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Novel Semiconductors for Energy Production via Electrochemical Processes

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Abstract:

This mini review summarizes the most recent advances in the field of photoactive materials employed in photoelectrochemical energy conversion, including electricity generation and hydrogen production. This work provides a brief narrative of some novel nanostructured materials employed as photoanodes in photoelectrochemical systems along with a short description of their working principles. It highlights the latest progress in the field and has the ambition to be a short and useful guide for young and experienced researchers that are interested in.

Keywords: nanostructured semiconductors, photoanodes, photoelectrochemical cells,

electricity generation, hydrogen production

Introduction

Photoelectrochemical cells are on the forefront of the research concerning the production of electrical and chemical energy from renewable resources. Designated by the seminal works of Fujishima and Honda[1] and later of O'Regan and Grätzel[2], photoelectrochemical devices may be classified accordingly in two categories, namely "photosynthetic" and "regenerative" solar cells. The former is associated with the hydrogen produced during photoinduced water splitting procedures while the latter follow another progress line that starts with Dye Sensitized Solar Cells (DCCSs) and ends up with the recently developed Perovskite Solar Cells. Whether water-soluble organic pollutants are added within a photosynthetic device, what we get is a Photocatalytic Fuel Cell (PFC) or simply a Photofuel Cell. In general, the term Photoelectrocatalytic Cell (PECs) is usually employed to describe both photosynthetic and photofuel cells. An archetypal PEC consists of a light-sensitive semiconductor as the photoanode, a strongly reductive catalyst as the cathode and a usually aqueous electrolyte bringing in electric contact the corresponding electrodes. In photo fuel cells, the electrolyte may contain organic pollutants which while being consumed by the photoanode, enhance the efficiency of the PEC, offering a double environmental benefit, clean energy production along with environmental protection from hazardous substances[3].

The operation of a PEC (Fig. 1a) briefly can be described as follows: The photoanode, absorbs sunlight and electron-hole pairs are created. The electrons flow through an external circuit to the cathode while the holes take part in oxidation reactions, reacting with water/water-soluble pollutants. The oxidation reactions depend on the nature of pollutants and on the pH of the electrolyte. The reduction half reactions at the cathode depend on the pH and the presence or the absence of oxygen. When a PEC runs in an aerated environment only electricity is produced, while in inert atmosphere both hydrogen and electricity are delivered.

Some popular nanostructured materials incorporated in the photoanode comprise TiO_2, $BiVO_4$, WO_3 and Fe_2O_3. The most significant characteristic of an effective photoanode towards hydrogen production is the level of its energy bands against the water redox potentials, Figure 1.

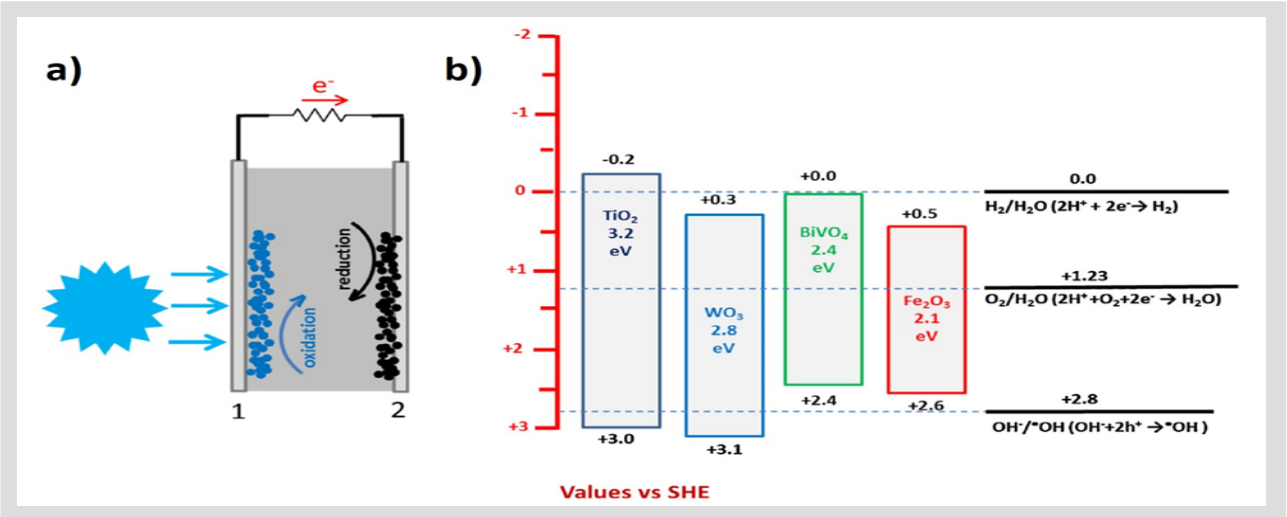

***Figure 1**. a) Schematic illustration of a PEC device consisting of an irradiated photoanode and a cathode, both immersed in an electrolyte. Oxidation reactions take part at the anode while reduction reactions take part at the cathode. The electrons flow through the external circuit. b) Energy levels of some common photocatalysts in comparison to redox potentials of the reactions taking part at the cathode. The redox potential of the production of hydroxyl radicals is also shown. Reprinted with permission by Ref.[3].*

The driving force promotes the transfer of the electron from the anode to the cathode is proportional to the energy difference between the Fermi level of the photocatalyst and the redox potential of the corresponding reactions. As shown in Fig.1b only titania has theoretically the appropriate conduction band (CB) level value in order to provoke hydrogen production at the cathode. However, due to energy losses during operation, hydrogen production is possible only under additional external bias. On the other hand, in an aerated environment all the depicted materials (TiO_2, $BiVO_4$, WO_3, Fe_2O_3) possess a CB that can reduce oxygen leading to free operation of the cell that produces electric power. Moreover, TiO_2 and WO_3 in Fig. 1b have suitably located valence bands (VB) which favor oxidation reactions like the formation of hydroxyl radicals and may act as strong oxidizers against any organic pollutant. Many studies focus on the semiconductors bang gap engineering so that the light-harvesting properties are improved. Recent literature works deal with tungsten trioxide (WO_3), which justifies a broader application field, including electrochromic systems, energy conversion devices, and gas sensors. WO_3 is a non-toxic semiconductor with high chemical stability and an ideal band gap (Eg=2.4–2.8 eV). Other visible-light activated (VLA) oxide catalysts, such as Cu_2O (Eg=2.17 eV), Fe_2O_3 (Eg=2.2 eV), and $BiVO_4$ (Eg=2.4 eV), have been investigated because of their Interesting optoelectronic properties.

Titanium dioxide (TiO_2)

Titanium dioxide in the form of mesoporous nanoparticulated anatase structural modification is the unambiguous most investigated and most effective photocatalyst,[4,5,6]although exceptional 1D nanostructures[7] have been also proposed as alternatives. Titania which can be deposited by a variety of methods (spin coating, spray pyrolysis, doctor blade), is a very effective photocatalyst and a huge number of papers are published every year on its photoinduced properties and related photocatalytic applications[8]. However popular, there are some disadvantages, namely low conductivity and extended defects that provoke electron-hole recombination. Thus, metal doping[9], graphene introduction[10] and coupling with other semiconductors[11] have been proposed to surpass these drawbacks.

Tungsten Trioxide (WO_3)

WO_3 is also a very popular n-type semiconductor. It has a diffusion length (150nm), in comparison to titania (10^4 nm) and the location of its energy band render it suitable for water oxidation. However, in order to be used for hydrogen production, an extra bias is necessary since its CB is located at 2.8-3.1eV vs SHE. The expected Solar-to-Hydrogen Efficiency (SHE)[12] for a WO_3 photocatalyst is 4.8%, higher than titania's (2.2%). WO_3 is stable only in low pH environments, while oxygen evolution takes place in a very slow rate, thus WO_3 is often coupled with oxygen evolution catalysts. Like titania it is more effective in the presence of pollutants. Shao et al.[13] presented the fabrication of a WO_3 photoanode with tunable oxygen vacancy densities in the bulk and on the surface using a two-step flame heating approach.

Using this WO_3 photoanode as a model, it was found that both the conductivity and trapping state density increases with the oxygen vacancy density in the bulk, therefore observing a volcano-like effect on the charge separation/transport kinetics. By tuning the oxygen vacancy density on the surface and in the bulk simultaneously, the PEC performance of the WO_3 photoanode was increased by circa 10 times[13]. Moreover, the WO_3 photoanode exhibited good photostability in both acid and neutral solution.[13] Similar works that clarify the influence of oxygen vacancies in the bulk and on the surface, respectively, on the PEC performance of WO_3 photoanodes, can be further performed to guide the optimization of other PEC devices through delicate oxygen vacancy engineering.

Bismuth Vanadate ($BiVO_4$)

$BiVO_4$ has been considered as a promising material for photoelectrochemical (PEC) hydrogen production. $BiVO_4$ has a 2.4eV bandgap with a theoretical maximum SHE of 9.1%. However, it is characterized by low charge mobility and extended electron-hole recombination rates. Like other counterparts, it is usually doped with metals to get its electronic properties improved. [14] It is also characterized by slow oxygen evolution kinetics, thus appropriate co-catalysts are used in order to decrease the corresponding overpotentials. To improve the charge transport performance of $BiVO_4$ photoanodes, functional nanostructured $BiVO_4$ array photoanodes were developed[15]. Wang et. al. proposed a novel and simple way to develop high-quality $BiVO_4$ array photoanodes via an in situ transformation strategy ($WO_3 \rightarrow Bi_2WO_6 \rightarrow BiVO_4$) that was designed to fabricate a nanoporous $BiVO_4$ nanoflake array (NFA) film, where the nanoflakes were composed of wormlike-shaped particles. The as-prepared $BiVO_4$ NFA photoanodes exhibited excellent visible-light PEC performance. At 1.23 V vs. RHE, photocurrent density values as high as 1.0 mA cm^{-2} were reached under visible light illumination, without the presence of any co-catalyst.

Hematite (a-Fe_2O_3)

Hematite is a promising photocatalyst, characterized by a low band gap that enables enhanced visible light absorption. It is readily synthesized and is non-toxic and stable in a range of pH values. Interestingly, the expected STH efficiency of a-Fe_2O_3 exceeds 15%, however what we really get is much lower due to low conductivity and high charge recombination rates. Like most analogous semiconductors, the hematite photoanode is suitable for water oxidation but insufficient for water reduction, thus an extra bias is necessary for hydrogen production. The material may be deposited by chemical vapor deposition, electrodeposition, and hydrothermal treatment. However, metal doping is often employed in order to improve its performance by decreasing recombination rate and increase photocurrent. Singh et al[16] prepared hematite (α-Fe_2O_3) thin films onto an indium-doped tin oxide (ITO) substrate by e-beam evaporation of Fe, followed by air annealing at 350 and 500 °C. The samples annealed at 500 °C show an in-situ diffusion of indium from the ITO substrate to the surface of α-Fe_2O_3, where it acts as a dopant and enhances the photoelectrochemical properties of hematite. The corresponding in situ diffused α-Fe_2O_3 photoanode exhibits an improved photoelectrochemical performance, with a photocurrent density of 145 µAcm^{-2} at 1.23 VRHE, compared to 37 µA cm^{-2} for the photoanode prepared at 350°C. In addition, the photocurrent onset potential also decreases from 1.13 V to 1.09 V, resulting to devices with improved performance in solar water splitting.

Heterostructures

The development of heterojunctions is an effective strategy to improve efficiency and enhance charge separation.[17,18] When two photocatalytic materials are coupled, an internal electric field is typically created at the junction. Many studies have reported that the induced electric field at the interface can promote charge separation by driving electron–hole pairs to move in opposite directions, thus leading to a lower recombination rate. Zhang et al.[19] demonstrated that PEC water-splitting efficiency of the WO_3/Cu_2O heterojunction photoelectrode significantly increased by 3.51 times than that of a single WO_3 photoanode. The desirable morphology and film quality can simply be modified by varying synthesis parameters, such as growth rate and annealing temperatures. S. Phiankoh et al.[20] also investigated the PEC performance of $WO_3/BiVO_4$ heterojunction thin film photoanodes and the optimization of thermal treatment processes, namely pre-annealing and annealing steps. They demonstrated that the thermal treatment strongly affected the structure and morphology of the WO_3/ $BiVO_4$ heterojunction thin-film photoanodes prepared by solution-based processing using a spin-coating deposition technique. The authors reported that pre-annealing optimization results in large surface area and highly porous films with improved crystallinity, uniformity and optical absorbance, thus leading to an enhancement of the amount of photogenerated charge carriers.

Conclusion

In this review, we briefly summarized some of the most intriguing UV and visible light activated photocatalysts for photoelectrocatalytic applications. Since titania has been exhaustingly investigated as a photoanode in relevant applications, $BiVO_4$, WO_3 and Fe_2O_3 are also very promising materials that deserve further investigation especially in the presence of organic pollutants acting as extra electron donors. Since sole semiconductors are insufficient for effective water splitting, coupling of two or more semiconductors is a perspective worth to be further explored.

Conflict of Interest

The authors declare no conflict of interest.

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