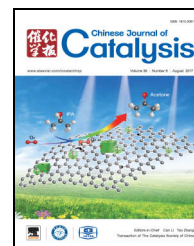


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## Review

# Nanoheterostructured photocatalysts for improving photocatalytic hydrogen production



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## ABSTRACT

Rapid industrialization has accordingly increased the demand for energy. This has resulted in the increasingly severe energy and environmental crises. Hydrogen production, based on the photocatalytic water splitting driven by sunlight, is able to directly convert solar energy into a usable or storable energy resource, which is considered to be an ideal alternative energy source to assist in solving the energy crisis and environmental pollution. Unfortunately, the hydrogen production efficiency of single phase photocatalysts is too low to meet the practical requirements. The construction of heterostructured photocatalyst systems, which are comprised of multiple components or multiple phases, is an efficient method to facilitate the separation of electron-hole pairs to minimize the energy-waste, provide more electrons, enhance their redox ability, and hence improve the photocatalytic activity. We summarize the recent progress in the rational design and fabrication of nanoheterostructured photocatalysts. The heterojunction photocatalytic hydrogen generation systems can be divided into type-I, type-II, pn-junction and Z-scheme junction, according to the differences in the transfer of the photogenerated electrons and holes. Finally, a summary and some of the challenges and prospects for the future development of heterojunction photocatalytic systems are discussed.

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## 1. Introduction

### 1.1. Research background

Industrialization has meant that the exhaustion of fossil energy sources and the deterioration of the environment have become serious bottlenecks to constrain further economic and social development. The demand for energy necessitates the search for renewable and clean alternative resources to supplement and eventually replace our dependence on fossil fuels

[1]. Solar energy is a free, abundant, and renewable clean energy and is one of the most promising options to ease the energy and environmental strain. Therefore, the harvest and conversion of solar energy into a usable energy by using photocatalytic processes is highly desirable [2,3]. The incident solar energy at the surface of the Earth is over  $1.3 \times 10^5$  TW, which far exceeds the current global energy consumption rate ( $\sim 16.9$  TW in 2013). Since Honda and Fujishima [4] discovered photoelectrochemical (PEC) water-splitting over a  $\text{TiO}_2$  electrode in 1972, solar  $\text{H}_2$  production from semiconductor-based photo-

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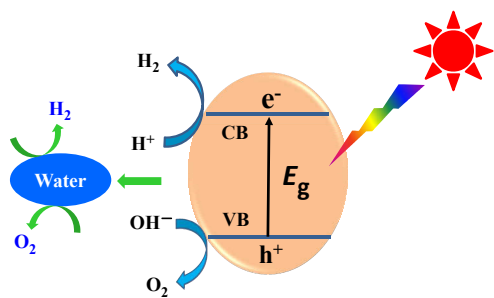
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catalytic water splitting has become a promising method to convert solar energy into clean and carbon-neutral chemical energy. It has been proposed that the photocatalytic H<sub>2</sub> production technology process could be used for commercial application when the solar energy conversion efficiency is above 10% [5].

The key factors influencing the efficiency of solar fuel synthesis include: (1) light absorption, (2) e<sup>-</sup>/h<sup>+</sup> separation and transport, and (3) the photo-electron chemical reaction. Thus, the design of efficient photocatalysts for producing molecular H<sub>2</sub> from water splitting by harvesting solar energy is one of the foremost challenges in the development of a solar hydrogen economy. In the past 40 years, great efforts have been made to synthesize new materials and enrich the photocatalytic theory [6–13]. In the past 10 years, the funding for clean energy research has been increasing in China and from other governments around the world, which has greatly promoted the development of photocatalytic hydrogen production. Many different kinds of semiconductor materials have been researched and developed as photocatalytic hydrogen production materials, such as: ion-doped TiO<sub>2</sub> with visible-light catalytic activity [14–17]; doping of indium-tantalum-oxide with nickel (In<sub>0.9</sub>Ni<sub>0.1</sub>TaO<sub>4</sub>) inducing direct splitting of water under visible-light irradiation with a quantum yield of approximately 0.66% [18]; highly efficient hydrogen production over lanthanum-doped NaTaO<sub>3</sub> photocatalysts with a quantum yield of approximately 56% at 270 nm [19]; cadmium sulfide [20–23] and (AgIn)<sub>x</sub>Zn<sub>2(1-x)</sub>S<sub>2</sub> [24] with a high hydrogen production efficiency in sacrificial agent solution; GaN-ZnO solid solution with high activity for photocatalytic H<sub>2</sub> generation [25–28]; and metal-free polymeric photocatalyst g-C<sub>3</sub>N<sub>4</sub> that can produce hydrogen from water under visible-light irradiation [9,29].

### 1.2. Reaction mechanisms of photocatalytic H<sub>2</sub> production

A schematic illustration of the photocatalytic H<sub>2</sub> production on a semiconductor is shown in Fig. 1. When the photocatalyst is illuminated with a light source, the electrons in the valence band (VB) of the photocatalyst are excited to the conduction band (CB) while the holes are left in the VB, which creates the electron-hole (e<sup>-</sup>-h<sup>+</sup>) pairs. The photogenerated electrons and holes, which do not undergo recombination, migrate towards the surface of the photocatalyst, where they act as the reducing agent and oxidizing agent to result in the reduction and oxidation reactions, respectively. The photocatalytic splitting of wa-



**Fig. 1.** Schematic illustration of semiconductor-based water splitting for photocatalytic H<sub>2</sub> production.

ter into hydrogen and oxygen is a thermodynamically “uphill” reaction, involving a large positive change in the Gibbs energy ( $\Delta G^0 = 237$  kJ/mol). To achieve an overall water splitting, both the reduction and oxidation potentials of water should lie within the band gap of the photocatalyst. The bottom of the CB should be more negative than the reduction potential of H<sup>+</sup>/H<sub>2</sub> (0 V vs. normal hydrogen electrode (NHE)), while the top of the VB must be more positive than the oxidation potential of O<sub>2</sub>/H<sub>2</sub>O (1.23 V vs. NHE). Therefore, the minimum photon energy thermodynamically required to drive the reaction is 1.23 eV, which corresponds to a wavelength of ~1000 nm, in the near-infrared region. To absorb the visible-light irradiation from sunlight, E<sub>g</sub> should be lower than 3.0 eV (>400 nm). Hence, the band gap of the photocatalyst must match up with the CB and VB potentials, which is a critical factor to facilitate both the reduction and oxidation of H<sub>2</sub>O by photoexcited electrons and holes.

### 1.3. Processes of water splitting on semiconductor photocatalysts

In practical applications, a more negative CB potential and a more positive VB potential are thermodynamically beneficial for the reduction and oxidation of reactants, respectively. However, this will also widen the bandgap of the photocatalyst, resulting in a poor solar-light absorption power conversion efficiency. Therefore, it is difficult for a single-component photocatalyst to exhibit both a strong redox ability and wide light-absorption range at the same time. Moreover, in the one-phase photocatalysts, the photoexcited electrons in the CB can easily return to the VB and recombine with the photogenerated holes, which seriously hinders the effective use of solar energy [30]. Therefore, a great deal of effort has been devoted to enhancing the efficiency of the photocatalytic process of one-phase materials, such as doping, sensitizing, morphology control, crystal lattice control and surface modification [31–36]. Among these approaches, the formation of semiconductor heterostructures has attracted vast attention because their performance for photocatalytic H<sub>2</sub> generation can be enhanced by combining semiconductors with different electronic structures that are capable of harvesting visible light and can regulate the electron transfer, thus drastically expanding the research scope [37–43].

Depending on the difference in transfer mechanism of photogenerated charge carriers, the heterostructured photocatalysts can be divided into two categories as follows. (1) Heterojunctions with a classic carrier transfer mechanism (Fig. 2(a)) formed from wide band gap semiconductors-A with a lower CB energy level and narrow band gap semiconductors-B with a higher conduction band energy level. The narrow band gap semiconductors can effectively expand the light response range of heterojunctions owing to their wider light absorption range. The photogenerated electrons of B can transfer to A, which leads to the dramatic increase in the number of photogenerated electrons, and consequently the photocatalytic H<sub>2</sub> generation performance is enhanced. Meanwhile the bottom of the CB of A and B must be more negative than the H<sup>+</sup>/H<sub>2</sub> reduction poten-

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