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Review

Prospects of electrochemically synthesized hematite photoanodes for photoelectrochemical water splitting: A review

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ABSTRACT

Hematite (α-Fe_2O_3) is found to be one of the most promising photoanode materials used for the application in photoelectrochemical (PEC) water splitting due to its narrow band gap energy of 2.1 eV, which is capable to harness approximately 40% of the incident solar light. This paper reviews the state-of-the-art progress of the electrochemically synthesized pristine hematite photoanodes for PEC water splitting. The fundamental principles and mechanisms of anodic electrodeposition, metal anodization, cathodic electrodeposition and potential cycling/pulsed electrodeposition are elucidated in detail. Besides, the influence of electrodeposition and annealing treatment conditions are systematically reviewed; for examples, electrolyte precursor composition, temperature and pH, electrode substrate, applied potential, deposition time as well as annealing temperature, duration and atmosphere. Furthermore, the surface and interfacial modifications of hematite-based nanostructured photoanodes, including elemental doping, surface treatment and heterojunctions are elaborated and appraised. This review paper is concluded with a summary and some future prospects on the challenges and research direction in this cutting-edge research hotspot. It is anticipated that the present review can act as a guiding blueprint and providing design principles to the scientists and engineers on the advancement of hematite photoanodes in PEC water splitting to resolve the current energy- and environmental-related concerns.

Contents

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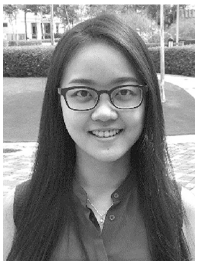
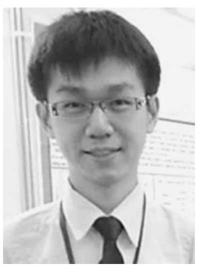


Yi Wen Phuan received her BEng and Ph.D. degrees in Chemical Engineering from Monash University in 2013 and 2017, respectively. Her recent research focuses on design and development of nanostructured semiconductor photocatalysts system for energy and environmental applications through the photoelectrochemical water splitting process.



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1. Introduction

The building of a sustainable society will necessitate reduction in the amount of environmental pollution and dependency on fossil fuels. At present, over 80% of the world's energy demand is derived from fossil fuels which will eventually lead to their foreseeable depletion [1]. The vast consumption of fossil fuels will cause global climate change and environmental deterioration. All these issues have become the main drivers in accelerating the transition from the utilization of exhaustible fossil fuels to clean and renewable energy sources toward achieving sustainability without compromising the environmental. Recently, the utilization of solar energy has gained a lot of attention since it is the largest renewable energy source on Earth [2–9]. If the energy from the sun can be efficiently harvested, it will provide adequate power for all future energy requirements [10]. Amid the wide availability of various solar energy conversion options, photoelectrochemical (PEC) water splitting process is considered to be one of the most promising options in mimicking the natural photosynthesis process in plants that reorganizes electrons in water (H_2O) and carbon dioxide (CO_2) to store solar energy in the form of carbohydrates [11–17]. Notably, it uses the inexhaustible solar energy and converts the electromagnetic energy directly into chemical energy in the form of molecular bonds, such as hydrogen (H_2). H_2 is regarded as a clean and renewable energy fuel as well as an important future energy carrier where the oxidation of H_2 produces energy with water as the only by-product. In view of this, PEC process is an attractive and excellent technological solution to surmount the present energy- and environmental-related issues encountered by the contemporary society [18–23].

The PEC effect was first discovered by the French scientist Edmond Becquerel in 1839 [24]. In the 1960s, Russian and Japanese research groups began to study zinc oxide (ZnO) and titanium dioxide (TiO_2) for heterogeneous photooxidation [25]. Later on, interests were reignited after the pioneering studies by two Japanese researchers, Fujishima and Honda on photocatalytic water splitting using TiO_2 under near-ultraviolet (UV) light in 1972 [26]. Four years after, Hardee and Bard constructed iron oxide (Fe_2O_3) photoanode via chemical vapor deposition (CVD) method [27] and over the next decade, numerous articles were published on the fabrication of Fe_2O_3 by different synthesis methods. Since then, a large array of semiconductor photocatalysts including TiO_2 [28–37], ZnO [38–40], Fe_2O_3 [41–44], CdS [45–47], $ZnIn_2S_4$ [48–50], WO_3 [51–55], Cu_2O [56–58], $BiVO_4$ [59–62], TaON [63,64], g-C_3N_4 [65–68], metal-organic-framework [69–71] and combinations thereof have been extensively investigated. To date, however, no single semiconductor photocatalyst can fulfil the essential and desirable requirements in achieving remarkable PEC performance, such as narrow band gap energy for wider spectral range of light absorption, conduction band (CB) and valance band (VB) energies that straddle the water redox potentials, high solar-to-hydrogen (STH) efficiency, high stability and durability in aqueous environment as well as affordability [11,72].

Among the various semiconductor photocatalysts, TiO_2 is the most widely used and well-known photoanode material for PEC application. Nevertheless, the major drawback of TiO_2 is that it absorbs only the UV light spectrum ($\lambda \leq 380$ nm) owing to its relatively wide band gap of 3.2 eV. Alternatively, WO_3 is a stable and inexpensive semiconductor metal oxide that can be used as a photoanode material in the PEC process. However, the unfavorable position of the CB edge of WO_3 limits its ability to reduce hydro-