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Invited Review

Chemically modified nanostructures for photoelectrochemical water splitting

Gongming Wang[a], Yichuan Ling[a], Hanyu Wang[a], Xihong Lu[a,b], Yat Li[a,*]

[a] Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, United States
[b] KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

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ABSTRACT

Hydrogen gas is chemical fuel with high energy density, and represents a clean, renewable and carbon-free burning fuel, which has the potential to solve the more and more urgent energy crisis in today's society. Inspired by natural photosynthesis, artificial photosynthesis to generate hydrogen energy has attracted a lot of attentions in the field of chemistry, physics and material. Photoelectrochemical water splitting based on semiconductors represents a green and low cost method to generate hydrogen fuel. However, solar to hydrogen conversion efficiency is quite low, due to some intrinsic limitations such as bandgap, diffusion distance, carrier lifetime and photostability of semiconductors. Although nanostructured photoelectrodes improve the photoelectrochemical water splitting performance to some extent, by increasing electrolyte accessible area and shortening minority carrier diffusion distance, nanostructure engineering cannot change their intrinsic electronic properties. More importantly, recent development in chemically modification of nanostructured electrodes, including surface modification with catalyst and plasmonic metallic structures, element doping and incorporation of functional heterojunctions, have led to significant enhancements in the efficiencies of charge separation, transport, collection and solar energy harvesting. In this review, we provide an overview of the recent process in photoelectrochemical water splitting by using chemically modified nanostructured photoelectrodes. Finally, we also discuss the current challenges and future opportunities in the area of photoelectrochemical water splitting.

Contents

* Corresponding author. Tel.: +1 8314591952.
E-mail address: yli@chemistry.ucsc.edu (Y. Li).

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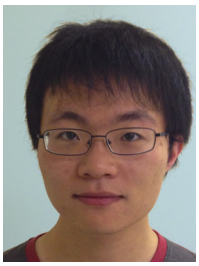
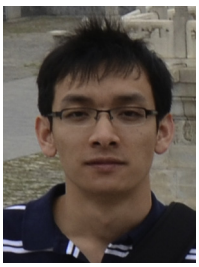
Gongming Wang received his B.S. degree in chemistry from the University of Science & Technology of China in 2008. He joined Prof. Yat Li's group at University of California, Santa Cruz in the fall of 2008 and received his PhD degree in chemistry in 2013. His research focuses on chemically modified nanostructures for energy conversion and storage.

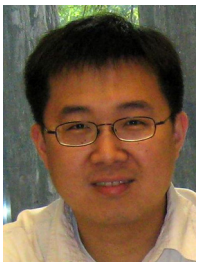


Yichuan Ling is currently a 5th year chemistry PhD student at University of California, Santa Cruz, under the supervision of Prof. Yat Li. He received his B.S. degree in chemistry from Fudan University, China in 2009. His research focuses on the synthesis of hematites and III-V semiconductor nanomaterials and investigates their applications for solar energy conversion.

Hanyu Wang received her B.E. degree in chemical engineering and technology from Qingdao University, and her M.S. degree in chemistry from Shandong University. She is a 4th year chemistry PhD student in Prof. Yat Li's group at University of California, Santa Cruz. Her research focuses on the development of high performance nanostructured metal oxide electrodes for photoelectrochemical and microbial photoelectrochemical systems.



Xihong received his B.S. degree in applied chemistry from Sun Yat-sen University in 2008, and then earned his doctor degree in 2013 under the guidance of Prof. Yexiang Tong from Sun Yat-sen University. During 2011–2013, he was a visiting graduate student in Prof. Yat Li's lab at University of California, Santa Cruz. He is now a lecturer in the school of chemistry and chemical engineering at Sun Yat-sen University. His research interests center on the development of nanostructured materials for the application of supercapacitors, photocatalyst and functional absorber materials.



Yat Li received his B.S. and PhD in chemistry from the University of Hong Kong. He was a postdoctoral research fellow at Harvard University, from 2003 to 2007, under the supervision of Prof. Charles M. Lieber. He joined UC Santa Cruz in 2007 and he is now an associate professor of chemistry at UC Santa Cruz. His research focuses on the design and synthesis of semiconductor nanostructures, investigation of their fundamental properties and exploration of their potentials for solar energy conversion and storage.

1. Introduction to photoelectrochemical water splitting

With the ever-growing of global population, there is a continuously increasing energy demand. Renewable solar energy is believed to be a potential solution to energy sustainability. However, the intermittent solar irradiation poses a new challenge for solar energy utilization. To obtain continuous and stable power supply, it requires efficient and cost effective methods to store the excess energy generated in daytime. One of the most attractive ways is storing solar energy in the form of chemical fuels, such as alcohols and hydrogen gas. Inspired by natural photosynthesis, research efforts have been devoted to mimic this process by using photoactive materials. One of the major directions is hydrogen generation via photoelectrochemical (PEC) water splitting.

1.1. Principle of PEC water splitting

Water cannot be directly decomposed by light, because it is transparent to visible light, but only with the irradiation wavelength shorter than 190 nm (deep ultraviolet light) [1]. For electrochemical water electrolysis, a minimum voltage of 1.23 V is required to split water. This voltage is equivalent to the energy irradiance with a wavelength of ~1000 nm. Therefore, if solar energy can be effectively used in the electrochemical system, water splitting can be achieved under visible light irradiation. The first artificial photosynthesis of generating H_2 by water splitting was demonstrated by Honda and Fujishima in 1972, using semiconductor titanium dioxide (TiO_2) as photoanode in a PEC cell [1]. Fig. 1 shows the configuration of PEC cell with *n*-type semiconductor TiO_2 photoanode and a Pt counter electrode. When the semiconductor is contacted with the electrolyte, the charge transfer occurs at the interface between semiconductor and electrolyte, and leading to surface charging. As a result, electronic bands bend upward. The potential barrier created by the band bending is known as Helmholtz barrier, which depends on the nature of the aqueous electrolyte and the semiconductor electrode [2]. This interfacial potential barrier could facilitate the separation of electron and hole pairs, which can be photogenerated when TiO_2 photoelectrode is irradiated with light with photon energy larger than or equal to its band gap. The photoexcited electrons transfer to Pt counter electrode and reduce water to generate H_2, while holes diffuse to the surface of TiO_2 and oxidize water to form O_2 [2–5]. The reaction equations on each electrode are shown in the following:

$$\text{Photoanode}: \quad H_2O + 2h^+ \rightarrow 2H^+ + 1/2O_2 \quad E^\circ_{ox} = -1.23\,V$$

$$\text{Cathode}: \quad 2H^+ + 2e^- \rightarrow H_2 \quad E^\circ_{red} = 0\,V$$

According to the Nernst equation, water electrolysis requires a minimum energy of 1.23 V. To gain the required electrochemical energy, the photoelectrode must absorb light with photon energy larger than 1.23 eV. Fig. 2 shows the solar energy spectrum plot as a function of number of photons and radiation energy [2]. Theoretically, the minimum energy required for PEC water splitting is 1.23 eV. However, in practice, photons with energy larger than the theoretical limit is needed due to the energy loss during PEC water splitting. The energy losses include electron-hole recombination, voltage losses at the contacts, and the potential loss due to

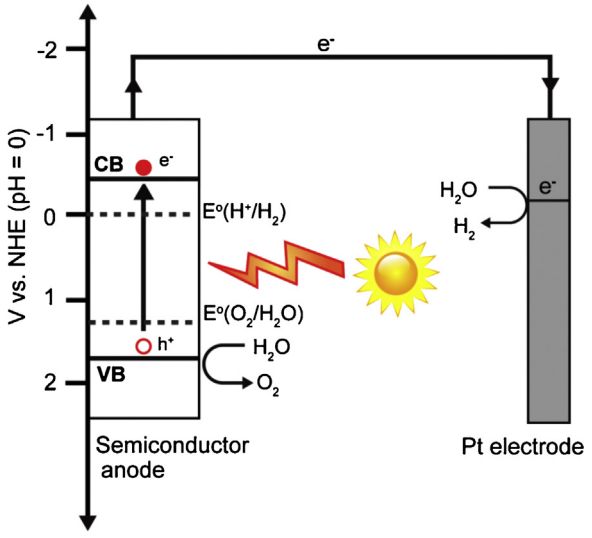


Fig. 1. Photoelectrochemical water splitting cell based on *n*-type semiconductor TiO_2 photoanode.
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