure 7 (a) The comparison of photocurrent of BiVO₄ photoanode with different proportion of (040) facet exposure and the corresponding electrochemical treated electrodes. Reprinted with permission from Ref. [35]. Copyright 2017, John Wiley & Sons, Inc. (b) The morphology of porous BiVO₄ electrode derived from BiOI nanoplate electrode. Reprinted with permission from Ref. [67]. Copyright 2014, the American Association for the Advancement of Science.

contact between the semiconductor layer and the conductive substrates. Many different methods are developed according to the semiconductor film so as to optimize the contact between semiconductor and substrate. A bottom-up method is always desired where the semiconductor film is epitaxially grown on the conductive substrate to minimize the impedance at the interfaces of substrate-particles and particles-particles. But limited by the substrate, a top-down method also will be used for film fabrication with the well-crystallized semiconductor particles. In general, these methods include wet chemical deposition, particle deposition, vapour phase deposition, and so on.

Wet chemical deposition

Hydrothermal method is a popular way for preparing metal oxide photoelectrode (e.g., TiO₂, WO₃, BiVO₄) with high degree of crystallization [28,35,64]. The morphology of the electrode can be well controlled *via* adding different capping reagent. For example, Wang *et al.* [35] reported that the exposed facet of BiVO₄ could be depressed when adding polyvinyl pyrrolidone (PVP) during the hydrothermal process. Since the (040) facet is regarded as the oxidative face, the decrease of (040) facet leads to the suppressed photoresponse (Fig. 7a). However, hydrothermal deposition is usually time-consuming and of low reproducibility due to the sensitivity to temperature, filling factor, etc.

Alternatively, electrodeposition is also an attractive method since it can facilitate control the thickness, morphology and even the phase of the semiconductor *via* controlling the applied bias, electrolyte pH and deposition temperature [65,66]. In 2014, Kim *et al.* [67] reported a facile BiVO₄ fabrication method *via* electrodeposition and calcination to achieve a porous photoelectrode (Fig. 7b). This method is easy to control and repeat, and many

exciting results have been reported based on it [36,68].

In addition, the chemical bath method is another widely used method in FeOOH, Cu₂O, NiOOH deposition [23,69,70]. Uniform films can be produced in the stock solution at ambient pressure below boiling point of solution. Similar to the chemical bath method, successive ion layer adsorption (SILA) is frequently used for depositing sulphide based film, such as CdS, MoS₂, due to a layer-by-layer alignment of the atoms in these crystal structure [71]. It is a useful strategy in modifying the chalcogenide based semiconductor which shares the same cations with the deposited layer. By controlling the number of deposition layer, the thickness can be easily controlled. Because the reaction occurs at relatively low temperature and ambient pressure, the as-prepared crystal is usually poorly crystallized. Moreover, the metal precursor is required to be stable in stock solution, which limits its application in depositing other films. Other methods, such as spin coating [72], spray pyrolysis [73], can be used to deposit uniform metal oxide film. But they usually lead to compact film with low specific area which is disadvantage for the surface reaction.

Particle deposition

Particle deposition can be considered as a top-down film deposition method with which the well crystallized semiconductor particles are prepared before being fabricated into photoelectrode with semiconductor films. The most popular method is doctor blading deriving from the research of dye-sensitized solar cell (DSSC) for which the semiconductor paste is spread on the conductive substrate with a spacer to control the film thickness [74]. Usually a following calcination is necessary for removing the organic additives in the paste and strengthening the particles connection. However, the heat treatment is not enough for forming tight crystal linkage and there still

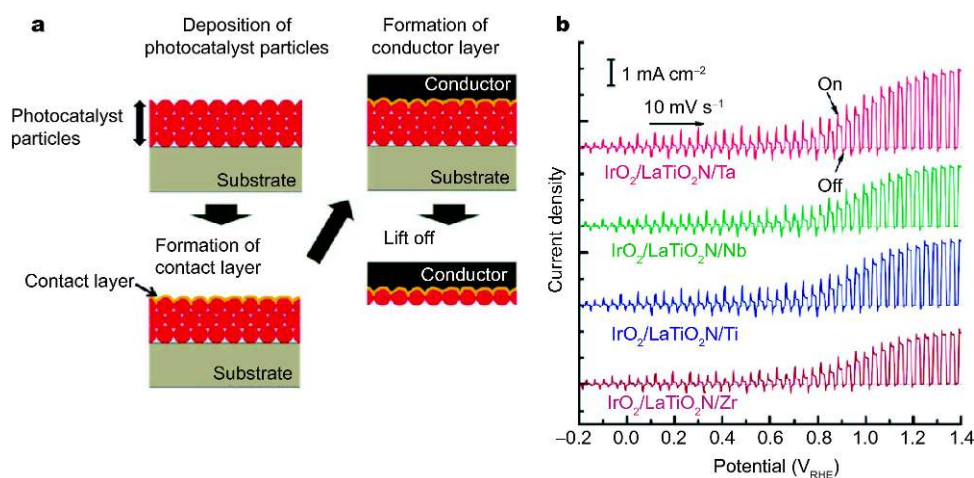


Figure 8 (a) The schematic illustration of particle transfer method. (b) The performance of LaTiO₂N photoelectrode with different contact layer. Reprinted with permission from Ref. [75]. Copyright 2013, the Royal Society of Chemistry.

exists abundant grain boundaries that can block the charge transfer. In order to improve the charge transfer process, a following necking treatment can be used to bridge the adjacent particles and provide a path for charge transportation. Wang *et al.* [18] performed a necking treatment on Ta₃N₅ particulate film fabricated by electrophoresis deposition method, which is another facile electrode fabrication method, and the photocurrent of Ta₃N₅ electrode increased profoundly.

Despite the success in fabricating Ta₃N₅ electrodes by the abovementioned methods, the connection between particles and substrate is too weak to bear harsh mechanical vibration (e.g., ultrasonic wave washing, crash). The particle-transfer method provides a good solution to this problem when the semiconductor particles are coated with a conductive layer before they are peeled off from the undelayed semiconductor film (Fig. 8a) [75]. It is a single crystal layer without particles stacking, so the charge transfer will be very convenient. With this method, the large LaTiO₂N particles are able to be fabricated into electrode with high performance (Fig. 8b). However, it should be mentioned that these methods have some limitations: the match between semiconductor and conductive layer is sensitive in determining PEC performance and the Ta contact layer prominently outcompetes the Zr layer for LaTiO₂N photoelectrode (Fig. 8b). Recently, Li's group [53,54] reported a moisture assisted particulate GaN:ZnO electrode fabrication. It is found that with the presence of moisture, the connection among GaN:ZnO particles was prominently enhanced, leading to over 10-time enhancement of the photocurrent compared to the one without moisture treatment. But for the

moisture assisted electrode fabrication, it is now only available in the GaN:ZnO semiconductor, more examples are under exploration to extend the application.

Vapour phase deposition

Films deposited from vapour have been well developed in physics, electronics, and semiconductor industry and the thickness can be controlled at several nanometer. As the most popular one, chemical vapour deposition (CVD) has been used to deposit electrode such as ZnO [76], SnS₂ [77], amorphous Si [78], and so on with well crystallization. The morphology can be well controlled during the CVD by changing the carrier gas, applying catalyst or other parameters. For example, oriented ZnO nanorod array can be deposited with Au as catalyst by CVD (Fig. 9a) [79]. This method can be used to prepare high quality ZnO nanowires. Moreover, cauliflower like Fe₂O₃ electrode has been reported *via* an ambient pressured CVD process with Fe-based organic precursor [39]. The materials prepared by CVD usually have high crystallinity, but it is hard to scale up.

Besides CVD, physical vapour deposition (PVD), including magnetron sputtering (MS), pulsed laser deposition (PLD), also have been applied in depositing semiconductor films. As for MS, it works under strong electric field between target and the substrate to allow the plasmonic precursor coating on the conductive layer. Changing the atmosphere (e.g., O₂, N₂ or NH₃) can produce different metal oxides and nitride, such as TiO₂, WO₃, ZnO, Ta₃N₅, etc. [81–84]. For PLD, it is a top-down film fabrication method where the target is well-prepared semiconductor and the film is formed by depositing the

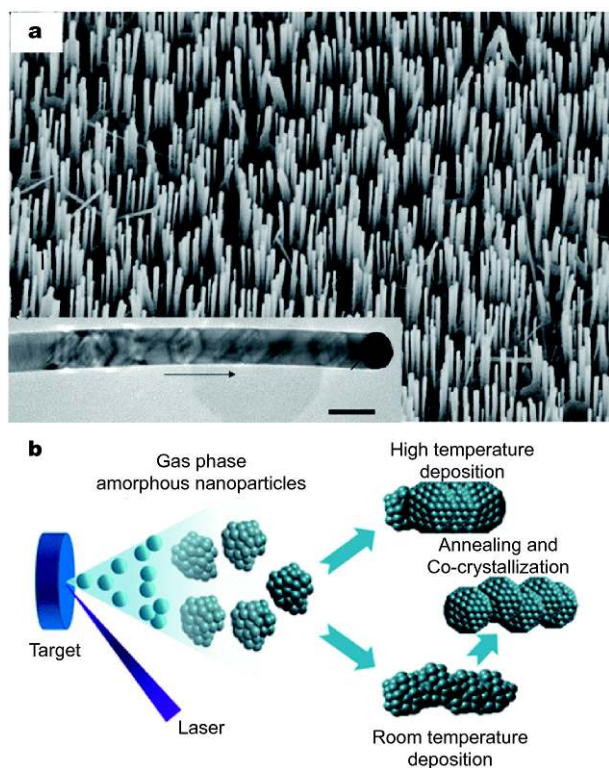


Figure 9 (a) The ZnO arrays prepared by CVD with gold as catalyst. Reprinted with permission from Ref. [79]. Copyright 2004, American Chemical Society. (b) The schematic illustration of different particle morphology deposited on films by PLD. Reprinted with permission from Ref. [80]. Copyright 2017, American Chemical Society.

tiny particles from the target onto the substrate (Fig. 9b). PLD has less requirement of the conductivity and magnetism of the target; so many candidates such as CaFe_2O_4 , SrTiO_3 , etc. have been reported to be used for film fabrication [85,86]. In addition, *via* changing the deposition temperature, it is possible to change the morphology from nanorods (at low temperature) to condensed film (at high temperature) as shown in Fig. 9b [80]. However, these physical vapour deposited films usually face the problem of low rough factor due to the plate-like film, too many defect states due to the abundant crystal stress, and so on. The shadow effect can be used to create an array like morphology and post-heat treatment also be able to release the stress in the film to some degree, but it is still not comparable to the wet-chemical method in the aspect of performance.

Other film deposition method

Besides the aforementioned methods, some other methods with special advantage also deserve our attention. Flame annealing method is reported by Zheng's group

[87–90]. The as-deposited TiO_2 nanotube, Fe_2O_3 nanorod, and so on undergo a fast annealing treatment to realize high crystallinity [87,90]. Using the annealing method, Han *et al.* [91] successfully prepared hematite photoelectrode with an onset potential as low as 0.5 V vs. RHE. Additionally, when adding the precursor source into the flame, it can realize an all-in-one process of particle formation, crystallization and film deposition (Fig. 10a). MoO_3 nanobelt (Fig. 10b) and WO_3 nanorod film have been fabricated in this way and the derived $\text{WO}_3/\text{BiVO}_4$ photoanode delivers a photocurrent as high as 3.1 mA cm^{-2} [89,92]. Molecular beam epitaxy (MBE) is another advanced film fabrication method in preparing film with high quality crystal. Uniform GaN nanorods are deposited on Si substrate by MBE method and show impressive photocurrent due to the high crystallization of GaN [93]. But MBE is an expensive method due to the equipment and the organic metal precursor, which limits its application in PEC.

PEC CHARACTERIZATIONS

Suitable characterization of the crystal structure, carrier diffusion, surface species, etc. is critical for deeply understanding the PEC process. Many routine technologies have been well applied in PEC research, such as X-ray diffraction (XRD) for phase detection, scanning electron microscopy (SEM) for morphology checking, transmission electron microscope (TEM) for fine structure identifying, and so on. But considering the complex process of water splitting, the above characterization cannot provide a comprehensive insight of the PEC reaction mechanism. Here, some advanced technologies for structure, carrier diffusion and surface reaction characterization in PEC will be briefly summarized.

Structure characterization

One of the most important things for PEC characterization is to identify the structure contributing to its performance. The X-ray absorption is a very powerful tool in disclosing the local atomic/electronic structure, such as surface distortion, distribution of dopants, defect types, dopant valance and chemical reaction progresses. In the presence of dopants or chemical valance change, the chemical bond will change in terms of the elemental absorption energy or the interatomic distance [94]. Based on the detected energy range, the X-ray absorption spectrum can be categorized into X-ray absorption near-edge structure (XANES, 30–50 eV above the absorption edge) and extended X-ray absorption fine structure (EXAFS, more than 50 eV above the absorption edge).

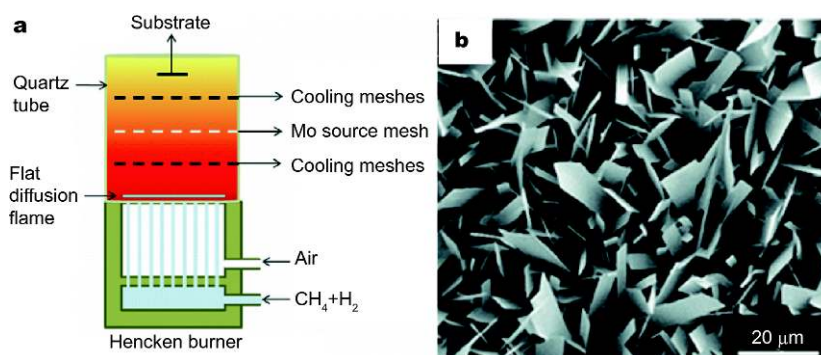


Figure 10 (a) The schematic illustration of equipment used for flame annealing electrode fabrication. (b) The MoO_3 nanobelts prepared by flame annealing method. Reprinted with permission from Ref. [92]. Copyright 2011, the American Chemical Society.

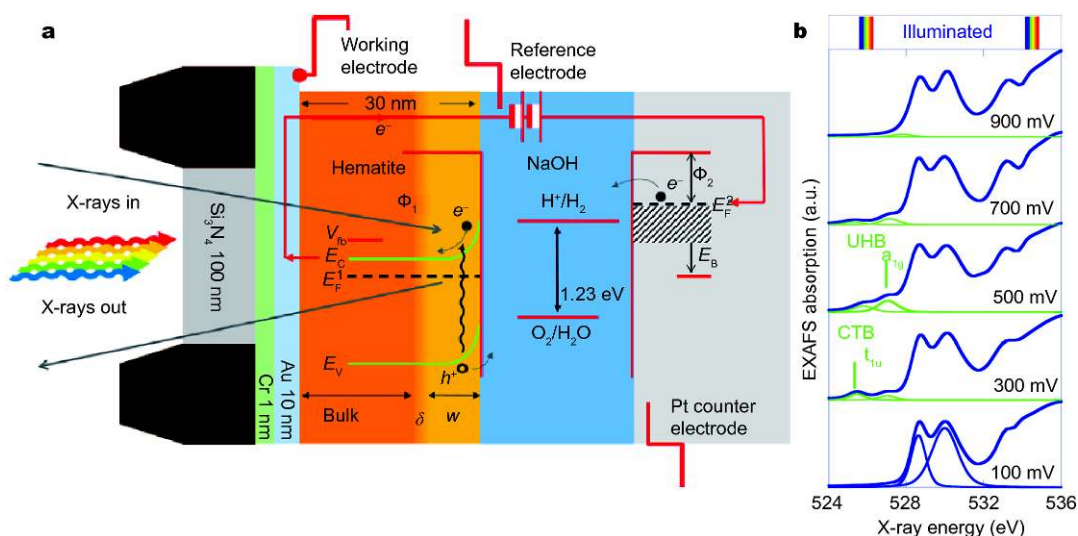


Figure 11 (a) The schematic illustration of *in-situ* X-ray absorption characterization of hematite electrode. (b) The O 1s EXAFS changes along with different applied bias under illumination. Reprinted with permission from Ref. [95]. Copyright 2012, the American Chemical Society.

They share the same fundament but have different analysing method. Braun *et al.* [95] used the EXAFS to study the charge transfer process on hematite electrode and claimed a two-hole accumulation process for PEC water oxidation (Fig. 11). A special PEC cell was designed for the *operando* X-ray absorption detection (Fig. 11a). And the change of O 1s EXAFS was claimed as the presence and transfer of photogenerated holes during the biased water oxidation (Fig. 11b). Other researchers focused on the cocatalyst (e.g., CoPi, CoO_x) change during the reaction where different chemical states may exist in the compound [96,97]. The X-ray absorption fine structure provides the detail about the metal–oxygen (M–O) bond and chemical valence change during the reaction. For the X-ray absorption technology, it usually needs a complex

data analysis process to gain the reasonable conclusion. So the sophisticated data analysis is important in building the structure–performance relationship.

Besides this, advanced electronic microscope, such as spherical aberration-corrected TEM, can be used to directly observe the structure change. It is very promising to use this technology in visually observing the structure change of the semiconductor or cocatalyst.

Carrier diffusion characterization

In addition to observing the structure change during the PEC reaction, it is also desired to detect the carrier diffusion process. The photogenerated holes and electrons usually have some characteristic light absorption whose intensity is proportional to the charge carrier's con-

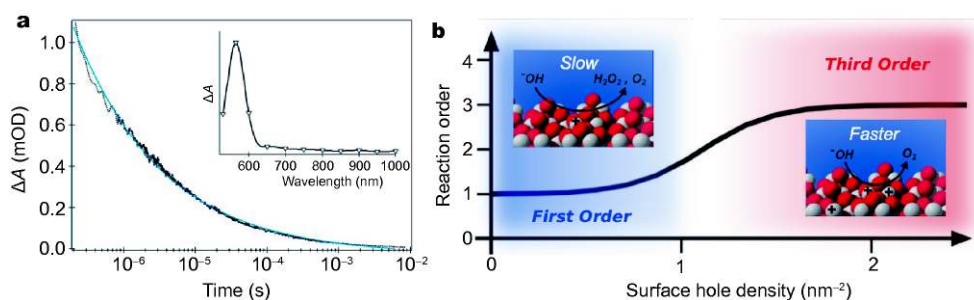


Figure 12 (a) The decay of hole absorption peaked at 580 nm as illustrated in the inserted pattern. Reprinted with permission from Ref. [98]. Copyright 2013, the Royal Society of Chemistry. (b) The reaction order change along with the surface hole density. Reprinted with permission from Ref. [99]. Copyright 2015, the American Chemical Society.

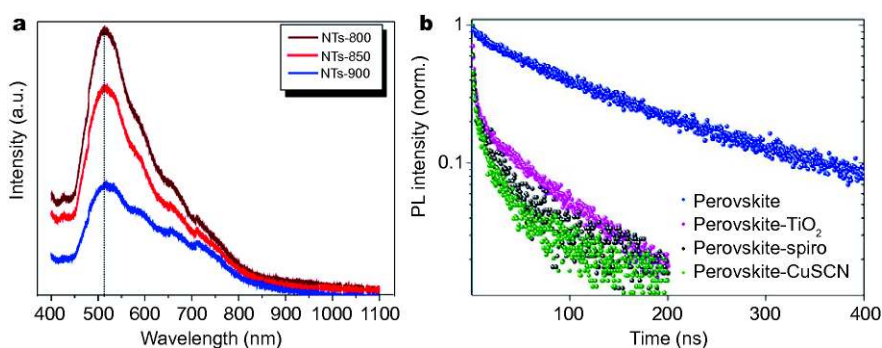


Figure 13 (a) The steady-state PL of Ta_3N_5 photoelectrode calcined at different temperature. Reprinted with permission from Ref. [103]. Copyright 2015, the American Chemical Society. (b) The TPL of perovskite film with different hole transfer layer to quench the PL. Reprinted with permission from Ref. [105]. Copyright 2017, the American Association for the Advancement of Science.

centration. This allows us to trace the carrier decay process with a transient absorption spectrum (TAS) since the amount of charge carriers will decay due to the charge recombination upon the charge production. For example, on hematite based PEC, the absorption at 580 nm in Fig. 12a is attributed to the photogenerated holes [98] and further kinetic study indicates that the reaction order changes from 1 under weak light intensity to 3 under strong light intensity (Fig. 12b) [99]. It is also possible to directly observe the absorption from photogenerated electrons *via* Fourier transform infra-red (FTIR) spectrum considering the very small energy gap among the photogenerated electrons. The time-resolved FTIR has been used to analyze the decay process on photocatalyst such as TaON, TiO_2 , and so on [100,101].

Besides direct observing the signal of photocharge, the photoluminescence (PL) process originating from electron-hole recombination can also be used to characterize the charge transfer process. For the steady-state PL, researchers usually hold the point that the lower the PL intensity is, the less the recombination centres will exist

[102,103]. It is widely used to characterize the defect state in Ta_3N_5 as demonstrated in Fig. 13a, where Khan *et al.* [103] attributed the lower PL intensity at higher temperature to the suppressed oxygen defect states. However, this is partially correct only when the recombination occurs *via* recombination centres rather than from the band-to-band recombination. Moreover, sometimes the light absorption of the semiconductor will decrease because of the shield effect from such as cocatalyst, surface species, and the PL intensity also will decrease due to the reduced pump light intensity, but not the recombination centres amounts. If a pulsed pumping laser is used to excite the PL, it is possible to observe the decay process of PL that is the so called time-resolved PL (TPL). The lifetime derived from TPL can indicate the charge recombination or charge diffusion process according to the test electrode structure [58,104]. The results from perovskite solar cell suggest that when the semiconductor film is deposited on insulator substrate (e.g., glass substrate), the fast decay process (short lifetime) usually suggests that there exist a large amount of recombination

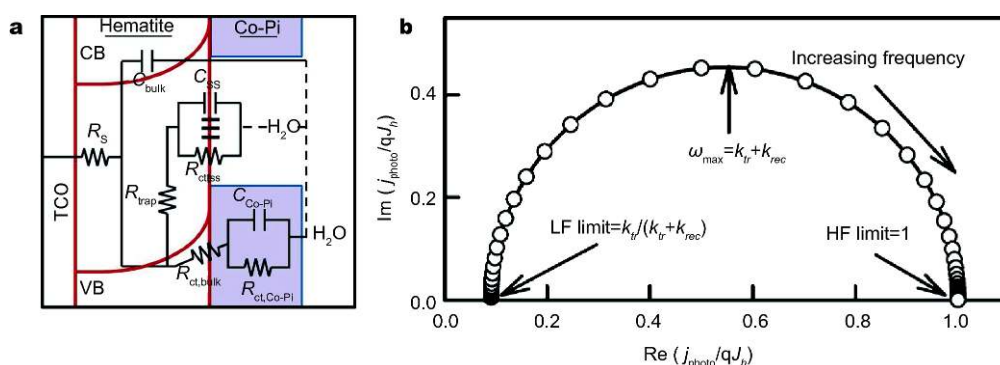


Figure 14 (a) The full equivalent circuit for interpretation of the $Fe_2O_3/CoPi$ system. Reprinted with permission from Ref. [106]. Copyright 2012, the American Chemical Society. (b) A calculated IMPS response when $k_{rec}=10k_{tr}$. Reprinted with permission from Ref. [108]. Copyright 2013, Springer.

centres. But if the film is deposited on conductive substrate (e.g., FTO or ITO) with the hole or electron transfer materials (TiO_2 , Spiro or $CuSCN$), the decay path is dominated by drawing the charges with the collector (Fig. 13b) [105]. Therefore, fast TPL decay process indicates fast charge transfer and collection process, which is beneficial to the whole photoelectric process. For the PEC research, the film is usually deposited on conductive substrate. When we try to explain the TPL spectrum, it is necessary to have a full consideration about the experiments fact and more evidences should be provided to support the conclusion derived by TPL or PL.

Reaction characterization

The above mentioned methods can provide the basic properties of the semiconductor electrode itself regardless of the reaction. To focus on the reaction process, the electrochemical method can be adopted, especially the frequency related methods, such as electrochemical impedance spectroscopy (EIS), intensity-modulated photocurrent spectroscopy (IMPS), which can provide abundant kinetic knowledge.

EIS can be used to analyze the energy loss process in PEC with the assistance of equivalent circuit (EC). Principally, the PEC system is viewed as a black box and many electric elements including resistor (R), capacitor (C), constant phase element (CPE), are used to fabricate the EC for simulating the frequency response of the PEC system. Bisquert's group [106,107] has applied the EIS to analyze the charge transfer on hematite photoanode and emphasized the important role of surface states on surface reaction and charge recombination, and from the result of $Fe_2O_3/CoPi$ system (Fig. 14a), they pointed out that the holes would accumulate at the electrode-electrolyte interface firstly before the charge consumption happened. Furthermore, IMPS provides an insight into the kinetics

of reaction and recombination *via* measuring the photocurrent under modulated light intensity [108]. Based on the IMPS response, the charge transfer and recombination kinetic constant can be derived from some characteristic frequency (Fig. 14b). By combining EIS with IMPS, it is possible to provide an all-sides view about the charge transfer mechanism and the kinetics which will provide us some guides on how to improve the system one step further.

But the explanation of EIS and IMPS strongly relies on the EC which is not easy to be confirmed without a deep understanding of the charge transfer path of the PEC system. For example, the full equivalent circuit of $Fe_2O_3/CoPi$ system is too complicate to derive any useful information (Fig. 14a). In order to trace the reaction mechanism, it is important to detect the reaction intermediate in a suitable way. It is highly desired to observe the surface reaction process *via* an *in-situ* or *operando* way since it can provide a direct picture about the structure or chemical states change during reaction. Some *operando* technologies such as Raman or X-ray photoelectron spectroscopy (XPS) have been applied in thermal- or electro- catalysis research [109,110], but for PEC research, due to the short lifetime and low concentration of the reaction intermediate, the progress in this field is so slow that more effort should be made to move it forward. Some other technologies, such as electron spin resonance (ESR), fluorescent molecular probe, Kelvin probe atomic force microscope (KPFM), also have the potential to be used to investigate the surface species and the surface charge distribution.

It is worth noting that Boettcher's group [111,112] has attempted to investigate the surface species under operation with a dual-working electrode system (Fig. 15). They found that the ion-permeable cocatalyst such as NiO_x could build an adaptive junction with the semi-

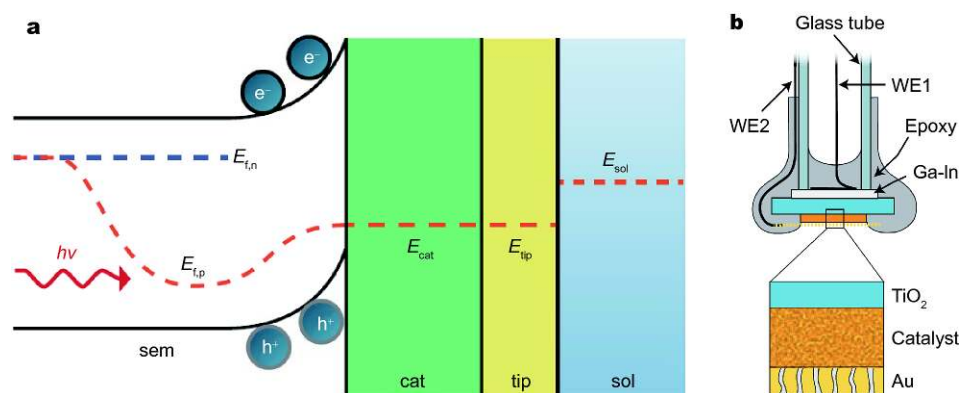


Figure 15 (a) The energy diagram to show the energy level alignment of a dual working electrode system. Reprinted with permission from Ref. [111]. Copyright 2018, Macmillan Publishers Limited. (b) The schematic show of the dual working electrode. Reprinted with permission from Ref. [112]. Copyright 2014, Macmillan Publishers Limited.

conductor which will allow Schottky barrier height changes along with the reaction to realize the optimized charge transfer. This technology can also be used to measure the surface electrochemical potential during operation.

CONCLUSION AND PERSPECTIVE

In this review, we summarized the recent progress in PEC water splitting in the aspect of materials, electrode fabrication methods and characterization methods. As the building block, the semiconductor materials have been largely expanded to the long-wavelength harvesting candidates. And many advanced electrode fabrication methods have been applied in preparing efficient photoelectrodes. Due to the great effort in recent years, the efficiency of PEC water splitting has a profound progress. For single photoelectrode, the highest applied bias photo-current efficiency has been over 2.5% and the nearly theoretical photocurrent of Ta_3N_5 photoelectrode suggests that PEC system can realize the utmost photocurrent under suitable strategies. For integrated system, the solar cell-PEC system has claimed to realize unbiased water splitting with the solar-to-hydrogen efficiency over 10%, which also demonstrated the feasibility of converting solar energy into hydrogen in a high efficiency. At the same time, some *operando* technologies, including X-ray absorption, transient light-absorption, have been applied to gain deep insight into the PEC reaction process and provide useful guidance for further improvement.

However, it should be mentioned that when taking the efficiency and cost into consideration, no existing system can meet the requirement for practical application. All current PEC systems have some shortages in the aspects of efficiency, stability or cost. Most of the reported highly

performed photoelectrodes are fabricated with expensive semiconductor, e.g., GaAs, crystal Si, Ta based semiconductor. By focusing on these prototypical photoelectrodes, we may figure out the criteria for realizing high solar conversion efficiency. It may provide the guidance for further improving the robust and cheap semiconductors such as Fe_2O_3 . The ideal system is single electrode with highly unbiased solar conversion efficiency since it has the lowest cost. Most of the existing materials cannot fulfil this requirement, so it is expected that the novel materials, such as organic-inorganic perovskite materials, MXene, metal-organic framework (MOF), can be possible to achieve that goals upon modification.

Meanwhile, the characterization technology is expected to have further progress so as to discover the underneath water splitting mechanism that will provide the direction for experimental research to release the bottleneck step and fabricate more effective photoelectrode. It is always desired to achieve a quantitative detection of the PEC system in order to have deep understanding of the photocatalytic process. For this purpose, some pending problems are urgent to be solved: 1) what is the reaction intermediate for PEC reaction, especially during water splitting? 2) How do we evaluate the driving force and overpotential for a PEC reaction? 3) What is the intrinsic role of surface states/cocatalyst during the surface reaction? 4) What does the photogenerated electron/holes experience? To answer all those questions, it requires a high resolution of the time, space and energy during the characterization.

PEC water splitting is a complex process related to materials, engineering, semiconductor physics, and electrochemistry that needs to pay continuous attention in this field. We strongly believe that these efforts will pave

the path towards a clean and sustainable future of our world.

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光电催化分解水: 电极材料, 电极组装和电极表征

王志亮, 王连洲*

摘要 光电催化分解水作为一种清洁可持续获取氢能的技术吸引了人们的广泛关注. 高效光电过程有赖于选择合适的半导体材料, 即: 具有较小的带隙以保障足够的光吸收; 优异的电荷分离以保障光生电荷向反应位点的迁移; 高效的表面催化能力以实现对光生电荷的充分利用. 同时, 合理的电极组装方法对于电荷的迁移与表面反应也起到至关重要的作用. 进一步, 强有力的表征技术为深入了解光电催化分解水的过程, 认清反应限速步骤并据此进一步优化电极设计提供了保证和依据. 本文着眼于实现高效的光催化分解水制氢过程, 综述了电极材料的开发, 电极组装手段和光电催化表征技术这三个方面的研究进展, 并期望为发展更加高效的光电催化分解水过程提供指导.