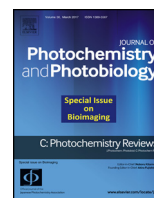




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Invited Review

## Interfacial charge transfer in semiconductor-molecular photocatalyst systems for proton reduction<sup>☆</sup>

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### ABSTRACT

Solar fuels have proven to be one of the important promising approaches to provide clean energy of H<sub>2</sub>. It is an effective strategy for H<sub>2</sub> production to construct photocatalytic systems using semiconductor as a sensitizer and molecular catalyst as the H<sub>2</sub> evolution catalyst. In the semiconductor-molecular photocatalyst systems (SMP systems) for proton reduction, the interfacial charge transfer, including electron and hole transfer, is the determining factor for the photocatalytic process from kinetic aspects. The knowledge of the interfacial charge transfer is of utmost importance for understanding the photocatalytic systems. This review focuses on the interfacial charge transfer in SMP systems for proton reduction, with a special emphasis on the advances in the studies on the kinetic aspects of interfacial charge transfer.

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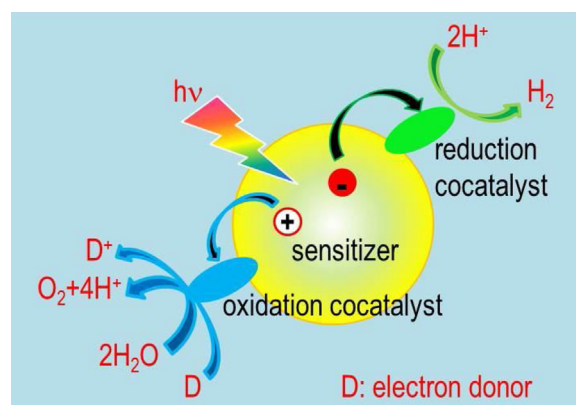
## 1. Introduction

Fossil fuels (*i.e.* oil, coal and natural gas) are still the dominating energy that human society relies on nowadays. The non-renewable fossil fuels were produced through natural photosynthesis in the past billion years. With the continuously increasing demand of energy resources, it is assumed that fossil fuels will be depleted within hundreds of years [1–3]. On the other hand, severe environmental issues accompanying with the utilization of fossil fuels, including air pollution and CO<sub>2</sub> emission, has become the huge problems [4–6]. Obviously, seeking for clean and sustainable alternative energy sources is paramount for the earth's sustainable development. Hydrogen is an ideal energy carrier molecule due to its high specific enthalpy of combustion and benign product H<sub>2</sub>O of combustion. Photocatalytic proton reduction, which converts solar energy into hydrogen energy, is a promising strategy to provide clean energy, as solar energy is the most abundant resources in the earth.

To improve the solar energy conversion efficiency, many strategies are developed, including construction of photocatalytic systems with heterojunction structure [7–9], and loading cocatalysts [10,11], *etc.* The semiconductor-molecular photocatalyst systems (SMP systems) have been reported to be effective for proton reduction in highly photocatalytic performance [12–15]. The SMP systems constructed with semiconductors as sensitizer and molecular catalyst as catalyst for proton reduction, can utilize the advantages of both semiconductor and molecular catalyst. Although the photocatalytic H<sub>2</sub> evolution has been well reported, the kinetic mechanism needs to be studied in order to understand the photocatalytic process. Especially, the interfacial charge transfer determines the charge separation efficiency, which will be a key kinetic factor in the systems. This review focuses on the interfacial charge transfer issues in SMP systems for proton reduction. Firstly, the SMP systems will be introduced briefly. Then the interfacial charge transfer mechanisms, including electron transfer, hole transfer and the roles of surface states, will be discussed and reviewed.

## 2. Semiconductor-molecular photocatalyst (SMP) systems

In the photocatalytic process, light absorption, charge separation, and catalytic reactions are three basic processes. A



**Scheme 1.** Schematic representation of photocatalytic systems.

photocatalytic system for H<sub>2</sub> production typically consists of a photosensitizer, cocatalysts for proton reduction, and cocatalysts for water oxidation or sacrificial agent oxidation, as shown in Scheme 1. The semiconductor as photosensitizer absorbs light irradiation to generate excited electrons and holes. On one hand, the excited electrons will transport to the semiconductor surface, and then further to the reduction cocatalyst loaded on the surface of the semiconductors. Molecular catalysts, such as complexes of cobalt [16], nickel [17], and iron [18–20], are reported to function as efficient catalysts for H<sub>2</sub> evolution. Moreover, [FeFe] hydrogenase ([FeFe]-H<sub>2</sub>ase) and its mimics [21–26], assemblies from Ni<sup>II</sup> salt and 2-mecaptoethanol or its derivatives [27], and metal salts (such as Ni<sup>2+</sup>) [28,29] can also efficiently catalyze the proton reduction. To date, it is demonstrated that the SMP systems are effective in realization of proton reduction [12–15]. On the other hand, the excited holes can transfer to the oxidation cocatalyst for water oxidation in overall water splitting. Although many molecular catalysts for water oxidation have been reported based on transition metal (Ru, Ir, Mn, Co, Fe, V, Ni, Cu, *etc.*) [30–39], it is still quite challenge to fabricate a stable SMP system for water oxidation.

Proton reduction to produce H<sub>2</sub> is a half reaction of photocatalytic water splitting. The other half reaction is water oxidation for O<sub>2</sub> evolution. Water oxidation has been proved to be the bottleneck of the water splitting reaction. It is still necessary to study the half reaction of proton reduction, not only to design proton reduction catalysts with high catalytic performances, but also to understand the fundamental scientific issues, especially the interfacial charge transfer kinetics. To extensively study the mechanism of proton reduction with electrons, the oxidation reaction should be a facile process so that using sacrificial hole scavenger instead of water oxidation. First of all, this strategy can be used to evaluate the photocatalytic rates of the reduction cocatalyst for proton reduction, since the hole oxidation reactions with sacrificial reagent (donor reagent) are much faster than the proton reduction reaction. More importantly, the photocatalytic mechanism studies on proton reduction can be conducted with the hole scavenger, assuming that the rate determining step is the reduction reaction because the sacrificial hole scavenger are readily oxidized by the photoinduced holes. The frequently used hole scavenger include ascorbic acid, alcohols, and tertiary amines [40].

The SMP systems have been reported for both water oxidation and proton reduction. The SMP systems for water oxidation are still challenge because the molecular catalyst for water oxidation is not stable enough. Among a few successful examples, the Co complex/BiVO<sub>4</sub> photocatalyst for photocatalytic water oxidation has been constructed, in which BiVO<sub>4</sub> as a photosensitizer and

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