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Cite this: *Inorg. Chem. Front.*, 2023, **10**, 4650

Recent progress in ammonia synthesis based on photoelectrocatalysis

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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 N₂ reduction are further summarized, followed by the current challenge and future prospects. This would guide both the productiveness and mechanism of NH₃ synthesis based on advanced PEC systems.

Received 13th April 2023,
Accepted 18th June 2023

DOI: 10.1039/d3qi00683b

rs.c.li/frontiers-inorganic

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.^{1,2} In nature, microorganisms depend on Mo-Fe protease to achieve the conversion of atmospheric N₂ to multipurpose NH₃.³ However, azotase is extremely sensitive to environmental

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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,⁴ 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.^{5–10} 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).^{11–13} 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.^{14,15} However, the deficient sites and hydrogen evolution reaction (HER) result in minimal yield and low Faradaic efficiency (FE) in electrocatalytic ammonia synthesis.^{16–19} 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.²⁰ 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).^{21–23}

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



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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.^{24–26} 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 , $W_{18}O_{49}$)^{27,28} and metal modifications,^{29,30} metal–organic frameworks with adjustable structures,³¹ and single atoms with remarkable active sites.³² 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.^{33,34}

Chemisorption is a crucial step for N_2 reduction because appropriate adsorption can destroy the molecular symmetry and enhance the proton affinity,³⁵ thus promoting N_2 hydrogenation. However, the bond energy (941 kJ mol^{-1}) and cleavage energy (410 kJ mol^{-1}) indicate that N_2 activation is challenging (Fig. 2a). Many studies have investigated activation mechanisms, such as vacancy engineering,^{27,36} large specific surface area, transition metal (TM)/non-metal doping,²⁵ 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 π^* orbital, thus producing a weak $N\equiv N$ bond through the ‘acceptor–donor’ route.³⁷ 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).^{37–40}

The research studies of electrocatalytic and photocatalytic ammonia synthesis are flourishing;^{42–45} 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.^{46,47} In particular, the electrocoupled 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.⁴⁸ 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.⁴⁹

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.^{49–51} Upon quenching photogenerated holes located on the valence band (VB),⁵² regulating the H^+ concentration on the surface of the catalyst,²⁷ 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.⁴⁸



Fig. 2 (a) N_2 molecular structure,⁴¹ 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.³⁸ Copyright 2018, American Association for the Advancement of Science.

2.2 Solar-driven and chemical bias-driven PEC N₂ reduction

Photocatalysts (such as g-C₃N₄, TiO₂, BiVO₄, *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 N₂ fixation can be carried out without electrochemical apparatus, and the formed anode photo-voltage contributes negative potential to N₂ reduction in the form of compensation voltage.^{53–55} 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 N₂ reduction and produced a high yield (13.3 mg m⁻² h⁻¹) under 2 sun radiation for the first time.²² 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.⁵⁶ Li *et al.* fabricated a photo-voltaic cell to realize PEC N₂ fixation with a high NH₃ yield (at the level of μmol h⁻¹ or even mmol h⁻¹) over the TiO₂/Au photocathode.⁵⁷ 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,²⁵ and the catalysts achieved a high FE (40.6%) and NH₃ yield (2.87 μmol h⁻¹ cm⁻²). The perovskite-based photocathode (TiO_x/CdS/Cu₂ZnSnS₄) achieved NH₃ production from NO₃⁻ reduction with a FE of 89.1% (Fig. 3).⁵⁸

Photocatalytic N₂ fixation is completed under the action of chemical bias induced by pH. Oshikiri's group was committed to research chemical bias-driven PEC N₂ fixation over Au/SrTiO₃ to improve NH₃ selectivity.^{30,59} The photo-excited hot

electrons from Au were transferred to the CB of SrTiO₃ to induce nitrogen reduction, and resulted in a hole on the SrTiO₃ 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 N₂ 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.⁶⁰ 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.^{61–63} 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 [Bi₂O₂]⁺ 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.⁶⁵ Due to improved electronic availability, the O_{vs} located on the BIOX (X = F, Cl, Br, I) surface is used as a reaction site to facilitate N₂ reduction.⁶⁶ Bai *et al.* synthesized O_{vs}-BiOI photocathodes by the *in situ* electrodeposition method (Fig. 4a),²⁴ and the adsorption capacity of R-BiOI to N₂ was significantly enhanced after introducing O_{vs} (Fig. 4b). The ammonia production rate is 1400 μmol m⁻² h⁻¹ (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_{vs}-BiOBr/TiO₂ photoelectrode, and the O_{vs} elevated the capacity of capturing photoelectrons. The bandgap of O_{vs}-BiOBr was reduced to 2.76 eV, indicating that O_{vs} can broaden the light absorption range (Fig. 4d). The O_{vs} is in favor of the formation of quasi-continuous defects that transport electrons under low-energy light irradiation, and O_{vs}-BiOBr/TiO₂ increases the NH₃ yield, which is 3.3 fold of the BiOBr/TiO₂ photocathode.²⁷ Mao *et al.* prepared LixMoO₃ nanosheets with O_{vs} through the lithiation strategy, and there are more abundant O_{vs} and Mo⁵⁺ in LixMoO₃ than in MoO₃ (Fig. 4e).⁶⁴ Density functional theory (DFT) calculations confirmed that LixMoO₃ nanosheets were favourable for the activation of N₂ and the formation of *N₂H (Fig. 4f). The experiments confirm that the effective NH₃ yield of LixMoO₃ nanosheets is 3.48 μg cm⁻² h⁻¹, 9 times that of MoO₃ nanosheets. The LDH systems with an abundance of surface oxygen vacancies or coordinatively unsaturated metal cations in ammonia synthesis were popular in N₂ reduction. Zhang *et al.* demonstrated a simple pretreatment of ZnCr-LDH,

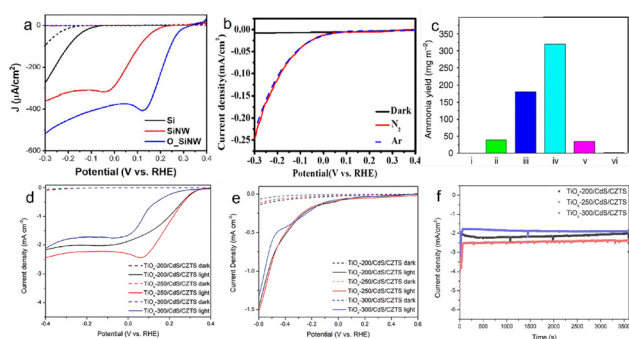


Fig. 3 The enhanced current density or improved NH₃ yield under light irradiation compared to that in the dark. (a) *J*-*V* plots of planar Si (black), Si nanowire (red), and highly ordered Si nanowire (blue) photocathodes for NO₃⁻ reduction in Ar-filled K₂SO₄ with KNO₃. Dashed lines represent dark current.⁵⁶ 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.²² Copyright 2016, Nature Publishing Group. (c) Linear sweep voltammetry (LSV) of the Ag/black Si electrode under N₂, Ar and dark conditions.²⁵ Copyright 2020, American Chemical Society. (d) The LSV of TiO_x/CdS/Cu₂ZnSnS₄ in KNO₃ and H₂SO₄ solution, (e) the LSV of TiO_x/CdS/Cu₂ZnSnS₄ and in K₂SO₄ solution, (f) the chronoamperometry curves of TiO_x/CdS/Cu₂ZnSnS₄ with different spray coating temperatures at 0 V vs. RHE.⁵⁸ Copyright 2022, Wiley-VCH.

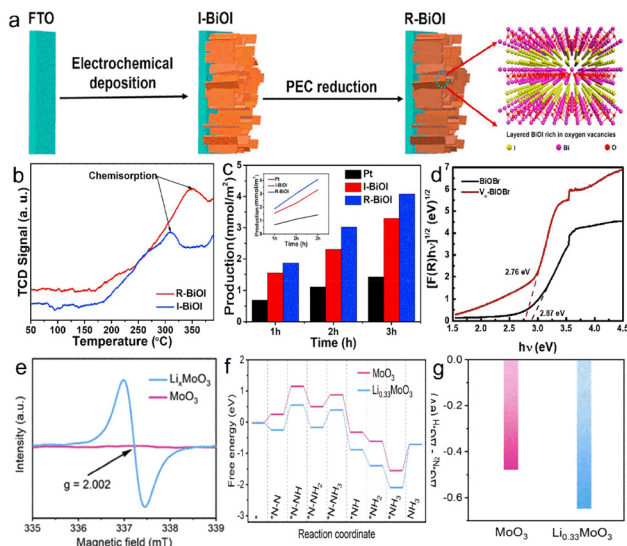


Fig. 4 (a) Schematic diagram of the synthesis process, of the I-BiOI/R-BiOI, (b) N_2 -TPD profiles of the I-BiOI/R-BiOI, (c) production rate of ammonia,²⁴ Copyright 2019, Elsevier. (d) the bandgap of O_{VS} -BiOBr and BiOBr,²⁷ Copyright 2022, Elsevier. (e) EPR of MoO_3 and $Li_{0.33}MoO_3$, (f) free 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).⁶⁴ 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 .⁶⁷

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} ,⁶⁸ 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.^{69,70} 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 σ -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.⁷¹ 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).²¹ 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.⁷³ Furthermore, non-metallic doping avoids the formation of recombination centers in N_2 reduction.^{74,75} Xu *et al.* synthesized B-doped Bi from layered BiOBr nanosheets with sodium borohydride ($NaBH_4$) as a reductant,⁷² 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 π electron delocalization.⁷⁶ 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.^{77,78} Nitrogen doping into carbon supporter generates regulated charge density, resulting in

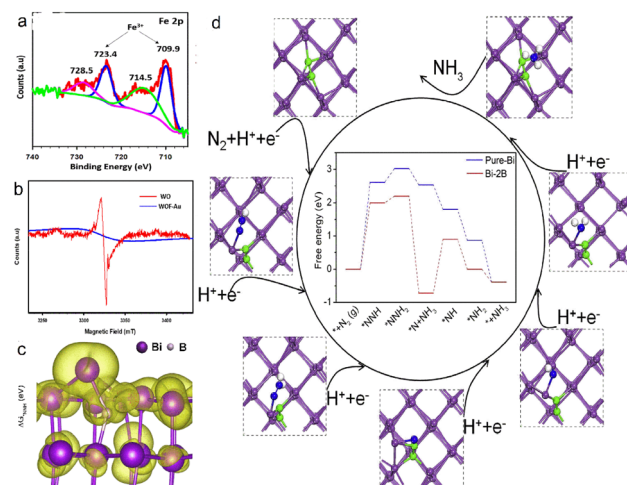


Fig. 5 (a) Fe 2p XPS of WOF-Au, (b) EPR of WO and WOF-Au,²¹ Copyright 2020, American Chemical Society. (c) Partial charge density of the Bi-2B (012) facet, (d) N_2 reduction progress on Bi-2B (012).⁷² Copyright 2020, Elsevier.

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.⁷⁹ 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.⁸⁰ 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,⁶² 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 2018.⁸¹ 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,⁸⁵ Copyright 2021, the Royal Society of Chemistry. (b) Lewis acidic boranes for N–N activation,⁸⁶ Copyright 2017, Wiley-VCH. (c) Schematic illustration of BCN for electrochemical nitrogen reduction,⁸³ Copyright 2022, Wiley-VCH. (d) Mechanism of over 10B/10Mo– C_3N_4 in the photocatalytic N_2 fixation strategy,⁸⁷ Copyright 2020, the Royal Society of Chemistry. (e) Gibbs energy over carborene-based FLPs for N_2 reduction.⁸¹ 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.⁸² 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.⁸³ 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.⁸⁴ Zhu *et al.* designed a variety of FLPs that have the ability to activate N_2 , and exhibit low ΔG values of -37.5 to $-51.0 \text{ kcal mol}^{-1}$ (Fig. 6e).⁸¹

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,⁸⁹ 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-

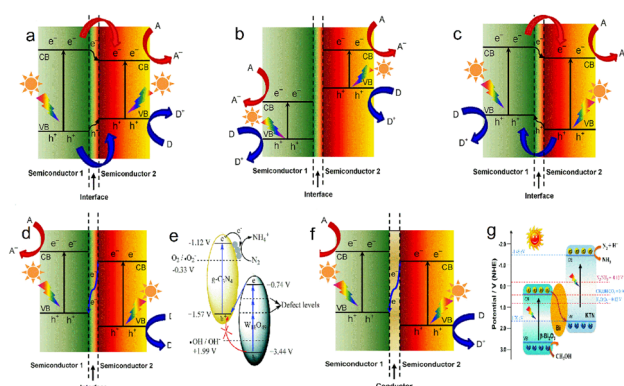


Fig. 7 Band structure of (a) type I, (b) type II, (c) type III, and (d) Z-scheme heterojunction in semiconductor–semiconductor and for example, (e) $g\text{-}C_3N_4/W_{18}O_{49}$,³³ Copyright 2017, the Royal Society of Chemistry. (f) Z-scheme in the semiconductor–electron mediator–semiconductor. A: electron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

structed type II systems, the main disadvantage is the lower oxidation and poorer reduction capabilities.⁹⁰ 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,⁹¹ 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.^{92,93} Liu *et al.* used the *in situ* chemical etching strategy to form Cu-MOFs on the Cu₂O surface with an organic ligand (H₃BTC), and the Cu-MOF amount can be determined by etching time (Fig. 8a).⁹⁴ The establishment of the Cu-MOF/Cu₂O heterostructure improves the carrier density and charge separation efficiency (Fig. 8b). Meanwhile, the NH₃ yield of Cu-MOF/Cu₂O is increased to 7.2 mmol m⁻² h⁻¹ due to unsaturated Cu(II) sites, which is 5 times that of Cu₂O (3.7 mmol m⁻² h⁻¹) and 3.9 times that of Cu-MOFs (1.9 mmol m⁻² h⁻¹). 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/CeO₂ heterostructure by the chemical deposition method, and CeO₂ is coated on the phthalocyanine copper surface.⁹⁵ UV-Vis absorption and electrochemical measurement make it clear that the phthalocyanine copper/CeO₂ heterostructure has a wide absorption range and a high electrochemical activity area. The PEC N₂ reduction performance reaches the best with an NH₃ yield of 1.16 μmol h⁻¹ cm⁻².

The C atom inserted into the Mo lattice shows a narrow metal band and exhibits similar Fermi level densities to noble metals, so Mo₂C is expected to perform well in catalysis.⁹⁸ However, Mo₂C is a matrix with poor electrical conductivity,⁹⁹ so it is necessary to consider the optimization of carrier migration for PEC N₂ reduction. Li *et al.* took graphite as a unit of the core-shell heterostructure, and wrapped it on the Mo₂C cluster surface based on *in situ* hydrothermal and calcination treatment, and effectively broke through the limitation of Mo₂C conductivity.¹⁰⁰ The graphitized carbon can accelerate electron transfer, which is conducive to the activation of N₂, with an NH₃ yield of 6.6 μg h⁻¹ mg⁻¹. In addition, MoSe₂ and the two-dimensional material g-C₃N₄ are assembled to form heterojunctions. Mushtaq *et al.* synthesized layered flower-like MoSe₂-g-C₃N₄,²⁶ and the Mo-N bond between MoSe₂ and g-C₃N₄ enhances the internal conductivity of MoSe₂. The absorption capacity of MoSe₂-g-C₃N₄ is enhanced (Fig. 8c), and the MoSe₂-g-C₃N₄ hybrid shows efficient PEC N₂ reduction performance with an FE of 28.91% and a yield of 7.72 mmol h⁻¹ cm⁻², respectively (Fig. 8d). The associative distal pathway and Gibbs free energy on MoSe₂@g-C₃N₄ heterojunctions are shown in Fig. 8e and f. The results show that N₂ is well adsorbed and activated on the MoSe₂-g-C₃N₄ (7 wt%) hybrid surface.

WO₃ 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 WO₃ and metal dichalcogenides (MoS₂, WSe₂), and proved that heterojunctions are stable in thermodynamics through calculation (Fig. 8g). In particular, optimized WO₃-MoS₂ has the lowest onset potential (0.25 V),⁹⁶ 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 N₂ 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.^{101–103} Porous CdS was obtained by growing CdS on Mo doped WO₃ hollow microspheres based on the hydrothermal method. The Mo-WO₃@CdS heterostructure¹⁰⁴ achieved a FE of 36.72% and an NH₃ yield of 38.99 μg h⁻¹ mg⁻¹. The DFT analysis suggests that Mo-W is the catalytic center of N₂ reduction, and CdS promotes the provision of electrons, thus accelerating PEC N₂ 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

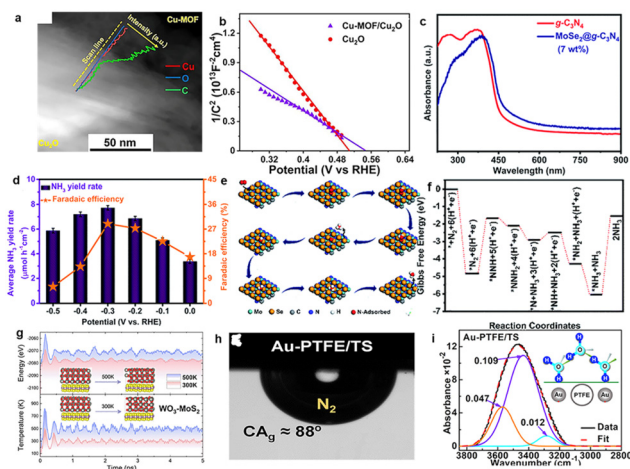


Fig. 8 (a) TEM images and EDS spectra of Cu-MOF/Cu₂O, (b) Mott-Schottky plot (frequency: 800 Hz),⁹⁴ Copyright 2021, Elsevier. (c) optical bandgap energy of g-C₃N₄ and MoSe₂@g-C₃N₄, (d) equivalent NH₃ yield and FE at different potentials on MoSe₂@g-C₃N₄ heterojunctions, (e) associative distal pathway for PEC N₂ reduction, (f) Gibbs free energy on MoSe₂@g-C₃N₄ heterojunctions,²⁶ Copyright 2020, the Royal Society of Chemistry. (g) Fluctuation of temperature and energy against the time of WO₃-MoS₂ at 300 K and 500 K,⁹⁶ Copyright 2022, American Chemical Society. (h) The image of an underwater N₂ 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.⁹⁷ 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.⁹⁷ Attenuated total reflection and caption-bubble measurements demonstrated that the porous framework of Teflon and Au created a gas-hydrophilic structure, which promoted N₂ 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 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.¹⁰⁵ Yan *et al.* constructed a CoVP@NiFeV-LDH heterojunction that has shown excellent electrocatalytic performance in the N₂ reduction reaction. The new three-dimensional hollow hierarchical structure provides abundant active sites for nitrogen adsorption and reduction to NH₃.¹⁰⁶

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.^{107,108} Ali *et al.* used plasma-enhanced black silicon decorated with Au nanoparticles (NPs) to achieve photoelectrically driven nitrogen conversion (Fig. 9a).²² When black silicon is replaced by unetched silicon, NH₃ 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 V (vs. RHE) .²⁵

Porous structures are also excellent to disperse and stabilize metal NPs. Peramaiah *et al.* deposited Au NPs on porous g-C₃N₄ with N defects, and then coated it on the n⁺np⁺-Si photocathode surface (Fig. 9b and c).¹⁰⁹ Silicon plays the roles of light collection and electrical management, Au is the active center to promote the conversion of N₂ to NH₃, and porous g-C₃N₄ with N-defects provides more N₂ 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 NH₃ molecule. Au/g-C₃N₄ exhibits excellent PEC N₂ reduction performance with a FE of up to 61.8% and an NH₃ yield of 13.8% $\mu\text{g h}^{-1} \text{ cm}^{-2}$. MoS₂ is an excellent carrier due to its well-dispersed layered structure, high conductivity and large specific surface area. Ye *et al.* dispersed TiO₂ NPs on MoS₂ nanosheets by the hydrothermal method, and the addition of MoS₂ leads to a smaller bandgap (2.98 eV) than that of TiO₂, and expedites the separation of electrons and holes.¹¹² Enhanced charge transfer maintains higher photoelectric voltage and slower decay behaviour. The results show that the NH₃ yield and FE are $1.42 \times 10^{-6} \text{ mol h}^{-1} \text{ cm}^{-2}$ and 65.52%, respectively, for MoS₂@TiO₂. Hydrophilic SnO₂ is uniformly dispersed on the surface of hydrophobic MoS₂, which leads to a change in the growth direction of MoS₂, 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 SnO₂ and MoS₂, with an NH₃ 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 SnO₂ and MoS₂ (Fig. 9d).

Quantum dots (QDs) possess superior properties that play important roles in N₂ reduction,¹¹³ such as small size, strong photostability, multiple excitation, exposed sites and electronic peculiarity. For example, Bi₂S₃ QDs have a high absorption coefficient and narrow bandgap.¹¹⁴ Gao *et al.* grew Bi₂S₃ QDs on MoS₂ through hydrothermal and solvothermal processes for photocatalytic reduction of N₂ to NH₃.¹¹¹ Bi₂S₃ QDs were dispersed on the MoS₂ surface, and the agglomeration of Bi₂S₃ QDs can be inhibited. The shift of binding energy indicates that there is an interaction between Bi₂S₃ QD and MoS₂ (Fig. 9e), thus leading to electron transfer from Bi₂S₃ to MoS₂ and accelerating the carrier separation (Fig. 9f). The FE of the Bi₂S₃ QD/15MoS₂ photocathode reaches 33%, and the NH₃ 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 SrTiO₃ (CQDs/STO) based on the small size and good conductivity.¹¹⁵ 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 N₂ conversion.



Fig. 9 (a) Corresponding TEM images of Au-coated silicon nanowires,²² Copyright 2016, Nature Publishing Group. (b) TEM images of Au/g-C₃N₄, (c) mapping of N, C, and Au.¹⁰⁹ Copyright 2021, Wiley-VCH. (d) XRD patterns of SnO₂/10MoS₂, SnO₂/10MoS₂ (silicomolybdic acid is not a precursor), MoS₂ (silicomolybdic acid is not a precursor) and SnO₂.¹¹⁰ Copyright 2022, Elsevier. (e) The XPS spectra of Bi₂S₃ QDs/15MoS₂. (f) photocurrent with a light on-off cycle.¹¹¹ 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.¹¹⁶ 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.¹¹⁷ 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%.¹¹⁸ In addition, this group has realized the ammonia synthesis by the phosphonium cation and isopropanol.¹¹⁹ 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).²³ 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

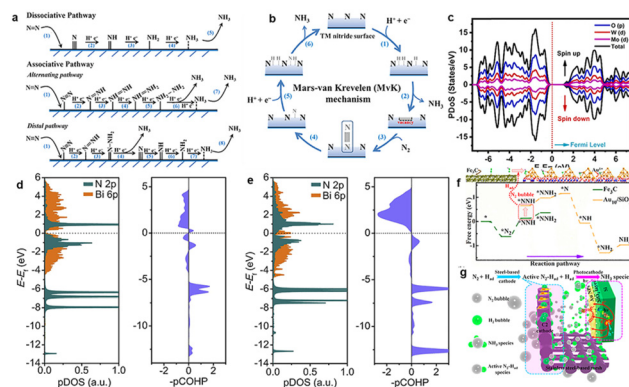


Fig. 10 (a) Dissociative, distal and alternating pathways for N_2 reduction, (b) MvK mechanism on the TM nitride surface,¹³² (c) atom projected density of states (PDOS) of $Mo-WO_3$,¹⁰⁴ Copyright 2022, Elsevier. (d and e) PDOS and projected crystal orbital Hamilton populations of the N atoms ($^{*}NNH$) on Bi (012) and (e) Bi-2B (012),⁷² 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/SiO₂/Si photocathode, (g) schematic representation of the catalytic and enhanced mechanism of the PEC NRR on the Au/SiO₂/Si photocathode.¹³³ 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,²⁶ 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 ₄ /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 ₃ | 300 W Xe lamp | −0.3 V vs. RHE | $1.915 \mu mol cm^{-2} h^{-1}$ | 115 |
| Cu ₂ O | 300 W Xe lamp | +0.4 V vs. RHE | $0.423 \mu mol cm^{-2} h^{-1}$ | 49 |
| PANI-ASSM/CdS-Co ₃ S ₄ | 40 W LED | −0.75 V vs. RHE | $12.33 \mu mol cm^{-2} h^{-1}$ | 120 |
| Vo-BiOBr/TiO ₂ | 300 W Xe lamp | −0.2 V vs. RHE | $1.475 \mu mol cm^{-2} h^{-1}$ | 27 |
| Cu-MOF/Cu ₂ O | 300 W Xe lamp | +0.5 V vs. RHE | $0.716 \mu mol cm^{-2} h^{-1}$ | 94 |
| MoSe ₂ @g-C ₃ N ₄ | 150 W Xe lamp | −0.3 V vs. RHE | $7.72 \mu mol cm^{-2} h^{-1}$ | 26 |
| Fe-doped W ₁₈ O ₄₉ | simulated solar light | −0.65 V vs. Ag/AgCl, | $0.577 \mu mol cm^{-2} h^{-1}$ | 21 |
| SnO ₂ /MoS ₂ | 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 ₃ @CdS | 300 W Xe lamp | −0.3 V vs. RHE | $38.99 \mu g h^{-1} mg_{cat}^{-1}$ | 101 |
| Mo ₂ 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. 10.¹²² The lattice N atoms of TMNs are hydrogenated to obtain NH_3 by lattice nitrogen reduction, followed by the regeneration of lattice nitrogen. Importantly, N_2 activation on TMNs requires a smaller overpotential for the MvK mechanism, which is more conducive to the formation of 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,^{75,123,124} 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).^{125–128} 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.¹²⁹ According to *in situ* SEIRAS, the possible nitrogen reduction pathway on the Ru surface in acidic solution was deduced.¹³⁰ Feng *et al.* observed that adsorbed H_2O molecules were located at the O_{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.¹³¹ 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 NH_3 from N_2 and H_2O is challenging against the HER (and/or N_2H_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 NH_3 and 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 H_2 is of first-order at a potential more negative than Us (Us refers to the potential to favourable H adsorption).¹³⁴ 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,¹³⁵ blanketing the catalyst with a hydrophobic protection layer,¹³⁶ and designing photoelectrocatalysts are several potential solutions to selectively block the proton transfer to the catalyst surface, thus hindering H_2 evolution. Increased loadings of H^+ and e^- equivalents can directly trans-

late to greater N_2H_4 yields, and the powerful reductant KC_8 and strong Brønsted acid can deliver H^+/e^- equivalents for the necessary proton-coupled electron transfer to improve the selectivity of N_2H_4 .¹³⁷ In addition, regulating the adsorption strength of N and H towards catalytic sites can alter the selectivity of 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 NH_3 selectivity.¹³⁸

5. Detection and quantification of nitrogen sources for ammonia

The accurate quantification of ammonia is restricted by many factors, such as trace 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 N_2 reduction, and we should maintain a rigorous scientific attitude and strive to accurately quantify 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 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 NH_3 quantification. (a) the UV-Vis absorption, (b) the corresponding calibration curve for the indophenol blue method,¹⁴⁷ Copyright 2019, Wiley-VCH. (c) ^1H NMR spectra of $^{15}\text{NH}_4^+$ standard solutions (0.1–2.0 mM), (d) the corresponding calibration curve for the NMR method,⁴⁹ Copyright 2020, American Chemical Society. (e) UV-Vis of standard solutions, and (f) the corresponding calibration curve with Nessler's reagent,¹⁴⁵ Copyright 2019, Nature Publishing Group. (g) (I) ^1H NMR of NH_4^+ in 100 μM 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 N_2 reduction, (h) calibration curve to determine the NH_4^+ concentration,¹⁴⁴ Copyright 2019, American Chemical Society. (i) UV-Vis absorption spectra and (j) the calibration curve using salicylic acid,¹⁰⁴ Copyright 2022, Elsevier. (k) FE of ammonia measured using Nessler's reagent or an enzymatic ammonia assay kit,¹⁴⁵ Copyright 2019, Nature Publishing Group. (l) The ion-selective electrode method.¹⁴⁸ 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.¹³⁹ Sodium salicylate is more steady than IB because salicylate can prevent the generation of toxic substances.¹⁴⁰ Nessler's method has wide pH applicability, however, some sacrificial agents (alcohol, glucose) are oxidized to carbonyl easily, thus resulting in misleading results.³⁵ Ion chromatography has high sensitivity and reliable results, among which the distraction of pH and sacrificial agents are avoided through appropriate detection methods.^{141,142} The ISE determines the concentration of ions in solution by a membrane potential based on the Nernst equation, which can be divided into the NH_4^+ -selective electrode and the NH_3 -selective electrode. The concentrated solution can further improve the accuracy of NH_3 detection when choosing an ISE.¹⁴³ The resonance signal obtained from ^1H can be qualitatively and quantitatively detected by NH_4^+ .¹⁴⁴ Nilander *et al.* reported a frequency-selective pulse NMR method for measuring 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 NH_3 assay kit (Sigma-Aldrich), and NMR to quantify ammonia accurately;¹⁴⁵ 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 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.¹⁴⁶

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,¹⁴⁹ especially for N-containing catalyst systems.¹²³ 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 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 NH_3 . However, there are fundamental challenges as follows:

(I) Disclosure of the essence of photo-electrical synergy. The catalytic performance of PEC 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 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 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 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 N_2 reduction to a large extent under environmental conditions in the future. The advantages of PEC 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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 22288201 and 22275021) and the Beijing Municipal Natural Science Foundation (Grant No. JQ20003).

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