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Review

Photochemical splitting of water for hydrogen production by photocatalysis: A review

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ABSTRACT

Hydrogen production from water using a catalyst and solar energy is an ideal future fuel source. The search for suitable semiconductors as photocatalysts for water splitting into molecular hydrogen and oxygen has been considered to be an urgent subject for our daily life. In this review, we aim to focus on the research efforts that have been made so far for H_2 generation from water splitting by UV and visible light-driven photocatalysis. A number of synthetic modification methods for adapting the electronic structure to enhance the charge separation in the photocatalyst materials are discussed. Sacrificial reagents and electron mediators for the overall water splitting are also reviewed. The quantum efficiency of photocatalyst materials upon visible and UV illumination will be reviewed, summarized and discussed.

Contents

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1. Introduction

Photocatalytic water splitting into H_2 and O_2 using semiconducting catalysts has received much attention due to the potential of this technology, as well as the great economic and environmental interest for the production of the clean fuel H_2 from water using solar energy. Fujishima and Honda demonstrated the potential of TiO_2 semiconductor materials to split water into H_2 and O_2 [1,2]. Their work triggered the development of semiconductor photocatalysis for a wide range of environmental and energy applications [1,2]. The photocatalytic activity of conventional metal-oxide photocatalysts for the overall water splitting is known to be heavily dependent on the crystallinity and the particle size of the material, as determined by the preparation conditions [3–5]. During the past 40 years, various photocatalyst materials have been developed to split water into H_2 and O_2 under UV and visible light illumination. The direct splitting of water using a particulate photocatalyst would be a good way to produce clean and recyclable H_2 on a large scale [6–9]. A number of photocatalysts have been proposed and achieved high quantum efficiencies under UV illumination. At present, there is a lack of suitable materials with sufficiently band gap positions for overall water splitting, and the stability necessary for practical applications. In general, efficient photocatalytic materials contain either transition-metal cations with a d^0 electronic configuration (e.g., Ta^{5+}, Ti^{4+}, Zr^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, and Mo^{6+}) or typical metal cations with d^{10} electronic configuration (e.g., In^{3+} and Sn^{4+}, Ga^{3+}, Ge^{4+}, Sb^{5+}) as principal cation components, the empty d or sp orbitals of which form the bottom of the respective conduction bands [6–9]. The tops of the valence bands of metal oxide photocatalysts with d^0- or d^{10}-metal cations usually consist of O2p orbitals, which are located at about +3 eV or higher versus normal hydrogen electrode (NHE) and, as such, produce a band gap too wide to absorb visible light [9]. Also, (oxy) nitrides containing d^0 transition-metal cations, such as Ta_3N_5, TaON, and $LaTiO_2N$, are potential photocatalytic materials to achieve water splitting [10]. The highest quantum efficiencies (QEs) have been reported for NiO-modified $La/KTaO_3$ (QE=56%) using water under UV light [11], QE=90% has been obtained for H_2 generation employing ZnS as photocatalysts in the presence of aqueous Na_2S/Na_2SO_3 as sacrificial reductant under UV illumination [12] and for Cr/Rh-modified GaN/ZnO (QE=2.5%), in pure water under visible light illumination [13–15]. So far, no material capable of catalyzing reaction (Eq. (1)) with visible light and a QE larger than 10% has been found [15]. Therefore, investigating the physical factors that govern the photocatalytic activity for H_2 production is an important and indispensable issue in the development of highly active photocatalysts. While a number of visible-light-driven photocatalysts have been proposed as potential candidates for the overall water splitting, a satisfactory material has yet to be devised [16–19]. At a power level of 1000 W/m^2 the solar energy incident on the earth's surface by far exceeds all human energy needs [20,21]. Photovoltaic and electrochemical solar cells that convert solar energy into electricity can reach up to 55–77% efficiency [22–25] but remain uneconomical because of high fabrication costs, insufficient light absorption [26], and inefficient charge transfer [22]. In a process that mimics photosynthesis; solar energy can also be used to convert water into H_2 and O_2, the fuels of a H_2-based energy economy (Eq. (1))

$$H_2O \rightarrow 1/2\ O_2(\Delta) + H_2(g);\quad \Delta G = +237\ \text{kJ/mol}(1.3\ \text{eV/e},\quad \lambda_{min} = 1100\ \text{nm}) \tag{1}$$

The development of a photocatalytic system that functions efficiently under visible light, representing almost half of the available solar energy on the surface of the earth, is therefore essential for the practical utilization of solar energy. In this review, we aim to summarize the research efforts having been made so far, for H_2 generation from water splitting employing UV and visible light-driven photocatalysts in combination with the view on inspiring new ideas to tackle this important challenge. A number of synthetic and modification techniques for adjusting the band structure of the photocatalyst to harvest visible light and to improve the charge separation in photocatalysis are discussed. Sacrificial reagents and electron mediators for the overall water splitting are also reviewed.

1.1. Basic principles of photocatalytic hydrogen generation

Fig. 1a shows a schematic diagram of water splitting into H_2 and O_2 over photocatalysts. Photocatalysis on semiconductor particles involves three main steps: (i) absorption of photons with energies exceeding the semiconductor bandgap, leading to the generation of electron (e^-) and hole (h^+) pairs in the semiconductor particles; (ii) charge separation followed by migration of these photogenerated carriers in the semiconductor particles; (iii) surface chemical

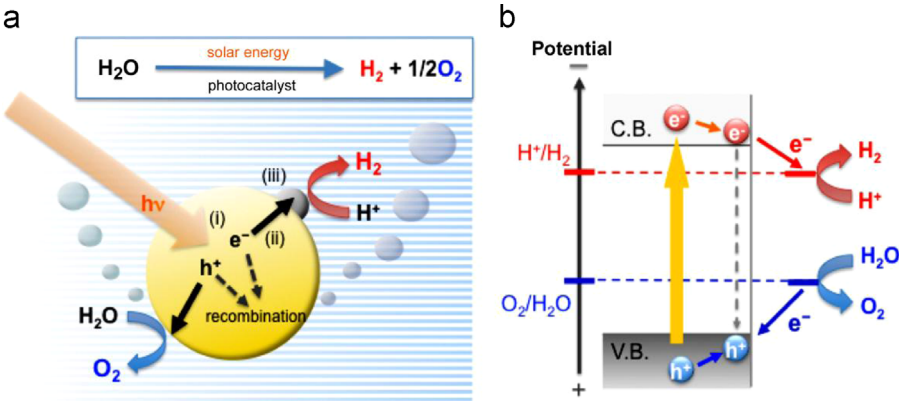

Fig. 1. Schematic illustration of water splitting over semiconductor photocatalysts. *Source*: Ref. [103].