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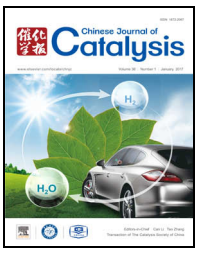

Minireview

Latest progress in hydrogen production from solar water splitting via photocatalysis, photoelectrochemical, and photovoltaic-photoelectrochemical solutions

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ABSTRACT

Hydrogen production via solar water splitting is regarded as one of the most promising ways to utilize solar energy and has attracted more and more attention. Great progress has been made on photocatalytic water splitting for hydrogen production in the past few years. This review summarizes the very recent progress (mainly in the last 2–3 years) on three major types of solar hydrogen production systems: particulate photocatalysis (PC) systems, photoelectrochemical (PEC) systems, and photovoltaic-photoelectrochemical (PV-PEC) hybrid systems. The solar-to-hydrogen (STH) conversion efficiency of PC systems has recently exceeded 1.0% using a $SrTiO_3$:La,Rh/Au/$BiVO_4$:Mo photocatalyst, 2.5% for PEC water splitting on a tantalum nitride photoanode, and reached 22.4% for PV-PEC water splitting using a multi-junction GaInP/GaAs/Ge cell and Ni electrode hybrid system. The advantages and disadvantages of these systems for hydrogen production via solar water splitting, especially for their potential demonstration and application in the future, are briefly described and discussed. Finally, the challenges and opportunities for solar water splitting solutions are also forecasted.

1. Introduction

The world's energy supply is based predominantly on the use of non-renewable energy resources such as oil, coal, and natural gas. A sustainable, scalable source of energy-dense chemical fuel is urgently needed to ensure the security of our energy supply for future generations [1,2]. Solar energy is the only renewable energy source of sufficient scale to replace fossil fuels and meet rising environmental demand [3,4]. Hydrogen is the cleanest energy with many potential applications, including the powering of nonpolluting vehicles, fuel cells, domestic heating systems, and aircraft [5–7]. Additionally, the use of hydrogen as an energy carrier is a long-term option for reducing worldwide CO_2 emissions via the hydrogenation of CO_2 to obtain high-value hydrocarbons [8–10]. Therefore, using solar energy to produce hydrogen by photocatalytic water splitting is one of the most promising ways to harness its power.

2. Mechanism of photocatalytic water splitting on a semiconductor-based photocatalyst

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The water splitting reaction ($H_2O \rightarrow 1/2O_2 + H_2$) is an thermodynamical uphill reaction with a net Gibbs free energy of 237 kJ/mol. Since the work by Fujishima and Honda [11] using rutile TiO_2 anode coupled with a platinum cathode for photoelectrochemical water splitting, extensive efforts have been made to construct efficient photocatalyst systems for solar energy utilization. Generally, the overall photocatalytic water splitting reaction on semiconductor-based photocatalysts involves three major steps: (1) electrons and holes are generated inside semiconductor particles by band-gap excitation, (2) the photogenerated electrons and holes are separated and transferred to the surface of the semiconductor, and (3) the photogenerated electrons and holes are trapped by surface active sites (reduction and oxidation co-catalysts) and consumed by catalytic water reduction and oxidation reactions (Fig. 1) [12–15]. The whole process spans more than 10 time orders from the absorption of light for the charge carrier generation to the surface catalytic reactions that produce gas, which is why photocatalytic water splitting is so challenging. Notably, the recombination of photoexcited carriers generally occurs on a very fast timescale alongside these reactions. Therefore, charge separation in the photocatalyst particles and the redox reactions on their surface must proceed within the lifetimes of the photoexcited carriers for successful water splitting [16]. Many useful strategies have been investigated for improving charge separation efficiency in both PC and PEC systems, e.g., constructing a heterojunction at the interfaces of different photocatalysts to form a built-in electronic field that provides a driving force for charge separation [17,18]. Such “junction” strategy can also be successfully introduced between different crystalline phases of the same photocatalyst (e.g., anatase and rutile phase TiO_2, α- and β-phase Ga_2O_3), named "phase junction" strategy [19,20]. For single photocatalysts without "junctions", morphology engineering, spatial charge separation between different exposed facets of semiconductor crystals, and surface modification by proper co-catalysts have been demonstrated to be useful strategies for improving photocatalytic performance [15,21,22].

3. General solutions for hydrogen production via solar water splitting

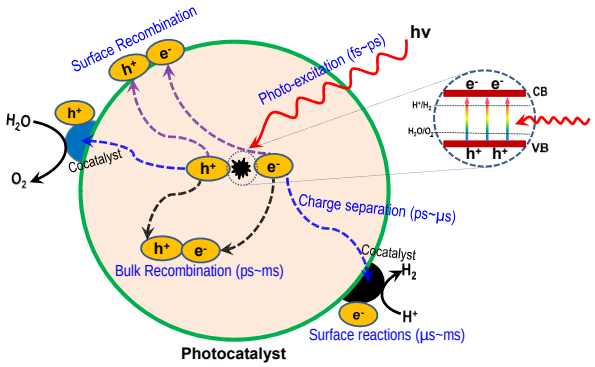

Fig. 1. The mechanism of photocatalytic water splitting on semiconductor-based photocatalyst.

Widely-used solutions for solar hydrogen production mainly fall into three categories: particulate photocatalyst (PC) systems, photoelectrochemical (PEC) systems, and photovoltaic-photoelectrochemical (PV-PEC) hybrid systems (Fig. 2). In PC systems, which are the simplest and lowest cost for potential scalable solar hydrogen production, photocatalyst powders are dispersed in water for hydrogen production under light irradiation. However, the necessity of H_2/O_2 gas separation and an enclosed reaction system on a large-scale are disadvantages in PC water splitting processes. The molecular sieving effect of microporous membranes has shown promise for the safe separation of the mixture of H_2 and O_2 gas. Great progress has been achieved in gas separation by zeolite membranes, and some reviews have highlighted the recent advances in both fundamental science and potential industrial applications [23–25]. The H_2/O_2 mixture produced in PC systems may be separated by molecular sieving based on the different kinetic diameters of the two gases (H_2, 2.9 Å; O_2, 3.5 Å). In photoelectrochemical systems, the photocatalysts must first be prepared on conductive substrates as electrodes and a small additional bias applied for water splitting. To make a PEC cell work, one or both of the electrodes should be a photoactive semiconductor, in which a space-charge layer forms at the semiconductor/liquid junction. Upon irradiation, photogenerated carriers are separated by the space-charge field and the minority carriers (holes for an n-type photoanode and electrons for a p-type photocathode) travel to the semiconductor-liquid interface for reaction [26]. There is no need for gas separation in PEC water splitting systems because the production of H_2 and O_2 is spatially separated at different electrode sides. PV-PEC hybrid system for hydrogen production is based on the coupling of highly efficient photovoltaic solar cells and with water electrolysis. PV-PEC systems have many advantages for hydrogen production compared with PEC systems if cost is not a major consideration. For example, for PEC systems the obstacles are a lack of efficient light absorber (for reasonable solar conversion efficiency, the band gap must be less than 2.0 eV), the corrosion of the semiconductor (thermodynamically, the most useful semiconductors are photochemically unstable in water), and the energetics (the difficulty of matching the semiconductor band-edge energies to the H_2 and O_2 evolution reactions) [27,28], all of which are not present for PV-PEC water splitting system. For the hydrogen production via solar water splitting, some latest reviews focusing on materials designing, engineering and energy evaluation have been comprehensively summarized [29–32]. In this mini-

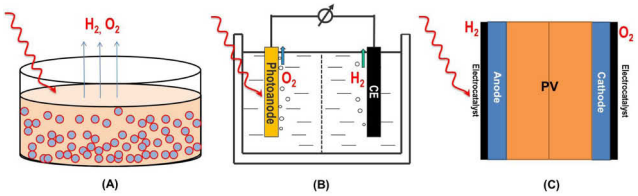

Fig. 2. The solutions for solar hydrogen via water splitting. (A) Particulate photocatalytic (PC) water splitting system, (B) photoelectrochemical (PEC) water splitting system and (C) photovoltaic-photoelectrochemical hybrid (PV-PEC) system.