

## REVIEW

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# Recent progress in ammonia synthesis based on photoelectrocatalysis

Pengyan Li,<sup>a</sup> Yumin Liu,<sup>a</sup> Muhammad Asim Mushtaq<sup>a,b</sup> and Dongpeng Yan<sup>\*a,b</sup>

Photoelectrocatalytic (PEC) ammonia synthesis from nitrogen and water is a promising approach for energy development and N-neutralization goal under mild conditions. Although significant progress has been made in the past few decades, the mechanisms underlying the synergistic effect between light and electricity are still challenging. One particular line of study is to improve the performances of PEC catalysts, such as selectivity, yield, and stability, etc. Here we review the recent progress in PEC ammonia synthesis. We first provide a systematic description of the driven bias in PEC ammonia processes, involving electrochemical apparatus, photovoltaic voltage, and chemical potential. The various strategies, including vacancy engineering, ion doping, frustrated Lewis pair design, heterojunction construction, cocatalyst loading and single atom synthesis to fabricate new catalysts, are then outlined. The performance and mechanism of PEC N<sub>2</sub> reduction are further summarized, followed by the current challenge and future prospects. This would guide both the productiveness and mechanism of NH<sub>3</sub> synthesis based on advanced PEC systems.

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## 1. Introduction

Ammonia synthesis provides an effective pathway to obtain fertilizers, medicines, chemicals and explosives from air, which is significant to human survival and industrial development.<sup>1,2</sup> In nature, microorganisms depend on Mo-Fe protease to achieve the conversion of atmospheric N<sub>2</sub> to multipurpose NH<sub>3</sub>.<sup>3</sup> However, azotase is extremely sensitive to environmental

<sup>a</sup>Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, and Key Laboratory of Radiopharmaceuticals, Ministry of Education, Beijing Normal University, Beijing 100875, People's Republic of China

<sup>b</sup>State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, People's Republic of China.

E-mail: yandp@bnu.edu.cn



Pengyan Li

Pengyan Li received her M.S. degree in Chemical Engineering from North China University of Science and Technology in 2020. She is now pursuing her Ph.D. degree at Beijing Normal University under the supervision of Prof. Dongpeng Yan. Her research interest is focused on energy and environmental catalysis by photo(electro)catalytic technology, such as CO<sub>2</sub> reduction, water splitting, N<sub>2</sub> reduction, and degradation of dye.

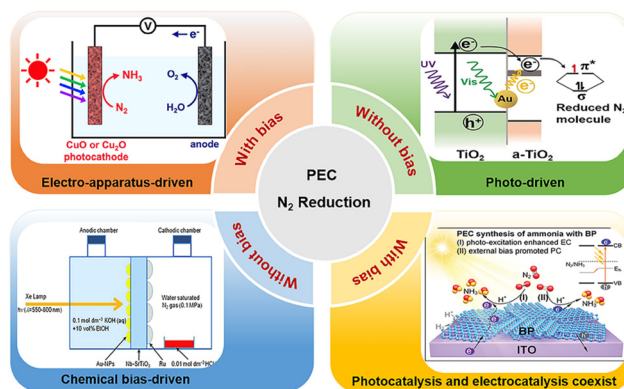


Yumin Liu

Yumin Liu earned her Ph.D. degree (2021) in Chemical Engineering from Tianjin University for research on pharmaceutical crystallisation under the supervision of Prof. Jingkang Wang and Prof. Junbo Gong. In 2017–2019, she joined the Crystal Chemistry and Particle Process Engineering (CCAPPE) research group at the University of Manchester, UK, as a visiting Ph.D. student. During this period, she studied crystal growth and worked with Prof. Roger Davey and Dr Aurora Cruz-Cabeza. She currently works as a Postdoc fellow with Prof. Dongpeng Yan at Beijing Normal University and focuses on functional molecular materials.

oxygen, so the evolution of rhizobium cultivation technology became the key to industrialization of biological  $N_2$ -fixing. As a paragon of artificial nitrogen fixation, the Haber-Bosch (H-B) reaction has contributed to the global economy in which Fe-based compounds show excellent catalytic performances under harsh conditions (temperatures: 300–500 °C, pressures: 150–300 atm) with  $N_2$  and  $H_2$  as feed gases. However, catalytic  $N_2$  hydrogenation consumes mass heat, and the production of feedstock  $H_2$  derived from methane steam reforming results in serious carbon emissions with more than 1% of global emissions,<sup>4</sup> furthermore, the whole H-B craft requires a large plant infrastructure. Therefore, it is essential to find alternative approaches for sustainable N-neutralization under ambient conditions.<sup>5–10</sup> Electrocatalysis and/or photocatalysis has become one of the promising strategies for realizing the N cycle due to its cost advantage, environmental friendliness, and significant  $N_2$  conversion efficiency.

Electrocatalytic  $N_2$  reduction in water involves electron-coupled proton transfer along with various product distributions ( $NH_3$ ,  $N_2H_2$ ,  $N_2H_4$ , and  $H_2$ ).<sup>11–13</sup> Generally, the bias can induce the first electron transfer progress ( $N_2 + e^- \leftrightarrow N_2^-$ ;  $-3.37$  V vs. RHE, pH = 14) and the first-H addition reaction ( $N_2 + H^+ + e^- \leftrightarrow N_2H^+$ ;  $-3.20$  V vs. RHE) that are not favourable thermodynamically, and accomplish continuously the following reduction.<sup>14,15</sup> However, the deficient sites and hydrogen evolution reaction (HER) result in minimal yield and low Faradaic efficiency (FE) in electrocatalytic ammonia synthesis.<sup>16–19</sup> Most studies have proved that Bi-based materials and layered double hydroxides (LDHs) have the



**Fig. 1** Schematic diagram of multiform PEC nitrogen fixation driven by an external bias, solar energy, chemical potential under irradiation, and coexistence of photocatalytic and electrocatalytic  $N_2$  reduction.

ability to undergo photocatalytic  $N_2$  reduction even if the band structures do not meet the requirements of the first electron transfer and the first-H addition, which contribute to considerable  $N_2$  activation, accelerated charge separation, and desired electron generation with strong reducibility.<sup>20</sup> Currently, the integration of electrocatalysis and photocatalysis serves as an effective way to improve the yield and selectivity of  $NH_3$  by virtue of the bias of electrocatalysis and the abundant sites of photocatalysts (Fig. 1).<sup>21–23</sup>

PEC  $N_2$  reduction is a process in which catalysts are excited under irradiation to generate carriers, and then carriers are



**Muhammad Asim Mushtaq**

*Muhammad Asim Mushtaq received his Master's degree in 2015 from the University of Engineering and Technology Lahore, Pakistan. He obtained his Ph.D. degree in Chemical Engineering and Technology (2021) from Beijing University of Chemical Technology (BUCT), PR China. Recently, he joined as a Postdoc fellow at Shenzhen University, Guangdong, PR China. He worked under the supervision of Prof. Dongpeng*

*Yan and Prof. Shengfu Ji at the Beijing Key Laboratory of Energy Conversion and Storage Materials, Beijing Normal University (BNU), and the State Key Laboratory of Chemical Resource Engineering, BUCT, PR China. His research focuses on the design and synthesis of catalytic materials for photo/electrochemical catalysis.*



**Dongpeng Yan**

*Dongpeng Yan obtained his Ph.D. degree under the supervision of Prof. Acad. Xue Duan from Beijing University of Chemical Technology (BUCT, China) in 2012. Then, he became an associate professor at BUCT. In 2014, he moved to Beijing Normal University (China) as a full professor. In 2011 and 2013, as a visiting scholar, he studied at the University of Cambridge (UK) and University College London (UK). His research topics are functional molecular materials, host-guest chemistry, and photo-electrochemistry. He has received the Tang Aqing Chemical Scholarship (2011) and the Outstanding Doctoral Dissertation Prize in Beijing (2013) amongst others. His interest focuses on the chemistry of functional materials and photo(electro)catalysis. As a corresponding author, he has published more than 150 scientific papers (such as in Chem. Soc. Rev., Angew. Chem., JACS, Adv. Mater. and Nature Commun.). He was awarded the Newton Advanced Fellowship of Royal Society and the Royal Society of Chemistry Fellowship*

separated into electrons and holes, finally, electrons migrate rapidly and participate in  $N_2$  reduction on the surface sites assisted with the bias. In addition, the photoelectric synergy is reflected in the coexistence of photochemical and electrochemical reactions. Therefore, PEC  $NH_3$  synthesis is considered as a promising approach that possesses advantages from photocatalysis and electrocatalysis simultaneously to efficiently complete  $N_2$  conversion.<sup>24–26</sup> A classical double chamber contains a photocathode (*i.e.* catalysts), anode (*i.e.* counter electrode), electrolyte,  $N_2$  and proton exchange membrane for PEC  $N_2$  fixation. Candidate photocathodes include inorganic semiconductors with suitable bandgaps ( $g\text{-}C_3N_4$ , BiOI,  $TiO_2$ ,  $Cu_2O$ ,  $W_{18}O_{49}$ )<sup>27,28</sup> and metal modifications,<sup>29,30</sup> metal–organic frameworks with adjustable structures,<sup>31</sup> and single atoms with remarkable active sites.<sup>32</sup> In consideration of the fact that the more negative position of the conduction band (CB) minimum and the enhanced capacity of electron reduction are favourable to  $N_2$  reduction in the PEC strategy, vacancy engineering, heteroatom-doping, heterostructure construction, and single atom synthesis are promising approaches to improve  $N_2$  reduction ability. What's more, the extended light response capacity to the near-infrared region is a potential idea for solar-based economy in PEC  $N_2$  reduction.<sup>33,34</sup>

Chemisorption is a crucial step for  $N_2$  reduction because appropriate adsorption can destroy the molecular symmetry and enhance the proton affinity,<sup>35</sup> thus promoting  $N_2$  hydrogenation. However, the bond energy ( $941\text{ kJ mol}^{-1}$ ) and cleavage energy ( $410\text{ kJ mol}^{-1}$ ) indicate that  $N_2$  activation is challenging (Fig. 2a). Many studies have investigated activation mechanisms, such as vacancy engineering,<sup>27,36</sup> large specific surface area, transition metal (TM)/non-metal doping,<sup>25</sup> and

thermal field coupling. The empty d orbital of the TMs can capture lone pair electrons from  $N_2$ , and the occupied d orbital donates electrons to the  $\pi^*$  orbital, thus producing a weak  $N\equiv N$  bond through the ‘acceptor–donor’ route.<sup>37</sup> In addition to metals, B-based molecules with empty orbitals and lone pair electrons have similar electronic structures to TMs, so  $N_2$  activation could be achieved through the ‘acceptor–donor’ pathway of B-containing catalysts (Fig. 2b and c).<sup>37–40</sup>

The research studies of electrocatalytic and photocatalytic ammonia synthesis are flourishing;<sup>42–45</sup> however, systematic summarizations of PEC  $N_2$  reduction are rather rare. Here, we review the various bias-driven photocatalytic ammonia processes, involving electrochemical apparatus, photovoltaic voltage and chemical potential. The various strategies and mechanistic understanding based on calculations and experiments are then outlined, furthermore, we summarize the methods of  $NH_3$  quantification, and highlight the necessity of nitrogen source determination.

## 2. Merging the solar strategy and the electrical strategy for PEC $N_2$ reduction

There are synergistic effects between light and electricity, which promote the PEC progress by taking advantage of both photocatalysis and electrocatalysis.<sup>46,47</sup> In particular, the electro-coupled photocatalysis strategy avoids  $NH_3$  oxidation, enhances the reduction ability of electrons, and boosts the carrier separation capacity, while photo-assisted electrocatalysis is more outstanding than single electrocatalysis progress, which contributes to the equilibrium of electron distribution under irradiation.<sup>48</sup> Besides, the synergistic effect is displayed in the form of the coexistence of photochemical and electrochemical processes, that is, the potential of electrons is determined by bias in electrocatalysis, and the reduction ability of photoelectrons depends on the minimum CB of semiconductors for photocatalysis.<sup>49</sup>

### 2.1 PEC $N_2$ reduction assisted by electrochemical apparatus

Generally, in the PEC process, light is absorbed to initiate the catalytic reaction directly, and the applied bias is used to promote the migration of the photogenerated electrons by changing the band bending.<sup>49–51</sup> Upon quenching photogenerated holes located on the valence band (VB),<sup>52</sup> regulating the  $H^+$  concentration on the surface of the catalyst,<sup>27</sup> and increasing the accumulation of electrons in the catalytic site, the catalytic performance of ammonia synthesis would be significantly improved. Electrocatalysis enhanced by photo-excitation and photocatalysis promoted by external bias occur simultaneously in PEC  $N_2$  reduction, which make the catalysis more effective than the individual electrocatalytic or photocatalytic nitrogen fixation. It was reported that black phosphorus on indium tin oxide showed extraordinary PEC  $N_2$  reduction properties, which benefit from the coexistence of electrocatalysis and photocatalysis.<sup>48</sup>



**Fig. 2** (a)  $N_2$  molecular structure,<sup>41</sup> Copyright 2020, American Chemical Society. (b) Mechanism of metal activation  $N_2$  (left) and boron activation  $N_2$  (right), (c) Outcomes of various reduction reactions of dihaloborane adduct 1, including generation of a transient dicoordinate borylene species (2) and its reaction with dinitrogen. Dip, 2,6-diisopropylphenyl; Dur, 2,3,5,6-tetramethylphenyl.<sup>38</sup> Copyright 2018, American Association for the Advancement of Science.



## 2.2 Solar-driven and chemical bias-driven PEC N<sub>2</sub> reduction

Photocatalysts (such as g-C<sub>3</sub>N<sub>4</sub>, TiO<sub>2</sub>, BiVO<sub>4</sub>, etc.) exhibit inefficient electrocatalytic performance due to poor conductivity, and there is an obvious side reaction (HER) for the electrochemical apparatus-assisted PEC strategy. The current studies have proved that PEC N<sub>2</sub> fixation can be carried out without electrochemical apparatus, and the formed anode photovoltage contributes negative potential to N<sub>2</sub> reduction in the form of compensation voltage.<sup>53–55</sup> The photovoltage from plasma-induced semiconductors shows huge potential for efficient ammonia synthesis in PEC cells without apparatus. Ali *et al.* described a solar-driven PEC cell over plasmon-assisted Si for atmospheric N<sub>2</sub> reduction and produced a high yield (13.3 mg m<sup>-2</sup> h<sup>-1</sup>) under 2 sun radiation for the first time.<sup>22</sup> Lee *et al.* reported that the photovoltage generated from Au modified ordered Si nanoarrays can reduce nitrate to ammonia with a FE of 95.6% at 0.2 V vs. RHE.<sup>56</sup> Li *et al.* fabricated a photovoltaic cell to realize PEC N<sub>2</sub> fixation with a high NH<sub>3</sub> yield (at the level of μmol h<sup>-1</sup> or even mmol h<sup>-1</sup>) over the TiO<sub>2</sub>/Au photocathode.<sup>57</sup> Inspired by the successful construction of Au-loaded black silicon, Wu's group synthesized Ag-loaded black silicon for PEC nitrogen fixation without external bias,<sup>25</sup> and the catalysts achieved a high FE (40.6%) and NH<sub>3</sub> yield (2.87 μmol h<sup>-1</sup> cm<sup>-2</sup>). The perovskite-based photocathode (TiO<sub>x</sub>/CdS/Cu<sub>2</sub>ZnSnS<sub>4</sub>) achieved NH<sub>3</sub> production from NO<sub>3</sub><sup>-</sup> reduction with a FE of 89.1% (Fig. 3).<sup>58</sup>

Photocatalytic N<sub>2</sub> fixation is completed under the action of chemical bias induced by pH. Oshikiri's group was committed to research chemical bias-driven PEC N<sub>2</sub> fixation over Au/SrTiO<sub>3</sub> to improve NH<sub>3</sub> selectivity.<sup>30,59</sup> The photo-excited hot

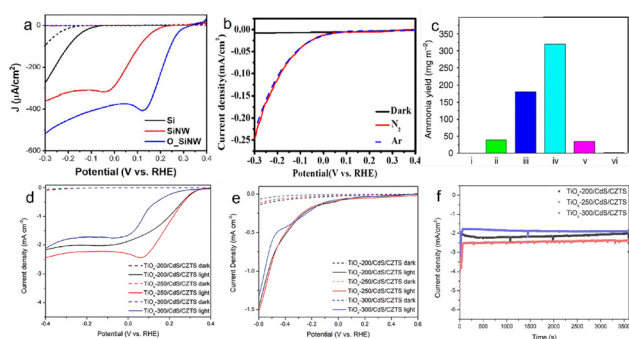
electrons from Au were transferred to the CB of SrTiO<sub>3</sub> to induce nitrogen reduction, and resulted in a hole on the SrTiO<sub>3</sub> surface for the oxidation reaction. There is an accelerated reaction under the action of chemical bias that was generated when the anode potentials move negatively and the cathode potentials move positively.

## 3. Synthesis and performance of advanced catalysts for PEC N<sub>2</sub> reduction

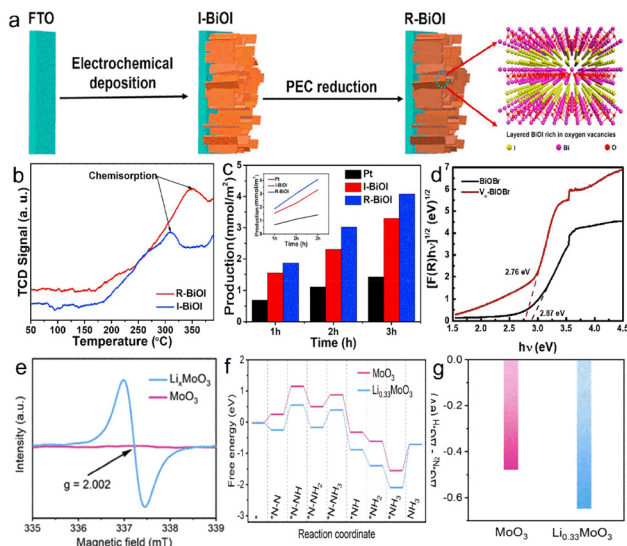
### 3.1 Vacancy engineering

Thermal vibration may cause atoms to deviate from the equilibrium position or escape from the surface lattice, and form vacancies.<sup>60</sup> As one of the most common defects on atomic-scale surfaces, vacancies can promote charge separation, anchor single atoms, and act as adsorption sites by breaking N≡N.<sup>61–63</sup> Therefore, the creation of vacancies significantly improved PEC performance for ammonia synthesis.

The methods for constructing oxygen vacancies have been widely studied, and the nitrogen fixation performance has been significantly improved. BiOF, BiOCl, BiOBr and BiOI are metallic compounds consisting of a [Bi<sub>2</sub>O<sub>2</sub>]<sup>+</sup> layer and a F/Cl/Br/I atomic layer through Van Der Waals interaction. The induced dipole action between the layered structures is favourable to form an electric field, thus passivating the recombination of photogenerated carriers.<sup>65</sup> Due to improved electronic availability, the O<sub>vs</sub> located on the BIOX (X = F, Cl, Br, I) surface is used as a reaction site to facilitate N<sub>2</sub> reduction.<sup>66</sup> Bai *et al.* synthesized O<sub>vs</sub>-BiOI photocathodes by the *in situ* electrodeposition method (Fig. 4a),<sup>24</sup> and the adsorption capacity of R-BiOI to N<sub>2</sub> was significantly enhanced after introducing O<sub>vs</sub> (Fig. 4b). The ammonia production rate is 1400 μmol m<sup>-2</sup> h<sup>-1</sup> (Fig. 4c) at 0.4 V vs. RHE, which is 1.3 times higher than that of the anaerobic catalyst. Similarly, Lin *et al.* prepared an O<sub>vs</sub>-BiOBr/TiO<sub>2</sub> photoelectrode, and the O<sub>vs</sub> elevated the capacity of capturing photoelectrons. The bandgap of O<sub>vs</sub>-BiOBr was reduced to 2.76 eV, indicating that O<sub>vs</sub> can broaden the light absorption range (Fig. 4d). The O<sub>vs</sub> is in favor of the formation of quasi-continuous defects that transport electrons under low-energy light irradiation, and O<sub>vs</sub>-BiOBr/TiO<sub>2</sub> increases the NH<sub>3</sub> yield, which is 3.3 fold of the BiOBr/TiO<sub>2</sub> photocathode.<sup>27</sup> Mao *et al.* prepared LixMoO<sub>3</sub> nanosheets with O<sub>vs</sub> through the lithiation strategy, and there are more abundant O<sub>vs</sub> and Mo<sup>5+</sup> in LixMoO<sub>3</sub> than in MoO<sub>3</sub> (Fig. 4e).<sup>64</sup> Density functional theory (DFT) calculations confirmed that LixMoO<sub>3</sub> nanosheets were favourable for the activation of N<sub>2</sub> and the formation of \*N<sub>2</sub>H (Fig. 4f). The experiments confirm that the effective NH<sub>3</sub> yield of LixMoO<sub>3</sub> nanosheets is 3.48 μg cm<sup>-2</sup> h<sup>-1</sup>, 9 times that of MoO<sub>3</sub> nanosheets. The LDH systems with an abundance of surface oxygen vacancies or coordinatively unsaturated metal cations in ammonia synthesis were popular in N<sub>2</sub> reduction. Zhang *et al.* demonstrated a simple pretreatment of ZnCr-LDH,



**Fig. 3** The enhanced current density or improved NH<sub>3</sub> yield under light irradiation compared to that in the dark. (a) *J*-*V* plots of planar Si (black), Si nanowire (red), and highly ordered Si nanowire (blue) photocathodes for NO<sub>3</sub><sup>-</sup> reduction in Ar-filled K<sub>2</sub>SO<sub>4</sub> with KNO<sub>3</sub>. Dashed lines represent dark current.<sup>56</sup> Copyright 2022, Wiley-VCH. (b) ammonia yield on various substrates: (i) P-type Si, (ii) black Si, (iii) Au/black Si, (iv) Au/black Si/Cr, and (v) Au/Si/Cr under photo-radiation, (vi) Au/black Si/Cr under dark conditions.<sup>22</sup> Copyright 2016, Nature Publishing Group. (c) Linear sweep voltammetry (LSV) of the Ag/black Si electrode under N<sub>2</sub>, Ar and dark conditions.<sup>25</sup> Copyright 2020, American Chemical Society. (d) The LSV of TiO<sub>x</sub>/CdS/Cu<sub>2</sub>ZnSnS<sub>4</sub> in KNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> solution, (e) the LSV of TiO<sub>x</sub>/CdS/Cu<sub>2</sub>ZnSnS<sub>4</sub> and in K<sub>2</sub>SO<sub>4</sub> solution, (f) the chronoamperometry curves of TiO<sub>x</sub>/CdS/Cu<sub>2</sub>ZnSnS<sub>4</sub> with different spray coating temperatures at 0 V vs. RHE.<sup>58</sup> Copyright 2022, Wiley-VCH.



**Fig. 4** (a) Schematic diagram of the synthesis process, of the I-BiOI/R-BiOI, (b)  $N_2$ -TPD profiles of the I-BiOI/R-BiOI, (c) production rate of ammonia,<sup>24</sup> Copyright 2019, Elsevier. (d) the bandgap of  $O_{VS}$ -BiOBr and BiOBr,<sup>27</sup> Copyright 2022, Elsevier. (e) EPR of  $MoO_3$  and  $Li_{0.33}MoO_3$ , (f) free energy on oxygen vacancies ( $O_{VS}$ ) of  $MoO_3$  (010) and  $Li_{0.33}MoO_3$  (010), (g) Gibbs free energy difference between  $^*N_2$  and  $^*H$  over  $MoO_3$  (010) and  $Li_{0.33}MoO_3$  (010).<sup>64</sup> Copyright 2022, Elsevier.

ZnAl-LDH, and NiAl-LDH nanosheets with aqueous NaOH, thus enhancing the concentration of oxygen vacancies to significantly improve photocatalytic activity for  $N_2$  reduction to  $NH_3$ .<sup>67</sup>

Nitrogen vacancies ( $N_{VS}$ ) exhibit enhanced performance for PEC  $N_2$  reduction. Li *et al.* used 3-amino-1,2,4-triazole treated with NaOH as a precursor to prepare  $g-C_3N_5$  with  $N_{VS}$ ,<sup>68</sup> and the  $N_{VS}$  realized charge separation by accepting electrons of  $g-C_3N_5$ . BiOBr/ $g-C_3N_5$  heterostructures with  $N_{VS}$  are synthesized to realize the double-electron transfer mechanism (DETM). The DETM delays the recombination of carriers to ensure high-quality electrons, which is manifested through increased ammonia yield (BiOBr:  $2.5 \mu g \text{ mg}^{-1} \text{ h}^{-1}$ ;  $N_{VS}$ - $g-C_3N_5$ :  $14.8 \mu g \text{ mg}^{-1} \text{ h}^{-1}$ ,  $N_{VS}$ - $g-C_3N_5$ /BiOBr:  $29.4 \mu g \text{ mg}^{-1} \text{ h}^{-1}$ ).

### 3.2 Heteroatom doping

Metal/non-metal ion doping could adjust the electronic structure, redistribute the electron density, and construct surface defects.<sup>69,70</sup> The unoccupied orbitals of the TMs capture lone pair electrons of  $N_2$  molecules due to matched orbital energy and symmetry, while the occupied d orbitals donate electrons in reverse to the anti-bonding orbitals of the  $N_2$  molecule. Therefore, the strong triple bond of  $N_2$  is weakened when the TM-N  $\sigma$ -bond is formed, thus promoting the activation of  $N_2$ . The most studied metal doping for photocatalytic nitrogen fixation is an iron ion with abundant unfilled 3d orbitals, variable valence and considerable cost. Schrauzer *et al.* improved the nitrogen-fixing activity of  $TiO_2$  by doping Fe, Co, Mo or Cr, and found that 2%Fe-doped  $TiO_2$  exhibited the best performance in photocatalytic  $NH_3$  synthesis.<sup>71</sup> Vu *et al.* synthesized

Fe- $W_{18}O_{49}$  nanorods with Au modification by two-step approach, in which the Fe existed in the form of  $Fe^{3+}/Fe^{2+}$  (Fig. 5a).<sup>21</sup> Fe- $W_{18}O_{49}$  enhanced light absorption ability and improved the separation capacity of electron-hole pairs, and achieved a high yield of  $NH_3$  ( $9.82 \mu g \text{ h}^{-1} \text{ cm}^{-1}$ ) under PEC conditions.

The doping of non-metallic atoms (such as B, P, N, *etc.*) is used to increase the VB position and reduce the bandgap through orbital hybridization or defect engineering.<sup>73</sup> Furthermore, non-metallic doping avoids the formation of recombination centers in  $N_2$  reduction.<sup>74,75</sup> Xu *et al.* synthesized B-doped Bi from layered BiOBr nanosheets with sodium borohydride ( $NaBH_4$ ) as a reductant,<sup>72</sup> and the injection of B atoms enhanced the polarization of Bi (012), and Bi provided electrons to the neighbouring B atoms, resulting in the change of the Bi oxidation state and surface geometry (Fig. 5c). The Bi surface with a high curvature promoted  $N_2$  adsorption, and the accumulation of electrons on Bi facilitated the entry of electrons into the anti-bonding orbital of  $^*NNH$ , thus promoting the elongation of the N-N bond of  $^*NNH$ . The energy barrier of the potential-determining step was reduced to 2.00 eV, showing that B doping had a positive role in  $N_2$  reduction (Fig. 5d). The B-doped Bi showed excellent PEC  $N_2$  reduction performance ( $NH_3$  yield:  $29.2 \text{ mg g}_{cat}^{-1} \text{ h}^{-1}$ ), far exceeding that of bismuth ( $10.6 \text{ mg g}_{cat}^{-1} \text{ h}^{-1}$ ).

As a burgeoning class of two-dimensional materials, graphene is sought in the field of photocatalysis and electrocatalysis. Nitrogen doping can regulate the optical bandgap of graphene to endow favourable optical and electrical features through expanded  $\pi$  electron delocalization.<sup>76</sup> The introduction of nitrogen affects both the crystal structure and electronic structure of graphene, in addition, the polarity, electronic donor property, conductivity and chemical stability of graphene can be improved.<sup>77,78</sup> Nitrogen doping into carbon supporter generates regulated charge density, resulting in



**Fig. 5** (a) Fe 2p XPS of WOF-Au, (b) EPR of WO and WOF-Au,<sup>21</sup> Copyright 2020, American Chemical Society. (c) Partial charge density of the Bi-2B (012) facet, (d)  $N_2$  reduction progress on Bi-2B (012).<sup>72</sup> Copyright 2020, Elsevier.

complex reactions related to the multi-proton and electron transfer in  $N_2$  reduction. Meanwhile, studies have shown that the graphene lattice that is rich in nitrogen dopants contributes to the formation of n-type semiconductors.<sup>79</sup> Generally, nitrogen doped reduced graphene oxide (RGO) shows potential for p–n heterojunction construction, which is conducive to the formation of an electric field. Paramanik *et al.* constructed the composite of  $CoTiO_3$  and N-RGO, where an electron is confined in the atomic layer when N-RGO grows on the surface of  $CoTiO_3$ . In addition, N-RGO/ $CoTiO_3$  achieves a shorter diffusion distance of electrons, rapid charge transfer and small interface resistance.<sup>80</sup> In addition, the synergistic interaction between the rod-like structure of  $CoTiO_3$  and the rough surface of N-RGO contributes to the overall improvement of the catalytic performance. The optimized 1N-RGO/ $CoTiO_3$  has a quenching rate of 54.89% for photogenerated carriers, and possesses an electron lifetime of 3.0 ms. The photocatalytic and PEC activities are more than  $1.7 \text{ mmol}^{-1} \text{ h}^{-1}$  and  $16 \mu\text{g cm}^{-1} \text{ h}^{-1}$ , respectively.

Although nonmetallic doped catalysts have improved performance, the mechanism and stability still need to be further explored in view of the fact that the introduced elements may become the quenching sites of electrons and holes,<sup>62</sup> so it is indispensable to study the stabilization strategy for doping non-metallic elements.

### 3.3 Frustrated Lewis pairs (FLPs)

Metal-free catalytic ammonia synthesis with high selectivity and ideal yield faces challenges until the breakthrough of  $N_2$  activation based on the frustrated Lewis pairs (FLPs) in 2018.<sup>81</sup> FLPs with an electrophilic acid and nucleophilic base are favorable for the breaking of  $N\equiv N$  through the electron transfer between the unoccupied orbitals of electrophilic acid and the nonbonding orbitals of nucleophilic base (Fig. 6a).

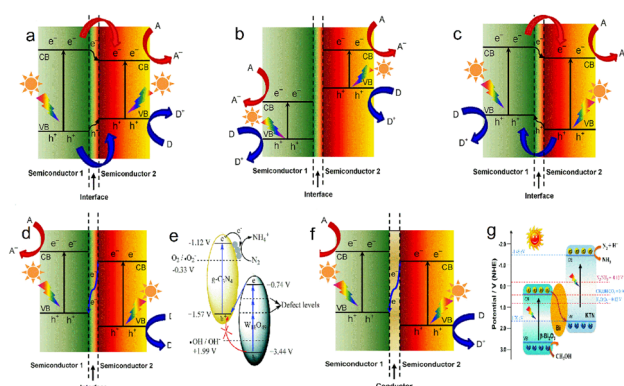


**Fig. 6** (a) Illustration of artificial frustrated Lewis pairs to adsorb and activate  $N_2$ , C–N coupling reaction,<sup>85</sup> Copyright 2021, the Royal Society of Chemistry. (b) Lewis acidic boranes for N–N activation,<sup>86</sup> Copyright 2017, Wiley-VCH. (c) Schematic illustration of BCN for electrochemical nitrogen reduction,<sup>83</sup> Copyright 2022, Wiley-VCH. (d) Mechanism of over 10B/10Mo- $C_3N_4$  in the photocatalytic  $N_2$  fixation strategy,<sup>87</sup> Copyright 2020, the Royal Society of Chemistry. (e) Gibbs energy over carborene-based FLPs for  $N_2$  reduction.<sup>81</sup> Copyright 2022, American Chemical Society.

Stephan *et al.* reported the space blockage in inhibiting the capture of  $N_2$  in the synthesis of  $Ph_2CN_2B(C_6F_5)_3$  with carbene,  $N_2$  and borane as reactants.<sup>82</sup> Dai *et al.* presented boron carbon nitride (BCN) with the abundant unsaturated B (Lewis acid sites) and N atoms (base sites), and the results showed that FLPs adsorb  $N_2$  molecules to form six membered ring intermediates, which reduces the energy of  $N\equiv N$  breaking.<sup>83</sup> Chen *et al.* proposed an alternative strategy based on FLP catalysts to stabilize  $N_2H^+$  intermediates, that is, substituting two-dimensional black phosphorus co-doped with TMs and boron atoms for FLPs.<sup>84</sup> Zhu *et al.* designed a variety of FLPs that have the ability to activate  $N_2$ , and exhibit low  $\Delta G$  values of  $-37.5$  to  $-51.0 \text{ kcal mol}^{-1}$  (Fig. 6e).<sup>81</sup>

### 3.4 Heterojunction construction

Different from the inherent band structure of single-phase catalysts, heterojunction materials have the advantages of regulating the threshold of light absorption, accelerating the separation of carriers by changing the band structure, and passivating the recombination of electrons and holes. A typical heterojunction is an interface formed through the contact of two different semiconductors, which is mainly divided into types I, II and III (Fig. 7a–c). In type I, the VB and the CB of one semiconductor are more negative than those of another semiconductor, and there is no photocatalytic activity because the carriers cannot be effectively separated under photoexcitation. In type III heterojunction, the band positions of one semiconductor are all above the band positions of another semiconductor, and the formed interface has almost no catalytic activity in type III. For type II, the band positions are staggered between the two semiconductors, thus forming an upward or downward bending of the band,<sup>89</sup> which causes the charge carriers to migrate in the opposite direction, thus prolonging the life of electrons and holes and improving the redox ability. Although effective charge separation is accomplished in con-



**Fig. 7** Band structure of (a) type I, (b) type II, (c) type III, and (d) Z-scheme heterojunction in semiconductor–semiconductor and for example, (e)  $g-C_3N_4/W_{18}O_{49}$ ,<sup>33</sup> Copyright 2017, the Royal Society of Chemistry. (f) Z-scheme in the semiconductor–electron mediator–semiconductor. A: electron acceptor, D: electron donor; and for example, (g)  $Bi-Bi_2O_3/KTa_{0.5}Nb_{0.5}O_3$ .<sup>88</sup> Copyright 2022, the Royal Society of Chemistry.



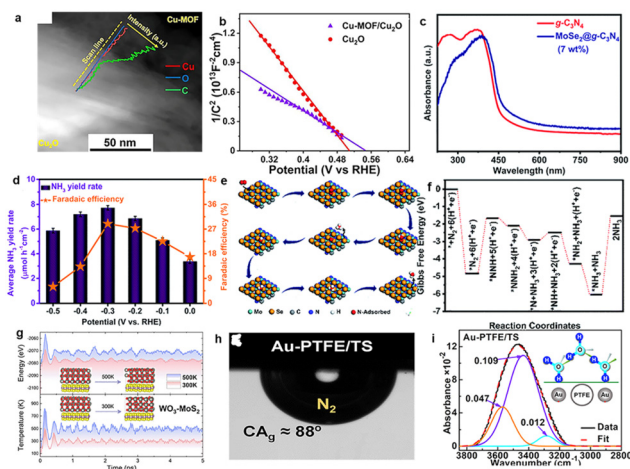
structed type II systems, the main disadvantage is the lower oxidation and poorer reduction capabilities.<sup>90</sup> The Z-scheme heterojunctions achieve rapidly separated carriers and strong redox ability, which can be attributed to the recombination of holes on the VB for one semiconductor and electrons on the CB for another semiconductor (Fig. 7d and e). The Z-scheme heterojunctions are divided into semiconductor-semiconductor (that is the S-scheme) and semiconductor-mediator-semiconductor depending on whether there is an electronic mediator between two semiconductors. Researchers have focused on the construction of different heterojunction nanocomposites,<sup>91</sup> aiming to boost the utilization of ultraviolet light or near-infrared light and to promote carrier separation for PEC nitrogen fixation.

Owing to the controllable chemical environment, metal-organic frameworks (MOFs) are used in the preparation of heterostructures as photoelectrodes.<sup>92,93</sup> Liu *et al.* used the *in situ* chemical etching strategy to form Cu-MOFs on the Cu<sub>2</sub>O surface with an organic ligand (H<sub>3</sub>BTC), and the Cu-MOF amount can be determined by etching time (Fig. 8a).<sup>94</sup> The establishment of the Cu-MOF/Cu<sub>2</sub>O heterostructure improves the carrier density and charge separation efficiency (Fig. 8b). Meanwhile, the NH<sub>3</sub> yield of Cu-MOF/Cu<sub>2</sub>O is increased to 7.2 mmol m<sup>-2</sup> h<sup>-1</sup> due to unsaturated Cu(II) sites, which is 5 times that of Cu<sub>2</sub>O (3.7 mmol m<sup>-2</sup> h<sup>-1</sup>) and 3.9 times that of Cu-MOFs (1.9 mmol m<sup>-2</sup> h<sup>-1</sup>). Phthalocyanine copper is used for ammonia synthesis due to strong photoresponsiveness. However, the surface of phthalocyanine copper lacks an active site and does not have the desired surface reaction kinetics. Li *et al.* prepared a phthalocyanine

copper/CeO<sub>2</sub> heterostructure by the chemical deposition method, and CeO<sub>2</sub> is coated on the phthalocyanine copper surface.<sup>95</sup> UV-Vis absorption and electrochemical measurement make it clear that the phthalocyanine copper/CeO<sub>2</sub> heterostructure has a wide absorption range and a high electrochemical activity area. The PEC N<sub>2</sub> reduction performance reaches the best with an NH<sub>3</sub> yield of 1.16 μmol h<sup>-1</sup> cm<sup>-2</sup>.

The C atom inserted into the Mo lattice shows a narrow metal band and exhibits similar Fermi level densities to noble metals, so Mo<sub>2</sub>C is expected to perform well in catalysis.<sup>98</sup> However, Mo<sub>2</sub>C is a matrix with poor electrical conductivity,<sup>99</sup> so it is necessary to consider the optimization of carrier migration for PEC N<sub>2</sub> reduction. Li *et al.* took graphite as a unit of the core-shell heterostructure, and wrapped it on the Mo<sub>2</sub>C cluster surface based on *in situ* hydrothermal and calcination treatment, and effectively broke through the limitation of Mo<sub>2</sub>C conductivity.<sup>100</sup> The graphitized carbon can accelerate electron transfer, which is conducive to the activation of N<sub>2</sub>, with an NH<sub>3</sub> yield of 6.6 μg h<sup>-1</sup> mg<sup>-1</sup>. In addition, MoSe<sub>2</sub> and the two-dimensional material g-C<sub>3</sub>N<sub>4</sub> are assembled to form heterojunctions. Mushtaq *et al.* synthesized layered flower-like MoSe<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub>,<sup>26</sup> and the Mo-N bond between MoSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> enhances the internal conductivity of MoSe<sub>2</sub>. The absorption capacity of MoSe<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> is enhanced (Fig. 8c), and the MoSe<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> hybrid shows efficient PEC N<sub>2</sub> reduction performance with an FE of 28.91% and a yield of 7.72 mmol h<sup>-1</sup> cm<sup>-2</sup>, respectively (Fig. 8d). The associative distal pathway and Gibbs free energy on MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> heterojunctions are shown in Fig. 8e and f. The results show that N<sub>2</sub> is well adsorbed and activated on the MoSe<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> (7 wt%) hybrid surface.

WO<sub>3</sub> is widely used as a photo/electrocatalyst due to its tunable composition, favourable stability and abundant availability. Guo *et al.* simulated a heterojunction constructed by WO<sub>3</sub> and metal dichalcogenides (MoS<sub>2</sub>, WSe<sub>2</sub>), and proved that heterojunctions are stable in thermodynamics through calculation (Fig. 8g). In particular, optimized WO<sub>3</sub>-MoS<sub>2</sub> has the lowest onset potential (0.25 V),<sup>96</sup> and its catalytic performance is enhanced by re-positioning the d-band center that is precisely controlled to a higher energy level. Furthermore, in order to improve the N<sub>2</sub> reduction activity, porous skeleton structures are used in heterojunction construction engineering. Multiple scattering and absorption of light in the porous structure are conducive to the efficient capture of sunlight.<sup>101–103</sup> Porous CdS was obtained by growing CdS on Mo doped WO<sub>3</sub> hollow microspheres based on the hydrothermal method. The Mo-WO<sub>3</sub>@CdS heterostructure<sup>104</sup> achieved a FE of 36.72% and an NH<sub>3</sub> yield of 38.99 μg h<sup>-1</sup> mg<sup>-1</sup>. The DFT analysis suggests that Mo-W is the catalytic center of N<sub>2</sub> reduction, and CdS promotes the provision of electrons, thus accelerating PEC N<sub>2</sub> hydrogenation. Meanwhile, the development of porous structures provides the basis for functionalized heterogeneous structures. The Au modified porous polytetrafluoroethylene (PTFE) skeleton dispersed on a silicon-based electrode was synthesized. The



**Fig. 8** (a) TEM images and EDS spectra of Cu-MOF/Cu<sub>2</sub>O, (b) Mott-Schottky plot (frequency: 800 Hz),<sup>94</sup> Copyright 2021, Elsevier. (c) optical bandgap energy of g-C<sub>3</sub>N<sub>4</sub> and MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub>, (d) equivalent NH<sub>3</sub> yield and FE at different potentials on MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> heterojunctions, (e) associative distal pathway for PEC N<sub>2</sub> reduction, (f) Gibbs free energy on MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> heterojunctions,<sup>26</sup> Copyright 2020, the Royal Society of Chemistry. (g) Fluctuation of temperature and energy against the time of WO<sub>3</sub>-MoS<sub>2</sub> at 300 K and 500 K,<sup>96</sup> Copyright 2022, American Chemical Society. (h) The image of an underwater N<sub>2</sub> bubble on the Au-PTFE/TS surface, (i) original (black line) and deconvoluted (red line) spectra of interfacial water at the Au-PTFE/TS surface.<sup>97</sup> Copyright 2019, Elsevier.

silicon and the porous PTFE skeleton were used as the light absorber and gas diffusion channels, respectively, while Au was used as the reaction site.<sup>97</sup> Attenuated total reflection and caption-bubble measurements demonstrated that the porous framework of Teflon and Au created a gas-hydrophilic structure, which promoted N<sub>2</sub> enrichment and controlled proton activity in aqueous solution (Fig. 8h and i). The optimal ammonia production rate of the photocathode is about 18.9  $\mu\text{g cm}^{-2} \text{h}^{-1}$ , and the FE is 37.8% at  $-0.2 \text{ V vs. RHE}$ . The LDH plays a key role in the fields of photocatalysis/electrocatalysis and energy conversion due to easily controllable composition and abundance of surface oxygen vacancies or coordinatively.<sup>105</sup> Yan *et al.* constructed a CoVP@NiFeV-LDH heterojunction that has shown excellent electrocatalytic performance in the N<sub>2</sub> reduction reaction. The new three-dimensional hollow hierarchical structure provides abundant active sites for nitrogen adsorption and reduction to NH<sub>3</sub>.<sup>106</sup>

### 3.5 Cocatalyst loading

Noble metal catalysts have the advantages of high catalytic activity, stability and selectivity. For effective utilization of noble metals, it is necessary to load them onto the host matrix. For example, black silicon serves as a carrier, and it can also enhance light absorption and suppress reflection.<sup>107,108</sup> Ali *et al.* used plasma-enhanced black silicon decorated with Au nanoparticles (NPs) to achieve photoelectrically driven nitrogen conversion (Fig. 9a).<sup>22</sup> When black silicon is replaced by unetched silicon, NH<sub>3</sub> production is 11% of that generated by Au/black Si/Cr. Black silicon provides a large surface area for Au loading. Au-coated black silicon has a higher ammonia yield (more than 13  $\text{mg m}^{-2} \text{h}^{-1}$ ) than black silicon. Wang *et al.* realized the PEC process of converting nitrogen into ammonia, when black silicon was used to enhance light absorption, and silver was used as an active site with a FE of 55.05% at  $-0.1 \text{ V (vs. RHE)}$ .<sup>25</sup>

Porous structures are also excellent to disperse and stabilize metal NPs. Peramaiah *et al.* deposited Au NPs on porous g-C<sub>3</sub>N<sub>4</sub> with N defects, and then coated it on the n<sup>+</sup>np<sup>+</sup>-Si photocathode surface (Fig. 9b and c).<sup>109</sup> Silicon plays the roles of light collection and electrical management, Au is the active center to promote the conversion of N<sub>2</sub> to NH<sub>3</sub>, and porous g-C<sub>3</sub>N<sub>4</sub> with N-defects provides more N<sub>2</sub> adsorption sites. Each N atom is alternately associated with the first and second hydrogenation; then, the third hydrogen is added to destroy the N-N bond; finally, the distal N atom is reduced thoroughly with the release of the first NH<sub>3</sub> molecule. Au/g-C<sub>3</sub>N<sub>4</sub> exhibits excellent PEC N<sub>2</sub> reduction performance with a FE of up to 61.8% and an NH<sub>3</sub> yield of 13.8%  $\mu\text{g h}^{-1} \text{cm}^{-2}$ . MoS<sub>2</sub> is an excellent carrier due to its well-dispersed layered structure, high conductivity and large specific surface area. Ye *et al.* dispersed TiO<sub>2</sub> NPs on MoS<sub>2</sub> nanosheets by the hydrothermal method, and the addition of MoS<sub>2</sub> leads to a smaller bandgap (2.98 eV) than that of TiO<sub>2</sub>, and expedites the separation of electrons and holes.<sup>112</sup> Enhanced charge transfer maintains higher photoelectric voltage and slower decay behaviour. The results show that the NH<sub>3</sub> yield and FE are  $1.42 \times 10^{-6} \text{ mol h}^{-1} \text{cm}^{-2}$  and 65.52%, respectively, for MoS<sub>2</sub>@TiO<sub>2</sub>. Hydrophilic SnO<sub>2</sub> is uniformly dispersed on the surface of hydrophobic MoS<sub>2</sub>, which leads to a change in the growth direction of MoS<sub>2</sub>, so as to induce the growth of the (002) crystal plane. The improved transfer and separation of carriers are attributed to the strong interaction between SnO<sub>2</sub> and MoS<sub>2</sub>, with an NH<sub>3</sub> yield of 19.6 at  $-0.3 \text{ V } \mu\text{g h}^{-1} \text{mg}^{-1}$  and a FE of 40.34%, much higher than those of individual SnO<sub>2</sub> and MoS<sub>2</sub> (Fig. 9d).

Quantum dots (QDs) possess superior properties that play important roles in N<sub>2</sub> reduction,<sup>113</sup> such as small size, strong photostability, multiple excitation, exposed sites and electronic peculiarity. For example, Bi<sub>2</sub>S<sub>3</sub> QDs have a high absorption coefficient and narrow bandgap.<sup>114</sup> Gao *et al.* grew Bi<sub>2</sub>S<sub>3</sub> QDs on MoS<sub>2</sub> through hydrothermal and solvothermal processes for photocatalytic reduction of N<sub>2</sub> to NH<sub>3</sub>.<sup>111</sup> Bi<sub>2</sub>S<sub>3</sub> QDs were dispersed on the MoS<sub>2</sub> surface, and the agglomeration of Bi<sub>2</sub>S<sub>3</sub> QDs can be inhibited. The shift of binding energy indicates that there is an interaction between Bi<sub>2</sub>S<sub>3</sub> QD and MoS<sub>2</sub> (Fig. 9e), thus leading to electron transfer from Bi<sub>2</sub>S<sub>3</sub> to MoS<sub>2</sub> and accelerating the carrier separation (Fig. 9f). The FE of the Bi<sub>2</sub>S<sub>3</sub> QD/15MoS<sub>2</sub> photocathode reaches 33%, and the NH<sub>3</sub> yield is 19  $\mu\text{g h}^{-1} \text{mg}^{-1}$ . Carbon quantum dots (CQDs) are narrow-gap semiconductor materials, and Hu *et al.* synthesized CQD-modified hydrogenated mesoporous SrTiO<sub>3</sub> (CQDs/STO) based on the small size and good conductivity.<sup>115</sup> The ammonia yield of CQDs/STO is 143  $\mu\text{mol g}^{-1} \text{h}^{-1}$  and is 7 times that of STO without a sacrificial agent. Furthermore, heterogeneous CQD/STO with a defective STO (200) surface can promote catalytic N<sub>2</sub> conversion.



**Fig. 9** (a) Corresponding TEM images of Au-coated silicon nanowires,<sup>22</sup> Copyright 2016, Nature Publishing Group. (b) TEM images of Au/g-C<sub>3</sub>N<sub>4</sub>, (c) mapping of N, C, and Au.<sup>109</sup> Copyright 2021, Wiley-VCH. (d) XRD patterns of SnO<sub>2</sub>/10MoS<sub>2</sub>, SnO<sub>2</sub>/10MoS<sub>2</sub> (silicomolybdic acid is not a precursor), MoS<sub>2</sub> (silicomolybdic acid is not a precursor) and SnO<sub>2</sub>.<sup>110</sup> Copyright 2022, Elsevier. (e) The XPS spectra of Bi<sub>2</sub>S<sub>3</sub> QDs/15MoS<sub>2</sub>. (f) photocurrent with a light on-off cycle.<sup>111</sup> Copyright 2022, Elsevier.

### 3.6 Other advanced catalysts and strategies for nitrogen fixation

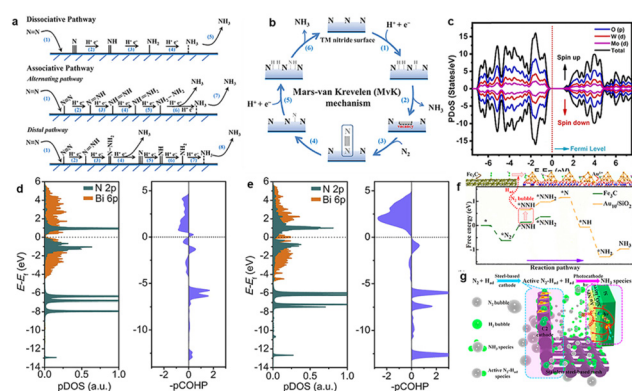
Single atomic alloy catalysts have broad application prospects in electro-catalytic nitrogen reduction because of the highly exposed active sites. However, there are limited comprehensive



experiments and theoretical research on the conversion of  $N_2$  to nitrogen-containing molecules. Chuk *et al.* reported that the yield of  $NH_3$  in the nitrogen reduction reaction was  $111.9 \mu g h^{-1} mg^{-1}$  using single atom PdFe alloy.<sup>116</sup> In addition, compared with the pristine Ru, the use of Ru–Cu alloy showed that the addition of Cu improved the FE of  $NH_3$  (31%) through enhanced  $N_2$  adsorption and a reduced H barrier.<sup>117</sup> Li-mediated  $N_2$  reduction is flexible in the electrocatalytic approach, which has practical significance for realizing the nitrogen cycle; however, the yield and FE are not optimistic. Du *et al.* studied the properties of the interface generated by the imide-based Li salt electrolytes. The constructed interface can provide a substantial  $NH_3$  yield of  $150 \pm 20 nmol s^{-1} cm^{-2}$ , and a FE of up to 100%.<sup>118</sup> In addition, this group has realized the ammonia synthesis by the phosphonium cation and isopropanol.<sup>119</sup> Therefore, the development of non-metallic materials with high nitrogen fixation efficiency is of great potential. Recently, both experiments and theoretical calculations have suggested that traditional semiconductor materials are promising photoelectrocatalysts for  $N_2$  reduction under ambient conditions, as listed in Table 1.

## 4. Mechanism of PEC $N_2$ reduction for ammonia synthesis

It is generally believed that PEC  $N_2$  reduction on a heterogeneous catalyst surface undergoes two mechanisms, namely the associative reaction and dissociative reaction (Fig. 10a).<sup>23</sup> For dissociation, the triple bond of  $N_2$  is cracked before hydrogenation, and two separate N atoms are reduced to form  $NH_3$  independently through hydrogenation steps, which is similar to the H–B process that requires more energy. In the association pathway, two nitrogen atom centers are combined together when the  $N_2$  molecule is hydrogenated, and  $NH_3$  is released with the breaking of the  $N \equiv N$  bond. The hydrogenation in the association mechanism can take place in two possible ways, namely distal and alternative pathways. When  $N_2$  appears in the mode of terminal coordination, hydrogenation is inclined to occur on the nitrogen far from the catalysts, thus



**Fig. 10** (a) Dissociative, distal and alternating pathways for  $N_2$  reduction, (b) MvK mechanism on the TM nitride surface,<sup>132</sup> (c) atom projected density of states (PDOS) of  $Mo-WO_3$ ,<sup>104</sup> Copyright 2022, Elsevier. (d and e) PDOS and projected crystal orbital Hamilton populations of the N atoms ( $^{*}NNH$ ) on Bi (012) and (e) Bi-2B (012),<sup>72</sup> Copyright 2021, Elsevier. (f) Free energy and optimized geometric structure of distal mechanisms on the  $Fe_3C$  sites and  $Au^{1+}$  sites of the Au/SiO<sub>2</sub>/Si photocathode, (g) schematic representation of the catalytic and enhanced mechanism of the PEC NRR on the Au/SiO<sub>2</sub>/Si photocathode.<sup>133</sup> Copyright 2021, American Chemical Society.

leading to the generation of  $NH_3$  molecules, and leaving the metal nitrogen unit to react with  $H^+$  to generate another  $NH_3$  molecule. The alternative route requires that two nitrogen centers alternate between two N atoms on the catalytic surface. After the first  $NH_3$  is removed, the second  $NH_3$  will be released immediately. Our group has reported the possible route (distal pathway) of  $NH_3$  synthesis on the  $MoSe_2-g-C_3N_4$  surface based on the Gibbs free energy,<sup>26</sup> that is, the adsorbed  $N_2$  is hydrogenated by  $H^+$  adsorption and electron transfer to form an  $N_2H^+$  group at the Mo site. And then  $H^+ + e^-$  reacts with N to form  $N_2H^+$ . The adsorption of  $H^+$  on the pre-hydrogenated N site of  $N_2H^+$  yields an  $NH_3$  molecule, leaving the remaining N at the Mo atom. After that, another three  $H^+$  ions are coupled to the electron, hydrogenating the remaining  $N^+$  molecule to give a second  $NH_3$ .

Researchers proposed a new reaction mechanism in recent years, namely Mars–van–Krevelen (MvK), based on transition

**Table 1** The catalytic performance of PEC  $N_2$  reduction to  $NH_3$  over various catalysts

Catalyst	Irradiation source	Bias [V]	Rate of $NH_3$	Ref.
BiVO <sub>4</sub> /PANI	300 W Xe lamp	−0.1 V vs. RHE	$0.055 \mu mol cm^{-2} h^{-1}$	52
BiOI	100 mW $cm^{-2}$	+0.4 V vs. RHE	$0.140 \mu mol cm^{-2} h^{-1}$	24
CQDs/SrTiO <sub>3</sub>	300 W Xe lamp	−0.3 V vs. RHE	$1.915 \mu mol cm^{-2} h^{-1}$	115
Cu <sub>2</sub> O	300 W Xe lamp	+0.4 V vs. RHE	$0.423 \mu mol cm^{-2} h^{-1}$	49
PANI-ASSM/CdS-Co <sub>3</sub> S <sub>4</sub>	40 W LED	−0.75 V vs. RHE	$12.33 \mu mol cm^{-2} h^{-1}$	120
Vo-BiOBr/TiO <sub>2</sub>	300 W Xe lamp	−0.2 V vs. RHE	$1.475 \mu mol cm^{-2} h^{-1}$	27
Cu-MOF/Cu <sub>2</sub> O	300 W Xe lamp	+0.5 V vs. RHE	$0.716 \mu mol cm^{-2} h^{-1}$	94
MoSe <sub>2</sub> @g-C <sub>3</sub> N <sub>4</sub>	150 W Xe lamp	−0.3 V vs. RHE	$7.72 \mu mol cm^{-2} h^{-1}$	26
Fe-doped W <sub>18</sub> O <sub>49</sub>	simulated solar light	−0.65 V vs. Ag/AgCl,	$0.577 \mu mol cm^{-2} h^{-1}$	21
SnO <sub>2</sub> /MoS <sub>2</sub>	300 W Xe lamp	−0.3 V vs. RHE	$19.6 \mu g h^{-1} mg_{cat}^{-1}$	110
B-doped Bi nanorolls	300 W Xe lamp	+0.48 V vs. RHE	$29.2 mg h^{-1} g_{cat}^{-1}$	72
Mo-doped WO <sub>3</sub> @CdS	300 W Xe lamp	−0.3 V vs. RHE	$38.99 \mu g h^{-1} mg_{cat}^{-1}$	101
Mo <sub>2</sub> C/C	100 mW $cm^{-2}$	+0.2 V vs. Ag/AgCl	$6.6 \mu g h^{-1} mg_{cat}^{-1}$	121

metal nitrides (TMNs: V-N, Zr-N, Nb-N) as shown in Fig. 10.<sup>122</sup> The lattice N atoms of TMNs are hydrogenated to obtain  $\text{NH}_3$  by lattice nitrogen reduction, followed by the regeneration of lattice nitrogen. Importantly,  $\text{N}_2$  activation on TMNs requires a smaller overpotential for the MvK mechanism, which is more conducive to the formation of  $\text{NH}_3$  than association and dissociation reactions.

DFT studies are used for energy assessment and catalyst design on the basis of experimental results, including the calculations of adsorption energy, Gibbs free energy,<sup>75,123,124</sup> the density of states analysis, the Bader charge analysis, and the crystal orbital Hamilton population analysis. In addition, advanced *in situ* monitoring technologies are meaningful for verifying the reaction mechanisms, dynamics of molecular catalyst interactions, and revealing the structure of intermediates, especially for *in situ* observation of catalytic reaction intermediates under practical operation, such as synchrotron radiation, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning tunnelling microscopy (STM), X-ray absorption spectroscopy (XAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and surface-enhanced infrared absorption spectroscopy (SEIRAS).<sup>125–128</sup> Yang *et al.* used *in situ* XPS and *in situ* XAS to reveal that  $\text{VN}_{0.7}\text{O}_{0.45}$  was the active site rather than VN, and they monitored that the catalyst underwent passivation due to a change in  $\text{VN}_{0.7}\text{O}_{0.45}$  to form VN.<sup>129</sup> According to *in situ* SEIRAS, the possible nitrogen reduction pathway on the Ru surface in acidic solution was deduced.<sup>130</sup> Feng *et al.* observed that adsorbed  $\text{H}_2\text{O}$  molecules were located at the  $\text{O}_{\text{vs}}$  site based on *operando* STM equipment, which accelerated the electrocatalytic HER process, and provided a rich route for revealing the kinetic process of nitrogen fixation.<sup>131</sup> Various *in situ* characterization techniques can be used not only independently, but also in combination to obtain accurate and multi-dimensional research results. In the future, *in situ* characterization technology will make a breakthrough in cost and universality, which further deepens our understanding of catalytic mechanisms.

The selectivity of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2\text{O}$  is challenging against the HER (and/or  $\text{N}_2\text{H}_4$ ), and numerous computational simulations and experimental attempts have been conducted to elucidate the essence of selectivity. Singh *et al.* provided some guidance that the selectivity between  $\text{NH}_3$  and  $\text{H}_2$  can be determined through a competition between the binding energies of N and H. They found that the generation rate of ammonia is of zero-order at electron and proton concentrations, while the rate of  $\text{H}_2$  is of first-order at a potential more negative than Us (Us refers to the potential to favourable H adsorption).<sup>134</sup> And the strategies of proton/electron availability have been proposed due to the significant impact of the proton concentration on HER performance, so employing an aprotic solvent,<sup>135</sup> blanketing the catalyst with a hydrophobic protection layer,<sup>136</sup> and designing photoelectrocatalysts are several potential solutions to selectively block the proton transfer to the catalyst surface, thus hindering  $\text{H}_2$  evolution. Increased loadings of  $\text{H}^+$  and  $\text{e}^-$  equivalents can directly trans-

late to greater  $\text{N}_2\text{H}_4$  yields, and the powerful reductant  $\text{KC}_8$  and strong Brønsted acid can deliver  $\text{H}^+/\text{e}^-$  equivalents for the necessary proton-coupled electron transfer to improve the selectivity of  $\text{N}_2\text{H}_4$ .<sup>137</sup> In addition, regulating the adsorption strength of N and H towards catalytic sites can alter the selectivity of  $\text{NH}_3$ . It is reported that the adsorption energy of H on Ru is smaller than that on N, which indicates that N atoms are preferably adsorbed on H atoms, thus obtaining higher  $\text{NH}_3$  selectivity.<sup>138</sup>

## 5. Detection and quantification of nitrogen sources for ammonia

The accurate quantification of ammonia is restricted by many factors, such as trace  $\text{NH}_3$  yield intrinsically, ammonia pollution from the environment, tedious ammonia separation from electrolytes, solution pH, and interferants. Serious concerns exist on a reliable quantitative method of ammonia concentration for  $\text{N}_2$  reduction, and we should maintain a rigorous scientific attitude and strive to accurately quantify  $\text{NH}_3$  based on different catalytic systems (Fig. 11). Currently, spectrophotometry and ion chromatography are common methods with the advantage of simplicity. In addition, the use of ion-selective electrodes (ISEs) and colorimetric  $\text{NH}_3$  assay kits, and nuclear magnetic resonance (NMR) methods can significantly improve the sensitivity, however, the experimental cost is increased to a certain extent.



**Fig. 11** Calibration curves for  $\text{NH}_3$  quantification. (a) the UV-Vis absorption, (b) the corresponding calibration curve for the indophenol blue method,<sup>147</sup> Copyright 2019, Wiley-VCH. (c)  $^1\text{H}$  NMR spectra of  $^{15}\text{NH}_4^+$  standard solutions (0.1–2.0 mM), (d) the corresponding calibration curve for the NMR method,<sup>49</sup> Copyright 2020, American Chemical Society. (e) UV-Vis of standard solutions, and (f) the corresponding calibration curve with Nessler's reagent,<sup>145</sup> Copyright 2019, Nature Publishing Group. (g) (I)  $^1\text{H}$  NMR of  $\text{NH}_4^+$  in 100  $\mu\text{M}$   $\text{NH}_4^+$  in various solvents, (II) NMR spectra of a mixture of  $^{14}\text{NH}_4^+$  +  $^{15}\text{NH}_4^+$ , (III) NMR of the  $\text{LiClO}_4/\text{THF}$  electrolyte after  $\text{N}_2$  reduction, (h) calibration curve to determine the  $\text{NH}_4^+$  concentration,<sup>144</sup> Copyright 2019, American Chemical Society. (i) UV-Vis absorption spectra and (j) the calibration curve using salicylic acid,<sup>104</sup> Copyright 2022, Elsevier. (k) FE of ammonia measured using Nessler's reagent or an enzymatic ammonia assay kit,<sup>145</sup> Copyright 2019, Nature Publishing Group. (l) The ion-selective electrode method.<sup>148</sup> Copyright 1969, Springer Nature.

The universal chemical chromogenic approaches are indophenol blue (IB) and Nessler's reagent based on the calibration curve, and they all have limitations. The IB test is usually used under neutral and acidic conditions because the generated indophenol dye could react with other amine groups under alkaline conditions.<sup>139</sup> Sodium salicylate is more steady than IB because salicylate can prevent the generation of toxic substances.<sup>140</sup> Nessler's method has wide pH applicability, however, some sacrificial agents (alcohol, glucose) are oxidized to carbonyl easily, thus resulting in misleading results.<sup>35</sup> Ion chromatography has high sensitivity and reliable results, among which the distraction of pH and sacrificial agents are avoided through appropriate detection methods.<sup>141,142</sup> The ISE determines the concentration of ions in solution by a membrane potential based on the Nernst equation, which can be divided into the  $\text{NH}_4^+$ -selective electrode and the  $\text{NH}_3$ -selective electrode. The concentrated solution can further improve the accuracy of  $\text{NH}_3$  detection when choosing an ISE.<sup>143</sup> The resonance signal obtained from  $^1\text{H}$  can be qualitatively and quantitatively detected by  $\text{NH}_4^+$ .<sup>144</sup> Nieler *et al.* reported a frequency-selective pulse NMR method for measuring  $\text{NH}_3$  concentration in electrolytes and quantified the common Berthelot method. The reliability of the results can be greatly improved by using various methods simultaneously to realize the quantitative determination of ammonia. Hao *et al.* used a colorimetric method with Nessler's reagent, an enzymatic  $\text{NH}_3$  assay kit (Sigma-Aldrich), and NMR to quantify ammonia accurately;<sup>145</sup> they found that the FEs measured using Nessler's approach or the enzymatic ammonia assay kit are persuasive. Zhang *et al.* used Nessler's approach, ion chromatography and the indole phenol method to quantify  $\text{NH}_3$ , and the results showed that the three methods had good coordination at low concentrations ( $0\text{--}500\ \mu\text{g L}^{-1}$ ). However, Nessler's approach and ion chromatography are more suitable for the quantification of ammonia than the indole phenol method at high concentrations.<sup>146</sup>

In order to scale up the PEC ammonia synthesis technology, the most essential progress is to confirm the true role of the catalysts. The primary task of removing nitrogen pollution is to ensure that the feed gases and catalysts are not polluted by nitrogen containing substances, including nitrate, nitrite and other contaminants before the experiment. Considering serious ammonia pollution in the environment, the  $^{15}\text{N}_2$  labeling experiment is necessary to provide direct evidence,<sup>149</sup> especially for N-containing catalyst systems.<sup>123</sup> However, many researchers often ignore the problem of  $^{15}\text{N}_2$  pollution, so it is only used as a qualitative method. Therefore, we need to accurately present the nitrogen fixation performance of the catalysts from multiple views. In addition, the background experiment is another piece of evidence to assist in proving the role of catalysts. The development of a combined technology of ammonia synthesis and ammonia detection can avoid ammonia pollution and realize the *in-situ* detection and online quantification of ammonia.

## 6. Conclusion

The above achievements have proved that PEC  $\text{N}_2$  reduction is a promising route to realize the N-cycle goal under environmental conditions, and multiple catalytic strategies are proposed to improve the yield and selectivity of  $\text{NH}_3$ . However, there are fundamental challenges as follows:

(I) Disclosure of the essence of photo-electrical synergy. The catalytic performance of PEC  $\text{N}_2$  reduction is more excellent than that of individual photocatalysis or electrocatalysis; however, this collaborative technology causes obstacles to the mechanistic understanding and revelation of photogenic/electrical effects. Most studies show that light irradiation promotes the electrocatalytic process, and bias accelerates the separation of photogenerated carriers, and few works reveal the coexistence of photocatalytic and electrocatalytic processes.

(II) Reliable methods in consideration of  $\text{NH}_3$  quantification and N-source determination. Although the spectral analysis is maneuverable, the accuracy usually is disturbed by pH, ionic strength and sacrificial agents. Therefore, it is necessary to combine it with other quantitative experiments, such as ion chromatography and NMR, to obtain accurate  $\text{NH}_3$  concentrations. In addition, researchers judge the rationality of catalytic performance by testing the recommended benchmark catalyst.

(III) Rigorous mechanistic insights. The active sites, free energies and possible reaction paths are revealed on the basis of theoretical exploration. The available theoretical methods, catalyst model and computing power are the driving force behind accurate calculations.

(IV) Advanced *in situ* characterization. It is difficult to predict the reconstruction of the surface structure, including the change of valence states, the identification of reaction intermediates and active centers, and real-time monitoring of reaction processes. For example, *in situ* surface enhanced infrared absorption spectroscopy and high-resolution electron energy loss spectroscopy showed potential for understanding the  $\text{N}_2$  reduction pathway due to its high sensitivity to the catalyst surface. In conclusion, reasonable catalysts are designed based on calculation and experiment, which will promote the rapid development of PEC  $\text{N}_2$  reduction to a large extent under environmental conditions in the future. The advantages of PEC  $\text{N}_2$  reduction are higher than those of individual photocatalysis or electrocatalysis. The correlation between PEC performance and the structures could be established at the molecular level to achieve industrial capabilities. In addition, strengthening durability testing is the key to proving the practicality at the industrial level. Finally, large-scale synthesis of catalysts should be considered.

## Author contributions

Pengyan Li: methodology, investigation, and writing – original draft. Yumin Liu: supervision. Muhammad Asim Mushtaq: supervision. Dongpeng Yan: supervision and writing – review



& editing. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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