Photocatalytic Reduction of N₂ for Ammonia Production

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Abstract Photocatalytic fixation of dinitrogen has become a research hotspot in recent years. Compared with traditional processes for the production of ammonia, photocatalysis exhibited superiorities, such as easy-to-operate, mild operating conditions and low cost. However, the production rate of ammonia from photocatalytic reduction of N₂ is pretty low. Also, the selectivity of ammonia is very low as regards the influence of water splitting. Lots of works have been reported with the presence of these hindrances. This is a challenge as well as an opportunity for global researchers. With this perspective in view, a recommendation for future work was included.

Keywords N₂ fixation, photocatalysis, Haber-Bosch, ammonia, solar energy

In the earth's atmosphere, dinitrogen (N₂) gas accounts for the highest amount with a concentration of 78%. All organisms need a steady supply of nitrogen because it is a building block of deoxyribonucleic acid (DNA), ribonucleic acid (RNA) and proteins. The three macromolecules are vital to organisms to build genetic information (DNA and RNA) and to carry out many of the processes of life (proteins). However, N₂ gas cannot be directly used by organisms, and it must be converted into another form, ammonia (NH₄⁺) before most organisms can absorb it. The process of converting N₂ into ammonia is defined a nitrogen fixation, and this process is naturally accomplished by bacteria. The generated ammonia was absorbed by plants, and animals get their nitrogen by eating plants or other animals. With the occurrence of population explosion, the demand of food increased sharply. Hence, this led to the invention of the Haber-Bosch process in 1900s to artificially fix nitrogen for the production of ammonia. The produced ammonia was an important component of fertilizers to promote the production of crops. A century after the invention of Harber-Bosch process, its application is in use till today worldwide to produce more than 500 million tons of artificial fertilizer annually. Fertilizer produced from this process was estimated to be responsible for sustaining roughly 40% of the world's population and is the source for 40%–60% of the nitrogen in the human body as reported in 2004.^[1] Harber-Bosch process has been regarded as the most important invention of the 20th century.^[2] However, this advanced process requires critical conditions (pressures higher than 200 bar and temperature higher than 673 K) for the production of ammonia.^[3] In addition, hydrogen with a high purity is required, being one of the reactants. It is industrially produced via a steam reforming process, which is also operated at an extremely high temperature (700–1100 °C). The production of hydrogen gas together with the high temperatures and pressures required for the Haber-Bosch process, inevitably consumes 1%–2% of the world's total annual energy supply.^[4] It has become an attractive research field to find alternative processes conducted at atmospheric pressure and room temperature for a clean, safe and sustainable ammonia production.

Recently, developed alternative processes in nitrogen fixation include primarily homogeneous catalysis, heterogeneous thermocatalytic process, biological approaches based on

nitrogenase enzyme, electrochemical and electrocatalytic process, and photocatalysis.^[5–9] Among these processes, photocatalysis is a process that converts light energy into chemical energy, and solar light may be a potential energy source for this process. In addition to the free source of energy, photocatalytic processes are operated at atmospheric pressure and room temperature. With these superiorities, photocatalysis in N₂ reduction has gained popularity in recent years. Comprehensive reviews on this subject were reported by Chen *et al.*^[10] and Medford *et al.*^[11] Photocatalytic reduction of N₂ for ammonia production can be described by Eq. (1):

This process with $\Delta H_{298\text{ K}} = -92.2\text{ kJ}\cdot\text{mol}^{-1}$ is thermodynamically accessible. However, this process cannot occur spontaneously under ambient conditions. Two possible mechanisms, namely associative and dissociative pathways, were generally adopted to explain a nitrogen reduction process.^[12] The cleavage and hydrogenation of dinitrogen are two primary hindrances. Typically, N₂ with a triple bond is very inert, and an energy of 410 kJ·mol^{−1} required for the cleavage of first bond of the triple bond in N₂. Two intermediates of this process are diazene (N₂H₂) and hydrazine (N₂H₄), which are produced via hydrogenation of dinitrogen. Energies of 212.9 kJ·mol^{−1} and 95.35 kJ·mol^{−1} are required to form N₂H₂ and N₂H₄, respectively. Another hindrance is the low selectivity of ammonia. This process occurs in water, and water splitting may also occur as a side reaction. From the aspect of electrochemical properties of these two processes, a reduction potential of −0.42 V is for the process of water splitting to evolve hydrogen (Table 1). Comparatively, a reduction potential of −3.2 V is required for the hydrogenation of dinitrogen, which is the first step of activation of N₂. It suggests that an electron with the capacity to reduce N₂ is also capable of reducing water with the H₂ evolution. The later process (hydrogen evolution reaction, HER) is much easier, compared to the reduction of N₂. As a result, the reduction of N₂ process occurs simultaneously with the evolution of H₂, which may reduce the selectivity of the production of ammonia. Approaches to overcome these hindrances are required to

improve the production rate of ammonia from a photocatalytic process. These approaches include primarily following categories: (1) novel materials preparation, (2) modifications of photocatalysts, and (3) process engineering via photoreactor design. It should be noted that oxygen vacancies (OVs)-promoted photocatalysis in the reduction of N_2 has become more prevalent.^[13-15] OVs can modulate both the coordination structures and electrical states of adsorbates via the surface dangling bonds and localized electrons, thus influencing the kinetics, energetics, and further the mechanisms of catalytic process, but an in-depth scenario depicting the interactions between OVs and molecular processes of photocatalytic reactions is still unclear.^[14,16]

Table 1 Reduction potentials (vs. NHE at pH 0) of typical hydrogenation reactions related to the reduction of N_2 to NH_3 ^[10]

Reaction	E^0/V
$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	0.81 ^a
$2H^+ + 2e^- \rightarrow H_2$	-0.42 ^a
$N_2 + e^- \rightarrow N_2^-$	-4.16
$N_2 + H^+ + e^- \rightarrow N_2H$	-3.2
$N_2 + 2H^+ + 2e^- \rightarrow N_2H_2$	-1.10 ^b
$N_2 + 4H^+ + 4e^- \rightarrow N_2H_4$	-0.36
$N_2 + 5H^+ + 4e^- \rightarrow N_2H_5^+$	-0.23
$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$	0.55
$N_2 + 8H^+ + 8e^- \rightarrow 2NH_4^+$	0.27

^a Reduction potential E^0 vs. NHE at pH 7; ^b Reduction potential E^0 vs. RHE.

More researchers will focus on this subject matter, photocatalytic N_2 fixation, due to the great potential of this process. Below are some recommendations for future works are listed below:

(1) Materials preparation to imitate the composition of nitrogenase enzyme may accelerate the screening process to find the photocatalyst with high activity;

(2) Optimization of materials preparation methods may boost the photocatalytic N_2 fixation efficiency, as different preparation approaches often lead to great differences of photocatalytic properties;^[17]

(3) Inactive photocatalytic oxidation activity may be in favor of suppressing the back reaction of the oxidization of ammonia into nitrates;

(4) Adoption of accurate ammonia detection method will make the testing results more convincing, as a significant interference of the solution condition was recently reported;^[18]

(5) Technologies integration: combination of photocatalysis with electrocatalysis/electrochemistry, or combination of photocatalysis with biotechnology may further improve the

photocatalytic activity;

(6) Photoelectrocatalysis may be promising, but the efficiency should be compared with considerations of economic cost and the pure electrocatalytic efficiency;

(7) Process engineering should be considered when a photocatalyst with a relative high activity is used in the photocatalytic reduction of ammonia. This process possesses the potential to favor scaling up and attain an improved activity.

Overall, we believe that photocatalytic conversion of N_2 for ammonia production will be comprehensively studied and start a revolution of renewable energy for practical benefits and future commercialization.

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