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Review

Recent progress in enhancing solar-to-hydrogen efficiency

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HIGHLIGHTS

- Recent progress in enhancing solar-to-hydrogen (STH) efficiency is reviewed.
- Light absorption, charge separation-migration and surface reaction are evaluated.
- Doping, quantum dot, and plasmon enhancement are the keys to high STH efficiency.
- Co-catalysts and nanostructured surfaces improve surface reactions effectively.
- Multiple excitons, upconversion, and synergic strategies are promising areas.

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ABSTRACT

Solar water splitting is a promising and ideal route for renewable production of hydrogen by using the most abundant resources of solar light and water. Focusing on the working principal of solar water splitting, including photon absorption and exciton generation in semiconductor, exciton separation and transfer to the surface of semiconductor, and respective electron and hole reactions with absorbed surface species to generate hydrogen and oxygen, this review covers the comprehensive efforts and findings made in recent years on the improvement for the solar-to-hydrogen efficiency (STH) determined by a combination of light absorption process, charge separation and migration, and catalytic reduction and oxidation reactions. Critical evaluation is attempted on the strategies for improving solar light harvesting efficiency, enhancing charge separation and migration, and improving surface reactions. Towards the end, new and emerging technologies for boosting the STH efficiency are discussed on multiple exciton generation, up-conversion, multi-strategy modifications and the potentials of organo-metal hybrid perovskite materials.

1. Introduction

Growing economy and increasing population are demanding an increased energy supply. A recent BP report of the 2030 Energy Outlook predicts that an additional 1.3 billion people will become new energy consumers by 2030 [1]. Fossil fuels are the popular energy sources because of relative low-cost and high energy density. But the limited fossil fuel deposits cannot afford the predicted energy demands. On the other hand, the global warming caused by the greenhouse gas emission from the refineries and combustion of fossil fuels is becoming one of the most serious environmental issues.

Solar energy is a decentralized and inexhaustible natural resource. The magnitude of the available solar power striking the earth's surface at any instant is equivalent to the power supply by 130 million of 500-MW power plants. Harvesting energy directly from sunlight offers an ideal approach to fulfilling with minimal environmental impact the need for clean and renewable energy [2]. It is therefore desirable to efficiently convert the energy from the sun into chemical fuels that can be stored, transported and used upon demand.

Hydrogen has been identified as a clean chemical fuel or a potential energy carrier in many low greenhouse gas energy scenarios because of the relative abundance of its source of generation

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(water), high gravimetric energy density, small environmental footprint thanks to its zero post-combustion pollutants and carbon dioxide emissions. Advantages of hydrogen fuel also include the ease of conversion to electricity or other forms of fuel with relatively high efficiencies and the convenience of storage and transmission compared with electrons. Since the discovery of hydrogen production through water splitting over a single crystal titania (TiO_2) photoanode under the illumination of ultraviolet (UV) light by Fujishima and Honda in 1972 [3], the technology of semiconductor-based photocatalytic water splitting to produce hydrogen using solar energy has been considered as one of the most important approaches to solving the world energy crisis. Indeed, photoelectrolysis of water using semiconductors as both light absorber and energy converter to store solar energy in the simplest chemical bond, H_2, is seen as the "Holy Grail" of solar energy conversion and storage [2,4], and tremendous amount of research has been conducted [5].

For a practical water splitting system, at least 10% of solar-to-hydrogen efficiency is necessary [6]. However, at present, less than desired solar-to-hydrogen efficiency, high cost and/or short lifetime of the photocatalysts are still the bottle-necking factors for realizing the industrial application of semiconductor-based photocatalytic hydrogen generation.

There were a series of articles addressing water splitting issues, including those in solar water splitting cells [2], photoelectrochemical tandem cells [7], and Z-scheme water splitting devices employing two different semiconductors [8]. Some individual enhancement strategies were also discussed such as those involving nanostructures [9–11], plasmon enhancements [12–14], and co-catalysts [15]. In this review, we focus on a comprehensive evaluation of fundamentally important strategies, parameters, and factors that affect the efficiency of the photocatalytic water splitting processes to reflect most recent developments in this specific research area.

Photocatalytic water splitting reaction on a semiconductor photocatalyst occurs in three steps as shown in Fig. 1:

1) Photocatalyst absorbs photon energy greater than the bandgap energy of the material and generates photo-excited electron–hole pairs (excitons or carriers) in the bulk;
2) Photo-excited carriers separate and migrate to the surface without recombination; and
3) Adsorbed species are reduced and oxidized by the photo-generated electrons and holes to produce H_2 and O_2 respectively [16].

The first two steps relate to the photon absorption and charge carrier transfer in the semiconductor, which are analogous to the photovoltaic process, and the last step is about electrochemistry and photochemistry. In order to achieve high solar-to-hydrogen efficiency, the efficiency-determining steps or all of the three steps, i.e. light absorption efficiency, charge separation and transport efficiency, and surface chemical reaction efficiency, have to be adequately addressed and optimized. Photocatalytic water splitting requires a semiconductor material that has robust capability for efficient harvesting of a large portion of the solar spectrum, supports charge separation and rapid transfer to the semiconductor/aqueous interface, and exhibits long-term stability.

2. Efficiency of light absorption process

Thermodynamically, the overall water splitting reaction is an uphill reaction with a free energy change (Gibbs free energy) of 237.2 kJ mol^{-1} corresponding to $\Delta E^0 = 1.23$ V per electron transferred [17]. Fig. 2 shows a schematic illustration of the basic principle of overall water splitting on a photocatalyst.

$$4h^+ + 2H_2O \rightarrow O_2 + 4H^+$$

$$2e^- + 2H^+ \rightarrow H_2$$

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \quad \Delta G = +237.2 \text{ kJ/mol}$$

For high efficient and long-term overall water splitting, the semiconductor photocatalyst must have a bandgap narrower than 3 eV to harvest visible light. In addition, the band edge potentials have to be suitable for overall water splitting and the semiconductor photocatalyst needs to be stable in the photocatalytic reactions. Because semiconductors with a bandgap wider than 3 eV can only absorb ultraviolet light which only constitutes 4–5% of the

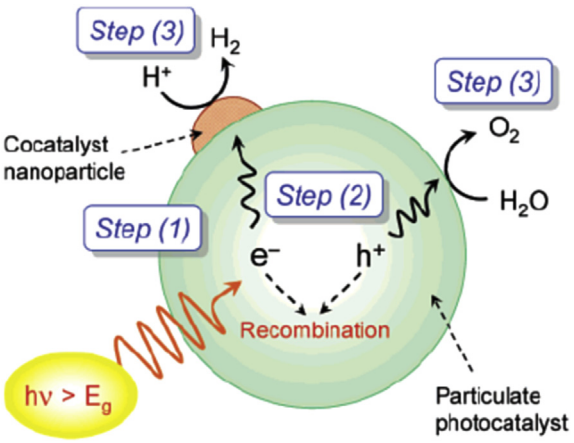

Fig. 1. Processes in photocatalytic overall water splitting on a semiconductor particle [16]. Reprinted with permission from ref 16. Copyright 2007, American Chemical Society.

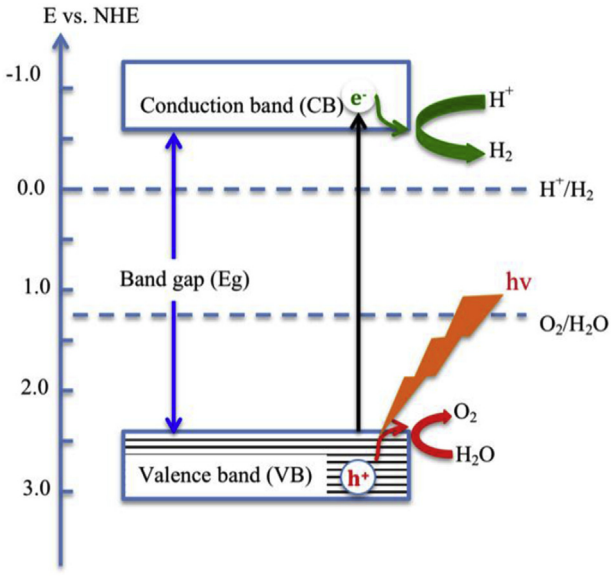

Fig. 2. Overall water splitting on a photocatalyst superimposed with a bandgap chart. The y axis E vs NHE refers to the potential, in unit V, as measured against the normal hydrogen electrode.