2-2-7. Photo-Nitrogen Reduction Reaction

Overview

The photo-nitrogen reduction reaction (photo-NRR), which synthesizes ammonia using water and solar light, is an energy-storage process classified as artificial photosynthesis. Ammonia has garnered significant attention as an energy carrier in addition to fertilizers and chemical reactants. Recently, advancements in photo-NRR systems have been made from the perspectives of photo- and molecular catalysis science and nanophotonics. Future process developments need to address practical applications, such as the selective conversion of gas-phase N_2 to ammonia and the separation of ammonia.

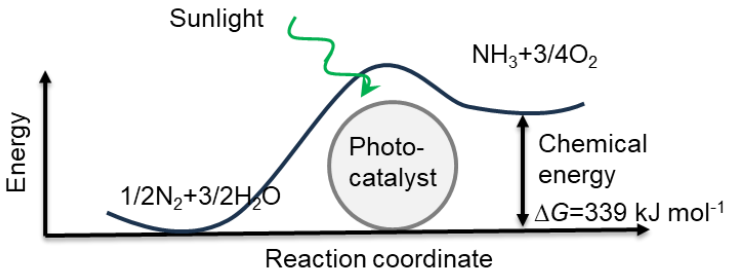

Figure 1. Schematic of photo-NRR.

Current Status and Frontiers

Ammonia is expected to be a novel chemical energy source due to its ease of liquefaction and its ability to retard the risks associated with hydrogen, such as embrittlement. The synthesis of ammonia via photo-NRR is considered to be a significant candidate for green ammonia production. The initial report of ammonia synthesis through photo-NRR is published in the 1970s. Subsequently, reliable photo-NRRs were reported in the 2000s, attributed to advancements in reaction and detection technologies for ammonia.

In Japan, active research has been conducted on photo-NRR using diverse methodologies. Notably, nitrogen photoreduction employing water as an electron donor at ambient temperature and atmospheric pressure has been successfully

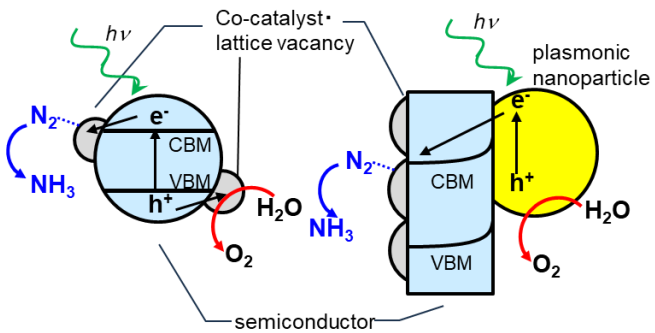

Figure 2. Photo-NRRs using semiconductor photocatalyst (left) and plasmon-enhanced photoelectrode (right).

realized. Some research examples are introduced below.

1. Photo-NRR via semiconductor photocatalysis

The activity and selectivity of substrate reactions facilitated by photocarriers generated in semiconductor photocatalysts can be enhanced using an appropriate co-catalyst. Instead of a co-catalyst, it has been demonstrated that oxygen vacancies on the surface of titanium dioxide can effectively adsorb nitrogen molecules, thereby enabling their reduction to ammonia. Additionally, efforts have been made to reduce nitrate ions, an environmental pollutant, to ammonia using a similar approach (Shiraishi et al.).

2. Photo-NRR utilizing plasmon-enhanced photoelectrode

Localized surface plasmons exhibited by metal nanoparticles generate hot carriers. The transfer of hot carriers into a semiconductor facilitates charge separation independent of the active wavelength of the semiconductor. Utilizing this phenomenon, ammonia synthesis through photo-NRR was achieved on a photoelectrode, which is composed of gold nanoparticles, strontium titanate, and zirconium, using water as an electron donor under visible light irradiation (Oshikiri and Misawa et al.).

3. Photo-NRR via molecular complex catalysis

Ammonia production from nitrogen and water under visible light irradiation using molybdenum and iridium complex catalysts has been reported. Although this method requires the consumption of an organophosphorus compound as a reducing agent, a high quantum yield exceeding 20% was achieved (Nishibayashi et al.).

References

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Future Perspectives and Directions

Issues that need to be solved and realized within the next 10 years: Achieving both reaction selectivity and efficiency. Improving the efficiency of visible light utilization. Separation and storage process for ammonia and its compounds.

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