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Nanostructured Materials for Photoelectrochemical Water Splitting

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Chapter 1

Fundamentals of photoelectrochemical water splitting

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Due to the storage restrictions of fossil fuels and petroleum and excessive carbon dioxide emissions after combustion, the search for alternatives to traditional fuels has been studied for many years. In recent years, the use of hydrogen as a fuel has received widespread attention. Photoelectrochemical (PEC) water splitting is a high-potential technology and has become an important production method that can be used to produce sustainable, renewable, low cost, and high-efficiency clean energy-hydrogen fuel. However, PEC water splitting still faces limitations and challenges such as limited solar energy absorption, rapid carrier recombination, and a lower rate of charge separation. This chapter introduces the principle and process of PEC water splitting and novel photoanode materials to overcome PEC application challenges and problems, such as photocurrent generation and hydrogen evolution efficiency. Simultaneously, we review the latest development of various technologies and methods of PEC water splitting.

1.1 Introduction

The rapid growth of industrialization and urbanization not only requires more energy supply but also generates more environmental pollution. Energy consumption and environmental pollution are the main issues encountered by human beings. In order to meet the demand for power generation, finding new energy and storage methods is an important direction of current research, and the main goal is to produce low-cost, clean, and abundant energy. In recent years, the impact of carbon dioxide emissions on climate change has received more attention. Storage of traditional chemical fuels is not easy, only unlimited renewable energy such as solar energy converted into other forms of energy can be stored to meet the demand for power supply. According to US reports, if the pollution trend continues, we will face

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global warming of 1.5°C from 2030 to 2052, which will have serious impacts on the environment such as rising temperatures in the land and oceans, droughts, extreme heatwaves, rainstorms, and ecosystems destroyed. In order to curb the impact of global warming, it is necessary to reduce emissions by 2030 to about half what they were in 2010, and achieve zero net emissions by 2050 in order to effectively achieve the goal of reducing greenhouse gas emissions. Among these strategies, the energy sector is the most important part, which can effectively improve the impact caused by traditional fossil fuels. Therefore, when renewable energy can provide about 70%–85% of electricity, this goal can be effectively achieved.

Solar energy is an unlimited, clean and low-cost renewable energy source. It is widely recognized due to its operation without noise, toxicity, and greenhouse gas emissions [1–5]. The total amount of solar power irradiated in the Earth is approximately 120 000 terawatt each year, and the energy consumption of traditional fuels can be replaced by solar energy that absorbs less than 1% of the annual radiation. It has the characteristic of being inexhaustible. By 2040, solar energy and wind energy will account for more than 2/3 of all renewable energy, and the power generation will increase from 13% to 18% [6]. A clean energy technology will help us efficiently and economically use solar energy to generate, convert and store electricity. In order to effectively complete this process, an environmentally friendly photoelectrochemical cell (PEC) should be created. It is composed of suitable and stable semiconductor materials, and an appropriate PEC reaction occurs at the interface between the semiconductor and the solution [7]. The PEC hydrolysis driven by visible light produces oxygen and hydrogen fuels and converts them into electricity, and this has become an important direction for the development of clean energy. During the reaction process of the PEC cell, the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) can be obtained simultaneously, as shown in figure 1.1. The O_2 oxidation reaction ($2H_2O \rightarrow 4H^+ + O_2 + 4e^-$) occurs at the photoanode; the H_2reduction reaction ($2H^+ + 2e^- \rightarrow H_2$) occurs at the cathode. More researches have been made on hydrogen to replace fossil fuel resources. Hydrogen provides a way to store electrical energy, and the production and consumption with zero carbon emissions, which can reduce carbon dioxide

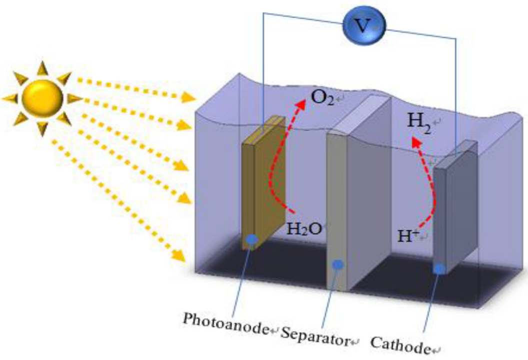

Figure 1.1. Scheme of a basic photoelectrochemical cell.

emissions to protect the environment. The production of hydrogen is highly efficient and promising in the foreground among renewable resources [8–10]. The specific energy of hydrogen (J kg^{-1}or m^{2}s^{-2}) is three times that of gasoline, with water and energy as the products after combustion, so it can be seen as a clean and sustainable fuel [11].

Semiconductor materials can naturally absorb the solar spectral region for a water splitting reaction, but the oxygen evolution reaction is kinetic and thermodynamically challenging, and the photoanode material will be destroyed by an oxidation reaction [16]. Meanwhile, the semiconductor materials are selective in absorbing light, which limits the use of the solar spectrum. Therefore, it is an important key to select suitable semiconductor materials to absorb solar energy and transfer it into some useful energy sources. The electron energy gap of the semiconductor material is consistent with the redox potential of water, which is a crucial key to water splitting. Figure 1.2 shows the comparison of the band gap in different semiconductors and the redox potential in the water. The positions of the band gap, conduction band (CB), and valence band (VB) of most semiconductors are not suitable for water splitting [12–14]. Among many semiconductors, TiO_2has characteristics of low cost, non-toxicity, self-cleaning, ease of operation, strong photocatalytic activity, and anti-light corrosion stability, and it has become the main material for PEC water splitting [15–17]. Moreover, the positions of the CB and the VB of $TiO_2$are consistent with redox potential of water, making TiO_2a suitable material for water splitting. However, the wide energy gap (3.0–3.2 eV) of TiO_2 only absorbs ultraviolet light and the high recombination rate of electron/ hole pairs reduces the degrade efficiency of TiO_2 in water splitting. Therefore, a low

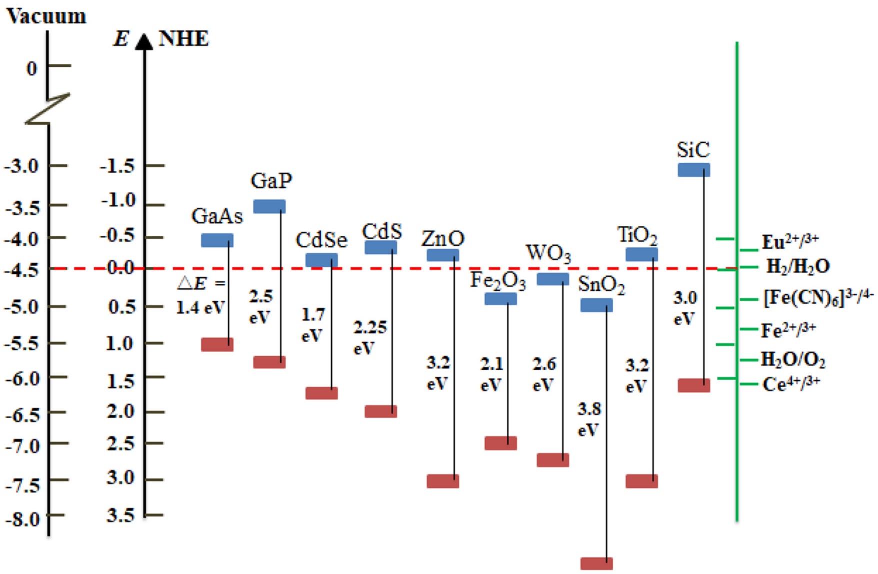

Figure 1.2. The energy gap of different semiconductor materials.

energy gap material and changing the position of the TiO_2 CB or VB will be necessary to effectively improve the photocatalytic efficiency. Further, to improve the migration of photo-generated charge carriers, various surface modification techniques can be used to improve the performance of water splitting under visible light irradiation [18, 19].

This chapter provides an important overview of PEC water splitting, including the basic principles and applications of PEC hydrogen production. First, we introduce the mechanism and process of PEC water splitting, and then discuss semiconductor materials suitable for hotoelectrochemical reactions and compare their performance. Finally, the possible influencing factors for PEC water splitting are proposed and its future applicability is evaluated.

1.2 Basis of PEC water splitting

In recent years, Osterloh proposed a classification dependent on reaction thermodynamics, and the thermodynamically advantageous system is considered to be photocatalysis (PC). In this system, photons can increase the reaction rate of favorable reactions. In contrast to PC, the disadvantageous system in which the free energy generated by thermodynamics is higher than the reactant is called photosynthesis (PS) [20]. For the photosynthetic system, the reverse reaction is thermodynamically advantageous, hence one must prevent the reverse reaction from occurring during the separation of the reaction products. The products of the water splitting (WS) process are hydrogen and oxygen. Figure 1.3 shows three main processes: (1) The excitation of electrons in the photocatalyst valence band generates charge carriers (electron–hole pairs) through photon absorption, leading to charge carriers entering the conduction band. The distance between the

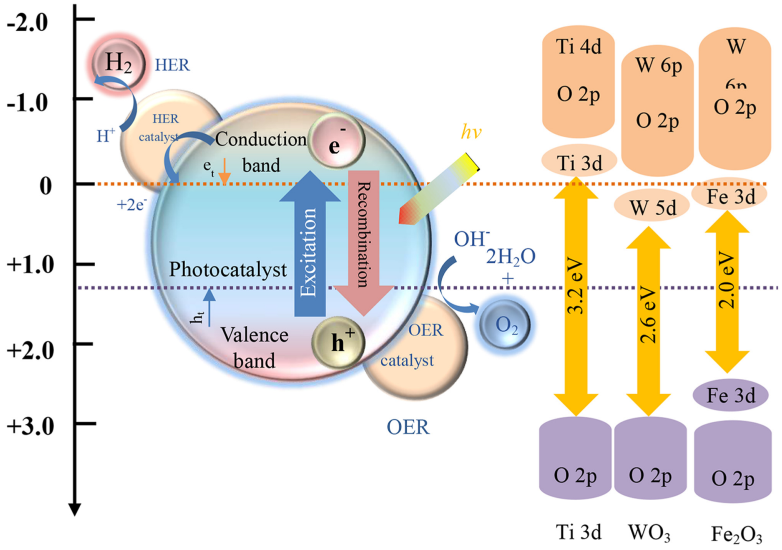

Figure 1.3. Overview of the WS process.

valence band and conduction band is called the band gap, i.e., E_g, which represents the minimum energy required for photon-induced electron excitation. (2) Unless there is a driving force like an electric field or $e^-$and h^+scavenger that hinders natural decay, the separation of charge carriers will recombine. Make the charge carriers migrate to space areas where an electrochemical reaction will occur. (3) The water is oxidized (OER) by holes on the catalyst surface, while electrons drive the reduction of water (HER) [11].

1.2.1 Principle of PEC water splitting

Among the current renewable energy sources, hydrogen produced through WS is very important. Figure 1.4 is a schematic diagram of the basic principle of photoexcited electron–hole pairs. When the semiconductor absorbs energy more than the band gap, electrons in VB are excited and leave holes. However, the photogenerated $e^-$and h^+have not effectively separated, which leads to their recombination immediately and the release of photons or heat energy. Therefore, charge separation is a key factor in any photocatalytic activity. If the charges are successfully separated, they will migrate to the semiconductor surface and participate in oxidation and reduction. Under standard conditions, the free energy change of a molecule of H_2O into H_2 and 1/2 O_2 is $\Delta G = 237.2\ \text{kJ mol}^{-1}$. According to the Nernst equation, each electron transmitted is $\Delta E = 1.23$ V. The relationship between eV energy and λ (wavelength) nm can be expressed by energy (eV) = $1240\ \lambda^{-1}$(nm). Therefore, the semiconductor must receive the energy of more than 1.23 eV (light wavelength at 1008 nm), and convert that energy into H_2 and O_2, as shown in figure 1.5.

To complete WS without providing additional energy, the bottom of the CB should be located at a position that is more negative than the reduction potential of H^+ to H_2 (relative to the normal hydrogen electrode (NHE) at 0 V when the pH is 0). The top of the VB should be at a more positive position than the oxidation potential of H_2O to O_2 (1.23 V versus NHE). NHE is a redox electrode dependent on a redox half-cell $2H^+(aq) + 2e^- \rightarrow H_2(g)$, that is, the potential of a platinum electrode under 1 N acid solution. Therefore, the difference between the two reduction potentials is that the minimum photon energy required for driving the thermodynamics reaction is 1.23 eV, which belongs to the visible light spectral range in the near-infrared region. Since there is an activation barrier between photocatalyst and water

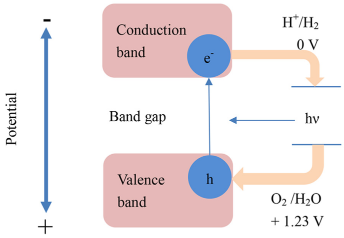

Figure 1.4. Principle of overall WS on photocatalyst of heterogeneous semiconductor.

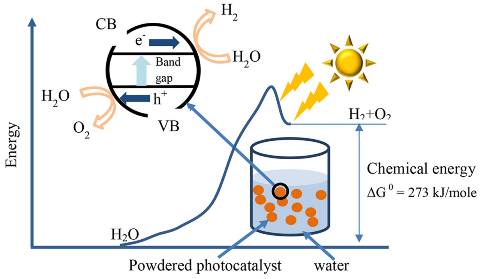

Figure 1.5. Photocatalytic WS via semiconductor photocatalyst.

molecule during the charge transfer process, the photon energy is required to be larger than the band gap of the photocatalyst for driving the entire WS reaction. In addition, the thickness of the photocatalyst is also key. When the diffusion length of charge carriers is less than the thickness of the photocatalyst, the recombination reaction of charge carriers may occur before they reach the semiconductor surface

The PEC process uses a photocatalyst to catalyze the WS reaction to separate water into O_2 and H_2. The water splitting reaction requires photon energy to overcome the positive change of Gibbs free energy produced by PEC WS (equation 1.1) [21]. Take the n-type TiO_2 photocatalyst as an example, when the energy of absorbed photons ($h\nu$) is larger than their own band gap, it will promote the light-driven WS process. This light absorbed generates the electron in the CB and the hole in the VB (equation 1.2). These holes on the TiO_2 electrolyte interface oxidizing water molecules resulting in generation of O_2 and H^+ ions (equation 1.3). The electrons will pass through the external circuit to reach the counter electrode and H^+ ions are reduced because of the electric field or external bias, thereby forming H_2 molecules (equation 1.4).

$$2H_2O\,(l) \rightarrow O_2(g) + 2H_2(g) \tag{1.1}$$

$$TiO_2 + 2\,hv \rightarrow TiO_2 + 2e^- + 2h^+ \tag{1.2}$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \tag{1.3}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{1.4}$$

1.2.2 Process of PEC water splitting

Generally, PEC is divided into four steps to complete the PEC WS reaction, as shown in figure 1.6: (1) the photocatalyst absorbs photon energy greater than the band gap of the semiconductor material; (2) light-excited electron–hole pairs are generated; (3) light-excited electrons and holes are separated and migrate to the smallest recombination surface. In the last two processes, the induced e^-/h^+ pairs can be combined or effectively separated in the materials; (4) The chemical reaction of surface. The adsorbed substances are reduced and oxidized by photogenerated

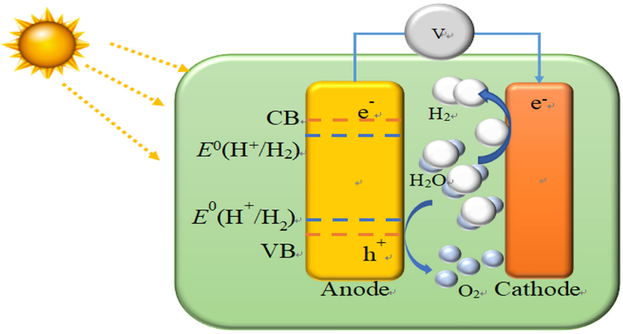

Figure 1.6. WS cell of the photoelectrochemical under n-type semiconductor TiO_2 photoanode.

electrons and holes, in which the H_2 and O_2 are generated at different surface reaction sites, respectively [22]. From these reaction steps, it is known that the structure, electronic and morphological properties of the photocatalyst are the main factors affecting the performance of the first and second steps. Meanwhile, the reverse reaction of H_2 and O_2 recombination to produce water must be suppressed, and the photocatalyst must be stable during the reaction. Some information can be obtained from these reaction processes. First, a semiconductor with an energy gap greater than 1.23 eV can generate electron–hole pairs by absorbing light, so that the WS reaction can occur on the surface of the semiconductor. Second, the amount of water molecules adsorbed on the photocatalyst increases as the surface area of the photocatalyst increases; therefore, increasing the surface area will enhance the reaction of light-excited electron holes on the substrate. On the other hand, the increase in surface area will generate defect centers in the photocatalyst. Since the surface of the catalyst is considered to be the defect site, that is as the electron–hole recombination centers. With a larger surface area, the faster the reaction, while the smaller the surface area, the less electron–hole recombination. Therefore, the appropriate performance of the photocatalyst requires a suitable surface area and crystallinity. Third, the solid cocatalyst can promote this step. Usually, the cocatalysts are noble metals (such as Pt) or metal oxides (such as RuO_2) as a dispersion of nanoparticles supported on the surface of the photocatalyst to generate active sites and to reduce the activation energy of gas release.

Nano-sized catalysts can enhance effective charge transport and contacting surface area during catalysis. In order to further increase the production of H_2, the cocatalyst is loaded on the semiconductor, which can provide active sites and reduce the activation energy of WS. Noble metals like platinum and ruthenium have been considered as typical promoters for promoting hydrogen production. Hydrogen can be used as fuel, so it is very important to increase the yield of hydrogen. The commonly used organic holes scavenger is ethylene diamine tetra-acetic acid (EDTA), due to it being easily oxidized by holes so that the electrons on the conduction band generate hydrogen. The ability order of some hole scavengers to generate hydrogen is the following: EDTA > methanol > ethanol > lactic acid. The decomposition of the reagent increases the production of hydrogen [23].

1.3 Materials for PEC

The most important factor that determines the spectral range of light absorbed by a semiconductor is the band gap energy (E_g). Since only 1.23 V is required for water splitting, the minimum band gap is 1.23 eV. According to the standard AM 1.5 G solar spectrum (approximately 100 mW cm^{-2}), assuming that there is no loss, the maximum overall conversion efficiency of solar energy to hydrogen (STH) for such a band gap semiconductor is 47.4% [24]. However, the semiconductor photocatalyst will inevitably have energy loss in the solar energy conversion process. When sunlight radiates on the photocatalyst, the absorption energy of the photon is larger than the photocatalyst's band gap, which will excite electrons from the VB into the CB. For this case, the recombination of e^-/h^+pairs will occur quickly, and energy is released by heat or photons form. Additional possible energy losses include electron transport of sample during the separation of charge carriers, electron transport of working anode to the counter electrode, and Joule heat generated by the electron flow from the external circuit process. In the actual PEC WS system, the energy loss will be greater than 0.8 eV [25]. Therefore, the photocatalyst used in the PEC WS cell is at least about 2.0 eV of the band gap [26], which corresponds to the absorption range of about 650 nm [27]. In addition, to achieve the US Department of Energy's (DOE) solar-to-hydrogen (STH) target efficiency of 10%, the minimum photocurrent density must reach 8 mA cm^{-2}, indicated that the maximum band gap must be approximately 2.3–2.4 eV. Therefore, the band gap of optimal should be between 2.0 and 2.4 eV. Semiconductors are in direct contact with electrolytes in darkness and light, they must have high chemical stability. Generally, the stability of corrosion resistance increases as the semiconductor band gap increases, but a larger band gap limits the absorption of visible light.

The important component of the PEC system is the semiconductor photoanode. In order to meet the effective splitting of water, some basic requirements must be met [27–30]:

1. Strong (visible) light absorption;
2. The long-term stability of the material in an aqueous solution and anti-photocorrosion during photoelectrolysis;
3. The band gap of the semiconductor material should be > 1.7 eV, to overpotential loss and the energy required during the WS process;
4. Suitable band edge position to catalyze the reduction and oxidation of water. The conduction band level of the material should be more negative than the H_2 generation energy level ($EH_2 = H_2O$), and the valence band level to generate effective H_2, should be more positive than the water oxidation level ($EO_2 = H_2O$);
5. Effectively separate/transport charge carriers in semiconductor materials to keep the WS reaction faster;
6. A lower charge transfer resistance is shown between the liquid and semiconductor interface;
7. The yield is abundant and cost-effective.

In the past few decades, different metal oxides (such as TiO_2, ZnO, WO_3, $BiVO_4$, Cu_2O, α-Fe_2O_3, etc.) and non-oxide (such as silicon, GaAs, CdS, GaP, Ta_3N_5, etc.) semiconductors have been applied extensively [31–33]. Metal oxides are generally considered suitable for a PEC to oxidize water and to generate molecular oxygen [34–39], mainly due to their general stability in aqueous solutions and relatively low cost. Figure 1.2 shows the band edges positions of different semiconductors in the normal hydrogen electrode serve as the standard for zero potential in the water oxidation/reduction process. Seeing the band position, semiconductors of TiO_2, CdSe, CdS, ZnO, and SiC meet the thermodynamic requirements for overall WS. Among those semiconductors, CdSe and CdS have lower band gap and suitable band edge positions. However, CdSe and CdS are inappropriate due to their instability in the water oxidation reaction and the anions of these materials are more easily oxidized than water, leading to CdS and CdSe being oxidatively degraded [40, 41]. ZnO meets the thermodynamic requirements for the WS reaction. However, it is difficult to get a well-organized nanostructure for ZnO, which makes the application of PEC WS limited. Among available semiconductor photocatalysts, TiO_2 has potential in PEC WS and is very suitable to serve as the photoelectrode for the PEC system [42–44].

1.3.1 TiO_2 photoanode

TiO_2 is an n-type semiconductor photocatalyst, mainly derived from the rutile titania photoanode made by Honda and Fujishima in 1972 [45]. TiO_2 is considered to be the most suitable in the application of water splitting with visible light and has a suitable energy band level, non-toxicity, and light stability. Currently, there are many studies to prepare synthetic nano-sized titanium dioxide. However, the TiO_2 larger band gap (anatase: 3.2 eV; rutile phase: 3.1 eV) limits its light absorption to the UV range only absorbing 5% of the solar spectrum, which reduces widespread use and leads to low efficiency of theoretical STH. Recently, many research works have taken the approach to combine TiO_2 with different cations or anions to extend the useful range to the visible light region to improve the overall absorption efficiency and maintain its good light stability and low cost [46]. So far, these methods such as doping [47–49], heat treatment [50], and chemical modification [51, 52] have been widely used for improving the PEC performance in TiO_2 materials.

In addition, surface plasmon resonance (SPR) has also been used in the photon-current efficiency (PCE) water electrolysis process, which extends the light absorption in the entire visible range of the solar spectrum [53, 54]. For example, the Au-doped TiO_2 nanowire electrode produced excellent photocurrent and improved photoactivity, which is attributed to the SPR excitation of Au [55]. Moreover, there have been important studies on Ag doping on TiO_2 electrodes. Ag nanoparticles act as electron absorbers in the effect of Ag SPR on photo-induced electron–hole pairs, thereby improving PEC performance [56, 57]. The use of other lower band gap semiconductor-loaded TiO_2 photoanode materials to produce heterojunctions is another way to trend visible light. The heterojunction material has an internal potential bias, which effectively promotes the separation and transport of excited holes and electrons, resulting in reduced charge carrier recombination. Recently, a heterojunction CdTe/TiO_2 photoelectrode has been developed, and the improvement of PEC efficiency is attributed to the optimization in Fermi level, band position, and conductivity of CdTe layer [58]. Moreover, TiO_2 nanotube arrays can be modified with Cu_2O semiconductors [59, 60].

1.3.2 Fe_2O_3 photoanode

Another photocatalyst for PEC WS with visible light reactivity is hematite [61–63]. Especially, α-Fe_2O_3 has more advantages than others. α-Fe_2O_3 has attracted attention due to the favorable position of the valence band. This material has high chemical inertness, low toxicity, and high yield. In addition, its band gap is about 1.9 to 2.3 eV, which allows visible light absorption and translates to the maximum theoretical STH efficiency. α-Fe_2O_3 maintains more positive proton reduction potential at the CB position, and has the ability to PEC oxidize water under an external bias. However, α-Fe_2O_3 has some disadvantages, including: (1) short carrier lifetime, resulting in a rapid combination of a large number of carriers; (2) low charge carrier (hole) mobility; (3) low water oxidation power leads to higher surface recombination rate. In order to solve these problems, atoms such as Sn, Ti, Zr, Si, and Nb have been effectively doped into the α-Fe_2O_3 photoanode [64–68], and α-Fe_2O_3 film doped with Si, in particular, can show excellent PEC behavior. In addition, it has been found that the modification of the cocatalyst, such as Co–Pi or FeOOH can accelerate the oxidation kinetics of water [69]. Finally, adding a thin metal oxide bottom/upper layer on α-Fe_2O_3 can significantly improve PEC performance. These layers will affect the passivation of the surface state and lead to an increase in the concentration and mobility of charge carriers [70].

1.3.3 $BiVO_4$ photoanode

$BiVO_4$ is also a suitable photoanode material for PEC WS [71–74]. The direct band gap of $BiVO_4$ is 2.4–2.5 eV and it is an n-type semiconductor (with a photocurrent of about 7.5 mA cm^{-2}), covering the entire visible light range of the solar spectrum, being alkaline with neutral friendly conditions, non-toxic and relatively cheap [75]. However, the slow electronic performance of $BiVO_4$ leads to low solar energy conversion efficiency, thereby limiting commercial use in PEC systems. Therefore, it is extremely important to incorporate effective and stable catalysts into photoactive semiconductor materials. There have been studies using ion doping [76–78], nanostructures [79], passivation layer or electrocatalyst for surface modification [80, 81], and synthesis [73] to solve the above problems. $BiVO_4$ achieves the maximum catalytic performance at a conversion efficiency of STH 8.1% through a double junction GaAs/InGaAsP photovoltaic (PV) device [82]. The PEC performance of $BiVO_4$ is significantly improved when loaded on the nanostructured WO_3 layer, mainly due to the synergistic reaction between $BiVO_4$ and WO_3 [83–85]. Different semiconductor combinations have been widely used, such as Si/TiO_2/$BiVO_4$, SnO_2/$BiVO_4$ and Ag_3PO_4/$BiVO_4$ [86–88], which have a significant improvement effect on the WS reaction. There have been studies on the modification of $BiVO_4$ with Fe_2O_3

nanoparticles, in which Fe_2O_3 is used as an effective carrier catalyst to catalyze the degradation of organic pollutants [89]. The functional of $BiVO_4$ photoanode is improved through the heterogeneity method with Fe_2O_3. Wang *et al* showed that electrolysis performance of PEC water increased by about 20 times [90] after Co_3O_4 deposited on $BiVO_4$.

1.3.4 Oxynitride photoanode

In recent years, various oxynitride photoanodes for PEC water oxidation have been established, including $LaTiO_2N$, $SrNbO_2N$, $ZnTaO_2N$, $BaNbO_2N$ [91–95]. Related semiconductor photoanodes modified with perovskite-based oxynitrides and appropriate co-catalysts have shown to be a new method for increasing PEC WS reaction [96, 97]. In recent years, low-cost nickel and cobalt-based oxide have been used in different fields [98, 99]. Although it has the ability to absorb visible light and chemical stability, the PEC activity of nitrogen oxides is affected by lower photon absorption, the high recombination rate of light-excited charge carriers, and OER power. To solve those limitations, an oxynitride photoanode can be combined with a co-catalyst material to promote the absorption of visible light photons. Currently, oxynitride materials like $LaTiO_2N/CoOx$, $BaTaO_2N/BaZrO_{3,}$and $BaNbO_2N$ [100–103] have been shown to absorb photons with the help of suitable sacrificial reagents. Especially, efforts have been made to develop low band gap semiconductor photoanodes with visible light active (<2 eV). Studies have shown that the photoanode band gap of $SrNbO_2N$ is 1.8 eV. Compared with RHE, their incident photon-current efficiency (IPCE) efficiency is 10% at 400 nm and 1.23 V [104]. Moreover, studies have also shown that the preparation of $LaTaO_2N$ photocatalyst materials has improved PEC performance in water oxidation reactions [105].

1.3.5 Noble metal and nanostuctrue photoanode

For the noble metal/TiO_2 nanocomposites, noble metals can generate other charge carriers for water oxidation. Studies have reported that under visible light irradiation, the presence of gold nanoparticles in the TiO_2 film enhances the water splitting of PEC by 66 times [106], which is mainly due to the increased photon absorption rate of TiO_2. Gao has reported that gold nanopillars can improve the photocatalytic activity on iron oxide [107]. Studies have shown that the implantation of noble metals (such as AuNP or AgNP) can significantly enhance the photocurrent density of TiO_2 and ZnO photoanodes.

Nano-material photoanodes are attractive in thermal electrochemical WS because they can change their bandwidth characteristics through structure and morphology. Since the larger surface area ratio, nanomaterials help separate charges and limit the recombination of electrons and holes. Crystalline nanomaterials exhibit better PEC properties, including the generation of photocurrent, stability, and HER. As the crystallinity of nanomaterials increases, the possibility of hole and electron recombination decreases, which will effectively increase the photocurrent. For nanostructures, one-dimensional nanostructures including TiO_2 nanotubes, nanowires of zinc oxide and cadmium sulfide, and carbon nanotubes are high-efficiency photoelectrodes for

PEC WS; two-dimensional nanostructures have a larger surface area. Compared with nanowires and nanorods, most of the visible light can be absorbed, thereby enhancing the HER; three-dimensional nanomaterials can accelerate the release of hydrogen and increase the photocurrent density.

Generally, bulk TiO_2 has more charge recombination. In order to inhibit recombination, TiO_2 nanotubes with a smaller band gap have been made to increase the activity of PEC. Nano-structured TiO_2 improves the PEC performance due to improved carrier transmission. α-Hematite has high stability in aqueous media and is resistant to light corrosion. α-Fe_2O_3 nanorods can provide a large number of electrons and help the carrier to transport between the electrode–electrolyte interface, thus improving the performance of PEC. The loading of metallic platinum nanoparticles can enhance the HER on the surface of a semiconductor photocatalyst. Therefore, the development of a nanoparticle cocatalyst is very important, as it can improve the overall splitting efficiency of PEC water. For example, Pt and Rh can be used as good cocatalysts for HER, while IrO_2 can be used as an OER cocatalyst.

1.4 Factors of PEC water splitting

1.4.1 Crystallinity and surface area

The rate of photocatalytic WS depends on the surface area and crystallinity of the photocatalyst. Generally, for a photocatalyst with a large surface area, the photocatalytic activity is high. The water molecules on the surface are increased with the specific surface area, in which a large amount of matrix surrounds and reacts with photogenerated electron–hole pairs. In addition, a higher surface area may also induce the generation of more electron–hole pairs. When the particle size is reduced, the distance of the electrons and holes transfer to the reaction sites of the surface is shortened, which leads to a decrease in their recombination rate, thereby increasing the photocatalytic activity. When the recombination rate of electron/hole pair is decreased and the number of water molecules surrounding them increases, the reaction rate is effectively increased. However, the defects and grain boundaries increase with reducing the particle size, which will increase the recombination rate of the electron–hole pair and further reduce photoactivity. Since the catalyst surface is considered to be a defect site of the crystal, charge carrier recombination may occur there. Therefore, an increase in the electron–hole recombination rate, higher surface area, or lower crystallinity of semiconductor photocatalyst will result in a lower rate in photocatalytic activity. In other words, crystallinity and particle size are two important factors that control the WS reaction of the PEC. When the surface reaction rate of the photocatalyst is greater than the recombination rate, a photocatalyst with a larger surface area is better. In contrast, when the recombination rate is dominant, a photocatalyst with a lower surface area and higher crystallinity is advantageous. There have been some studies reporting the optimal crystallinity of the photocatalyst to obtain the maximum hydrogen photocatalytic yield [106, 107].

1.4.2 Photoanode material

Materials can be divided into stable, abundant, and low-activity materials (called earth-abundant materials) and unstable, rare, and highly active materials (called high-efficiency materials). The earth-abundant materials are stable oxides such as TiO_2, Fe_2O_3, Cu_2O, ZnO, and WO_3. The high-efficiency materials belong to rare materials with relatively high cost, such as GaAs and CdSe. However, instability and corrosion mean that high-efficiency materials must have anti-corrosion protection. Recently, the use of atomic deposition of TiO_2 has achieved certain results in material protection materials, which can achieve effective corrosion protection with minimal loss. In addition, the IPCE of earth-rich materials is relatively low. When the system is operated with zero bias, it can be improved by doping. For example, the STH of $BiVO_4$ doped with Mo or W is higher than for the original [108–110] to achieve a commercially feasible degree in the future.

1.4.3 Cell type and radiation time

Generally, we can consider the following conditions to obtain higher efficiency: (1) the electrocatalyst is used for driving the reactions of HER and OER; (2) photovoltaic bias (PV) is used with additional driving force; (3) two/three junction is used to generate potential driving forces; (4) use of high-efficiency materials instead of earth-abundant materials.

The IPCE of high-efficiency materials is higher than that of the Earth-abundant materials, so one needs to consider the trade-off between cost and efficiency. In addition, it is worth noting that the STH conversion rate of 20%–25% has not been reached for PEC hydrogen generation. In order to break through this problem, the combination of a double or triple system is required to take the efficiency to more than 20%, and the efficiency of high-efficiency catalysts can reach 28.3%. For the three-junction system, part of the disadvantage is that it takes six photons to produce a hydrogen molecule, so the overall hydrogen production efficiency may be limited to 25.4% [110]. The two-junction or three-junction system can actually achieve the required STH efficiency. In addition, the H_2 and O_2 produced by PEC catalytic WS increase with light irradiation time. In addition to measuring the reaction rate, the photocatalytic activity at a fixed time can also be tested to obtain the stability of the catalyst under the reaction conditions.

1.5 Conclusion

The PEC WS technology has great potential to produce hydrogen. Hydrogen can be used as an energy carrier and does not cause environmental pollution after combustion. This chapter has reviewed the basic principles of PEC WS, discusses various photoanode materials and possible challenges of WS. Depending on the principle, for successful WS through a semiconductor photoanode, the band gap position must be consistent with the oxidation and reduction potential of water, and then the light-induced charge carriers are used for the HER and OER reactions, respectively. The most appropriate photocatalyst for PEC is TiO_2. It is inexpensive and chemically stable but has a band gap limitation in the visible light region which is not suitable for visible light absorption. Other materials such as Fe_2O_3 and $BiVO_4$ have relatively wide visible light absorption, but fast recombination of light-induced charge carriers and the slow kinetics of water oxidation lead to failure to reach the maximum photocurrent. Therefore, we mentioned surface modification or doping through noble metal nanoparticles to improve it. This is the primary mission of semiconductor photoanode breakthrough to achieve adequate light absorption and charge separation. The development of the high active photoanode materials will be necessary work in the future.

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