

Recent advances in photocatalytic nitrogen fixation and beyond

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Minireview

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Recent advances in photocatalytic nitrogen fixation and beyondYunxia Wei^{a,1} Wenjun Jiang^{b,1} Yang Liu^{c,1} Xiaojuan Bai^d, Derek Hao^{e*} and Bing-Jie Ni^{e*}

The traditional synthesis of ammonia is an industrial process with high energy consumption and serious pollutions, thus, it is urgent to develop cost-effective approaches to synthesize ammonia under ambient conditions. In recent years, photochemical synthesis of ammonia became a hot research frontier. In this minireview, we summarized recent advances in materials sciences for photocatalytic nitrogen fixation. Beyond nitrogen fixation, we talked about the alternative for artificial ammonia synthesis and coupling reactions with other reactions for the synthesis of other high-value chemicals. The results and findings of this review will help the development of ammonia synthesis and the synthesis of other high-value chemicals.

1. Introduction

Nitrogen is an irreplaceable element for the growth and development of plants, because it is the source for the generation of chlorophyll and amino acids.¹ Plants cannot utilize the atmospheric nitrogen until it is converted from free state to compound state, which is called nitrogen fixation.² In the natural environment, the nitrogen fixation process is mainly achieved by lightning and nitrogen-fixing microorganisms. However, it is not enough to support human demand. To achieve a sustainable agricultural industry for the increasing population, more and more nitrogen-based fertilizers are required, thus artificial nitrogen fixation is invented. The current commercial artificial nitrogen fixation is achieved through the Haber process, which is a milestone for human development.³ However, a huge amount of energy is required to finalize this process. As a result, about 2% of global energy is consumed by the Haber process each year and it should be responsible for 1.6 % of global CO₂ emission.⁴ To reduce energy consumption and CO₂ emission, researchers are seeking for new approaches to replace the Haber process. Recently, photocatalytic nitrogen fixation has become a hot research frontier, which has broad potential to be utilized on large scale.⁵⁻⁸ Compared with the traditional Haber process, photocatalytic nitrogen fixation has some distinctive advantages (Table 1). In detail, the hydrogen source of photocatalytic nitrogen fixation is water, rather than natural gas, which means that high temperature is not required to convert the natural gas to hydrogen. The photocatalytic nitrogen fixation reaction can be completed under ambient conditions, without the requirement of high temperature and high pressure.^{9, 10} More importantly, the photocatalytic nitrogen fixation reaction is driven by solar energy, rather than fossil fuel, indicating the consumption of traditional energy and the emission of CO₂ can

be significantly decreased. However, there is still a huge gap for the photocatalytic nitrogen fixation to be applied in mass production, due to the low ammonia yield rate. Therefore, it is urgent to develop novel materials to improve photocatalytic nitrogen fixation efficiency.

Table 1. The differences between the Haber process and photocatalytic nitrogen fixation process.

	Haber process	Photocatalytic nitrogen fixation
Hydrogen source	Natural gas	Water
Catalysts	Iron catalyst	Semiconductors
Temperature	400–500 °C	Room temperature
Pressure	200 atm	1 atm
Energy source	Fossil fuel	Solar energy

In this review, we introduced the mechanisms for nitrogen fixation and then summarized recent advances in nanomaterial photocatalysts. After that, we proposed several approaches that can efficiently boost photochemical nitrogen fixation performance. This review may provide some new ideas and inspirations for the development of artificial ammonia synthesis under ambient conditions.

2. Mechanisms of photocatalytic ammonia synthesis

The detailed understanding of fundamental nitrogen fixation mechanisms is important, because the more we know the reaction process, the more we can work to improve the nitrogen fixation efficiency with pertinence. Currently, there are three kinds of well-recognized mechanisms including four pathways for catalytic nitrogen fixation, which include the dissociative, distal associative, alternative associative and enzymatic pathways.¹¹ In the dissociative pathway (Fig. 1a), strong energy is used to completely break the tripe bonds of nitrogen molecules, after which, hydrogenation will happen, and ammonia can be formed.¹² In the Haber process, the dissociative pathway is the approach how ammonia is generated. In the two kinds of associative pathways, the hydrogenation happens with the step-by-step cleavage of the N≡N, but the hydrogenation

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occurs differently. In the distal associative pathway (Fig. 1b), the hydrogenation firstly occurs to the nitrogen atom further away from the catalysts. The hydrogenation will happen to the second nitrogen atom until the first ammonia molecule is released. In the alternative associative pathway (Fig. 1c), the hydrogenation appears to the two nitrogen atoms simultaneously. As for the enzymatic pathway (Fig. 1d), it usually occurs in the reactions carried out by nitrogenases and some catalysts. Different from the mentioned pathways, herein, the nitrogen molecule is adsorbed on the nitrogenases or catalysts by the edge of each atom, rather than one side of only one atom. In this pathway, hydrogenation also appears to each nitrogen atom simultaneously.

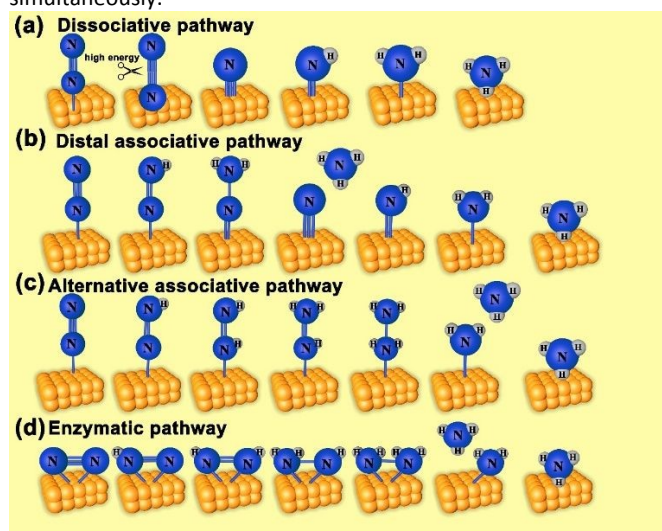


Fig. 1 The pathways of nitrogen fixation to ammonia (a) dissociative pathway, (b) distal associative pathway, (c) alternative associative pathway, and (d) enzymatic pathway. Reused with permission.¹³ Copyright 2021, Elsevier.

In 2019, Ling et al. proposed a new nitrogen reduction mechanism called surface hydrogenation mechanism that can happen on the surface of noble-metal-based metal catalysts (Fig. 2).¹⁴ The first step of this mechanism is converting H^+ to $*H$ using minor energy and it is regarded as a potential determining step. After that, nitrogen molecules will directly react with the $*H$ to form $*N_2H_2$ with higher energy. Then the $*N_2H_2$ will react with H^+ and e^- to form ammonia. Since alkali-metal cations can work the same as H^+ in N_2 activation, increasing the concentration of alkali-metal cations may be a high potential approach to accelerate the nitrogen fixation reaction.

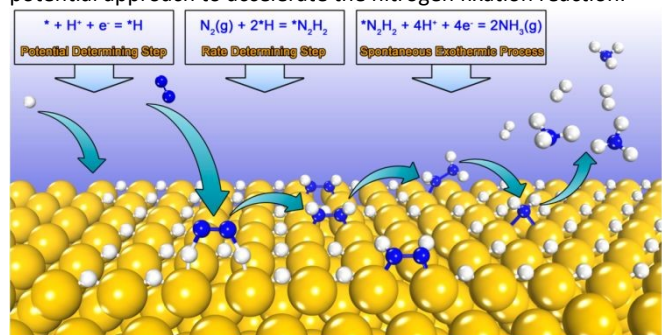


Fig. 2 Scheme of the surface hydrogenation mechanism for nitrogen reduction on noble metal catalysts. Reused with permission.¹⁴ Copyright 2019, American Chemical Society.

3. Recent materials advances in photocatalytic ammonia synthesis

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Different materials have different properties. In recent years, various kinds of materials have been developed to boost artificial photochemical nitrogen fixation efficiency. These methods and strategies may provide some inspiration for future development in this topic. In this chapter, some recent materials advances in photocatalytic ammonia synthesis are summarized and discussed.

3.1 Bismuth-based photocatalysts for ammonia synthesis

Bismuth-based photocatalyst is a kind of emerging material with a lot of advancements including facile preparation, non-toxicity, controllable band structure, high solar-energy utilization etc. More importantly, bismuth is a less hydrogen evolution reaction (HER) active material, making the competing HER reaction obstructed, which can significantly boost the nitrogen fixation.⁴ Using the surface plasmon resonance (SPR) of bismuth is regarded as an efficient way to improve the photocatalytic nitrogen reduction activity. For example, Wang et al. reported a $Bi/InVO_4$ photocatalyst with 5.2-fold enhanced photocatalytic ammonia yield rate than pure $InVO_4$.¹⁵ The photogenerated electrons on the conduction band (CB) of $InVO_4$ and transfer to Bi because of the thermodynamic potential gap, as a result, the charge transfer is boosted and the nitrogen fixation increased a lot. The strategies can also be used to modify other semiconductors to boost photochemical nitrogen fixation.¹⁶⁻¹⁸ Element doping is another way to improve the photocatalytic activity of bismuth-based photocatalysts. For instance, Meng et al. prepared a Fe-doped Bi_2MoO_6 for efficient photocatalytic N_2 fixation. The photocatalytic activity of the best sample can reach $106.5 \mu\text{mol/g/h}$ and it is 3.7-time as that of pure Bi_2MoO_6 . The dope of Fe can not only increase the surface area of the catalysts, but also increase the light absorption. Other than that, the Fe-doping can likewise further develop the charge assortment through a Fe^{3+}/Fe^{2+} redox pathway, which fills in as active sites for nitrogen reduction.¹⁹ It has been approved that many kinds of bismuth-based photocatalysts can be used for ammonia synthesis like $Bi_3FeMo_2O_{12}$,²⁰ bismuth oxyhalides,²¹ $Bi_2O_2CO_3$,²² Bi_2O_3 ,²³ etc. Using defect engineering is a good strategy to boost the catalytic efficiency as it can work as the active site. Feng et al. prepared a series of $Bi_2O_2CO_3$ with abundant oxygen vacancies via the addition of glyoxal during the hydrothermal reaction.²² The oxygen vacancies made the photocatalytic ammonia yield rate increase by 10 times, because the vacancies can boost the chemisorption and activation of nitrogen molecules. Bismuth-based semiconductors are good photocatalysts for ammonia synthesis. More importantly, metallic bismuth has SPR effect and it can be used to activate nitrogen molecules.^{24, 25} Currently, the photocatalytic activity of bismuth-based materials for nitrogen fixation still need improvement. Besides, the cycle stability of bismuth-based materials is usually not really good as bismuth is beam sensitive.²⁶

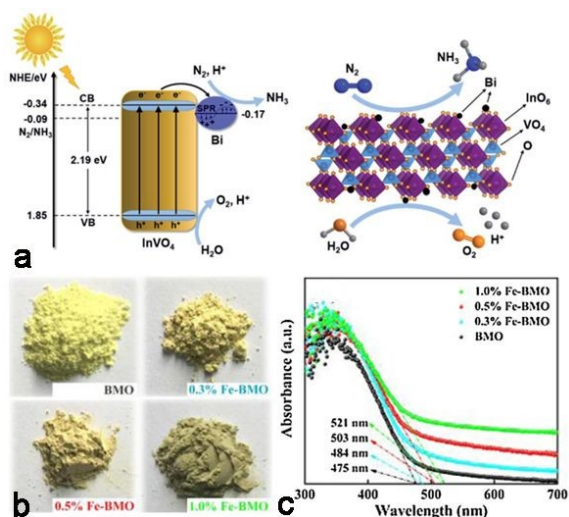


Fig. 3 (a) The scheme of Bi doped InVO_4 for the highly efficient nitrogen reduction. Reused with permission.¹⁵ Copyright 2020, Royal Society of Chemistry. (b) The optical images and (c) UV-vis DRS of BiMoO_6 and Fe-doped BiMoO_6 samples. Reused with permission.¹⁹ Copyright 2019, Elsevier.

3.2 Noble metal-modified photocatalysts for ammonia synthesis

Noble metal-modified photocatalysts are generally divided into noble metal-based photocatalysts and noble metal-doped photocatalysts. Noble metals with surface plasmon resonance, such as gold, silver, etc., can inject active high-energy hot electrons into the anti-bonding orbital of nitrogen molecules, thereby reducing the chemical bond energy of nitrogen molecules, making it easier to complete the first step of hydrogenation.^{27, 28} Plasma-enhanced noble metal-based photocatalysts can bypass the linear constraints of conventional catalytic processes and it is a very promising direction in the research of nitrogen reduction. For example, Hu et al. designed an "AuRu core-antenna nanostructure", where gold nanocrystals were selected as plasmonic nanostructures to obtain a wide range of light absorption. This mixed structure with Au as the core Ru as the antenna promoted the activation process of nitrogen molecules on Ru and achieved an ammonia yield of 101.4 $\mu\text{mol/g/h}$.²⁹ Chen et al. developed a MOF film encapsulating gold nanoparticles for the direct immobilization of photocatalytic nitrogen.³⁰ The "gas-membrane-solution interface" composed of it can achieve effective gas diffusion. Each Au nanoparticle is dispersed in the MOF matrix and simultaneously acts as a photosensitizer (acquiring light and generating electrons) and an auxiliary catalyst (catalytic reduction of nitrogen). In the design of the reaction interface, the porous MOF substrate (such as UiO-66) not only serves as a stable substrate, but also ensures the contact of these AuNPs with N_2 molecules and protons, and also provides an interconnected nanoreactor with ultra-high surface area. Zheng et al. designed a hydrophobic PTFE porous framework on a silicon substrate as a gas diffusion layer, and gold nanoparticles covering the PTFE porous framework as photocatalytic active sites.³¹ Such a hydrophilic-hydrophobic structure helps to improve nitrogen solubility. The solubility of the catalytic site and the effective inhibition of the hydrogen evolution reaction have achieved a Faraday efficiency of 37.8% at the highest. The development of noble metal photocatalysts with different shapes and array structures based on the plasma enhancement effect still has great potential. Metal-semiconductor heterostructures composed of precious metals and semiconductor materials have also been developed. Recently, Yang et al. reported a strategy of immobilizing gold nanoparticles on titanium dioxide

nanosheets for photocatalytic nitrogen fixation.³² The oxygen vacancies on the surface of titanium dioxide can pre-adsorb and activate nitrogen molecules, and then the nitrogen molecules will be reduced by the hot electrons generated by the plasma excited gold nanoparticles to form a "working-in-tandem" pathway, which achieves a quantum efficiency of 0.82% under 550nm light. Wang et al. reported a heterojunction photocatalyst composed of Ru, RuO_2 and $\text{g-C}_3\text{N}_4$.³³ Under light irradiation, electrons in $\text{g-C}_3\text{N}_4$ transition from the valence band to the conduction band and can be easily captured by Ru. Finally, the electrons are transferred to the π^* anti-bond orbital of the nitrogen molecule to promote the cleavage and activation of the nitrogen-nitrogen triple bond. The holes are transferred to RuO_2 , which reacts with methanol in the solution and is consumed, finally achieving an ammonia yield of 13.3 $\mu\text{mol/g/h}$. Oshikiri et al. reported a photoelectrocatalytic cathode nitrogen reduction catalyst with hemispherical gold nanoparticles supported on strontium titanate, and achieved an ammonia yield of 10 nmol/h/cm^2 .³⁴ The author also studied the effect of solution pH and bias voltage on the final product. The noble metal with good nitrogen fixation activity can not only serve as a catalytically active site after being combined with a semiconductor, but also promote the movement of electrons in the semiconductor to the surface, inhibit the recombination of holes and electrons, and improve light utilization. It is a high-efficiency catalyst design strategy with more research value. Li et al. reported a photocatalyst with monoatomic platinum anchored at -N₃ site in covalent triazine framework nanosheets.³⁵ Theoretical calculations show that the alternating mechanism is more energy-efficient than the remote mechanism, and the single-atom dispersed platinum atoms help the electron-hole separation. The transfer of electrons in the conduction band to platinum atoms can promote the activation and reduction of adsorbed nitrogen molecules. Without sacrificial agents, an ammonia yield of 171.40 $\mu\text{mol/g/h}$ was achieved. Although the SPR of noble metals can significantly improve the activation nitrogen molecules, they are not cost-effective to achieve mass production. Strategies should be developed to find a balance amount of the utilization of noble metals to get the best photocatalytic activity.

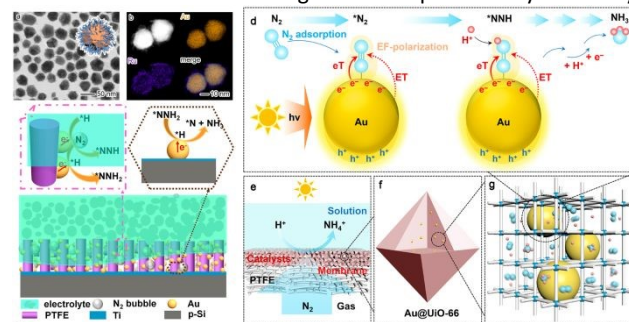


Fig. 4 (a) The TEM image and (b) EDS-mapping of the Au-Ru core-shell nanoparticles. Reused with permission.²⁹ Copyright 2019, American Chemical Society. (c) The aerophilic-hydrophilic heterostructure composed of Au nanoparticles in a poly(tetrafluoroethylene) porous framework d on Si-based photocathode for N_2 fixation. Reused with permission.³¹ Copyright 2019, Elsevier. (d-g) The structure of Au@UiO-66 and the scheme illustration how it worked as a photocatalyst for nitrogen reduction. Reused with permission.³⁰ Copyright 2019, American Chemical Society.

3.3 Metal-free semiconductor photocatalysts for ammonia synthesis

$\text{g-C}_3\text{N}_4$ is one of the most popular metal-free semiconductor photocatalysts, which is widely used for photocatalytic ammonia

synthesis. However, pure $g\text{-C}_3\text{N}_4$ shows poor photocatalytic ammonia synthesis performance on account of the severe recombination of photo-generated carriers, the limited adsorption and activation capacity of nitrogen. Great efforts have been made to solve these problems. Nonmetallic doping (B, P, S, I) is an effective way to promote the photocatalytic ammonia synthesis activity of $g\text{-C}_3\text{N}_4$. Lv et al. reported a single B atom anchored on holey $g\text{-C}_3\text{N}_4$ (B@ $g\text{-CN}$) for photocatalytic ammonia synthesis.³⁶ As shown in Fig. 5a, strong covalent B–N bonds were formed between B atoms and sp^2 -bonded N atoms. As a result, one empty sp^2 orbital and one half-occupied sp^2 orbital of B atom could promote the N_2 activation (Fig. 5b). Three possible mechanisms (distal, alternating, and enzymatic) for N_2 reduction were proposed in Fig. 5c. DFT calculations prove that the enzymatic pathway is the most rational mechanism, and the accelerated activity comes from the “ σ donation– π^* back-donation” mechanism.

Metallic doping (Cu, K, Co, Fe, Ag) is also widely adopted to accelerate the photocatalytic ammonia photosynthesis. Huang et al. reported a single Cu atom modified $g\text{-C}_3\text{N}_4$ (Cu-CN) for ammonia synthesis with a quantum efficiency of 1.01% at 420 nm.³⁷ X-ray absorption fine structure (XAFS) demonstrates that threefold coordination of Cu atoms was formed (Fig. 5d). *In situ* FTIR spectra proved that N–H bonds (1553 and 1685 cm^{-1}) were formed under light irradiation thanks to the decoration of a single Cu atom (Fig. 5e). DFT calculations prove that valence-electron showed isolation from the conjugated π electron cloud (Fig. 5f), which is beneficial for the adsorption and activation of N_2 over the positively charged metal ions.

Defect strategies provide an efficient way of adjusting the properties of the photocatalysts since the defect sites could act as the active centre for the ammonia synthesis and further increase the intrinsic activity. Wang et al. prepared $g\text{-C}_3\text{N}_4$ with N vacancy ($V_{\text{N}}\text{-P-GCN}$) for N_2 fixation by replacing the corner-site C with P (Fig. 5g).³⁸ The chemical environment was changed on account of the synergy of P doping and N vacancies. Both the CB and VB of $V_{\text{N}}\text{-P-GCN}$ exhibited an upshift compared to GCN (Fig. 5h). In addition, DFT calculations prove that the introduction of P could boost the activation ability of N vacancies to the adsorbed N_2 , which is beneficial for the N_2 photo fixation performance.

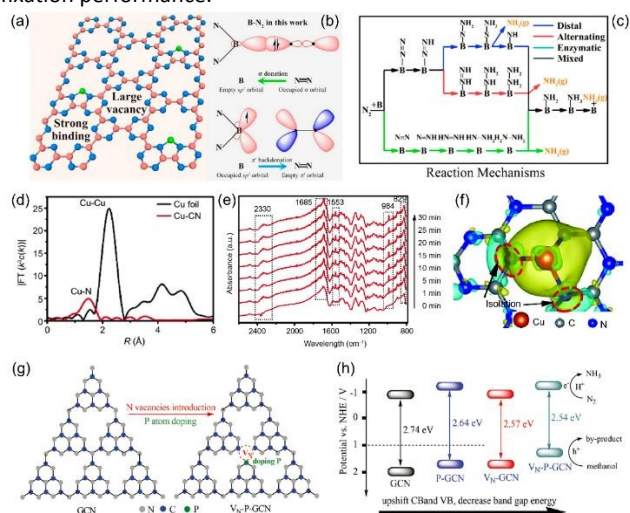


Fig. 5 (a) Structure of B@ $g\text{-CN}$; (b) Schematic plot for N_2 bonding to B; (c) Three possible reaction paths for N_2 reduction over B@ $g\text{-CN}$ (distal, alternating, and enzymatic pathways). Reproduced with permission.³⁶ Copyright 2019, American Chemical Society. (d) FT-EXAFS plots for Cu foil and Cu-CN; (e) *In situ* FTIR spectra for Cu-CN; (f) Top view of the electron density distribution for Cu-CN.

Reproduced with permission.³⁷ Copyright 2018, Science China Press and Springer-Verlag GmbH Germany, part of Springer Nature. (g) The structure diagram for VN-P-GCN; (h) Band diagram for as-prepared samples. Reproduced with permission.³⁸ Copyright 2019, The Royal Society of Chemistry.

Coupling with other semiconductors is also a beneficial strategy to promote the separation efficiency of carriers. Qiu reported a black phosphorus nanosheets-modified $g\text{-C}_3\text{N}_4$ (BPCNS) for photocatalytic ammonia synthesis.³⁹ Electron paramagnetic resonance showed that the peak intensity of BPCNS under visible light was much higher than that of CNS, demonstrated that the electrons of BPCNS are much easier to be excited thanks to the change of the π -conjugate system induced by the C-P bonds (Fig. 6a). The fluorescence lifetime of BPCNS was longer than that of CNS, demonstrating the effective electron transfer from CNS to BP (Fig. 6b and 6c).

Covalent triazine framework is also a potential candidate for ammonia synthesis thanks to its high adsorbing capability of visible light and adjustable π -conjugated units. Single Pt atom decorated covalent triazine framework was synthesized by Li et al.³⁵ The isotopically labeled experiment demonstrated that the generated NH_4^+ indeed came from ammonia synthesis (Fig. 2d). Both the CB and VB of Pt-SACs/CTF exhibited an upshift compared to CTF-PDDA-TPDH (Fig. 2e), which is thermodynamically beneficial for the reduction of N_2 . DFT calculations proved that Pt– N_3 sites were the active sites (Fig. 2f) and the alternating pathway is the main reaction path other than the distal pathway.

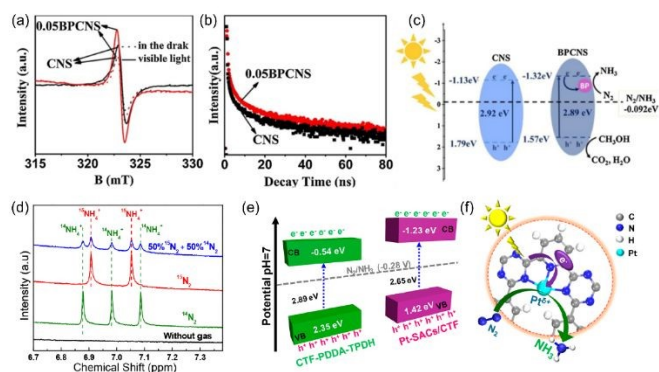


Fig. 6 (a) EPR spectra and (b) time-resolved fluorescence spectra of CNS and 0.05BPCNS; (c) Reaction mechanism for 0.05BPCNS. Reproduced with permission.³⁹ Copyright 2017, Elsevier B.V. (d) ^1H NMR spectra of solution after the reaction for the Pt-SACs/CTF; (e) Band position for CTF-PDDA-TPDH and Pt-SACs/CTF; (f) Possible reaction mechanism over Pt-SACs/CTF. Reproduced with permission.³⁵ Copyright 2020, American Chemical Society.

There are still several key issues that need to be addressed although a large number of articles concerning $g\text{-C}_3\text{N}_4$ have been published. Firstly, the ammonia production should be measured with caution since it is possible for $g\text{-C}_3\text{N}_4$ to break down to produce nitrogen-containing groups during the reaction. These nitrogen-containing groups may have an impact on the test results. Secondly, ethanol and heavy metal ions used in the synthesis of $g\text{-C}_3\text{N}_4$ may also affect the accuracy of the Nessler's reagent method.⁴⁰ In addition, ethanol is widely used as the sacrificial agent of holes, which is an interference factor that affects the detection results. In the name of accuracy, it is necessary to detect ammonium ions by NMR or ion chromatography.^{41–43} Thirdly, most of the current research about metal-free semiconductor photocatalysts focuses on $g\text{-C}_3\text{N}_4$. The

exploitation of new metal-free semiconductor photocatalysts beyond $g\text{-C}_3\text{N}_4$ is urgently needed.⁴⁴

3.4 Other semiconductor photocatalysts

Currently, the researches on photocatalysts for nitrogen fixation are mainly focused on bismuth-based materials, $g\text{-C}_3\text{N}_4$ -based materials and metallic materials with SPR. However, some other kinds of semiconductors also showed broad potential in this application. Titanium dioxide (TiO_2) is a wide-studied photocatalyst, and it has been confirmed to be a good photocatalyst for photocatalytic nitrogen fixation. Meanwhile, some recent achievements have been accomplished to improve the photocatalytic nitrogen reduction activity. For example, Zhang et al. constructed a tunable defective TiO_2 via heating TiO_2 with NaBH_4 under high temperature (310–360 °C) in Ar atmosphere.⁴⁵ As shown in Fig. 7, the color of the TiO_2 samples became darker with temperature increased. At the same time, the absorption edge showed a redshift. Among all the samples, the one obtained at 340 °C can reach the highest ammonia yield of 324.86 $\mu\text{mol/h/g}$, which is 3.85-fold as pristine TiO_2 . The oxygen vacancies can increase the adsorption capacity of nitrogen, as well as boosting the charge separation, leading to a significantly increased photocatalytic activity. The construction of heterojunction can also improve the photochemical nitrogen fixation performance of TiO_2 . For instance, Rong et al. reported a Z-scheme $\text{TiO}_2/\text{ZnFe}_2\text{O}_4$ heterojunction photocatalyst, which showed a much higher photocatalytic activity than single TiO_2 or ZnFe_2O_4 .⁴⁶ The Z-scheme heterojunction can boost the transfer and separation of electron-hole pairs, leading to good photocatalytic activity.

With proper modification, some other kinds of novel photocatalysts for nitrogen fixation have been developed and they also have some potential to be further used. For example, Luo et al. reported a Fe doped SrMoO_4 and it showed much better photocatalytic activity for nitrogen fixation.⁸ The reason why the catalytic activity can be improved, is because of the narrower bandgap, expanded light absorption, and the newly formed Fe-Mo active centres. Constructing heterojunctions is a highly efficient approach to boost the separation and transfer of photogenerated electron-hole pairs. $\text{CeO}_2/\text{FeS}_2$ heterojunction, $\text{CeCO}_3\text{OH}/g\text{-C}_3\text{N}_4/\text{CeO}_2$ heterojunction have been reported to be good photocatalysts for nitrogen fixation.^{47,48} Defect engineering is the most widely used approach for the modification of catalysts to achieve highly efficient nitrogen fixation. Sun et al. prepared a sulfur vacancy-rich oxygen-doped MoS_2 modified CdS nanorods, which exhibited a photochemical ammonia synthesis rate of 8.2 mmol/L/g/h .⁴⁹ They found that sulfur vacancy and the incorporation of oxygen can improve the conductivity as well as reduce the energy barrier for nitrogen reduction, and that is the key factor for the excellent photocatalytic activity. Recently, Zhang et al. found that layered double hydroxides (LDH) can be used as photocatalysts for nitrogen reduction.⁵⁰ They used Vo and Cu^{2+} to modify ZnAl-LDH and got an ammonia yield rate of 110 $\mu\text{mol/g/h}$.

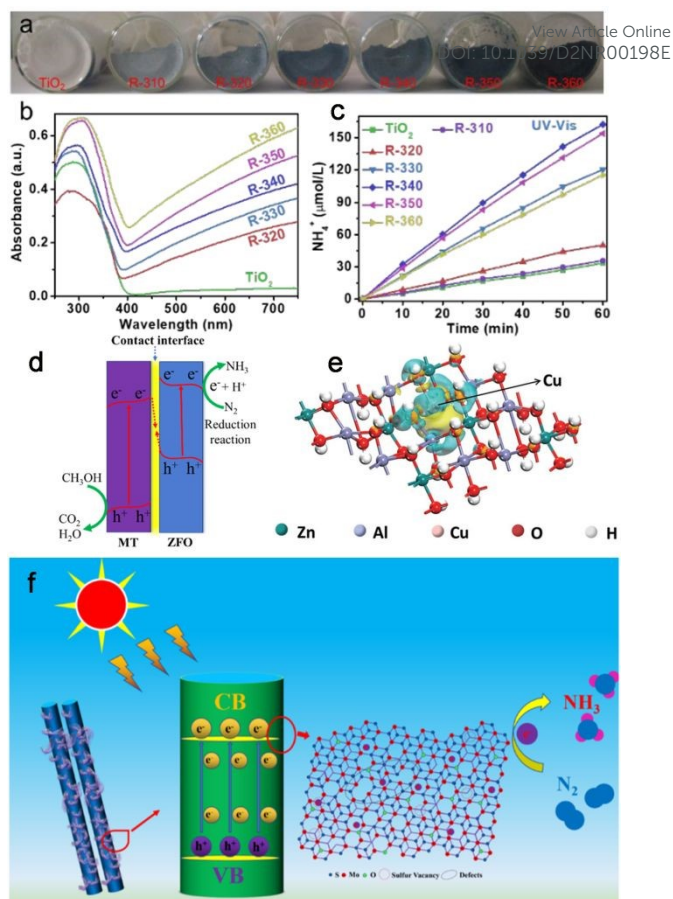


Fig. 7 The optical images (a), UV-vis DRS (b) and photocatalytic activity for ammonia generation (c) of TiO_2 samples. Reused with permission.⁴⁵ Copyright 2020, Royal Society of Chemistry. (d) The nitrogen fixation mechanism of the Z-scheme $\text{TiO}_2/\text{ZnFe}_2\text{O}_4$ heterojunction photocatalyst. Reproduced with permission.⁴⁶ Copyright 2019, Elsevier. (e) The crystal structure and charge density distribution on the surface of ZnAl-LDH . Reproduced with permission.⁵⁰ Copyright 2020, Wiley. (f) The scheme for charge separation and nitrogen fixation mechanism on MoS_2/CdS composite photocatalysts. Reproduced with permission.⁴⁹ Copyright 2020, American Chemical Society.

4. Beyond nitrogen fixation

4.1 Alternative nitrogen sources for ammonia synthesis

Due to the high bond energy, high stability and poor solubility of nitrogen molecules, the current photocatalytic nitrogen fixation rate is too low to meet mass production. Alternatively, there are many kinds of other nitrogen-based compounds that can be used as nitrogen sources, like nitrate, nitrite, nitrogen oxides, etc. In this way, we do not need to worry about the cleavage of nitrogen molecules, more importantly, the potential environmental hazards can be converted into valuable chemicals. It will be easier and more meaningful than nitrogen fixation for sustainable development and a green planet.

4.2 Generation of other valuable chemicals

As an important chemical raw material, ammonia is widely used for the synthesis of a lot of cleaning and pharmaceutical products. Except for the synthesis of ammonia, coupling CO_2 reductions with N reductions, a lot of other high-value chemicals can be synthesized

(Fig. 8).⁵¹ In 2020, Chen et al. reported the direct electrochemical synthesis of urea by coupling N_2 and CO_2 in water under ambient conditions.⁵² The reactions were completed utilizing an electrocatalyst comprising of PdCu alloy nanoparticles on TiO_2 nanosheets. It opened a new avenue for the catalytic synthesis of high-value chemicals. Recently, there are some significant achievements in photocatalytic urea synthesis. Maimaiti et al. achieved the photochemical synthesis of urea using N_2 , CO_2 and H_2O , with TiO_2 loaded on Fe-carbon nanotube.⁵³ The urea yield can reach $710.1 \mu\text{mol}/(\text{Lg})$ in four hours.

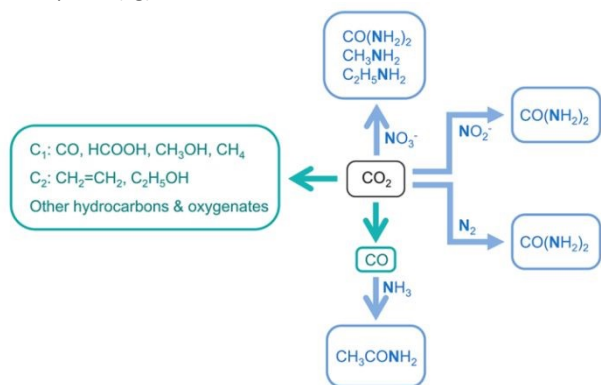


Fig. 8 Major products of electrocatalytic CO_2 reduction and demonstrated syntheses of organonitrogen compounds from N-integrated electrocatalytic CO_2 reduction. Reused with permission.⁵¹ Copyright 2021, American Chemical Society.

4.3 Lithium-mediated nitrogen fixation

In electrochemical ammonia synthesis, lithium-mediated nitrogen fixation has attracted broad interest because Li is an excellent material for N_2 activation with small energy barriers.⁵⁴ Recently, some important findings on this topic have been published. For instance, Kim et al. developed a biphasic system of aqueous 1 M $LiClO_4$ and 1 M $LiClO_4$ /propylene carbonate reinforced with poly(methyl methacrylate), which is membrane-free and can reach a high faradaic efficiency of 57.2% of nitrogen reduction.⁵⁵ Suryanto et al. used a phosphonium salt as a proton shuttle to boost the lithium-mediated nitrogen fixation, and a high faradaic efficiency of $69 \pm 1\%$ was achieved.⁵⁶ In the lithium-mediated nitrogen fixation process, Li^+ firstly react with electrons to form Li^0 . Then the Li^0 will react with nitrogen to generate Li_3N , which can further react with H^+ to obtain ammonia and Li^+ . Although some great achievements have been made in electrochemical lithium-mediated nitrogen fixation, but it has not been applied in photochemical ammonia synthesis. The key reason is that the reduction potential of Li^+ to Li^0 is -3.04 V (vs. SHE).⁵⁵ This step is difficult to be achieved by most of the photocatalysts. However, photoelectrocatalysis can overcome this problem and lithium-mediated photoelectrocatalytic nitrogen fixation may be a good topic that worth investigation.

5. Summary and outlook

Until now, many kinds of novel photocatalysts have been developed to improve photocatalytic nitrogen fixation performance. A lot of photocatalysts including TiO_2 , g- C_3N_4 , Bi-based semiconductors etc. have shown broad prospects in ammonia synthesis. However, the current ammonia yield is still too low to meet mass production. Due to the strong bond energy of $N \equiv N$, it is challenging to achieve mass nitrogen fixation under ambient conditions. Nevertheless,

photoelectrocatalytic lithium-mediated nitrogen fixation might be a good way to overcome the problem. Besides using another nitrogen source like nitrate, nitrate or nitrogen oxides is more promising. Meanwhile, coupling N-reduction with CO_2 reduction deserves more investigation as it will create more economic value, being more sustainable for the planet.

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