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Principles on design and fabrication of nanomaterials as photocatalysts for water-splitting

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ABSTRACT

As an energy carrier, hydrogen has been extensively studied to satisfy the increasing demand on green energy. Efficiently producing hydrogen from water under sunlight is one of the challenging and important topics in hydrogen energy technology. Photocatalyst plays a critical role for the photo-production of hydrogen from water. It is essential to design novel photocatalysts with enhanced efficiency for the increasing demand on energy. In this paper, recent development on novel strategies to design photocatalysts and novel nanomaterials for efficient production of hydrogen is comprehensively reviewed based on fundamental principles. The strategies, including codoping, hydrogenation, defect engineering, sensitization, formation of heterojunction, metal decoration, band-edge-states modification, and novel designs of cell structures (tandem cell), are systematically discussed. Nanomaterials, including oxides (such as TiO_2, Ta_2O_5, Fe_2O_3 and $SrTiO_3$) and nitrides (such as GaN, graphitic carbon nitride, and Ta_2N_3), are investigated. It is shown that these strategies can generally apply to all of materials, such as oxide and nitride semiconductors. It is believed that maximal conversion efficiency could be achieved by optimizing the electronic structures of photocatalysts and engineering the structures of cells.

Contents

1. Introduction

As world demand for energy rapidly expands, transforming the way we generate, supply, transmit, store, and use energy will be one of the defining global challenges in the 21st century. The incremental advances in current energy technologies will not be

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sufficient to supply this demand in a sustainable way. Finding sufficient supplies of clean energy for the future is one of society's most daunting challenges [1]. Sunlight is a compelling solution to our need for clean, abundant sources of energy in the future. It is readily available, secure from geopolitical tension, and poses no threat to our environment through pollution or to our climate through greenhouse gases [2]. Sunlight provides by far the largest of all carbon-neutral energy sources. More energy from sunlight strikes the Earth in one hour (4.3×10^2 J) than all the energy consumed on the planet in a year (4.1×10^{20} J). However, the utilization of solar energy only provided less than 2% of the world's energy. The huge gap between our present use of solar energy and its enormous undeveloped potential defines a grand challenge in energy research.

Three technologies according to their primary energy products have been developed to take advantage of solar energy, including solar electricity (such as photovoltaic cell (PV)), solar fuels (such as photo-electrochemical cell (PEC)), and solar thermal systems. The PV cell involves the direct conversion of solar radiation to electrical energy via the photovoltaic effect. The PEC cell involves water-splitting to oxygen and hydrogen, so as to convert the solar energy into chemical energy. The solar thermal systems convert the solar energy to thermal energy. Each of the three generic approaches to exploiting the solar resource has untapped capability well beyond its present usage.

Because of the versatile applications of hydrogen and oxygen gases, such as directly used as a fuel, the PEC has attracted substantial attention since the discovery of water splitting property of TiO_2 electrodes under ultraviolet (UV) illumination in 1972 [3]. However, its efficiency of water splitting is limited by its wide band gap (~3.0 eV) because the UV irradiation only counts for 5% of the solar spectrum (Fig. 1). This triggered the surge in research for a suitable material for such solar water splitting, especially with a huge interest in visible-light-driven water splitting as visible light contributes to a majority (~46%) of the total solar energy. Design of novel materials as photocatalysts for water splitting with optimal performance is thus a critical step to solar energy harvesting. There have been a lot of reviews on photocatalysts for hydrogen production [4–7]. In the review, we present the recent development on the design and fabrication of nanomaterials in application of water-splitting, focusing on the new technologies. In Section 1, we introduce the current situation on energy assumption, and possible ways to satisfy the increasing demand by focusing on solar energy harvesting through hydrogen production. In Section 2, we give a brief introduction on the principles of water splitting in sunlight irradiation and the general criteria to the design of photocatalyst. In Section 3, we focus on the design of TiO_2-based nanomaterials for water splitting. Especially, we systematically discuss the various methods, including codoping, hydrogenation, surface decoration, heterojunciton, and surface-plasma resonance, to improve conversion efficiency based on fundamental principles. In Section 4, we give a broad review on other oxides-based photocatalysts. In Section 5, nitrides-based photocatalysts and novel photoelectronchemical tandem cells are discussed for their applications in hydrogen production. A concluding remark and perspectives are given in Section 6.

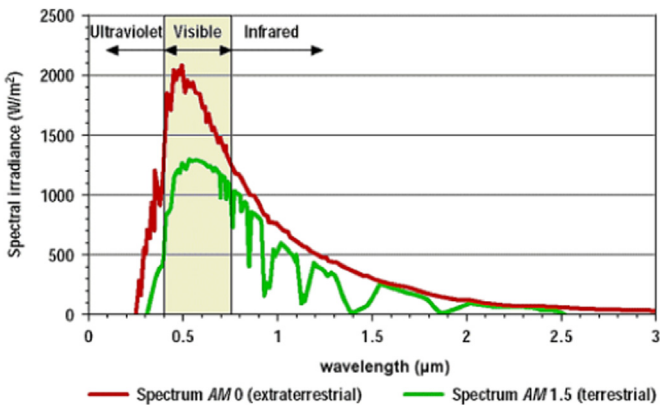

Fig. 1. Solar spectra.

2. Basic principles of water splitting and requirements of photocatalysts

Thermodynamically, the dissociation reaction, as shown in Eq. (1), is an uphill reaction with a positive Gibbs free energy.

$$H_2O\ (l) \rightarrow H_2\ (g) + \tfrac{1}{2}O_2\ (g) \quad (1)$$

The standard Gibbs free energy change (ΔG^0) of water dissociation is +238 kJ/mol or 1.23 eV. The half-cell reactions of formation of hydrogen and oxygen gas from water are shown in the equations below:

$$\text{Oxidation: } H_2O + 2h^+ \rightarrow \tfrac{1}{2}O_2 + 2H^+ \quad (2)$$

$$\text{Reduction: } 2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

Reduction potential of H^+/H_2 is 0 V vs. standard hydrogen electrode (SHE) and oxidation potential of O_2/H_2O is 1.23 V vs. SHE [8].

An ideal photocatalyst absorbs light irradiation, thus exciting electrons from the valence band (VB) to the conduction band (CB) while holes are created in VB. The excited electrons and holes will migrate to the surface of the catalyst. Water will be oxidized and reduced to oxygen and hydrogen gas by the photoexcited holes and electrons, respectively (Fig. 2). The process is repeated as long as irradiation of light continues. For the purpose, several fundamental requirements on the materials, which can efficiently dive the water-splitting reaction upon light absorption, can be categorized.

First, the photocatalyst should have an optimal band structure for maximal utilization of solar energy, which should be comparable to the photo's energy in the visible region (2.0–2.4 eV) but higher than 1.23 eV. A band gap of more than 1.23 eV is the thermodynamically required energy for water splitting, while 2.0–2.4 eV is the energy of a photon in visible light spectrum. In addition, due to energy losses from (i) loss imposed by thermodynamics due to the entropy change, and (ii) transport of electrons/holes to the surface of the photocatalyst, recombination of electron–hole pairs, kinetic losses, etc. [9]. The minimum band gap of an ideal photocatalyst should be adjusted higher. In real systems, about 0.8 eV can be allowed for global energy losses [10].

Secondly, the bottom level of the conduction band of the photocatalyst must be more negative than the reduction potential of H^+/H_2 and the top level of the valence band should be more

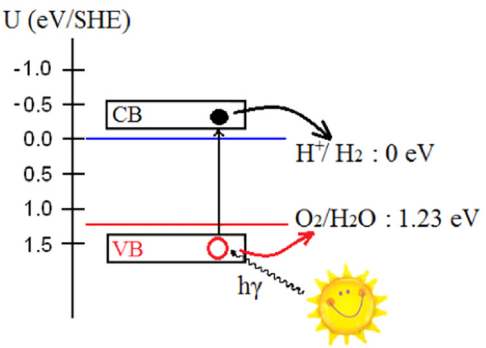

Fig. 2. Band alignment to H^+/H_2 and O_2/H_2O levels.