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Review

Photocatalytic nitrogen fixation: An attractive approach for artificial photocatalysis

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ABSTRACT

Ammonia synthesis via the Haber-Bosch process, which has been heralded as the most important invention of the 20th century, consumes massive amounts of energy, around ~1%–2% of the world's annual energy consumption. Developing green and sustainable strategies for NH_3 synthesis under ambient conditions, using renewable energy, is strongly desired, by both industrial and scientific researchers. Artificial photosynthesis for ammonia synthesis, which has recently attracted significant attention, directly produces NH_3 from sunlight, and N_2 and H_2O via photocatalysis. This has been regarded as an ideal, energy-saving and environmentally-benign process for NH_3 production because it can be performed under normal temperature and atmospheric pressure using renewable solar energy. Although sustainable developments have been achieved since the pioneering work in 1977, many challenging issues (e.g., adsorption and activation of nitrogen molecules on the surface of photocatalysts under mild conditions) have still not been well solved and the photocatalytic activities are generally low. In this miniature review, I summarize the most recent progress of photocatalytic N_2 fixation for ammonia synthesis, focusing specifically on two attractive aspects for adsorption and activation of nitrogen molecules: one is engineering of oxygen vacancies, and the other is mimicking natural nitrogenase for constructing artificial systems for N_2 fixation. Several representative works focusing on these aspects in artificial systems have been reported recently, and it has been demonstrated that both factors play more significant roles in photocatalytic N_2 reduction and fixation under ambient conditions. At the end of the review, I also give some remarks and perspective on the existing challenges and future directions in this field.

1. Introduction

Ammonia (NH_3) is not only an essential chemical in producing various chemicals, like fertilizers, in modern society, but it is also an important clean energy carrier and fuel. It is currently manufactured by the well-known industrial Haber-Bosch process using H_2 and N_2 under extremely high-pressure and high-temperature conditions, typically over an iron-based catalyst [1–5]. The discovery of the Haber-Bosch process for ammonia synthesis in 1909 resulted in 4 times multiplication of crop yield, which enabled the global population to nearly quadruple since the rapid implementation of the process in the early 20th century [6,7]. However, the dominance of the Haber-Bosch process leads to massive consumption of energy, ~1%–2% of the world's annual energy consumption, and generates large amounts of CO_2, putting enormous pressure on the

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world's energy demand and environmental issues [8]. Therefore, it is of great significance to develop green and sustainable strategies for NH_3 synthesis, especially using renewable energy under ambient conditions. Until now, various strategies that can be operated under mild conditions, including electrocatalysis [9–12] and photo(electro)catalysis [8,13–16], have been explored in regard to N_2 reduction for NH_3 synthesis, and some promising progress has been achieved. Artificial photosynthesis of ammonia directly from sunlight, N_2 and H_2O via photocatalysis, is regarded as an ideal, energy-saving and environmentally-benign process for NH_3 production since it can be performed at normal temperature and atmospheric pressure using renewable solar energy. The study of nitrogen fixation via artificial photosynthesis was first reported in 1977 by Schrauzer et al. [17], who employed the model photocatalyst TiO_2 as a proof-of-concept to convert N_2 into NH_3 and to oxidize H_2O to oxygen simultaneously under UV light irradiation. Since then, the research in this field had attracted many attentions in the last century, but further study has become much more challenging. With the increase in demands for renewable energy in the world, photocatalytic nitrogen fixation for ammonia synthesis has recently gathered momentum in terms of development.

2. Thermodynamics of nitrogen fixation

The principle of artificial photosynthesis for nitrogen fixation is similar to photocatalytic water splitting and CO_2 reduction [18–21] For artificial photosynthesis on semiconductor-based photocatalysts, the first step is photoexcitation, in which the electrons are excited onto the conduction bands leaving the photogenerated holes remain within valence band. Following is the dissociation of the photogenerated charges, so that the electrons and holes separate and diffuse to the surface of photocatalysts (Fig. 1). Finally, the electrons and holes participate in the redox reactions with the adsorbed molecules (e.g., N_2, H_2O) onto the reactive sites for the production of ammonia. Thermodynamically, photocatalytic N_2 fixation for NH_3 synthesis is an endothermic reaction, with a Gibbs free energy of 339 kJ/mol (Eq. (1)). In this reaction, H_2O is oxidized to O_2 and protons, while N_2 and protons are reduced to NH_3. As a result, NH_3 is produced from water and N_2 under ambient conditions, using sunlight as the energy source. Compared with water splitting reactions, the nitrogen fixation needs more energy to drive the reaction and is much more challenging than water splitting. The whole reaction can be separated into two sub-reactions, the initial reaction being H_2O splitting to H_2 and O_2, and the second being NH_3 synthesis using H_2 and N_2. Therefore, the first step for artificial photosynthesis for N_2 fixation is photocatalytic water oxidation to generate O_2 and protons, and the prerequisite for a potential photocatalyst is that it should satisfy the energy requirement for efficient water oxidation.

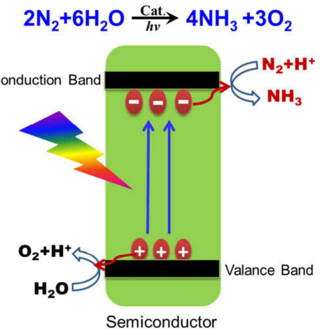

Fig. 1. Schematic of photocatalytic N_2 fixation to NH_3 on a semiconductor-based photocatalyst.

$$2N_2 + 6H_2O \rightarrow 4NH_3 + 3O_2\ (\Delta G = 339\ \text{kJ/mol}) \qquad (1)$$

The key reactions in artificial photosynthesis, that is photocatalytic water splitting, CO_2 reduction and nitrogen fixation, share many common challenges. For example, the primary step, water oxidation, is the most challenging, which directly determines whether the reactions can occur or not, and how efficient they will be. Therefore, a photocatalyst, which possesses good water oxidation ability and suitable band structures, is the prerequisite for all these artificial photosynthesis reactions. For CO_2 reduction and N_2 fixation, one of the most challenging issues is the activation of CO_2 and N_2 molecules, both of which are chemically stable molecules and need a high input energy to activate them. Therefore, CO_2 reduction and N_2 fixation reactions are more difficult than photocatalytic water splitting, and the reported efficiencies are consequently much lower than those of water splitting.

3. Oxygen vacancies in photocatalytic N_2 fixation

For the research of artificial photosynthesis for nitrogen fixation via photocatalytic processes, many semiconductor-based photocatalysts have been investigated and reported to be active, e.g., titanium oxides [15,22], bismuth oxyhalides [23,24], bismuth oxides [25], carbon nitrides [26], cadmium zinc sulfides [27], cadmium sulfides [28], and even diamond [29]. One of the big challenges in photocatalytic nitrogen fixation is the adsorption and activation of inert nitrogen molecules under ambient conditions, which is recognized to be the rate-determining step, as the cleavage of the N≡N triple bond needs an extremely high dissociation energy (~941 kJ/mol).

Oxygen vacancy-based semiconductors, with abundant localized electrons in oxides, can act as active sites and exhibit superior performances in various photocatalytic reactions [30–34]. Oxygen vacancies have been reported to be important in enhancing the adsorption and activation of O_2 molecules; oxygen vacancies in TiO_2 are able to activate O_2 to reactive oxygen species, such as peroxide and superoxide species [34,35] Vacancies and defect states always coexist in a specific photocatalyst, and there are many different opinions when it comes to the intrinsic role of oxygen vacancies or defect states in photocatalysis. In some cases, vacancies or defect states on the surface of photocatalysts can act as trapping sites for photogenerated electrons or protons to inhibit the charge recombination, so that the surviving charges can participate in the following photocatalytic reactions.

Oxygen vacancies have been demonstrated to be essential in the adsorption and activation of nitrogen molecules [16,23]. Li