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Nanomaterials for the electrochemical nitrogen reduction reaction under ambient conditions

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As an important chemical product and carbon-free energy carrier, ammonia has a wide range of daily applications in several related fields. Although the industrial synthesis method using the Haber–Bosch process could meet production demands, its huge energy consumption and gas emission limit its long-time development. Therefore, the clean and sustainable electrocatalytic N₂ reduction reaction (NRR) operating under conditions have attracted great attention in recent years. However, the chemical inertness of N₂ molecules makes it difficult for this reaction to proceed. Therefore, rationally designed catalysts need to be introduced to activate N₂ molecules. Here, we summarize the recent progress in low-dimensional nanocatalyst development, including the relationship between the structure and NRR performance from both the theoretical and experimental perspectives. Some insights into the development of NRR electrocatalysts from electronic control aspects are provided. In addition, the theoretical mechanisms, reaction pathways and credibility studies of the NRR are discussed. Some challenges and future prospects of the NRR are also pointed out.

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1 Introduction

Against the background of increasing population and global energy consumption connected with burning fossil fuels and worldwide environmental issues, creating an energy system based on efficient, clean and sustainable resources is particularly significant to secure our energy supply.^{1,2} Ammonia (NH₃) as one of the most widely produced industrial chemicals has found wide applications in the manufacture of fertilizers (at least 80% of total ammonia annually) and pharmaceuticals, as well as energy conversion.³ Particularly, compared to other energy carriers, NH₃ is recognized as an ideal storage medium for hydrogen (H₂), because it has a relatively high hydrogen content (17.6% by mass) and can exist easily in liquid form.^{4–8} Besides, nitrogen is an indispensable element of life and a crucial component of various bio-macromolecules (amino acids, nucleotides and the like). However, since the N≡N triple bond has a high bond energy of 945 kJ mol^{−1} at 298 K, it is difficult to crack and hydrogennate.⁹ Even though the atmospheric nitrogen (N₂) content is 78%, organisms normally obtain N in the form of NH₃ or nitrate (NO₃[−]) instead of directly using N₂ molecules. In nature, NH₃ can be obtained by fixing N₂ either by lightning or through the action of microbial nitrogenases.¹⁰ Generally, bacteria of the genus *Azotobacter* use adenosine triphosphate (ATP) as an energy transporter, and an iron–molybdenum–sulphur (FeMoS) core cluster as the main N₂ binding site to achieve the conversion of N₂ into NH₃ through migrating



multiple protons and electrons under ambient conditions.^{11–13} However, microorganisms containing nitrogenase in nature alone cannot sufficiently match the demand for fertilizer use. Industrially, the Haber–Bosch process with Fe-based^{14,15} or Ru-based^{16,17} catalysts has been the main NH₃ production method over the last 100 years, and is operated under harsh conditions (around 400 °C, 50 bar), thus suffering from high energy consumption and severe equipment requirements.^{18,19} In addition, H₂ is generally produced by the steam reformation of CH₄, which also depletes fossil fuels immensely and causes excessive CO₂ emissions. The social cost of CO₂ emissions and the impact of global fuel prices on geopolitics also limit the long-term development of conventional NH₃ processes.²⁰ Therefore, NH₃ synthesized from water and atmospheric N₂ using electric power is a promising method to convert unstably stored electricity into chemical energy. Moreover, feedstocks like water and N₂ are abundant and eco-friendly, acting as a proton source and N source, respectively. Since Davy's group developed the N₂ reduction reaction (NRR) method in 1807, researchers around the world have used various catalysts with different structures and compositions to activate N₂.²¹ Attracted by the attention of various countries and the huge prospects of electrocatalysis, the NRR field has developed tremendously over the past five years (Fig. 1a). So far, various active centre nanomaterials such as precious metals (Au, Ag, Ru, Pd, *etc.*), non-precious metals (Fe, Mo, Co, Ti, *etc.*), and metal-free (B, C, *etc.*) (Fig. 1c) have been investigated to match some suitable low-dimensional substrates to improve the catalytic performance of NH₃ yield and faradaic efficiency (FE). However, in some representative studies (Fig. 1b), around 70% of the catalysts appear in the low performance zone of low NH₃ yield

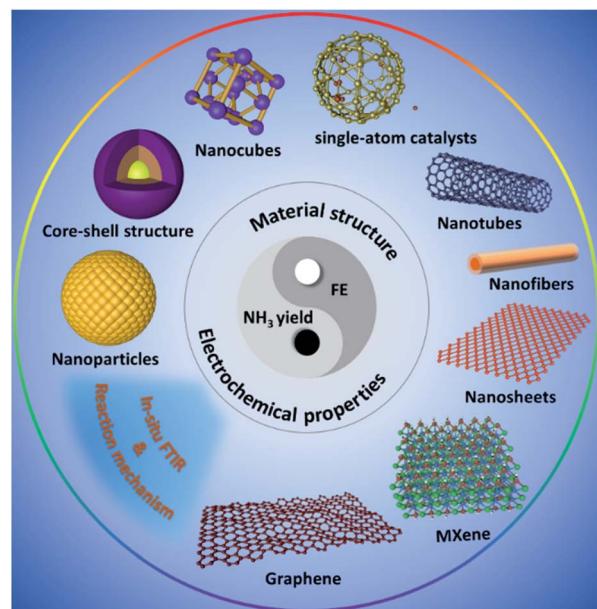


Fig. 2 Schematic overview of the NRR materials covered in this section.

or low FE, which is not conducive to the industrialization of the production process. According to S. Giddey's suggestion, the commercial process needs to achieve an NH₃ yield of 6.5×10^{-7} mol cm⁻² s⁻¹ or 3978 µg mg_{cat}⁻¹ h⁻¹ (mass loading: 0.1 mg cm⁻¹), and a FE of about 50%, with a current density above 0.25 A cm⁻².²² Therefore, these issues should be solved before attempting to produce NH₃ on a large scale: firstly, the N≡N bond is hard to activate – the high N≡N bond energy makes it difficult for the N₂ activation reaction to proceed. Therefore, some key strategies to improve the kinetics of the NRR need to be developed. Secondly, the competing hydrogen evolution reaction (HER) should be considered. Since the NRR and HER have similar reaction potentials, choosing a catalyst with high selectivity that can inhibit the HER is the key to finding an efficient and sustainable NH₃ synthesis route.²³ Moreover, a rational material morphology should be designed because of the significant difference in the reaction rates of materials on different exposed surfaces with different morphologies. Therefore, it is necessary to design a series of advanced catalysts to realize revolutionary progress in the NRR field.

In this review, we will mainly summarize the recent progress of some advanced low-dimensional nanomaterials in N₂ fixation under ambient conditions from experimental and theoretical perspectives, aiming at inspiring new perceptions for the future in this field. Firstly, we discuss the NRR mechanisms, reaction intermediates and credibility studies of the NRR. Then, we summarize some typical low-dimensional nanomaterials, discussing the relationship between the structure and NRR performance from both the theoretical and experimental perspectives. Finally, we provide some insights into the development of NRR electrocatalysts from the perspective of electronic control.

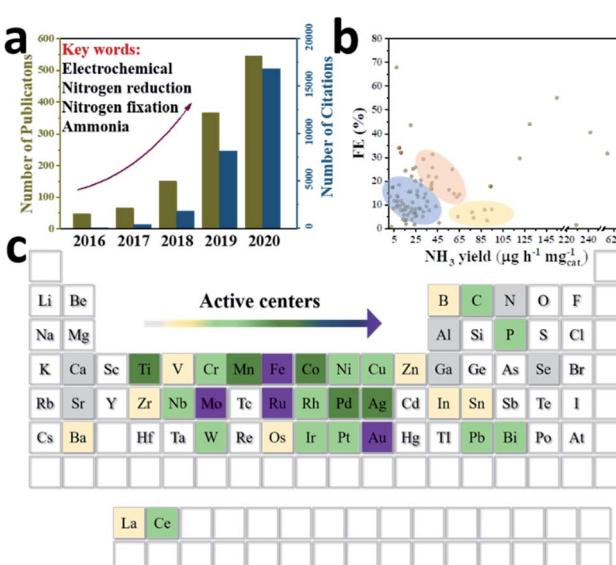


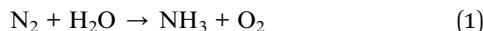
Fig. 1 (a) The number of publications and citations of NRR articles in the Web of Science in the last 5 years. (b) Reported NH₃ yield rate and FE of some representative articles. (c) The types of NRR electrocatalyst active centre published to date. The direction of the arrow represents the number of reports.



2 Reaction mechanisms

2.1 Theoretical basis

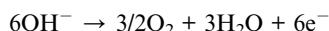
The electrochemical NRR is generally completed in an H-type cell. The overall reaction equation is shown in eqn (1):



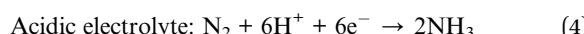
The anodic reaction is shown in eqn (2) and (3):



Alkaline or neutral electrolyte:



The cathodic reaction is shown in eqn (4) and (5):



Alkaline or neutral electrolyte:



The first important step of the NRR is the adsorption and activation of N_2 , which is highly related to the electronic state of the electrocatalyst. For the ground state of N_2 , the bonding HOMO is $3\sigma_g$, and the antibonding LUMO is $1\pi_g^*$. Taking transition metals as an example, N_2 donates electrons to the empty d orbital from its HOMO and accepts electrons to its LUMO, thereby being adsorbed on the catalyst and forming

bonds.²⁴ This electron donation and acceptance process is beneficial to adsorbing N_2 and weakening the $\text{N}\equiv\text{N}$ bonds.²⁵ The NRR is accompanied by a series of hydrogenation steps, including the breaking of $\text{N}\equiv\text{N}$ bonds and the formation of $\text{N}-\text{H}$ bonds. Generally speaking, N_2 hydrogenation has two main mechanisms, the dissociative mechanism and the associative mechanism (Fig. 3).^{26,27} In the dissociative mechanism, the $\text{N}\equiv\text{N}$ bond is broken before hydrogenation. Then, each N atom is hydrogenated separately until two NH_3 molecules are formed. This approach requires a high activation energy to overcome the high energy barrier during the direct cleavage of $\text{N}\equiv\text{N}$ bonds. In the associative mechanism, one N atom in the N_2 molecule is first adsorbed on the surface of the electrocatalyst, and then gradually hydrogenated. Generally, the mainstream pathways in the associative mechanism for converting N_2 to NH_3 can be classified into two hydrogenation routes, distal hydrogenation and alternating hydrogenation. In the distal hydrogenation path, H is added one by one to the N atom farthest away from the catalyst surface. When this N atom is converted to NH_3 , the N–N bond is broken. Then, the other N atom adsorbed on the surface of the catalyst is converted into NH_3 in the same way. In the alternating hydrogenation route, hydrogenation occurs alternately on the two N atoms. After the first N atom is converted to NH_3 , the remaining $-\text{NH}_2$ will absorb another proton to form a second NH_3 molecule. The enzymatic pathways belonging to the associative pathway exhibit the unique characteristics of lateral adsorption, rather than terminal adsorption in the alternating and distal pathways. The current research work shows that the N_2 fixation in the Haber–Bosch process is mainly caused by the dissociative

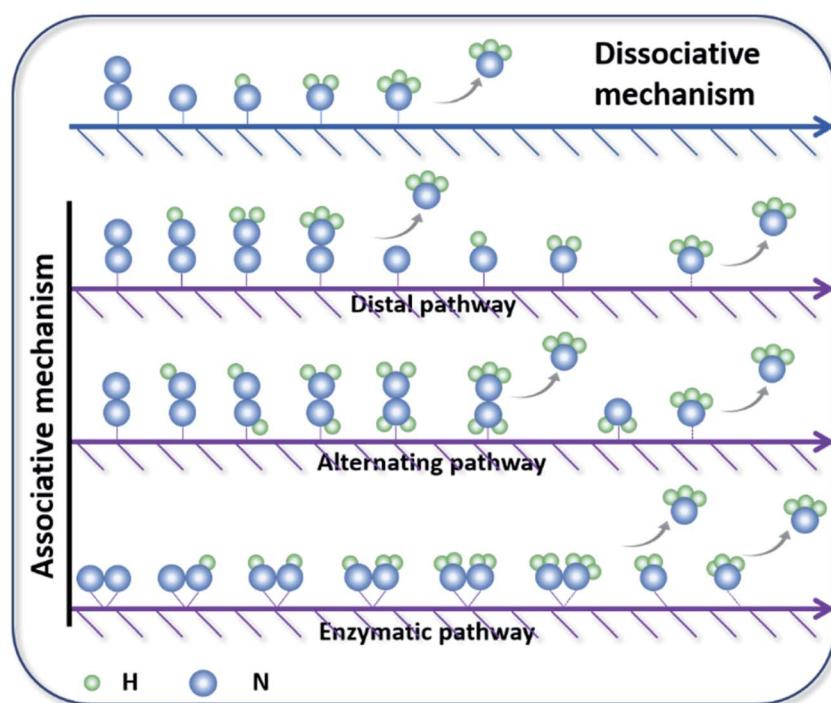


Fig. 3 Mainstream mechanisms for N_2 reduction to NH_3 on catalysts. Copyright 2016, Elsevier B.V.²⁶ Copyright 2016, American Chemical Society.²⁷



mechanism.²⁸ Therefore, high-temperature and high-pressure reaction conditions are necessary for the cleavage of $\text{N}\equiv\text{N}$ bonds. However, cleavage of the $\text{N}\equiv\text{N}$ bond in the associative mechanism is not necessary, which significantly reduces the energy input during the N_2 activation process, allowing the reaction to proceed under relatively mild conditions. Therefore, the separate or mixed partial radical steps of the distal, alternating, and enzymatic pathways dominate in the NRR.

2.2 Research on intermediate products

Although it is important to determine the NRR mechanism to further improve the absorbance and activation of N_2 on the surface of the catalyst, few experimental studies have been published on the significant effects of the NRR. *In situ* Fourier transform infrared spectroscopy (*in situ* FTIR) technology based on electrochemistry has become a new method to explore the N_2 reduction pathways, employed to detect the change of functional groups (like $^*\text{NNH}$, $^*\text{HNH}$, and $^*\text{NH}_3$) on the electrocatalyst surface during the NRR. By using *in situ* FTIR, key information about the real-time adsorption state of reactants and the structural transformation of intermediates on the catalyst surface could be obtained during the reaction process.²⁹ Shao's group investigated the composition and content of Pt and Au surface functional groups at different potentials by surface-enhanced infrared absorption spectroscopy (SEIRAS).³⁰ Fig. 4a shows the change in functional groups at the Au surface in N_2 -saturated solution under the first CV segment. It can be seen clearly that the intensity of $\delta(\text{H}-\text{N}-\text{H})$ and $\delta(\text{N}-\text{N})$ gradually increases as the potential grows more negative in the N_2 -saturated solution. At the Pt surface, the characteristic peaks

between 1300 and 1500 cm^{-1} are not observed (Fig. 4b), due to the much faster kinetics of the HER. Based on this analysis, it was believed that there was an associative reaction mechanism on the Au surfaces. Furthermore, they deduced a new possible NRR pathway on Rh surfaces by SEIRAS and differential electrochemical mass spectrometry (DEMS), that is, first reduction to N_2H_2 on the Rh surface, and then chemical dissociation in the electrolyte to form NH_3 .³¹ The optimal potential and materials have also been analysed by Yan.³² Combining LSV (Fig. 4c), *in situ* FTIR (Fig. 4d) and *in situ* Raman (Fig. 4e), they studied the catalyst reaction interface. Compared to the BCP (left) and PVDF@BCP (right) of ECOF@BCP (middle) additionally displayed obvious $\nu(\text{N}-\text{H})$ with increasing intensity as the potential became more negative, which is consistent with LSV. According to the position of the cathodic peak in the LSV, the potential of -0.3 V vs. RHE was selected for *in situ* Raman spectroscopy. Fig. 4e shows the gradual formation of NH_3 on the surface of ECOF@BCP.

2.3 Credibility studies

The fundamental problem with the NRR is that the amount of NH_3 produced is very small, yet NH_3 is a common contaminant in the laboratory environment, which has led to a large number of rigorous experiments being carried out to verify the reliability of the NRR activity of the material. The reasons for the discrepancies in the experimental data can be broadly classified as follows: contamination of the raw material (water, catalyst, catalyst carrier, electrolyte, and feed gas), air contamination, deterioration of the colour developer and decomposition of the catalyst. For feedstock contamination, eight sets of comparison

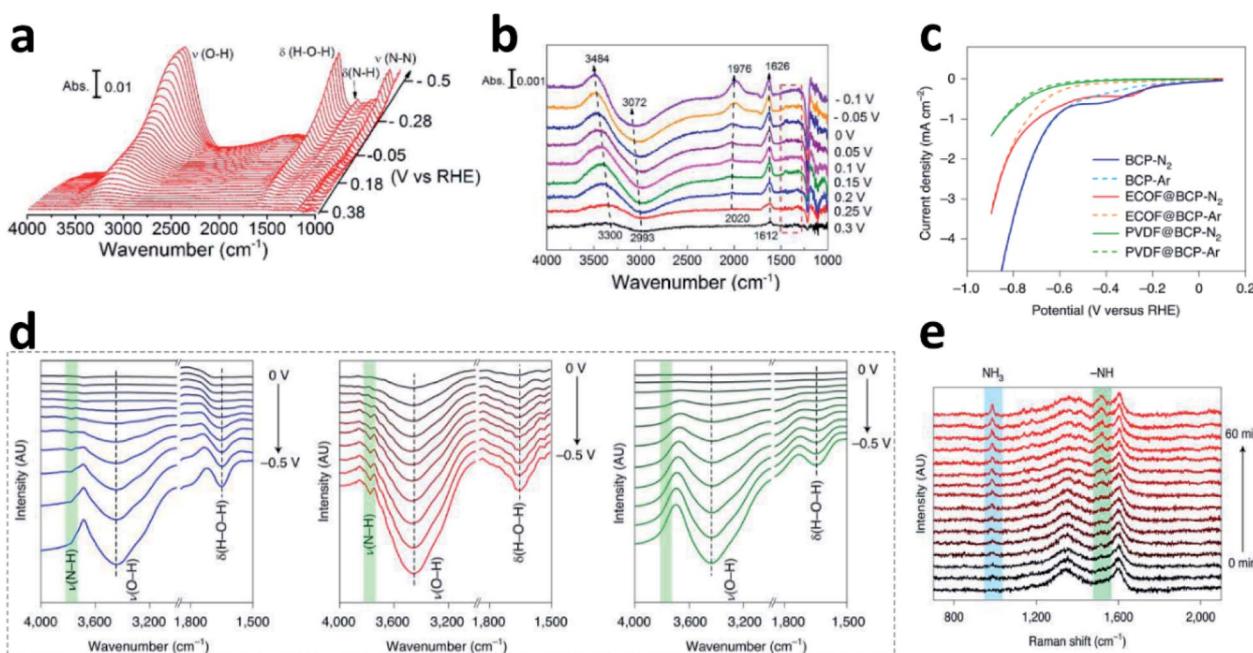


Fig. 4 FTIR spectra during the CV on the Au (a)/Pt (b) film in N_2 -saturated solution. Copyright 2018, American Chemical Society.³⁰ (c) LSV of different electrodes in feed gas. (d) *In situ* FTIR spectra of BCP (left), ECOF@BCP (middle) and PVDF@BCP (right) under feed gas. (e) *In situ* Raman spectra of ECOF@BCP at -0.3 V vs. RHE. Copyright 2021, Springer Nature.³²



experiments using the controlled variable method for NRR systems can be verified: (1) non-catalyst-Ar-open circuit voltage (OCV), (2) non-catalyst-N₂-OCV, (3) non-catalyst-Ar-working voltage (WV), (4) non-catalyst-N₂-WV, (5) catalyst-Ar-OCV, (6) catalyst-N₂-WV, (7) catalyst-Ar-WV, (8) catalyst-N₂-WV. For air contamination, the same volume of electrolyte placed daily on the operating table allows for monitoring of NH₃ contamination in the laboratory. For colour reagent deterioration, the standard curve should be calibrated weekly and all batches of electrolyte are coloured for the same time. For catalysts containing N, ¹⁵N NMR is necessary to ensure that the source of NH₃ is N₂ and not the decomposition of the catalyst.

3 Nanomaterial NRR electrocatalysts

For electrocatalytic N₂ fixation, nanomaterials have a uniform exposed lattice and can realize more exposed active sites under a certain mass loading compared with conventional bulk catalysts. Nanomaterials encompass a broad spectrum of tunable physical and chemical properties including a high surface to volume ratio and abundant active sites, making them immensely useful for a wide range of catalytic reactions. Low-dimensional nanocatalysts are highly designable because their surface structures and electronic properties are very sensitive to particle size and morphology. In this section, we will briefly summarize the synthetic methods and corresponding unique properties of these advanced nanomaterials, which are grouped into four categories based on material morphology (Fig. 2): zero-dimensional (0D) nanomaterials, including nanoparticles (NPs), nanospheres, quantum dots (QDs) and single-atom catalysts (SACs); one-dimensional (1D) nanomaterials such as nanofibers (NPs), nanowires (NWs), nanorods (NRs), and nanotubes (NTs); and two-dimensional (2D) nanomaterials

such as nanosheets (NSs), graphene (G), C₃N₄, MXene, and other non-layered carbon compounds.

3.1 Zero-dimensional (0D) nanomaterials

0D nanomaterials have ultra-small sizes, high specific surface area and huge numbers of active edge sites. The most typical 0D materials are NPs, which can be crystalline or amorphous, monometallic, multicomponent, or metal-free materials. In catalysis, NPs are the most common nanomaterials due to the relatively easier synthetic procedures. Over the past few decades, a rich variety of chemical methods (like chemical exfoliation, sonication-assisted exfoliation, chemical vapor deposition (CVD), solvothermal processing, cauterization technique, and laser ablation technique) have been developed to fabricate 0D NPs with well-controlled sizes and shapes.³³ In this section, we will briefly review the synthetic strategies for various 0D NRR catalysts. The performance of some 0D electrocatalysts is summarized in Table 1.

The NPs were fabricated applying a series of solvothermal strategies using various precursors. The general approach for preparing NPs is using a solvothermal process to prepare precursors followed by annealing treatment, or using sacrificial templates. Some pioneering researches on TiO₂ as the NRR nanocatalyst were done by Sun's group.^{54,55} They fabricated C-doped TiO₂ NPs by dispersing titanium butoxide in water/ethanol (5 : 30) solution, followed by hydrothermal and annealing treatment. A yield of 16.22 μg h⁻¹ mg_{cat}⁻¹ NH₃ was obtained with a 1.84% FE at -0.7 V vs. RHE in Na₂SO₄. However, the amorphous carbon may cover the active sites of the catalyst during the synthesis process, resulting in a relatively low yield of NH₃. Therefore, modulating the vacancy concentration and defect states may increase the active site density effectively.

Table 1 Summary of 0D nanomaterials for the NRR

Catalyst ^{ref.}	Electrolyte	NH ₃ yield (μg h ⁻¹ mg _{cat} ⁻¹)	NH ₃ yield (×10 ⁻¹⁰ mol s ⁻¹ cm ⁻²)	FE (%)	Potential (V vs. RHE)
MV-MoN@NC ³⁴	0.1 M HCl	≈76.90	—	6.90	-0.20
AuCu/ZIF-8 (ref. 35)	0.1 M HCl	63.90	—	5.00	-0.20
Pt/Au@ZIF ³⁶	THF + CF ₃ LiO ₃ S + 1% ethanol	>130	—	44.00	—
Au NPs ³⁷	0.1 M Na ₂ SO ₄	17.49	—	5.79	-0.14
Au ₁ Cu ₁ (ref. 38)	0.05 M H ₂ SO ₄	154.91	—	54.96	-0.2
Fe ₂ (MoO ₄) ₃ (ref. 39)	0.1 M Na ₂ SO ₄	18.16	—	9.10	-0.60
Mn ₃ O ₄ NPs ⁴⁰	0.1 M Na ₂ SO ₄	25.95	—	5.51	-0.50
ZrO ₂ NPs ⁴¹	0.1 M HCl	24.74	—	5.00	-0.45
C/Y stabilized ZrO ₂ (ref. 42)	0.1 M Na ₂ SO ₄	24.60	—	8.20	-0.50
np-PdH _{0.43} (ref. 43)	0.1 M PBS	20.40	—	43.60	-0.15
Body-centered cubic PdCu NPs ⁴⁴	LiCl	35.70	—	11.50	-0.10
B and N dual-doped C nanospheres ⁴⁵	0.05 M H ₂ SO ₄	15.70	—	8.10	-0.04
Defect-rich MoS ₂ nanoflowers ⁴⁶	0.1 M Na ₂ SO ₄	29.28	—	8.34	-0.40
BP QDs/MnO ₂ (ref. 47)	0.1 M Na ₂ SO ₄	25.30	—	6.70	-0.50
BP QDs@SnO _{2-x} (ref. 48)	0.1 M Na ₂ SO ₄	29.22	—	18.00	-0.40
Ru SAS/N-C ⁴⁹	0.05 M H ₂ SO ₄	120.90	—	29.60	-0.20
Fe-(O-C ₂) ₄ (ref. 50)	0.1 M KOH	32.10	—	29.30	-0.10
SACs-MoS ₂ -Fe ⁵¹	0.1 M KCl	613.70	15.93	31.60	-0.20
Ni _x -N-C-700-3h ⁵²	0.5 M Li ₂ SO ₄	—	18.79	21.00	—
SA-Mo/NPC ⁵³	0.1 M KOH	34.00	—	14.60	-0.30



Recently, Cu ions with mixed valences of +1 and +2 were also introduced into TiO_2 NPs by hydrothermal reaction to modulate the oxygen vacancy concentration and Ti^{3+} defect states (Fig. 5a).⁵⁵ Due to the chemical compensation effect, mixed-valent Cu can induce different electronic defect states in TiO_2 , thereby spontaneously adjusting the oxygen vacancies (OVs) concentration. Introduction of mixed valence Cu modulates the surface of TiO_2 (101) to generate OVs with different Ti^{3+} 3d¹ defect states below the Fermi energy. By adjusting the coordination structure, the activation and adsorption of N_2 can be enhanced effectively. Moreover, the catalytic performance is related to both Ti^{3+} and Cu contents. When the content of Cu was 6.9%, the Cu-doped TiO_2 NPs attained a high FE of 21.99% with $21.31 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ NH_3 yield at -0.55 V vs. RHE in 0.5 M LiClO_4 . Indeed, semiconductor materials with OVs can contribute to a certain NRR activity.⁵⁶ If combined with other NRR active components like noble Au, the catalytic performance may also improve synergistically. Due to the easy $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycle and abundant OVs, CeO_2 has been widely investigated as a catalyst.⁵⁷ Zhang's group reported a core-shell structure $\text{Au}@\text{CeO}_2$ with a small core layer of Au NPs ($<10 \text{ nm}$).⁵⁸ The combination of abundant OVs in the shell layer of CeO_2 NPs and small-sized Au NPs in the core layer enhances the NRR performance synergistically. The same group also developed core-shell Au/C NPs (Fig. 5b) by laser ablation, which consists of a spherical Au core and 1–2-layer graphite carbon shell with

a large number of defects.⁵⁹ The ultrathin carbon layer inhibits the aggregation of Au nanospheres effectively during the electrochemical reaction. Alternatively, there are a large number of carbon vacancies in the ultrathin carbon layer, which can provide additional catalytically active sites for the NRR. Hence, the core-shell Au/C NPs can afford an excellent performance (NH_3 : $241.9 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$, FE: 40.5%) at -0.45 V vs. RHE in neutral solution. Apparently, the synergistic effect between the carbon vacancies in the ultrathin graphitic carbon layer and the inner active Au nanospheres enhanced the NRR activity.

To utilize Au effectively, Jiang's group embedded Au subnanoclusters onto the TiO_2 surface and stabilized them with lattice oxygen to form Au–O–Ti bonds. The positively charged Au centre in the Au–O–Ti bond is the active site for forming the chemically adsorbed Au– N_2 bond. These small Au subnanoclusters ($\approx 0.5 \text{ nm}$) with few coordination sites as isolated precious metal active centres dispersed on the TiO_2 support lead to effective and stable NRR performance (Fig. 5c).⁶⁰ Xue and co-workers constructed inorganic donor–acceptor metal couples to increase electron density.⁶¹ The highly coupled Au_6/Ni NPs exhibited a high FE of 67.8% at -0.14 V vs. RHE. The author suggested that Ni provides numerous electrons for Au, which boosts the NRR activity of electron-rich Au. DFT calculations further proved that both the Gibbs free energy (ΔG) of N_2 dissociation and the desorption energy of NH_3 molecules on the electron-rich Au surface were reduced (Fig. 5d and e). Quantum

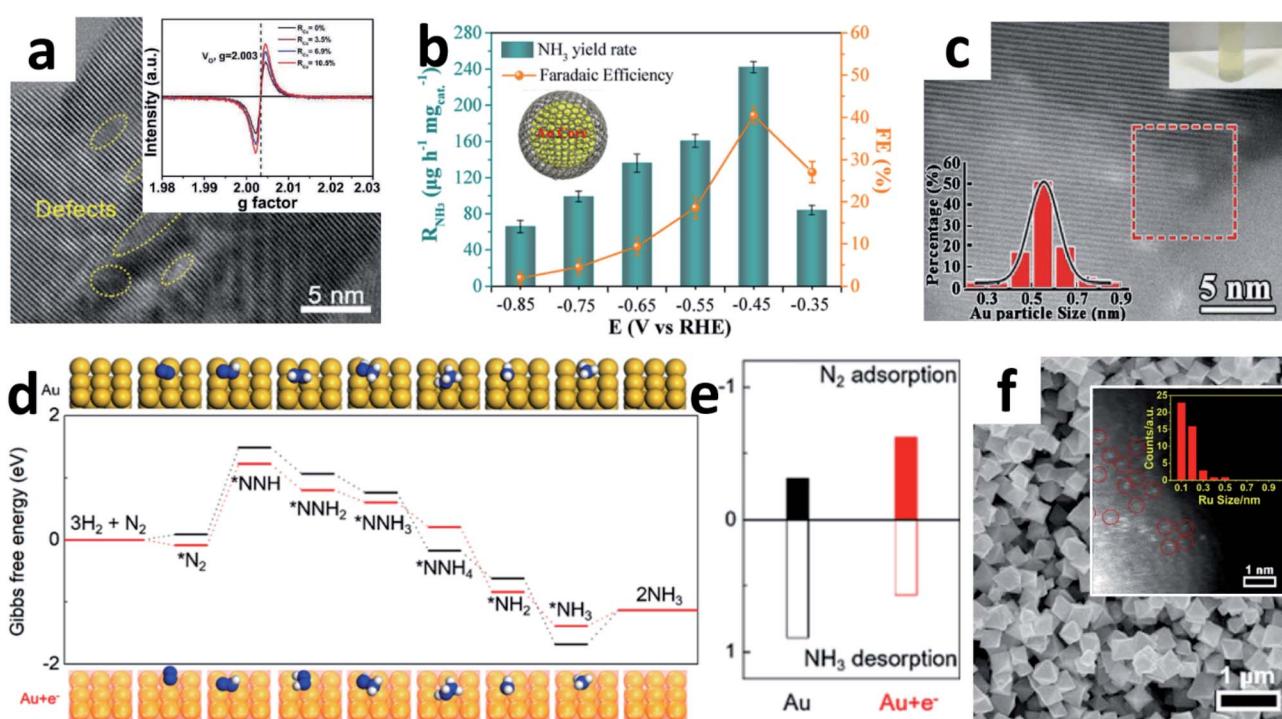


Fig. 5 (a) HRTEM image of $\text{Cu}-\text{TiO}_2$ NPs (inset: EPR spectra of $\text{Cu}-\text{TiO}_2$ with different Cu contents). Copyright 2020, Wiley-VCH.⁵⁵ (b) Performance of $\text{Au}@\text{C}$ at different applied potentials (inset: the structural diagram of $\text{Au}@\text{C}$). Copyright 2019, American Chemical Society.⁵⁹ (c) HAADF-STEM image of the TA-reduced Au/TiO_2 (top inset: the photograph of the catalyst suspended in water; bottom inset: Au particle size distribution). Copyright 2017, Wiley-VCH.⁶⁰ (d) Gibbs free energy diagram of the NRR for Au and $\text{Au} + \text{e}^-$ (insets: the corresponding optimized adsorption structures). (e) The calculated adsorption energies and desorption energies for adsorption onto Au and $\text{Au} + \text{e}^-$.⁶¹ (f) SEM image of $\text{Ru}@\text{ZrO}_2/\text{NC}$ (inset: the size-distribution histogram of Ru). Copyright 2019, Elsevier Inc.⁶⁹



dots (QDs) are nanoclusters that behave like atoms, which can significantly affect the chemical and physical properties of nanomaterials. Taking BP QDs as an example, the ultrafine BP QDs anchored on either MnO_2 NSs⁴⁷ or SnO_{2-x} NTs⁴⁸ could synergistically promote the NRR. Shao's group developed a 1T- MoS_2 /g-C₃N₄ with ultra-small sized MoS_2 QDs for the NRR.⁶² The metallic 1T- MoS_2 nanodots anchored on g-C₃N₄ NSs have abundant active sites and excellent conductivity, thereby achieving a comparable FE of 20.48% under demanding HER conditions.

Single-atom catalysts (SACs) are the ultimate form of 0D NPs, where all the atoms are surface active sites. Due to the homogeneity of the catalytically active sites, low coordination environment and maximal utilization efficiency, SACs have high catalytic activity, stability and selectivity for a series of electrochemical processes.^{63–66} Some reports have explored the application of SACs anchored on N-doped porous carbon for the NRR.^{53,67,68} In 2018, Zeng's group prepared single Ru atoms distributed on N-doped C by pyrolyzing a Ru-containing derivative of ZIF-8.⁴⁹ The isolated Ru atom was dispersed on the whole Ru SAs/N-C and without Ru–Ru bond contribution. The Ru SAs/N-C reached a high NH_3 production rate ($120.9 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$) and FE (29.6%) at -0.2 V vs. RHE. In particular, the FE of Ru SAs/N-C was 2.1 times higher than that of Ru NPs/N-C. Reducing the size of Ru particles to the atomic level should obviously improve efficiency. In addition, Tao *et al.* developed a thermal pyrolysis method anchoring single Ru atoms onto a Zr-based MOF to suppress the HER.⁶⁹ They claimed that control of the Ru size by the choice of ligand and the inhibitory effect of ZrO_2 on the HER facilitate the dissociation of N_2 . DFT also showed that the Ru sites with OVs were major active centres for enhancing N_2 fixation. Due to these remarkable properties, the Ru@ ZrO_2 /NC catalysts (Fig. 5f) achieved a significant NH_3 production rate of $3.665 \mu\text{g h}^{-1} \text{mg}_{\text{Ru}}^{-1}$ at -0.21 V vs. RHE. Moreover, the FEs of Ru@ ZrO_2 /C and Ru@ ZrO_2 /NC were significantly higher than those of Ru/C and Ru/NC, indicating that ZrO_2 could probably suppress the HER during the NRR.

3.2 One-dimensional (1D) nanomaterials

As an emerging class of nanomaterials, 1D materials exhibit excellent catalytic activity due to their fast charge transport, large active surface area and rapid mass transport.^{70–72} Compared with their bulk, 0D and 2D counterparts, the 1D structure has the following characteristics: first, the diameter of the material is limited to the nanoscale, so it shows high atom efficiency while preserving the relatively stable structure. Then, the large number of open spaces between adjacent 1D nanostructures facilitate both chemical accessibility and mass transport of electrolyte deep into the electrode.⁷³ Moreover, for electrocatalysis, the surface of the 1D nanomaterials can greatly facilitate the formation and release of bubbles, thus preventing them from occupying the active sites and hindering subsequent reactions.^{74–76} The synthetic methods for 1D nanomaterials include electrospinning, electrodeposition, solvothermal reactions, template-assisted methods, and mediated growth.^{70,71} Thus, advanced 1D nanomaterials including NFs, NWS, NTs and NRs will be briefly reviewed in this section. The performance of some 1D electrocatalysts is summarized in Table 2.

The electrospinning method is one of the most convenient methods for constructing complex 1D nanomaterials. Up to now, various 1D NWs and NTs have been synthesized by a spinneret electrospinning process for research on batteries and electrocatalysis.^{70,91} Yu's group designed an amorphous $\text{Bi}_4\text{V}_2\text{O}_{11}/\text{CeO}_2$ hybrid obtained by electrospinning.⁸⁸ The OVs and defective sites in $\text{Bi}_4\text{V}_2\text{O}_{11}/\text{CeO}_2$ are able to trap electrons in the metastable state, so that the electrons are injected into the antibonding orbital of the adsorbed N_2 , thereby weakening the $\text{N}\equiv\text{N}$ triple bond and promoting catalytic activity. Similarly, Sun's group also reported a novel metal oxide synthesized by this method.⁷⁷ The Nb_2O_5 NFs were shown to be a superior NRR catalyst with a high NH_3 yield ($43.60 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ at -0.55 V vs. RHE) and FE (9.26%). DFT calculations show that the electrocatalytic reaction takes place on the active sites on the surface (181), and the key energy barrier could be eliminated by applying a potential of -0.56 V. The same group also reported the Ti^{3+} self-doped TiO_{2-x}

Table 2 Summary of 1D nanomaterials for the NRR

Catalyst ^{ref.}	Electrolyte	NH_3 yield ($\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$)	NH_3 yield ($\times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$)	FE (%)	Potential (V vs. RHE)
Nb_2O_5 NF ⁷⁷	0.1 M HCl	43.6	—	9.26	-0.55
AuPdP NWs ⁷⁸	0.1 M Na_2SO_4	18.78	1.23	15.44	-0.30
$\text{CBC}/\text{V}_{\text{r}}\text{-ReSe}_2@\text{CBC}/\text{CBC}$ ⁷⁹	0.1 M Na_2SO_4	—	4.62	42.5	-0.25
Ti^{3+} self-doped TiO_{2-x} NWS ⁸⁰	0.1 M Na_2SO_4	—	0.35	14.62	-0.55
C@CoS@ TiO_2 NFS ⁸¹	0.1 M Na_2SO_4	—	8.09	28.60	-0.55
Fe-doped $\text{W}_{18}\text{O}_{49}$ NWS ⁸²	0.25 M LiClO_4	24.70	—	20.0	-0.15
Fe– MnO_2 (ref. 83)	0.1 M Na_2SO_4	39.20	—	16.80	-0.29
$\alpha\text{-Fe}_2\text{O}_3@\text{mTiO}_2$ (ref. 84)	0.1 M Na_2SO_4	27.20	—	13.30	-0.50
Fe–N/C-CNTs ⁸⁵	0.1 M KOH	34.83	—	9.28	-0.20
CoVP@NiFeV-LDH HHNTs ⁸⁶	0.05 M H_2SO_4	—	4.44	13.80	-0.30
Mo_2C NRs ⁸⁷	0.1 M HCl	95.10	—	8.13	-0.30
$\text{Bi}_4\text{O}_{11}/\text{CeO}_2$ (ref. 88)	0.1 M HCl	23.21	—	10.16	-0.20
CNT@C ₃ N ₄ –Fe & Cu ⁸⁹	0.25 M LiClO_4	9.86	—	34.00 (-0.80 V)	-1.20
Surface-rough Rh_2Sb NRs ⁷⁵	0.5 M Na_2SO_4	228.85	—	1.50	-0.45
IrP ₂ @PNPC-NF ⁹⁰	0.05 M H_2SO_4	94.00	—	17.80	-0.20



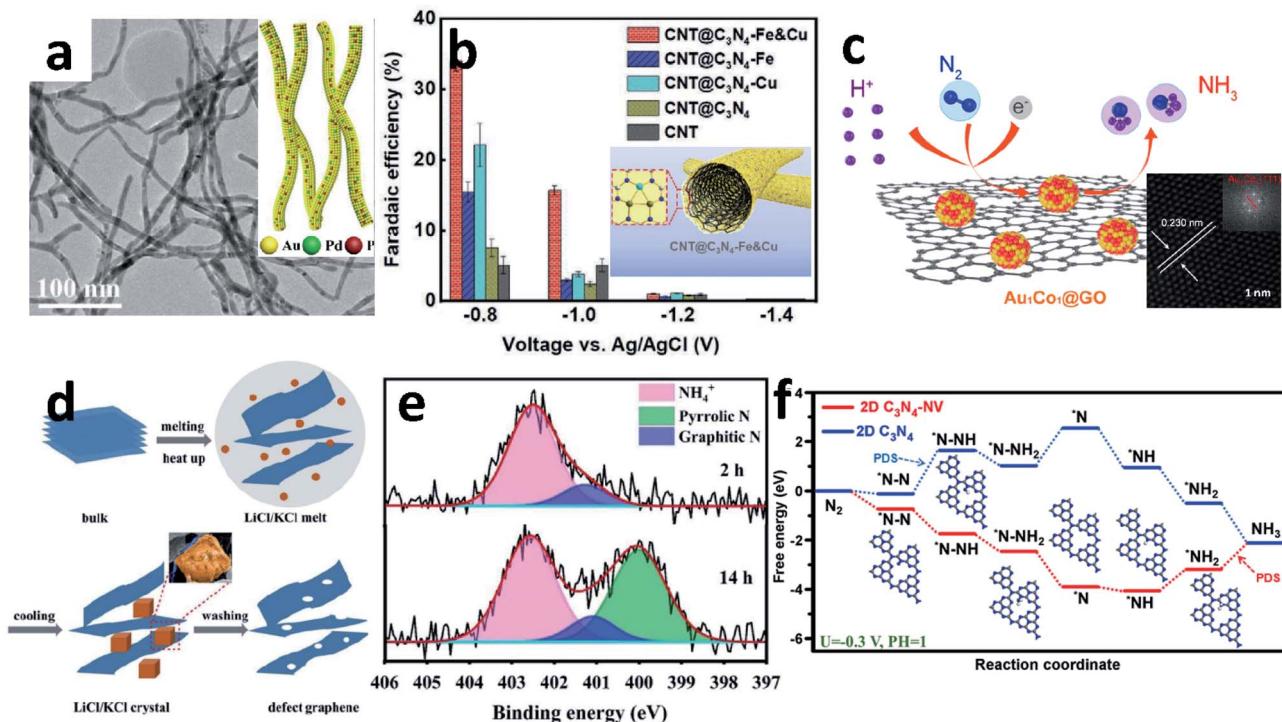


Fig. 6 (a) TEM image of AuPdP NWs (inset: schematic diagram of AuPdP NWs). Copyright 2019, American Chemical Society.⁷⁸ (b) The FE of different materials at different potentials (inset: schematic diagram of CNT@C₃N₄-Fe & Cu). Copyright 2020, Wiley-VCH.⁸⁹ (c) Schematic diagram of the NRR of Au₁Co₁@GO (inset: HRTEM image of Au₁Co₁@GO). Copyright 2019, American Chemical Society.¹¹⁷ (d) Schematic diagram of defect graphene (DG) synthesis. (e) N 1s spectra of DG-800 after reaction. Copyright 2020, The Royal Society of Chemistry.¹³¹ (f) Gibbs free energy of C₃N₄ and C₃N₄-NV for the NRR. Copyright 2021, Elsevier B.V.¹³⁸

NWs supported on Ti mesh.⁸⁰ Introducing Ti³⁺ into the TiO₂ surface could decrease the energy barrier of electron transfer and increase the number of active sites to obtain a higher NH₃ yield (3.51×10^{-11} mol s⁻¹ cm⁻²) with 14.62% FE at -0.55 V vs. RHE, compared to TiO₂/TM (1.89×10^{-11} mol s⁻¹ cm⁻², 6.49%). Wang *et al.* synthesized AuPdP NWs by simultaneously incorporating Pd and P into a controlled morphology Au particle (Fig. 6a).⁷⁸ There is a strong interaction between Au, Pd and P in the NWs. Pd, which has a stronger adsorption effect on H, improves the H adsorption on the Au surface;⁹² and the incorporation of P provides more valence electrons, which is beneficial to the selective hydrogenation of N₂ to NH₃. Thus, AuPdP NWs achieved an NH₃ yield of $18.78 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and FE of 15.44% at -0.3 V vs. RHE. Although defect engineering has been repeatedly proven as a rational strategy to enhance electrocatalytic performance, it has poor selectivity between the NRR and HER. The side-effects of the HER mean that the NRR is still far from commercialization. Recently, Liu *et al.* reported a novel “sandwich” structure, CBC/Vr-ReSe₂@CBC/CBC (CBC = carbonized bacterial cellulose, Vr-ReSe₂ = vacancy-rich ReSe₂).⁷⁹ The surface of the hydrophobic CBC layer resists the intimate contact between water molecules and Vr-ReSe₂@CBC NFs, and slightly increases the adhesive force to N₂ bubbles, so the FE is boosted by 32% at -0.25 V vs. RHE compared with Vr-ReSe₂@CBC without the CBC sandwich structure.

NRs are the most common 1D morphology because they contain exposed stepped faces, remarkably boosting their

catalytic performance.⁹³⁻⁹⁶ In 2017, Ren *et al.* demonstrated Mo₂N NRs as an efficient NRR electrocatalyst.⁹⁷ According to the DFT calculations, after nitrogenation, the ΔG of the potential determining step of the NRR on MoO₂ decreased dramatically. Later, this group developed MoC NRs based on Mo₂N, which was synthesized by pyrolyzing a Mo₃O₁₀(C₆H₈N)₂·2H₂O precursor in an Ar atmosphere. The FE of MoC is 1.8-fold that of Mo₂N.⁸⁷ Porous FeVO₄ NRs have been reported as an effective NRR catalyst contributing to the dual active centres.⁹⁸ The dual active centres of the Fe_{2c}-V_{2c} dimer can jointly back-donate their 3d-electrons into the antibonding $1\pi_g^*$ orbital of *N₂, and this process strongly polarizes and activates N₂, increasing the NH₃ yield up to $52.8 \mu\text{g h}^{-1} \text{mg}^{-1}$. Moreover, coordination of Fe and Cu also enhanced the NRR. From Chu's report, the ordered sub-nano space in the surface cavities of CNT@g-C₃N₄ can accommodate several Fe and Cu atoms, forming a sub-nano reactor with tight coordination between Fe and Cu.⁸⁹ Compared to their single-metal counterparts, the coordination between Cu and Fe can accelerate the adsorption of N₂ synergistically to optimize the reaction path and lower the energy barrier, thereby improving the FE to up to 34% (Fig. 6b).

3.3 Two-dimensional (2D) nanomaterials

2D materials have a single and fully exposed crystal surface and unique electronic state, arousing enormous interest over a wide field of energy and storage.^{99,100} Compared with their bulk, 0D



Table 3 Summary of 2D nanomaterials for the NRR

Catalyst ^{ref.}	Electrolyte	NH ₃ yield ($\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$)	NH ₃ yield ($\times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$)	FE (%)	Potential (V vs. RHE)
Co-FePS ₃ NSs ¹¹⁸	0.1 M KOH	90.60	—	3.38	-0.40
Sn/SnS ₂ (ref. 119)	0.1 M PBS	23.8	—	3.40	-0.80
B4C NSs ¹²⁰	0.1 M Na ₂ SO ₄	26.57	—	15.95	-0.75
Bi NS ¹⁰⁵	0.1 M Na ₂ SO ₄	13.23	0.42	10.46	-0.80
FeS ₂ -Mo _{17.3} NSs ¹²¹	0.1 M KOH	26.15	—	14.41	-0.20
Few-layer black phosphorus NSs ¹²²	0.01 M HCl	31.37	—	3.09	-0.70
Crystalline red phosphorus nanoribbons ¹⁰⁹	0.1 M Na ₂ SO ₄	15.40	—	≈ 3.00	-0.40
IrP ₂ @PNPC nanofilm ⁹⁰	0.05 M H ₂ SO ₄	94.00	—	≈ 10.00	-0.20
1T-MoS ₂ /g-C ₃ N ₄ (ref. 62)	0.1 M HCl	29.97	—	20.48	-0.30
Hydroxyl-rich Ti ₃ C ₂ T _x QDs ¹²³	0.1 M HCl	62.94	—	13.30	-0.50
Au/Ti ₃ C ₂ (ref. 124)	0.1 M HCl	30.06	—	18.34	-0.20
Rh ₂ P@NPC ¹²⁵	0.1 M Na ₂ SO ₄	37.60	—	7.64	-0.25
Au ₁ Co ₁ @GO ¹¹⁷	0.5 M K ₂ SO ₄	36.82	—	22.03	-0.20
CoO QD/RGO ¹¹¹	0.1 M Na ₂ SO ₄	21.50	—	8.30	-0.60
CoS ₂ /NS-G ¹²⁶	0.05 M H ₂ SO ₄	25.00	—	≈ 6.00	-0.20
rGO/Fe@Fe ₃ O ₄ /CP ¹²⁷	0.2 M NaHCO ₃	—	1.30	6.25	-0.30
Boron-doped graphene (BG) ¹²⁸	0.05 M H ₂ SO ₄	—	1.60	10.80	-0.50

and 1D counterparts, the 2D structure has the following characteristics: first, the 2D nanomaterials have exceptional flexibility and mechanical strength due to nanoscale thickness and strong in-plane covalent bonding. Then, thanks to their ultra-thin thickness and large transverse dimensions, 2D materials have a high specific surface area and surface atomic exposure. Moreover, for surfaces that expose a large number of atoms, researchers can design 2D nanomaterials for surface modification, elemental doping or vacancy engineering at the atomic level. Especially in recent years, various 2D nanomaterials (such as NSs, MXene, G, and C₃N₄) have been developed and utilized in the NRR electrocatalysis. The synthetic methods for 2D nanomaterials are mainly solvothermal reactions, CVD, template-assisted methods, topochemical transformations, salt-assisted synthesis, and self-assembly methods.¹⁰⁰⁻¹⁰³ The performance of some 2D electrocatalysts is summarized in Table 3.

Nørskov *et al.* suggested using a less reactive main group element, semiconductor or thin insulator, to suppress the HER process and enhance the FE.¹⁰⁴ Qiao's group reported a semi-conducting Bi NS with effective p-orbital electron delocalization and abundant exposure of edge sites, which exhibits a high NRR electrocatalytic activity.¹⁰⁵ Notably, materials with HER characteristics also promote the NRR. Wang's group developed ultra-thin carbon NSs with Mo₂C DQs, which have high reactivity for both the NRR and HER.¹⁰⁶ Unlike the back-donation process of the transition metal complex, the B atoms have the characteristics of monovalent borylene, and the N₂ unit can be used as a Lewis s-donor and p-receptor.¹⁰⁷ In 2019, Zhang *et al.* developed a novel boron NS (BNS), whose B atoms were oxidized and H deactivated as a NRR electrocatalyst with an NH₃ production rate of 13.22 $\mu\text{g h}^{-1} \text{ mg}_{\text{cat}}^{-1}$.¹⁰⁸ Compared with traditional NSs, 2D nanoribbons have stronger size confinement effects. Recently, Liu *et al.* reported triclinic crystalline red phosphorus (cRP) nanoribbons as a large-scale synthetic nanocatalyst for the NRR in 0.1 M Na₂SO₄.¹⁰⁹

As an ideal substrate to load electrocatalysts, graphene (G) has a large specific surface area and abundant material attachment sites, which can make the material grow evenly on the G surface to avoid agglomeration. Many G-based materials have been reported for the NRR.¹¹⁰⁻¹¹⁴ Recent work by Chu *et al.* developed an advanced electrocatalyst, CuO/RGO, which was synthesized by a microwave-assisted solvothermal method.¹¹⁵ The CuO/RGO exhibited a high NH₃ yield of $1.8 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ and FE of 3.9% at -0.75 V vs. RHE in 0.1 M Na₂SO₄, far outperforming the bare CuO or RGO alone. The highly stable and efficient mode for the N₂ adsorption activity of CuO was attributed to the (111) facet of surface end groups. Similarly, a Au/CeO_x-RGO achieved a comparable NH₃ performance due to the amorphous Au, which has more structural distortion and a higher concentration of catalytic NRR active sites.¹¹⁶ The alloyed Au₁Co₁ NPs dispersed on GO can also synergistically boost the activation of the N≡N bond, and its synergistic effect is mainly reflected in Au₁Co₁ (111) (Fig. 6c).¹¹⁷

G-Based materials are always modified by the introduction of defects¹²⁹ or heteroatoms¹³⁰ to improve their usage. Defective G disrupts the original electronic arrangement and improves the transfer of electrons from the electrocatalyst to the chemisorbed molecules. He's group prepared an ultrathin porous dopant-free defect G using the molten salt method (Fig. 6d).¹³¹ It is noteworthy that the defect G utilizes the product NH₃ from the NRR instead of N₂ as the N source for N doping (Fig. 6e). G can also be activated by lone pairs of electrons in electron-rich dopants, or by empty orbitals in electron-deficient dopants, thereby destroying the integrity of π -conjugation.^{132,133} Boron (B) is an effective doping example, which can cause electron deficiency in G and thus increase electrocatalytic activity.^{134,135} The local electron-deficient environment at the B-doped site provides a powerful binding site for the Lewis base, leading to improved electrocatalytic activity. Recently, Zheng's group reported B-doped G. In this work, the distribution structures and



contents of B have distinct effects on NH_3 yield and FE. Among the structure of BC_3 , BC_2O and BCO_2 , the G-like BC_3 -type bond plays a key role in enhancing N_2 fixation. At a doping level of 6.2%, the B-doped G achieves an NH_3 production rate of $9.8 \mu\text{g h}^{-1} \text{cm}^{-2}$ and a remarkable FE of 10.8% at -0.5 V vs. RHE in aqueous solutions. B doping in the G framework leads to the redistribution of electron density, where the electron-deficient boron sites provide enhanced binding capability to N_2 molecules.¹²⁸ Wang's group developed B, N co-doped G with abundant defects by thermal treatment of GO and boric acid under an NH_3 atmosphere followed by annealing. Edge carbon atoms occurring near B-N pairs were found to be the active sites for the NRR. Thus, the NRR with a high NH_3 production rate ($7.75 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$) and excellent FE (13.79%) was achieved at -0.3 V vs. RHE .¹³⁶

Analogous to G, the crystal structure of graphitic carbon nitride (C_3N_4) may be described as a hexagonal carbon framework with N-substituted carbon by the sp^2 hybridization of C and N atoms. C_3N_4 and related materials possess evenly distributed holes, a tunable electronic structure and uniform pyridinic-N coordinators rich in lone electron pairs able to capture metal ions in the ligands. C_3N_4 has a more negative conduction position relative to the reduction potential of N_2/NH_3 , which favours the activation of adsorbed N_2 .¹³⁷ The 2D C_3N_4 -NV, which has a larger specific surface area and abundant NVs, has a lower reaction ΔG (Fig. 6f).¹³⁸ This is because NVs can enrich electrons and transfer them to the $2\pi^*$ orbital of N_2 , thereby enhancing the adsorption effect.

MXenes have been widely reported in the electrocatalysis field due to their diverse metal active centres and abundant surface end groups.^{139–141} For example, $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T} = \text{F, OH}$),¹⁴² $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T} = \text{O, OH}$),¹⁴³ MXene/TiFeO_x-700,¹⁴⁴ and $\text{Ti}_3\text{C}_2\text{OH}$ QDs¹²³ achieved good NRR activities by modifying the surface end groups. Li and co-workers developed small sized fluorine-free $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T} = \text{O, OH}$) NSs for the NRR, synthesized by TMAOH intercalation and delamination.¹⁴³ The size effect and fluorine-free characteristics result in an NH_3 yield 1.8 times that of fluorine-based treatment. Tan's group reported a SAC Ru doped Mo_2CT_x NS material for the NRR in 0.5 M K_2SO_4 , which increased the FE to 25.77%.¹⁴⁵ Among them, the SAC Ru is the main electron back-donation centre for the absorbance and activation of N_2 molecules.

4 Modification of nanomaterials

4.1 Forming alloy centres

N_2 activation is a complicated process. Although the single active site can activate N to a certain extent, it cannot balance well the adsorption energy of multiple reaction intermediate species. Extending the single active site to dual or multiple sites may further improve the overall NRR performance of the catalyst.

Bimetallic nanocatalysts have been introduced into NRR systems to enhance selectivity for N_2 . In 2001, Jens K. Nørskov and co-workers reported a bimetallic ammonia synthesis strategy that used interpolation to find a rational catalyst in the periodic table.¹⁴⁶ They combined metals with high and low N_2

interaction energies to obtain the required interaction strength for preparation of NH_3 synthesis catalysts. By the introduction of N atoms to order the binary alloy, bimetallic catalysis could be achieved. Yu's group developed an amorphous BiNi alloy for the NRR, which was designed to activate N_2 molecules by optimizing the adsorption energy and adjusting the crystallinity.¹⁴⁷ The BiNi alloy has a significantly smaller area-specific impedance than Bi (Fig. 7c), indicating that the 3D nanoporous alloy framework promotes charge transport, thereby enhancing the NRR activity.

For metal–carbon-based materials, bimetallic alloying has been employed to alter such weak metal–carbon interactions into synergistic metal–metal interactions, thereby optimizing the electronic structure of monometals and accordingly, promoting the catalytic activity. Taking Pt/Au@ZIF as an example, ZIF electronically modified the d-band structure of the Pt/Au electrocatalyst and created electron deficient sites to achieve more favourable N adsorption of H (Fig. 7a).³⁶ According to the XPS spectra, after encapsulating the ZIF, the binding energy of Pt 4f shifts left and that of N 1s shifts right, clearly highlighting the electron density transfer from Pt to the ZIF framework by the Pt–N ZIF interaction (Fig. 7b). This electron migration from Pt to ZIF will form electron-deficient sites on the Pt surface, thereby forming N_2 adsorption sites. Moreover, the hydrophobic ZIF pores act as a barrier that prevents trace amounts of water from reaching the electrocatalytic sites, thereby inhibiting the HER. As a result, Pt/Au@ZIF has a FE >44 times that of Pt/Au ($\approx 1\%$), and reaches a high NH_3 production rate of $>161 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ under ambient conditions. AuCu/ZIF-8 was also reported for the NRR due to the large active surface areas and conductive carbon frameworks of the ZIF-8 precursor. The highly dispersed bimetallic active sites achieved an unprecedented NH_3 yield of $23.3 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$.³⁵

Due to the unique characteristics such as corrosion resistance under harsh conditions and adjustable performance (shorter distance between active sites facilitates component optimization), high-entropy alloys (HEAs) have also been applied in the NRR. The HEAs are synthesized by controlling the coordination entropy within 5 or more metal elements. Wang's group reported HEA RuFeCoNiCu NPs as a pH-universal NRR catalyst. When multiple H atoms are adsorbed, they are mainly distributed over the hollow positions, and the adsorption energy decreases rapidly with the H coverage.¹⁴⁸ Therefore, the surface H adsorption will affect the Co–Ni–Ni sites, but the optimal site of the NRR, t-Fe, is not at a hollow position and will not be affected significantly. Clearly, different metals may play different roles and work in a synergistic way to provide outstanding NRR performance (Fig. 7d). This catalyst has a surprising NH_3 yield of $57.1 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ at 0.05 V vs. RHE in 0.1 M KOH, and the corresponding FE is 38.5%. It also has excellent NRR activity in 0.1 M Li_2SO_4 , 0.1 M Na_2SO_4 , and 0.1 M HCl electrolytes.

4.2 Optimizing the valence state

N_2 activation is essentially an electron donating–accepting process between the catalyst surface and N_2 molecules. The



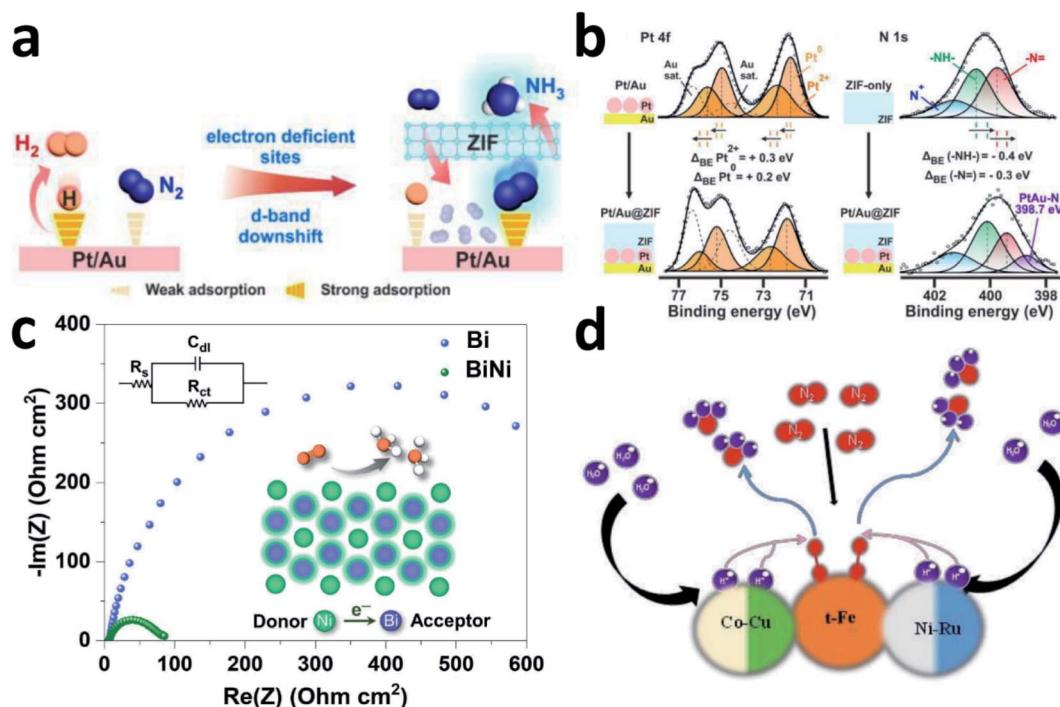


Fig. 7 (a) Schematic depicting the functions of Pt/Au@ZIF. (b) XPS investigations on the Pt/Au@ZIF platform. Copyright 2020, Wiley-VCH.³⁶ (c) EIS spectra of Bi and BiNi. Copyright 2020, Wiley-VCH.¹⁴⁷ (d) Schematic illustration of a possible mechanism of RuFeCoNiCu NPs. Copyright 2020, Wiley-VCH.¹⁴⁸

different valence states for the active centre atoms will affect the energy barrier of the activation of N_2 molecules. Although both NbO_2 and Nb_2O_5 have similar octahedral structures, the

catalytic properties differ significantly due to the different oxidation states of Nb (Fig. 8a). According to the report by Zheng's group, the FE of NbO_2 is almost 3.5 times higher than

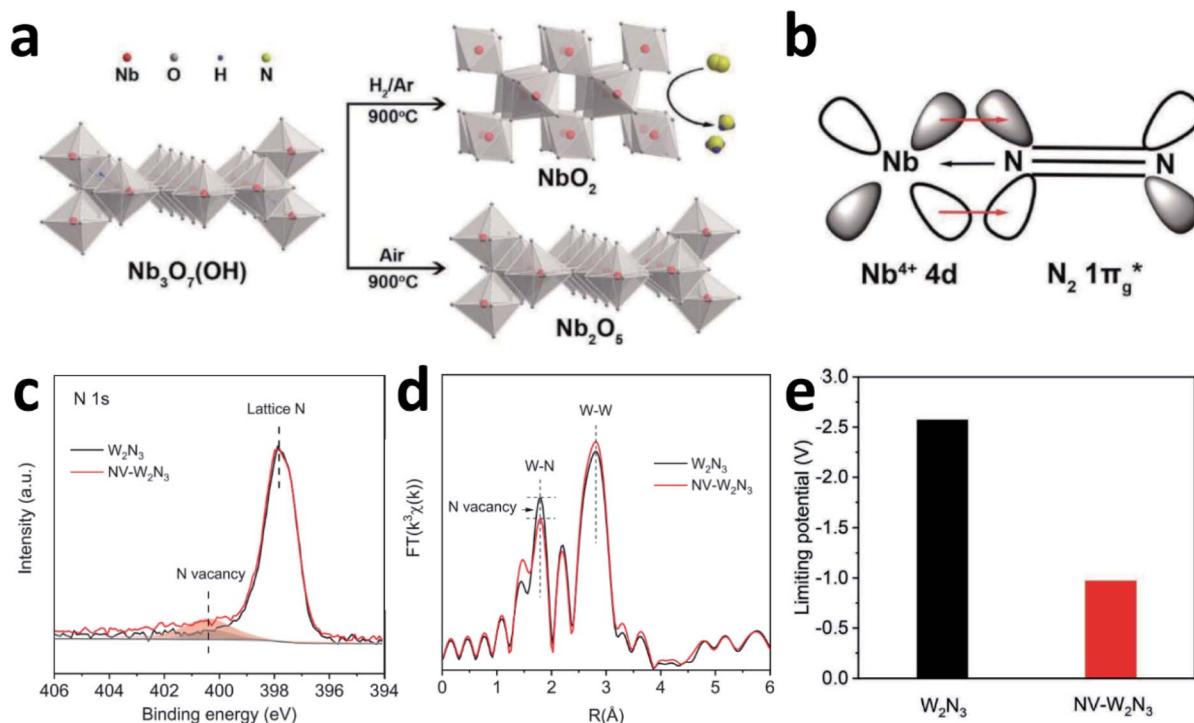


Fig. 8 (a) Synthetic schematic of NbO_2 and Nb_2O_5 . (b) The interaction between Nb^{4+} and N_2 . Copyright 2018, Wiley-VCH.¹⁰⁷ (c) N 1s spectra and (d) FT-EXAFS plots of the pristine W_2N_3 and NV- W_2N_3 . (e) Magnitudes of the theoretical limiting potentials of NH_3 production on W_2N_3 and NV- W_2N_3 . Copyright 2019, Wiley-VCH.¹⁵⁹



that of Nb_2O_5 . For Nb_2O_5 , the charge exchange and transfer mainly occur between the Nb atoms and N_2 , and the electrons on the adjacent Nb atoms are transferred back to weaken the $\text{N}\equiv\text{N}$ bond while strengthening the metal–N bond.¹⁰⁷ For NbO_2 , the Jahn–Teller distortion destroys degeneracy, causing the t_{2g} level to split into partially occupied d_{xy} orbitals and partially unoccupied d_{yz} and d_{xz} orbitals. Therefore, when N_2 molecules are adsorbed on NbO_2 , they not only bind electrons from its $3\sigma_g$ orbital to the empty orbital of Nb, but also accept d-electrons of Nb and back-donate to its anti-bonding $1\pi_g^*$ orbital (Fig. 8b). This back-donation can effectively weaken the $\text{N}\equiv\text{N}$ bond and activate the adsorbed N_2 molecules. For Nb^{4+} with an electron occupying a 4d orbital, it should be easier to form such a back donor than Nb^{5+} without 4d electrons, so it exhibits better N_2 fixation activity.²⁴ Moreover, introducing mixed valences into nanomaterials to modulate the vacancy concentration and metal defect states could also induce the NRR process. Sun's group introduced Cu ions with mixed valences of +1 and +2 to modulate the defect states in TiO_2 . Theoretical calculations suggest that when the Ti^{3+} 3d¹ defect states present the splitting of e_g and t_{2g} orbitals, the adsorption and activation of N_2 enhanced strongly.⁵⁵

4.3 Introducing vacancies

For a long time, surface chemical modifications like defect engineering and heteroatom doping have been regarded as efficient methods to boost NRR activity, due to the electronic structures of the electrochemical catalytic surfaces resulting in the modulation of adsorption properties.^{149,150} Some introduced vacancy nanomaterials are summarized in Table 4.

4.3.1 Oxygen vacancies. Oxygen vacancies (OVs) with low formation energy are the most common anionic vacancies in

transition metal oxides, which modulate the physicochemical properties of the material and thus influence the trapping and activation of inert N_2 molecules. $\text{W}_{18}\text{O}_{49}$ has exposed W sites and displays inherently weak binding of H_2 , which is not conducive to the choice of N or H for the catalytic site. Fe doping modifies the surface atomic structure of $\text{W}_{18}\text{O}_{49}$ for effective NRR electrocatalysis and suppresses the HER. For the defect-rich $\text{W}_{18}\text{O}_{49}$, the abundant tunnels in its lattice structure make it ideal for heteroatom doping. Especially, compared to the d-spacing of $\text{W}_{18}\text{O}_{49}$ (3.8 Å), the size of Fe atoms (1.2 Å) would greatly facilitate their intercalation into $\text{W}_{18}\text{O}_{49}$. By changing the Fe doping level, the construction and surface properties of $\text{W}_{18}\text{O}_{49}$ can be finely tuned, which results in an increase in the number of OVs for exposing more W active sites, thereby enhancing the binding capability for N_2 . Fe atoms are intercalated in the tunnels of $\text{W}_{18}\text{O}_{49}$, leading to the redistribution of the surface electrons of $\text{W}_{18}\text{O}_{49}$, thereby significantly minimizing the NRR overpotential, resulting in higher energy saving. The $\text{W}_{18}\text{O}_{49}$ –16Fe@CFP attained a high NH_3 yield rate (24.7 $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$) and FE (20.0%) at a very low overpotential of -0.15 V vs. RHE.⁸²

In contrast, Zhang's work anchored Fe atoms into OVs and doped Fe on the lattice, enhancing the adsorption and activation of N_2 on SnO_2 and improving the electrical conductivity of SnO_2 , respectively.¹⁷⁰ This Fe– SnO_2 catalyst had a unique surface structure. In state of metallic Fe NPs or clusters, the elemental Fe in Fe– SnO_2 is composed of oxygen vacancy-anchored SAC Fe and lattice doped Fe, which largely lowered the energy barrier for activating chemically inert N_2 molecules. The electron paramagnetic resonance (EPR) spectra confirmed that many OVs existed within SnO_2 and Fe– SnO_2 . However, the peak intensities of O 1s in the XPS and EPR spectra clearly decreased after Fe doping, which indicates that Fe may have

Table 4 Summary of introducing vacancy nanomaterials for the NRR

Catalyst ^{ref.}	Electrolyte	NH_3 yield ($\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$)	NH_3 yield ($\times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$)	FE (%)	Potential (V vs. RHE)
OVs-Bi- VO_4 (ref. 151)	0.2 M Na_2SO_4	8.60	—	10.04	-0.50
OVs-Mo O_2 (ref. 152)	0.1 M HCl	~12.20	—	8.20	-0.15
Bo-OV-Mn O_2 (ref. 153)	0.5 M LiClO_4	54.2	—	16.80 (-0.20 V)	-0.40
Au@ CeO_2 (ref. 58)	0.01 M H_2SO_4	10.60	4.61	9.50	-0.40
Al-doped Co_3O_4 (ref. 154)	0.1 M KOH	—	0.65	6.25	-0.20
OVs-Ce O_2 (ref. 155)	0.1 M Na_2SO_4	16.4	—	3.70 (-0.40 V)	-0.50
Polymeric CN-NVx (ref. 156)	0.1 M HCl	8.09	—	11.59	-0.20
NVs-CN/C ₆₀₀ (ref. 157)	0.1 M HCl	2.9	—	16.8	-0.30
S-NVs-C ₃ N ₄ (ref. 158)	0.5 M LiClO_4	32.7	—	14.1	-0.40
NVs-W ₂ N ₃ NS ¹⁵⁹	0.1 M KOH	11.66	0.38	11.67	-0.20
C ₃ N ₄ -NVs ¹³⁸	0.1 M HCl	17.85	—	10.96	-0.30
Vs-FePS ₃ NS ¹⁶⁰	0.1 M HCl	38.8	0.63	12.36 (-0.20 V)	-0.25
B-doped VS ₂ (ref. 161)	0.5 M LiClO_4	55.7	—	16.40 (-0.20 V)	-0.40
Mo-SnS ₂ -SV ₅ ¹⁶²	0.5 M LiClO_4	41.3	—	20.80 (-0.40 V)	-0.50
MoS ₃ -SV ₅ ¹⁶³	0.5 M LiClO_4	51.7	—	12.8	-0.30
MoS ₂ -SV ₅ ¹⁶⁴	0.1 M HCl	23.38	—	17.9	-0.35
Sb ₂ S ₃ -SV ₅ ¹⁶⁵	0.1 M Na_2SO_4	10.85	—	3.75 (-0.30 V)	-0.40
N-doped MoS ₂ (ref. 166)	0.1 M Na_2SO_4	69.82	—	9.14	-0.30
CoS _{1-x} (ref. 167)	0.05 M H_2SO_4	~12.1	—	~16.5	-0.15
SV-1T-MoS ₂ @MoO ₃ (ref. 168)	0.05 M H_2SO_4	116.1	—	18.9	-0.20
SVs-ZnS-rGO ¹⁶⁹	0.1 M HCl	51.2	—	28.2 (-0.10 V)	-0.15



been anchored by OVs. The extended X-ray absorption fine structure (EXAFS) of the catalyst showed a first-shell Fe–O contribution with a coordination number of about 3.6 at 2.01 Å, and a first-shell Fe–Sn contribution with a coordination number of about 0.4 at 3.12 Å, corresponding to lattice doped Fe. Moreover, the first-shell Fe–Sn contribution with a coordination number of about 4.4 at 3.87 Å can be ascribed to Fe anchored at OVs, forming a Sn–Fe–Sn structure. Therefore, the elemental Fe in Fe–SnO₂ can be categorized into isolated single-atom Fe on the surface with OVs, and lattice doped Fe. Consequently, the Fe–SnO₂ catalyst exhibited superior catalytic performance with a high NH₃ yield of 82.7 µg h⁻¹ mg_{cat.}⁻¹ and a high FE of 20.4%.

4.3.2 Nitrogen vacancies. Since nitrogen vacancies (NVs) exhibit the same situation as N atoms in N₂ and could affect the electronic and energy band structure in nanomaterials, NVs may also have an enhanced ability to activate N₂. The high N contents and layered structure of C₃N₄ could generate copious and homogeneously distributed NVs.¹⁵⁶ Compared to pristine C₃N₄, C₃N₄ with NVs has a higher NRR activity, which can be partly attributed to the improvement of N₂ chemical adsorption by the NVs. Compared to NV-C₃N₄, the filled S dopants could induce electronic modulation and break the *N₂H–*NH₂ scaling relation to effectively stabilize *N₂H and destabilize *NH₂ on S-NV-C₃N₄, leading to more optimized adsorption of the NRR intermediates and a significantly reduced energy barrier.¹⁵⁸ S-NV-C₃N₄ with a high S dopant concentration of 5.2% exhibited a comparable NRR performance.

Qiao's group experimentally and theoretically studied the NVs on W₂N₃, which acts as an efficient and stable NRR catalyst.¹⁵⁹ NV-W₂N₃ NSs were prepared by annealing under an NH₃ atmosphere, and the NVs were generated by further annealing (5% H₂/Ar at 500 °C for 3 h). According to the XPS N 1s spectra and EXAFS (Fig. 8c and d), compared to the pristine W₂N₃ NSs, the intensity of the peak (NVs) in NV-W₂N₃ increased and the coordination number of the W–N bond decreased, proving that vacancies were created. The authors also claimed that the high valence state of W and the surface distortion induced by the 2D morphology contribute to the good stability of NV-W₂N₃. Based on the pristine W₂N₃ theoretical model, they investigated the effect of introducing NVs on N₂ activation. When N vacancies are involved, significant charge transfer is observed between W₂N₃ and the adsorbed N₂ molecule. More importantly, inducing NVs decreases the theoretical limiting potentials of NH₃ production significantly (Fig. 8e), which is convenient for the NRR.

4.3.3 Sulfur vacancies. The O and S elements have very similar chemical properties, so the sulfur vacancies (SVs) are also expected to influence NRR performance by inducing additional sites for N₂ adsorption and activation. Hou's group reported the synthesis of porous FePS₃ NSs with abundant S vacancies (SVs-FePS₃ NSs) by electrochemical exfoliation in an organic electrolyte followed by hydrogenation treatment in a 5% H₂/Ar atmosphere.¹⁶⁰ The Fe species in the SVs-FePS₃ NSs were confirmed to be the true active sites by addition of the SCN⁻ ion as a poisoning agent, which was illustrated during chronoamperometry. XPS and EPR confirmed the formation of SVs. Residual electrons that are restrained in the Vs are more likely

to flow to the surrounding Fe atoms, which leads to a strong hydrogen attraction that can be induced by the delocalised electrons around the Fe atoms, thus promoting the hydrogenation of N₂. Electron delocalization of SVs also improved the conductivity of SVs-Sb₂S₃ and boosted the activation of N₂.¹⁶⁵ The B element could act as a promoter to optimize the NRR energetics of active sites. Li and co-workers co-introduced Vs and B-dopant into VS₂ basal planes to promote the activity and selectivity of the NRR.¹⁶¹ Compared with unsaturated Vs (1.13 eV), B-dopant unsaturated Vs (B-u-V) greatly exhibit the lower first hydrogenation step barrier of *N₂–*NNH (0.77 eV), thereby promoting the activation of N₂. Meanwhile, compared with the B-dopant (1.05 eV), B-u-V has a lower barrier of 0.77 eV in the last reaction step (*NH₂/NH₃), which is conducive to NH₃ formation and desorption. The metal dopants and SVs could also form multimeric catalytic sites *via* a side-on configuration, such as the Mo–SnS₂–SVs reported by Chu.¹⁶² Mo–Sn–Sn trimer active sites from DFT calculations confirm that more electrons are accumulated in the Mo/SV region of Mo–SnS₂–SVs compared to SnS₂. In total, the Mo–Sn–Sn trimer back-donates 0.55|e| to *N₂ (0.37|e| + 0.09|e| + 0.09|e|) according to Mulliken charge analysis. Upon N₂ adsorption, the large number of accumulated electrons induced by these Mo/SVs can be readily transferred into the antibonding orbitals of the N₂ molecule, thereby weakening and dissociating the N≡N bond.

5 Summary and outlook

Due to the urgent need to solve energy problems and the great attraction of finding new energy materials, the NRR is considered to be the most effective strategy for industrial production of NH₃ under mild conditions. Over the past five years, researchers from various countries have explored some effective and promising active centres to boost the adsorption and activation of N₂, combined with some low-dimensional nanomaterial substrates with high specific surface area, abundant exposed active sites, and unique electronic morphology to improve the performance of the NRR. In this review, we have briefly discussed some advanced low-dimensional nanomaterials with various structures in the development of the NRR, and also mentioned approaches to catalyst design and characteristics. In pursuit of more practical NRR catalysts with higher activity and selectivity, we provide some prospects for future research.

(1) Combination of theoretical calculations and some advanced characterization techniques (like NMR, XAFS, etc.) with experiments. A series of catalysts has been obtained using the results of theoretical calculations. Moreover, the adsorption energy of different sites on the catalyst surface could be explored by atomic-scale NMR technology. Using these two methods to design NRR catalysts in a targeted manner can save researchers time in screening catalysts.

(2) Improvement of the material preparation method. Constructing small-sized catalysts with diatomic or polyatomic active centres and combining them with low-dimensional nanomaterials. The diatomic or polyatomic active centres can reasonably regulate the adsorption process of each



intermediate product in the N_2 activation process. Compounding with low-dimensional nanosized substrates can effectively adjust the exposed crystal faces of the catalyst, which is convenient for researchers to screen for active crystal faces. High-porosity 3D nanomaterials also have comparable potential as suitable substrate supported catalysts.

(3) Some elements with mixed valences are selected as the components of the catalyst to adjust the defect concentration and metal defect valences. N_2 activation is essentially an electron donor-acceptor process between the catalyst surface and N_2 molecules. The different valences of the active centre atoms will affect the energy barrier for activation of N_2 molecules.

(4) Designing a strategy that combines defect engineering and heteroatom doping. Defect engineering and heteroatom doping can change the electronic structure of the electrochemical catalyst surface, enhance the electron cloud density of the active site, and promote the adsorption and activation of N_2 .

Conflicts of interest

There are no conflicts to declare.

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