A minireview on catalysts for photocatalytic N₂ fixation to synthesize ammonia

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Introduction

Ammonia (NH₃) is an important feedstock in chemical industry. Nowadays NH₃ is mainly produced via the industrialized Haber–Bosch process, which requires substantial energy input, since it operates at high temperatures (400–650 °C) and high pressures (20–40 Mpa). From the energy conservation point of view, it is of great significance to explore an alternative avenue to synthesize NH₃, which is in line with the concept of sustainable development. Very recently, photocatalytic N₂ fixation (PNF) has been discovered as a safe and green approach to synthesize NH₃, as it utilizes the inexhaustible solar energy and the abundant N₂ in nature to synthesize NH₃ under mild conditions. A highly efficient catalyst is the core of PNF. Up to now, extensive studies have been conducted to design efficient catalysts for PNF. Summarizing the catalysts reported for PNF and unraveling their reaction mechanisms could provide guidance for the design of better catalysts. In this review, we will illustrate the development of catalysts for PNF, including semiconductors, plasmonic metal-based catalysts, iron-based catalysts, ruthenium-based catalysts and several other catalysts, point out the remaining challenges and outline the future opportunities, with the aim to contribute to the development of PNF.

Industrially, NH₃ could be used to produce fertilizers, synthetic fibres, nitrile rubber and so on; medically, NH₃ is often utilized as a drug to treat dizziness and fainting; militarily, NH₃ could serve as a biological disinfectant to disinfect sarin agents. The wide applications of NH₃ make it essential in promoting the development of national economies.

At present, the Haber-Bosch process is the main approach to synthesize NH₃.⁵–⁶ However, the Haber-Bosch process is carried out under harsh reaction conditions (the pressure is high up to 20–40 MPa and the temperature is in the range of 400–650 °C), which consumes extensive energy.⁴ From the context of global

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energy crisis, it is necessary to search for an alternative avenue to synthesize NH₃ which is in line with the concept of sustainable development.

Photocatalytic N₂ fixation (PNF) is a process which utilizes the inexhaustible solar energy and the abundant N₂ in nature to synthesize NH₃ under mild conditions. It is a safe and green approach and has great potential to solve the problems encountered in the industrialized Haber-Bosch process, provided that efficient photocatalysts are adopted.

In photocatalytic N₂ fixation reaction, the cleavage of the N≡N bond is the rate determining step. That is, effective catalysts for PNF should be able to accelerate the N≡N bond cleavage process.

Over the past few years, an enormous amount of research effort has been devoted to explore effective catalysts for PNF. A large number of photocatalysts, such as semiconductors, plasmonic metal-based catalysts, iron-based catalysts, ruthenium-based catalysts and several other catalysts, have been designed for PNF (a schematic illustration is shown in Fig. 1).

For each type of these photocatalysts, a specific photocatalyst for PNF could be simply divided into two different functional units. One is the light harvesting unit (which is used to denote the active sites that could adsorb light) and the other is the thermal-driven active unit (which is referred as the active center that directly involves in the polarization and activation of N₂). The tailoring of each of the type of functional unit could contribute to the performance of a catalyst in PNF. In this review, we will summarize the photocatalysts that have been reported active for PNF, generalize the principles for the design of efficient catalysts (tailoring the light harvesting unit or the thermal-driven active unit), unravel their reaction mechanisms, point out the remaining challenges and prospect the future development, with the aim to provide guidance for the rational design of more efficient photocatalysts and contribute to the development of PNF.

**Photocatalysts for PNF**

In this section, the photocatalysts for PNF are classified into five categories, including semiconductors, plasmonic metal-based catalysts, iron-based catalysts, ruthenium-based catalysts and other catalysts. The progress of each category of photocatalysts is summarized and discussed in the following sub-sections.

**Semiconductors as photocatalysts for PNF**

When semiconductors are adopted to catalyse PNF, suitable energy band levels are required. Generally speaking, semiconductors for PNF are designed according to the following principles, (1) the semiconductor could absorb light efficiently and it could be excited by light easily, (2) the separation and transfer efficiency of the photogenerated electron hole pairs should be effective, and (3) the energy levels of the semiconductor photocatalyst could meet the standards for the two photo-induced half reactions, referring to the reduction of N₂ and the oxidation of H₂ or H₂O.

Some pristine semiconductors could meet the standards to drive PNF, however, their efficiencies are quite low. Introducing vacancies or foreign elements into the semiconductor, functionalizing the pristine semiconductor, constructing heterojunctions/homojunctions or design a semiconductor-based hydrophilic-hydrophobic catalyst, are approaches to extend the light harvesting spectrum, enhance the light harvesting capacity (which means its capacity to absorb more light), facilitate the separation and transfer of photoinduced electron hole pairs and further accelerate PNF.

**Pristine semiconductors.** Pristine semiconductors are a type of photocatalyst with only light harvesting unit for PNF. Pristine semiconductors are widely studied in PNF. The catalytic performance of pristine semiconductors could be improved by regulating their optical properties. Theoretical calculations suggest that (110) facet of rutile TiO₂ is capable of activating N₂ into NH₃ via both the associative and dissociative mechanism. (040) facet of BiVO₄ single crystal could catalyze PNF, with V⁴⁺/ V⁵⁺ as the active site, where V⁴⁺ chemisorbs N₂, V⁵⁺ serves as the electron transfer bridge and the photogenerated electrons are the driving force for PNF.

The activities of pristine semiconductors have been verified experimentally. For example, ultrathin MoS₂ could convert N₂ into NH₃ via a six-electron reduction process (Fig. 2), achieving...
a NH₃ synthesis rate of 325 μmol g⁻¹ h⁻¹ without any sacrificial reagents or co-catalysts. The electron-rich property of ultrathin MoS₂, as well as the high concentration of localized electrons upon light irradiation accounted for its activity. Bismuth monoxide (BiO) quantum dots, synthesized via a facile hydrothermal method, are reported as a highly efficient catalyst for PNF, recording a NH₃ generation rate of 1226 μmol g⁻¹ h⁻¹ without the assistance of any sacrificial reagents or co-catalysts. It is postulated that all the low valence Bi[II] in BiO were potential active sites for N₂ activation.

The catalytic activity of pristine semiconductor could be improved, in case that a 2-dimensional (2D) material is used as co-catalyst. For instance, P25 itself yielded NH₃ at a rate of 2.11 μmol g⁻¹ h⁻¹ under full spectrum light irradiation, while the activity was fivefold increased when Ti₃C₂ MXene was used as a co-catalyst. Similarly, the catalytic performance of CdS in PNF boosted obviously when black phosphorous nanosheet was adopted as a co-catalyst. It is reported that 2D co-catalysts facilitated the separation of electron–hole pairs and promoted N₂ chemisorption and activation.

Despite that some pristine semiconductors are active for PNF, their efficiencies are generally low. To further improve their efficiencies, multiple approaches are adopted to modify the pristine semiconductors.

**Semiconductors with vacancies.** Introducing vacancies into a semiconductor endows the pristine semiconductor additional properties. On one hand, vacancy introduction could tailor the light harvesting unit of the photocatalyst, such as narrow its band gap, extend its light harvesting range and enhance its light harvesting capacity. On the other hand, the vacancies occasionally serve as thermal-driven active sites for N₂ activation. Defective semiconductors have been widely applied in PNF. The functions of the defective sites vary with the catalytic systems.

1. The introduction of defective sites engineers the light harvesting unit, such as lowers the conduction band position, engineers the band gap and improves the light harvesting capacity of the semiconductor. Few-layer g-C₃N₄ (ref. 38) and one-dimensional g-C₃N₄ (ref. 39) are rich in N defects. The existence of N defects lowered the conduction band position and increased its light harvesting capacity, which then contribute to their performance in PNF. Band gaps and the light harvesting capacities could be consecutively tuned by dedicating controlling the content of surface vacancies.

2. The defective sites serve as the active sites to enhance the adsorption and activation of N₂. N vacancies on nitrides generally activate N₂ via a pathway analogous to Mar-van Krevelen mechanism. That is, N₂ is firstly activated at the N vacancies and then transformed into NH₃ by reacting with H₂ or H₂O. Wang et al.’s work is a typical example. In their work, a N deficient g-C₃N₄ catalyst was prepared by the dielectric barrier discharge plasma treatment method, which displayed a NH₃ production rate of 161.8 μmol g⁻¹ h⁻¹. Mechanism exploration disclosed that N₂ was activated via the two-path analogous Mar-van Krevelen mechanism.

3. Similarly, in addition to enhance the light harvesting capacity, the oxygen vacancies on BiOCl, TiO₂ and BiOBr also serve as the active sites for N₂ activation and reduction while the oxygen vacancies on BiₓFeMoO₆ help adsorb and stabilize the N–H intermediate during N₂ activation, which cooperatively boost NH₃ production via PNF (Fig. 3).

Intrinsic strain is occasionally induced by vacancies. Thereby the strain and vacancies cooperatively contribute to PNF. Zhang et al. synthesized an ultrathin TiO₂ nanosheet catalyst with...
abundant oxygen vacancies via a facile copper-doping method, which could absorb visible light high up to 700 nm.\textsuperscript{51} It was discovered that there was intrinsic compression strain in the as-prepared TiO\textsubscript{2} nanosheet. The oxygen vacancies and the strain worked in concert to chemisorb and activate N\textsubscript{2} and H\textsubscript{2}O effectively, leading to a high NH\textsubscript{3} production rate (78.9 \(\mu\)mol g\textsuperscript{−1} h\textsuperscript{−1}).\textsuperscript{53}

**Doped semiconductors.** Doping one or more foreign elements into a semiconductor is an important approach to mediate the light harvesting unit (such as introduce new energy levels, engineer its energy structure, tailor its light harvesting capacity) and/or manipulate the active sites for N\textsubscript{2} activation. Doped semiconductor is a category of catalysts for PNF. Here, based on the functions of the dopant, the doped semiconductor catalyst for PNF is review.

1. Suitable dopant could serve as active sites for promoting N\textsubscript{2} activation. For example, Mo\textsubscript{1−x}W\textsubscript{x}S\textsubscript{2} nanosheets, which could be considered as Mo doped WS\textsubscript{2}, recorded a NH\textsubscript{3} yield of 109.3 \(\mu\)mol g\textsuperscript{−1} h\textsuperscript{−1} NH\textsubscript{3} synthesis rate under visible light irradiation and an apparent quantum yield of 1.1% at 400 nm (Fig. 4b).\textsuperscript{29} Similarly, oxygen vacancies could also be generated by doping carbon into BiO\textsubscript{I}.\textsuperscript{44} Carbon dopant decreased the band gap, extended the light harvesting region, facilitated the separation and migration of electron–hole pairs and consequently hastened PNF, leading to a NH\textsubscript{3} generation rate of 311 \(\mu\)mol g\textsuperscript{−1} h\textsuperscript{−1} under the illumination of simulated sunlight.\textsuperscript{54}

As for doping, it is clear that most of the doped semiconductors exhibited a NH\textsubscript{3} production rate of \(\sim 100 \mu\)mol g\textsuperscript{−1} h\textsuperscript{−1}, with only two exceptions on B-g-C\textsubscript{3}N\textsubscript{4} and C–BiO\textsubscript{I}, who gave NH\textsubscript{3} yields over 300 \(\mu\)mol g\textsuperscript{−1} h\textsuperscript{−1}. Even though limited by the number of studies, it might provide a clue that nonmetal element doping could endow the doped semiconductors better performance in PNF.

**Functionalized semiconductors.** Grafting functional groups onto a semiconductor or modifying a pristine semiconductor is an important approach to mediate the two functional units and consequently enhance their performance for PNF.

1. Functionalized semiconductors with engineered light harvesting unit.

Acid treated semiconductors. Tian et al. reported that salicylic acid (SA) modification could enlarge the Brunauer–Emmett–Teller surface area, improve the optical absorption capacity as well as promote the separation of photoinduced electron–hole pairs in g-C\textsubscript{3}N\textsubscript{4}, which resulted in a much enhanced PNF activity over g-C\textsubscript{3}N\textsubscript{4}-SA.\textsuperscript{52}

Base treated semiconductors. It has been reported that base treated semiconductors exhibited improved electron–hole separation efficiency. Typical examples are given by Yangjie et al.\textsuperscript{61} and Wang et al.,\textsuperscript{64} who reported that MgO decorated g-C\textsubscript{3}N\textsubscript{4} and KOH treated g-C\textsubscript{3}N\textsubscript{4} gave superior performance in PNF than pristine g-C\textsubscript{3}N\textsubscript{4}, and the reduced recombination rate of electron–hole pairs was one of the reasons for their premier activities.

Metal decorated semiconductors. Cu, Fe, Ni and Pd decoration could promote the charge transfer efficiency. Cu, Fe or Ni decorated TiO\textsubscript{2}, synthesized via microwave assisted hydrothermal method, not only exhibited promoted charge transfer efficiency, but also had larger specific surface area and stronger capacity in harvesting visible light.\textsuperscript{54} As a result, they exhibited 1.9–6.0 times higher PNF activities than the pristine TiO\textsubscript{2} under simulated light irradiation.\textsuperscript{56} Pd decorated TiO\textsubscript{2}, prepared by one-pot microwave synthesis techniques, also demonstrated reduced recombination of photoinduced electron–hole pairs and led to a 4 fold higher NH\textsubscript{3} production rate than the unmodified one.\textsuperscript{66}

Quantum dots modified semiconductors. Graphene quantum dots modified Bi\textsubscript{2}W\textsubscript{6}O\textsubscript{24}, with graphene quantum dots uniformly dispersed on the surface of Bi\textsubscript{2}W\textsubscript{6}O\textsubscript{24}, exhibited remarkably enhanced PNF activity than the two single component counterparts. Characterization results implied that the recombination of photoinduced electron–hole pairs was
significantly reduced and the junction between graphene quantum dots and Bi$_2$WO$_6$ helped to boost the photocatalytic activity.²⁷

(2) Functionalized semiconductors with tailored active sites.

**Hydrogenated semiconductors.** Unsaturated Mo atoms in Bi$_2$MoO$_6$ are the active sites for N$_2$ chemisorption, activation and reduction, on the contrary, the Mo atoms within the crystal are always inert. Focusing on this standpoint, Zhang et al. hydrogenated Bi$_2$MoO$_6$ with the aim to expose more unsaturated Mo atoms by inducing the escape of oxygen atoms in saturated Mo–O bond and enhance its N$_2$ activation capacity. As expected, the hydrogenated Bi$_2$MoO$_6$ exhibited a NH$_3$ production rate 9.5 times higher than that of untreated one, up to 1.3 mmol g$^{-1}$ h$^{-1}$.

(3) Functionalized semiconductors with two functional units modified.

**Semiconductors with functional groups.** Grafting amine groups onto g-C$_3$N$_4$ could enhance the charge separation efficiency and consequently nearly double its activity in PNF.²⁹ Introducing cyano groups onto g-C$_3$N$_4$ not only improves the separation and migration of photoinduced electron–hole pairs but also enhances N$_2$ activation owing to its electron-withdrawing characteristics. Thus, cyano group functionalized g-C$_3$N$_4$ resulted in a 12.8 times promoted activity in PNF than pristine g-C$_3$N$_4$.³⁰ With the assistance of K$, the cyano group on modified g-C$_3$N$_4$ could be regenerated readily via the analogous Mars van Krevelen mechanism, which ensured the stability of the functionalized semiconductors.³¹

**Hydrogenated semiconductors.** Dong et al. reported that hydrogen treatment could withdraw the oxygen atoms and leave oxygen vacancies in BiOBr, which then broadened the photoelectricity absorption window, triggered the electron transfer from BiOBr to the adsorbed N$_2$, and responded for the 2.6 times improved PNF efficiency, compared to the untreated counterpart.³²

Acid treated semiconductors. Wang et al. reported that phosphate acid treated LaFeO$_3$ could catalyze PNF effectively, producing NH$_3$ at a rate of ~250 μmol g$^{-1}$ h$^{-1}$ under simulated light irradiation. Mechanism exploration suggested that phosphate acid served as the Lewis acid center, it worked synergistically with Fe in LaFeO$_3$ to activate N$_2$ via the “push–pull” hypothesis. That is, the electron density is pulled from Fe and pushed into N$_2$ by the adjacent hydrogen bonding sites. In addition, phosphate modification facilitated H$_2$O dissociation.³³

**Metal decorated semiconductors.** In case that a metal is decorated onto a semiconductor with vacancy sites, the doped metal and the vacancies work in concert to promote N$_2$ activation. For instance, Dong et al. constructed a Bi/BiOBr heterostructure with abundant oxygen vacancies via a one-step solvothermal strategy. In BiOBr, the oxygen defective sites were the active centers for N$_2$ adsorption. Bi and oxygen vacancies promoted the interfacial charge transfer from Bi/ BiOBr to the adsorbed N$_2$, facilitated charge separation efficiency and accounted for a remarkably high NH$_3$ production rate (1350 μmol g$^{-1}$ h$^{-1}$).³⁴

**Heterojunctions and homojunctions.** Heterojunctions and homojunctions are fabricated by integrating two or more semiconductors. Heterojunctions and homojunctions generally inherit the merits of each single semiconductor counterpart, exhibit stronger light harvesting capacities and deliver high photocatalytic activities. Further introducing other dopants or vacancies into heterojunctions or homojunctions might tailor the active centers for N$_2$ activation. The advantages of heterojunctions and homojunctions make them applicable in PNF.

(1) Heterojunctions/homojunctions with modified light harvesting unit. Bi$_2$Te$_2$/BiOCl,³⁴ g-C$_3$N$_4$/ZrO$_2$,³⁵ MoO$_2$/BiOCl³⁶ perovskite/attapulgite³⁷ and CdS/LDH (LDH: layered double hydroxide)³⁸ are typical heterojunctions that have been reported active in PNF. Here CdS/LDH is taken as an example for elaboration. In the case that CdS/LDH heterojunction was constructed between (003) or (012) facet of LDH and (002) facet of CdS, a build-in electric field would be induced under light irradiation, which promoted charge transfer from the heterostructure to the reaction media for N$_2$ activation via a favorable configuration and resulted in a better catalytic activity.³⁹
Z scheme is a special case of heterojunctions. Z schemes AgBr/Bi4O5Br2,79 Bi2O3@CoAl-LDHs,80 3,4-dihydroxybenzaldehyde-functionalized Ga2O3@g-C3N4,81 g-C3N4/Mg53.1Al0.3Fe0.1O1.7,82 nano-MOF@defected g-C3N4 (MOF: metal organic frameworks),83 and SiW9Co3/PDA/BWO (PDA: poly-dopamine; BWO: Bi2WO6)84 have been reported active in PNF. In these Z schemes, the separation of photoinduced electron–hole pairs was significantly improved, which played a dispensable role in boosting their catalytic activities.

(2) Heterojunctions/homojunctions with modified light harvesting unit and active sites. The catalytic activities of heterojunctions in PNF could be further improved by doping foreign elements, introducing defective sites or loading another component to one of the semiconductors of heterojunctions. N deficient g-C3N4/Cu2(OH)2CO3,85 N deficient g-C3N4/Ag2CO3,86 Bi2MoO6/oxygen-vacancy-rich BiOBr,87 MoS2/C–ZnO (C was loaded onto ZnO),88 TiO2@C g-C3N4,89 B doped g-C3N4/NiP90 and In2O3/In2S3 (oxygen vacancies are generated in situ)91 are representatives. In this type of heterojunctions, the junctions between the two semiconductors as well as the doped/loaded component or defective sites synergistically contributed to their activities in PNF.

Homojunction catalyst such as ordered/disordered TiO2 exhibited a superior activity in PNF, affording a NH3 formation rate of 432 μmol g−1 h−1 under solar illumination.92 In the homojunction catalyst, ordered TiO2 exhibited a stronger N2 adsorption capacity with a reduced activation barrier while the disordered TiO2 was rich in oxygen vacancies which selectively chemisorbed N2 and enhanced visible light harvesting. The synergistic effect between ordered TiO2 and disordered TiO2, together with the rapid interfacial charge separation, ensured its superior activity (Fig. 5).92

Semiconductor-based hydrophilic-hydrophobic catalyst. In case that H2O is the proton donor and solid catalyst is designed, PNF occurs at the gas (N2)–liquid (H2O)–solid (catalyst) triphase interface. The poor solubility and the poor diffusion rate of N2 in H2O severely limit the N2 fixation efficiency. In order to overcome this obstacle, Fan et al. designed a Bi4O2Br2/ZIF-8 catalyst (ZIF-8 is a kind of MOFs), where Bi4O2Br2 is hydrophilic whereas ZIF-8 is hydrophobic.93 Such a hydrophilic–hydrophobic catalyst allowed the direct delivery of N2 and H2O into the reaction interface, without the diffusion of N2 in H2O. The rapid supply of N2 ensured the efficient utilization of photoinduced electrons and led to a superior activity (NH3 production rate was high up to 327 μmol g−1 h−1).94

Plasmonic metal-based catalysts for PNF

Plasmonic metals, such as Au and Ag, exhibit localized surface plasmon resonance (LSPR) effect upon light irradiation. The LSPR effects empower the plasmonic metal-based catalysts applicability in PNF. Over most of the plasmonic metal-based catalysts, the light harvesting unit and the active center work synergistically for improved performance. As the particle sizes, morphologies as well as the particle–particle distances of plasmonic metals are crucial for their light harvesting capacities, the tailoring of these properties are generally adopted with the aim to accelerate the reaction rate of plasmonic metal-based catalysts in PNF.

For example, Wang et al. encapsulated Au nanoparticles into a MOF membrane (Uio-66) and realized a NH3 production rate of 359.1 μmol g−1 h−1 under visible light irradiation (λ > 400 nm, 100 mW cm−2).94 It was discovered that N2 adsorbed on Au nanoparticles. Upon light irradiation, hot electrons generated on Au nanoparticles. The hot electrons on Au activated N2 via two pathways, ① induced an electromagnetic field to polarize N2 and ② directly injected into the anti-bonding orbitals of N2 molecules (Fig. 6a). Moreover, the gas permeable nature of MOF membrane facilitated the mass transfer of the reactants, which further boosted its photocatalytic activity at

![Figure 5](image-url)
the gas (N₂)-membrane (Uio-66 encapsulated Au nanoparticles)-solution (H₂O) interface (Fig. 6b).²⁹

Yang et al. reported that Au nanoparticles supported on nitrogen deficient g-C₃N₄ could catalyze PNF, achieving a NH₃ production rate of ~783 μmol g⁻¹ h⁻¹ under visible light irradiation.³⁵ In this catalytic system, the nitrogen vacancy sites adsorbed N₂; Au and g-C₃N₄ harvested visible light and induced electrons upon light irradiation, which then injected into N₂ for its activation.³⁶ Liao et al. synthesized small Ag doped g-C₃N₄ catalyst and unraveled that Ag enhanced N₂ adsorption, generated more electrons, facilitated the separation and migration of photogenerated electron–hole pairs and consequently resulted in high activity in PNF.³⁶ Wang et al. supported Au nanocrystals onto Mo doped W₁₈O₄₉ and realized a NH₃ synthesis rate of ~399 μmol g⁻¹ h⁻¹.³⁷ Au not only harvested visible light but also decreased the desorption energy of the product NH₃, which accelerated the regeneration of the active sites for next catalytic cycle.³⁷ Introducing a moderate amount of alkali metal cations could further promote N₂ activation and then enhance the performance of these plasmonic metal-based catalysts in PNF.³⁸

Iron-based catalysts for PNF

Iron is the most active metal for N₂ activation. The strong N₂ activation capacity of iron makes it applicable as active center for PNF. However, the light harvesting capacity of iron is very weak. Integrating iron with a material that could harvest light efficiently is an approach to design the photocatalyst for PNF. Based on this principle, doping iron into semiconductors, loading iron onto semiconductors, constructing a Fe-based heterostructure catalyst and loading iron onto other light harvesting materials are promising avenues. Therefore, over most of the iron-based catalysts for PNF, both the light harvesting unit and the active center are regulated. Up to now, various iron-based catalysts have been designed. In this section, we will discuss the types of iron-based catalysts for PNF and emphasize their progress.

(1) Fe doped into semiconductors. Doping Fe into a semiconductor could tune the local electronic structure of the catalysts and thereby facilitate N₂ activation. For example, when Fe is doped into TiO₂, Fe will substitute Ti atoms in TiO₂ owing to their similar radii, which creates oxygen vacancies at the neighbor of Fe atoms to meet the local charge balance.³⁹ The Fe atoms and oxygen vacancies work in concert to facilitate N₂ adsorption and polarization, which enables N₂ hydrogenation via the favorable associative distal pathway and contributes to PNF. As shown in Fig. 7a and b, 5wt% Fe/TiO₂ (5-FTNFs) afforded a stable NH₃ production rate of ~64 μmol g⁻¹ h⁻¹ under the full spectrum illumination of a 300 W Xe lamp.³⁹ Isotope labeling experiment as well as ¹H-NMR (NMR: Nuclear magnetic resonance, Fig. 7c and d) indicated that the generated NH₃ was originated from N₂ instead of other contaminants.³⁹ Similarly, Fe-doped BiOBr with oxygen vacancies afforded a NH₃ yield of 46.1 μmol g⁻¹ h⁻¹ without any sacrificial reagent under 400 mW cm⁻² visible light irradiation.¹⁰⁰ The doped Fe and the oxygen vacancies synergistically modulated the band structure, improved charge transfer and thereby enhanced the photocatalytic activities.¹⁰⁰

Doping exerts functions beyond creating oxygen vacancies. For instance, the Fe atoms on the surface of Fe doped SrTiO₃ (FeₓSr₁₋ₓTiO₃) could not only chemisorb and activate N₂, but also promote the electron transfer from FeₓSr₁₋ₓTiO₃ to N₂, which resulted in high N₂ fixation capacity and a NH₃ production rate of 30.1 μmol g⁻¹ h⁻¹ over FeₓSr₁₋ₓTiO₃ (x = 0.1) under Xe lamp illumination.¹⁰¹ Doping Fe into Mo-based semiconductors could narrow their band gaps, extend their light absorption capacities as well as generate new Fe–Mo active centers, which enables Fe doped Mo-based semiconductor to harvest more solar light and facilitate the electron–hole separation and migration efficiency.¹⁰² Chang et al. doped Fe into 2D MoTe₂ nanosheets to construct Fe–Mo active centers.¹⁰³ It is reported that Fe doped into MoTe₂ facilitated the separation and transfer of photoinduced electron–hole pairs, prolonged their lifetime and accounted for an obviously boosted NH₃ production rate.¹⁰³ Similarly, Fe doped SrMoO₄ (Fe/Sr = 1.6) achieved a NH₃ production rate of 93.1 μmol g⁻¹ h⁻¹ under Xe lamp illumination.¹⁰²

(2) Fe loaded onto semiconductors. Zhang et al. reported that Fe/TiO₂–H₂ could serve as a dual temperature zone catalyst for

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**Fig. 6** (a) Schematic illustration of PNF over Uio-66 encapsulated Au nanoparticles. (b) Schematic illustration of the interface design for PNF. This figure has been adapted from ref. 94 with permission from Royal Society of Chemistry, copyright 2021.

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PNF. Under solar light irradiation, catalyst surface temperature reached 495 °C, with a temperature difference between Fe and TiO$_2$–H$_2$ of 137 °C, owing to the plasmonic local heating effect of Fe. Then Fe acted as the hot zone catalyst to dissociate N$_2$ via its photogenerated hot electrons, while TiO$_2$–H$_2$ accommodated the N atoms from Fe and hydrogenated them into NH$_3$. Fe/TiO$_2$–H$_2$ delivered a NH$_3$ concentration of 109.5 μmol g$^{-1}$ h$^{-1}$, an order of magnitude higher than the commercial Haber-Bosch Fe catalyst.$^{104}$

(3) Fe based heterostructure catalysts. Fe$_2$O$_3$/g-C$_3$N$_4$, prepared by thermal treatment method exhibited a NH$_3$ production rate of 7044 μmol g$^{-1}$ h$^{-1}$ under the illumination of a 300 W Xe lamp, where the heterostructure facilitated light harvesting and Fe$_2$O$_3$ played key roles in N$_2$ adsorption.$^{105}$ Oxygen deficient Fe$_2$O$_3$/ZnO could stably produce NH$_3$ at a rate of 80 μmol g$^{-1}$ h$^{-1}$ without any sacrificial agent under visible light irradiation.$^{106}$ Over Fe$_2$O$_3$/ZnO, the synergistic effect between oxygen vacancies and Fe$_2$O$_3$ activated N$_2$, while the heterostructure of Fe$_2$O$_3$/ZnO prohibited the recombination of electron–hole pairs, which accounted for its superior photocatalytic performance.$^{107}$ Fe-modified polygorskite supported FeS$_2$, synthesized by microwave hydrothermal method, could serve as a Z scheme type photocatalysts for PNF and recorded a NH$_3$ production rate of 147 μmol g$^{-1}$ h$^{-1}$ under solar light irradiation.$^{107}$ Its activity was ascribed to the narrowed band gap, widened light harvesting region of Fe-modified polygorskite as well as the facilitated charge transfer between Fe-modified polygorskite and FeS$_2$.$^{107}$

(4) Other light responsive materials, such as graphdiyne and MOFs, supported Fe catalysts. For instance, Li et al. reported that the morphology, coordination environment and the valence state of iron oxide could be manipulated by encapsulating versatile shaped Fe$_3$O$_4$ by graphdiyne.$^{108}$ The encapsulation of graphdiyne endowed Fe$_3$O$_4$@graphdiyne heterojunctions strong light harvesting capacity, a structural evolution during PNF, as well as a NH$_3$ yield of an unprecedented level of $\sim$1762 μmol g$^{-1}$ h$^{-1}$.$^{109}$ The Fe atoms in Fe-based MOFs (e.g., MIL-101(Fe), MIL-100(Fe), MIL-88(Fe)) have high electron densities, low reaction barriers for the activation of N$_2$ and H$_2$ to N–H bond, and could serve as the catalytic active center for PNF.$^{109}$ Taking MIL-101(Fe) as an example, it gave a NH$_3$ production rate of 100.7 μmol g$^{-1}$ h$^{-1}$ under the illumination of a 300 W Xe lamp.$^{109}$

Ruthenium-based catalysts for PNF

Ruthenium is another metal capable of activating N$_2$ under thermally-driven conditions. Ruthenium-based catalysts that could harvest solar light effectively have been successfully applied in PNF. Since the light harvesting capacity of ruthenium is weak, the light harvesting unit of ruthenium-based photocatalysts are generally semiconductors or other light responsive materials. Similar as iron-based catalysts, over most of the ruthenium-based catalysts for PNF, both the light harvesting unit and the active center are regulated. Based on the nature of the light responsive components, these ruthenium-based catalysts could be divided into the following categories.

(1) Semiconductor, such as TiO$_2$, GaN, C$_3$N$_4$ and CeO$_2$, supported ruthenium catalysts. For example, Ru/TiO$_2$, in which singly dispersed Ru atoms were decorated onto TiO$_2$ nanosheets rich in oxygen vacancies, is active for PNF.$^{110}$ Over Ru/TiO$_2$, the single Ru atoms were possibly located at the oxygen vacancy sites and stabilized by the vacancies.$^{111}$ The isolated Ru atoms promoted the chemisorption of N$_2$, boosted the electron–hole separation and overall recorded a NH$_3$ generation rate of 3.3 μmol g$^{-1}$ h$^{-1}$ upon irradiation by a 300 W high pressure Xe lamp.$^{110}$ Ru/P25, prepared by the facile synthetic method, exhibited Ru particle sizes of 2–3 nm. In PNF, Ru/P25 dissociated H$_2$O to hydrogen atoms continuously and then hydrogenated N$_2$ molecules via a distal reaction pathway at the gas (N$_2$)–liquid (H$_2$O) interface.$^{111}$ The NH$_3$ yield over Ru/P25 was high up to 5.2 μmol g$^{-1}$ h$^{-1}$ under the irradiation of a Xe lamp.$^{112}$ GaN supported Ru catalysts, Ru/GaN, behaved tailorable electronic and morphological properties.$^{113}$ The interfacial Schottky junction between Ru and GaN facilitated the electron transfer from GaN to Ru, then the electron tank in Ru promoted N≡N bond dissociation and achieved NH$_3$ synthesis at low temperatures. Notably, 5 wt% Ru/GaN afforded an average NH$_3$ production rate of 120 μmol g$^{-1}$ h$^{-1}$ after 2 h UV irradiation at 10 °C (Fig. 8)$^{112}$

Modifying the semiconductor supported Ru catalysts could speed up NH$_3$ production rate. For instance, modifying Ru/g-C$_3$N$_4$ or Ru/TiO$_2$ by K could enrich the electrons in Ru, enhance the catalyst capacities in activating N$_2$ and consequently improve NH$_3$ generation rate.$^{111,114}$ Doping Zr$^{4+}$ into CeO$_2$ could increase the electron densities on Ce and create oxygen vacancies, which strengthened the interactions between Ru nanoparticles and supports.$^{115}$ The strong interaction upshifted the Ru d-band center relative to Fermi level and enhanced N$_2$ cleavage.$^{116}$ Ternary heterostructure Ru/RuO$_2$/g-C$_3$N$_4$ catalyst gave an average NH$_3$ production rate of 13.3 μmol g$^{-1}$ h$^{-1}$, 6 times higher than Ru/g-C$_3$N$_4$.$^{116}$ Characterization results indicated that under light
irradiation, the electrons transferred to Ru whereas holes migrated to RuO₂ to facilitate the reduction and oxidation reactions, respectively, meanwhile, the electron-rich Ru activated N₂ effectively.¹¹⁶ Decorating Ru@g-C₃N₄ catalyst by S-deficient CoSₓ could construct a bimetallic center at the interface of Ru/CoSₓ, which facilitated N₂ polarization and activation via electron transfer from Ru and Co to N₂ upon light irradiation and ultimately gave a NH₃ production rate high up to 440 μmol g⁻¹ h⁻¹.¹¹⁷

(2) Other light responsive materials supported Ru catalysts. For example, coal-based carbon nanosheet supported Ru catalyst yielded 55.3 μmol g⁻¹ h⁻¹ NH₃ under a 300 W Xe lamp irradiation.¹¹⁸ Graphene oxide/silica could sufficiently disperse Ru and enhance the LSPR effect of Ru species, which excited more electron–hole pairs upon light irradiation and accelerated NH₃ generation.¹¹⁹ TiO₂–Mxene hybrid nanostructure supported Ru catalysts afforded an ammonia production rate of ~5.7 μmol g⁻¹ h⁻¹, which was principally stemmed from the synergetic effects among TiO₂, Mxene and Ru.¹²⁰

Other catalysts for PNF

Numerous other catalysts have also been designed for PNF. Phosphorus is one of them. Yu et al. disclosed that the edges of black phosphorus (BP) could absorb and reduce N₂. They synthesized an edge-rich BP nanostructure with a flake-like shape via chemical etching exfoliation method. The edge-rich BP is of good dispersibility in H₂O, which allows its full contact with the reactants. Owing to the abundant active sites for N₂ chemisorption and reduction as well as the efficient contact between the reactants and catalyst, the edge-rich BP delivered a NH₃ production rate of 2370 μmol g⁻¹ h⁻¹.¹²¹ Lin et al. loaded red phosphorus (RP) onto photoinactive SiO₂ via a facile sublimation-deposition method, in which RP was modified by in situ formed carbon.¹²² The hybrid SiO₂/C-RP catalyst was of large specific surface area, strong light harvesting capacity and high charge separation efficiency, which accounted for a NH₃ production rate of 36.5 μmol g⁻¹ h⁻¹.¹²³

MOFs have also been successfully applied in PNF. Chen et al. unraveled that the Ce species in MOF-76(Ce) was an electron tank, which accepted photoinduced electrons to its 4f orbitals and then donated the electrons to the anti-bonding orbitals of N₂.¹²⁴ As a result, MOF-76(Ce) gave an average NH₃ yield of 34 μmol g⁻¹ h⁻¹ under ambient conditions.¹²⁵ Ye et al. reported that functionalized MIL-125(Ti) could act as photocatalysts for PNF under visible light irradiation without any sacrificial reagent.¹²⁶ Notably, amine-functionalized NH₂-MIL-125(Ti) afforded a NH₃ production rate of 12.3 μmol g⁻¹ h⁻¹. The electron transfer from the ligand to metal in MIL-125(Ti) induced Ti³⁺, which was the active sites for N₂ activation. Functionalization extended the light harvesting capacity of MIL-125(Ti) and further enhanced catalyst activity in PNF.¹²⁷

LDH with oxygen defects and electron-rich metals have been discovered active in PNF, in which vacancies and metal centers synergistically promote N₂ adsorption, facilitate the separation of photoinduced electron–hole pairs, and thereby boost activity in PNF.¹²⁸,¹²⁹ Zhang et al. uncovered that 0.5% mol Cu modification could impart ZnAl-LDH oxygen vacancies and electron-rich unsaturated Cu⁵⁺ (δ < 2)¹³⁰ NaOH treatment could also induce vacancies and low-coordinated metal centers in ZnCr-LDH, ZnAl-LDH and NiAl-LDH.¹³¹ Taking Cu⁵⁺-ZnAl-LDH as an example, it realized a NH₃ production rate of 110 μmol g⁻¹ h⁻¹ under UV-vis light irradiation.¹³²

In addition, Mo-based catalysts (e.g., Mo₄/g-C₃N₄),¹³³ carbon-tungstic-acid hybrids,¹³⁴ Pr³⁺:LiNbO₃,¹³⁵ Pt GO/SiO₂ (GO: graphene oxide)¹³⁶ have also been utilized in PNF. These catalysts produce NH₃ at the magnitude of μmol g⁻¹ h⁻¹. Meanwhile, the studies on these catalysts are quite limited and the reaction mechanism is not fully understood.

Summary and outlooks

Ideally, PNF is a safe and green approach to synthesize NH₃ under ambient conditions, using the inexhaustible solar light as the sole energy input and the abundant N₂ as a reactant. Catalyst is the key for PNF. Over the past few years, extensive studies have been conducted to search for efficient catalysts for PNF. Semiconductor, plasmonic metal-based catalysts, iron-based catalysts, ruthenium-based catalysts and several other catalysts, have been reported active in PNF. Table 1 lists the

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Fig. 8 NH₃ production rate over (a) Ru/GaN of different Ru loadings, (b) 5 wt% Ru loaded onto various supports, and (c) NH₃ production rate as a function of time over 5 wt% Ru/GaN under UV irradiation, with reusability of 5 wt% Ru/GaN as an inset. This figure has been adapted from ref. 112 with permission from American Chemical Society, copyright 2019.
| Catalysts                                      | Catalytic types         | Reaction conditions                                                                 | NH₃ yield (μmol g⁻¹ h⁻¹) | Ref. |
|-----------------------------------------------|-------------------------|--------------------------------------------------------------------------------------|---------------------------|------|
| Ultrathin MoS₂                                | Pristine semiconductors | Water (200 mL), catalyst (15 mg), reaction temperature (25 °C), N₂ bubble, under light irradiation (500 W, λ > 420 nm, Xe lamp) | 325                        | 34   |
| BiO quantum dots                              | Pristine semiconductors | Water (200 mL), catalyst (50 mg), reaction temperature (25 °C), N₂ bubble, under light irradiation (500 W, Xe lamp) | 1226                       | 35   |
| PFL-g-C₃N₄ (PFL: porous few-layer)             | Defective semiconductors| 20% CH₃OH (100 mL), catalyst (20 mg), N₂ (30 min), under light irradiation (500 W, AM 1.5G, 100 mW cm⁻², Xe lamp) | 8200                      | 38   |
| D-CN (1D defective g-C₃N₄)                    | Defective semiconductors| 0.1 mol L⁻¹ K₂SO₄ solution (95 mL) and methanol (5 mL), catalyst (200 mg), reaction temperature (25 °C), N₂ bubble (2 h), under light irradiation (600 mW cm⁻²), reaction time (8 h) | 17.4                       | 39   |
| BOC/OV (surface oxygen vacancies modified micro-nanosheet structure Bi₂O₂CO₃) | Defective semiconductors| 0.1 mmol L⁻¹ Na₂SO₃ solution (50 mL), catalyst (10 mg), N₂ (30 min), under light irradiation (300 W, Xe lamp) | 14.7                       | 40   |
| A-SmOCl (amorphous SmOCl nanosheets)          | Defective semiconductors| Water (20 mL), catalyst (10 mg), N₂ (30 min), under light irradiation (250 mW cm⁻², 320-780 nm, Xe lamp) | 426                        | 42   |
| TiO₂ (B) nanotubes                            | Defective semiconductors| Water (90 mL) and methanol (10 mL), catalyst (25 mg), ultrasonic oscillation (10 min), reaction time (10 min), N₂ (30 min) under simulated sunlight irradiation (300 W, 60 min, AM 1.5G, Xe lamp) | 106                        | 48   |
| TiO₂-OVs (reduced TiO₂)                       | Defective semiconductors| Water (90 mL) and methanol (10 mL), catalyst (50 mg), ultrasonic oscillation (15 min), N₂ (30 mL min⁻¹), reaction temperature (25 °C), under light irradiation (300 W, Xe lamp) | 324.86                     | 49   |
| BCN (B-doped g-C₃N₄ nanosheets)               | Doped semiconductors    | Aqueous solution of Na₂SO₃ (40 mL, 1.0 × 10⁻³ mol L⁻¹), catalyst (20 mg), N₂ (30 mL min⁻¹, 30 min), reaction time (1 h), under light irradiation (250 W, λ > 400 nm, 500 mW cm⁻², Xe lamp) | 313.9                      | 55   |
| C-BiO (carbon-doped BiO)                      | Doped semiconductors    | Water (40 mL) and ethanol (10 mL), catalyst (50 mg), under light irradiation (300 W, Xe lamp) | 311                        | 61   |
| NCN/MgO (g-C₃N₄ nanosheets decorated with MgO nanoparticles) | Functionalized semiconductors | Water (10 mL) and 40 μL absolute ethanol (0.789 g L⁻¹), catalyst (40 mg), ultrasonic oscillation (6 min), N₂ (1 h), reaction temperature (25 °C), under light irradiation (500 W, 100 mW cm⁻², λ > 420 nm, Xe lamp) | 4554                       | 63   |
| KOH treated g-C₃N₄                            | Functionalized semiconductors | CH₃OH (150 mL), catalyst (20 mg), reaction temperature (25 °C), under light irradiation (300 W, 100 mW cm⁻², Xe lamp) | 3632                       | 64   |
| Cu/TiO₂ (transition metal modified TiO₂)      | Functionalized semiconductors | 5.0 wt% glycerol aqueous solution (200 mL), catalyst (100 mg), under simulating solar light irradiation (300 W, 100 mW cm⁻², Xe lamp) | 6780                       | 65   |
| P-LFO (phosphate modified LaFeO₃)             | Functionalized semiconductors | Water (100 mL), catalyst (10 mg), N₂ (80 mL min⁻¹, 30 min), reaction temperature (15 °C), under simulating solar light irradiation (300 W, 1.63 W cm⁻², Xe lamp) | 250                        | 72   |
| Bi@BiOBr                                     | Functionalized semiconductors | Water (100 mL), catalyst (10 mg), N₂ (80 mL min⁻¹, 30 min), reaction temperature (15 °C), under simulating solar light irradiation (300 W, 1.63 W cm⁻², Xe lamp) | 1350                       | 73   |
| MOF@DF-C₃N₄ (nano-MOF@defected thin film C₃N₄) | Heterojunctions and homojunctions | Water (100 mL), catalyst (10 mg), N₂ (80 mL min⁻¹, 30 min), reaction temperature (15 °C), under simulating solar light irradiation (300 W, 1.63 W cm⁻², Xe lamp) | 2320                       | 83   |
| MoS₂/C-ZnO                                   | Heterojunctions and homojunctions | Water (100 mL), catalyst (10 mg), N₂ (80 mL min⁻¹, 30 min), reaction temperature (15 °C), under simulating solar light irradiation (300 W, 1.63 W cm⁻², Xe lamp) | 49.1                       | 88   |
| TiO₂@C/g-C₃N₄                                | Heterojunctions and homojunctions | Water (100 mL), catalyst (10 mg), N₂ (80 mL min⁻¹, 30 min), reaction temperature (15 °C), under simulating solar light irradiation (300 W, 1.63 W cm⁻², Xe lamp) | 250.6                      | 89   |
| TiO₂@C/g-C₃N₄                                | Heterojunctions and homojunctions | Water (100 mL), catalyst (10 mg), N₂ (80 mL min⁻¹, 30 min), reaction temperature (15 °C), under simulating solar light irradiation (300 W, 1.63 W cm⁻², Xe lamp) | 432                        | 92   |
## Table 1 (Contd.)

| Catalysts | Catalytic types | Reaction conditions | NH$_3$ yield ($\mu$mol g$^{-1}$ h$^{-1}$) | Ref. |
|------------|-----------------|---------------------|----------------------------------------|------|
| Na$_4$Ar/R$_{O}$ (Na treatment of P25-TiO$_2$, A$_{dis}$: disordered anatase, R$_{dis}$: disordered rutile) | | Water (50 mL), catalyst (50 mg), isopropyl alcohol (7 mL), N$_2$ (0.3 L min$^{-1}$) under simulated AM 1.5G sunlight irradiation (1000 W, Xe lamp) in a double-layered jacket with cooling water circulating line | 16.4 | 93 |
| Bi$_2$O$_3$Br$_2$/ZIF-8 | Semiconductor-based hydrophilic-hydrophobic catalyst | Water (50 mL), catalyst (50 mg), N$_2$ (80 mL min$^{-1}$) under simulated sunlight irradiation (300 W, 200–800 nm, Xe lamp) | 359.1 | 94 |
| Au@UIO-66 | Plasmonic metal-based catalysts | Aqueous solution of K$_2$SO$_4$ (50 mL, 0.5 mol L$^{-1}$), catalyst (15 mg), N$_2$ (80 mL min$^{-1}$, 30 min), reaction temperature (25°C) under light irradiation (300 W, $\lambda >$ 400 nm, 100mW cm$^{-2}$, Xe lamp) | 783.4 | 95 |
| Au/HCNS-NV (HCNS: Hollow mesoporous carbon nitride sphere, NV: nitrogen vacancies) | Plasmonic metal-based catalysts | Mixture of water (50 mL) and methanol (20 mL), catalyst (50 mg), ultrasonic oscillation (10 min), reaction temperature (room temperature), N$_2$ (100 mL min$^{-1}$, 30 min), under light irradiation (300 W, Xe lamp) | 430 | 98 |
| Au/P25-K$^+$ | Plasmonic metal-based catalysts | Water (50 mL), catalyst (5 mg), N$_2$ (60 mL min$^{-1}$) under light irradiation (300 W, $\lambda >$ 400 nm, 100mW cm$^{-2}$, Xe lamp) | 129.08 | 103 |
| Fe–MoTe$_2$ | Iron-based catalysts | Milli-Q (80 mL), catalyst (10 mg), reaction temperature (25°C), N$_2$ (50 sccm, 60 min), under light irradiation (300 W, $\lambda <$ 420 nm, 400 mW cm$^{-2}$, h, Xe lamp) | 100.7 | 109 |
| MIL-101(Fe) | Iron-based catalysts | Water (100 mL), catalyst (50 mg), ultrasonic oscillation (10 min), reaction temperature (room temperature), N$_2$ (60 mL min$^{-1}$, 30 min), under simulated light irradiation (300 W, 1 h, Xe lamp) | 3.3 | 110 |
| Ru–TiO$_2$ | Ruthenium-based catalysts | 20% ethanol solution (100 mL), catalyst (40 mg), reaction temperature (25°C), N$_2$ (1 h), light irradiation (300 W, Xe lamp), reaction time (4 h) | 438 | 117 |
| Ru-Vecos/CN (Ru/CoS$_x$ with S-vacancy on graphitic carbon nitride nanosheets) | Ruthenium-based catalysts | 10% methanol solution (50 mL), catalyst (25 mg), N$_2$ (30 min), light irradiation (300 W, 200 mW cm$^{-2}$, Xe lamp) | 38.4 | 129 |
| SiO$_2$/C-RP (RP: red phosphorous) | Other catalysts | Water (40 mL), catalyst (20 mg), ultrasonic oscillation, N$_2$, reaction temperature (25°C) under light irradiation (300 W, 320 mW cm$^{-2}$, Xe lamp) | 36.5 | 122 |
| Mo–PCN SACs (PNG polymeric carbon nitride, SACs: single-atom catalysts) | Other catalysts | Water (6 mL), catalyst (3 mg), ultrasonic oscillation (60 min), pH = 5, N$_2$, reaction temperature (room temperature), reaction time (12 h), light irradiation (300 W, Xe lamp) | 830 | 127 |
| Pr$^{3+}$: LiNbO$_3$ | Other catalysts | Aqueous solution (100 mL), catalyst (40 mg), N$_2$ (30 min), reaction temperature (30°C), under light irradiation (300 W, $\lambda >$ 420 nm, Xe lamp) | 38.4 | 129 |
performances of some typical catalysts. This review summarizes the progress of each category of the catalysts designed for PNF, with a special attention on semiconductor-based catalysts. Generally speaking, the catalyst development is still in the infant stage and huge challenges need to be overcome.

(1) $\text{NH}_3$ production rates are still low. Over most of the catalysts, $\text{NH}_3$ production rates are in the magnitude of mmol g$^{-1}$ h$^{-1}$ or even $\mu$mol g$^{-1}$ h$^{-1}$. It is far away from the industrial applications. Meanwhile, other chemicals (e.g., $\text{N}_2$H$_4$) are occasionally generated as byproducts. Therefore, persistent efforts should be devoted to design catalysts that could drive PNF efficiently and selectively to the desired product $\text{NH}_3$. Adopting novel materials as catalysts for PNF might benefit this research area.

(2) There is a long way to make clear the reaction mechanism. In spite that some studies carried out mechanism explorations, little progress have been made in understanding the fundamental mechanism. The physicochemical properties of the photocatalysts under working states remain unclear; $\text{N}_2$ chemisorption, activation and reduction pathway on the active sites are not clarified; the electron–hole transfer and migration routes need to be understood; in-depth understanding on the structure/property–performance correlations in PNF needs to be unraveled. Theoretical studies together with in situ characterization techniques might offer potential approaches to make clear the reaction mechanism.

In summary, despite that the development of catalysts for PNF is still in the primary stage, progress has been made. PNF has been proved as a promising avenue to replace the industrialized Haber-Bosch process to produce $\text{NH}_3$. Numerous opportunities exist to move the research field forwards.

Conflicts of interest

The authors declare no competing interests.

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