INORGANIC CHEMISTRY
FRONTIERS

CHINESE CHEMICAL SOCIETY

ROYAL SOCIETY OF CHEMISTRY

REVIEW

View Article Online
View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2023, **10**, 3489

Recent progress and strategies on the design of catalysts for electrochemical ammonia synthesis from nitrate reduction

Wei Song,[a] Luchao Yue,*[a] Xiaoya Fan,[b] Yongsong Luo,[b] Binwu Ying,[b] Shengjun Sun,[c] Dongdong Zheng,[c] Qian Liu,[d] Mohamed S. Hamdy[e] and Xuping Sun*[b,c]

Received 27th March 2023,
Accepted 27th April 2023

DOI: 10.1039/d3qi00554b

rsc.li/frontiers-inorganic

Ammonia (NH_3) is an essential raw material in the production of fertilizers and a promising carbon-free energy carrier, however, its synthesis still depends on the energy- and capital-intensive Haber–Bosch process. Recently, the electrochemical N_2 reduction reaction has attracted significant interest as an emerging method for NH_3 synthesis under ambient conditions. However, the limited solubility of N_2 in aqueous electrolyte and the strong $N\equiv N$ bonds result in a low NH_3 yield rate, inferior faradaic efficiency and unsatisfactory selectivity, impeding its further practical application. Considering the high water solubility of nitrate (NO_3^-), the electrochemical NO_3^- reduction reaction (NO_3^-RR) has become a fascinating route for achieving sustainable production of NH_3, and enormous progress has been made in this field. As a consequence, this review discusses the reaction mechanism of the electrochemical reduction of NO_3^- and systematically summarizes the recent development of electrocatalysts for the NO_3^-RR, including noble-metal-based materials, single-atom metal catalysts, and transition-metal-based catalysts. Diverse design strategies of the catalysts to boost the NO_3^-RR performance, such as defect engineering, rational structure design, strain engineering and constructing heterostructures, are discussed. This is followed by an illustration of how a robust understanding of the optimization strategies affords fundamental insights into the NH_3 yield rate, faradaic efficiency, and selectivity of the electrocatalysts. Finally, we conclude with future perspectives on the critical issues, challenges and research directions in the design of high-efficiency electrocatalysts for selective reduction of NO_3^- to NH_3.

1. Introduction

Ammonia (NH_3) as a high-value-added chemical exerts a significant influence in the synthesis of fertilizers for sustaining the rising global population, and is also being considered as a promising alternative fuel for hydrogen storage in the future.[1–3] At present, the synthesis of NH_3 in industry mainly hinges on the traditional Haber–Bosch process (HBP). Such a reaction process is accomplished under tough operating conditions, including high temperature (400–550 °C) and high pressure (15–30 MPa), which is extremely energy-consuming.[4,5] Taking the enormous requirements into consideration (~170 Mt per year, over 80% of total content for fertilizers), the HBP consumes 1–2% of the world's energy supply and is accompanied by extensive CO_2 emissions.[6] Furthermore, the extensive centralized infrastructures involved in the HBP have to spend substantial capital, leading to a large innovation barrier and uneven regional distribution.[7] In this regard, exploring a clean and sustainable strategy for highly-efficient NH_3 production is highly desired, and presents great challenges in both fundamental science and engineering.

Recently, electrochemical NH_3 synthesis has provided an alluring research direction in the search for a substitute for the traditional HBP due to its moderate production conditions and ability to integrate with renewable energy resources.[8,9] Among them, the electrochemical N_2 reduction reaction (NRR) has drawn tremendous interest and achieved substantial progress. In NRR systems, the electrochemical synthesis of NH_3 directly originates from the reduction of N_2 and the

---

[a] School of Chemistry and Chemical Engineering & Shanxi Provincial Key Laboratory for High Performance Battery Materials and Devices, North University of China, Taiyuan 030051, Shanxi, China. E-mail: ylctyut@163.com
[b] Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, Sichuan, China. E-mail: xpsun@uestc.edu.cn, xpsun@sdnu.edu.cn
[c] College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, Shandong, China
[d] Institute for Advanced Study, Chengdu University, Chengdu 610106, Sichuan, China
[e] Catalysis Research Group (CRG), Department of Chemistry, College of Science, King Khalid University, P.O. Box 9004, 61413 Abha, Saudi Arabia

dissociation of H_2O under ambient conditions, in which the driving force is regulated by the applied voltage.[10–12] Consequently, the thermodynamic energy efficiency of the NRR is about 20% higher than that of the HBP.[1] Meanwhile, this method can achieve the decentralized and on-site/-demand production of NH_3, further supporting the fabrication of distributed fertilizers and reducing the cost of transportation. Nevertheless, the highly stable $N\equiv N$ bond with a bond energy of 941 kJ mol^{-1}, limited solubility of N_2, and the competing hydrogen evolution reaction (HER) cause the extremely low NH_3 yield rate, selectivity, and faradaic efficiency (FE), which are far from meeting the practical demands, and even result in unreliable quantifications experimentally owing to the trace amounts of contaminants.[13,14]

Recently, the electrochemical nitrate reduction reaction (NO_3^-RR) has been demonstrated as an alluring method for NH_3 synthesis at room temperature and atmospheric pressure, and its good performance may originate from the following aspects: (i) NO_3^- is highly soluble in water, has a relatively low $N{=}O$ dissociation energy of 204 kJ mol^{-1}, and has a more positive potential than N_2. These characteristics are beneficial to alleviate the competing HER and attain high NH_3 selectivity with only a small overpotential required, indicating that the NO_3^-RR process is more energy-efficient than the HBP and NRR; (ii) NO_3^- is abundant in industrial wastewater and polluted groundwater, with a maximum concentration up to 2.0 mol L^{-1}, and these can be considered as NO_3^- sources, providing a promising opportunity for large-scale fabrication of NH_3; (iii) converting NO_3^- into NH_3 alleviates the environmental degradation caused by excessive nitrate emission and maintains the balance of the perturbed nitrogen cycle. The reason is attributed to the fact that the accumulation of NO_3^- in drinking water will induce illness and jeopardize human health; (iv) this process utilized water as the proton source, eliminating fossil-fuel consumption and CO_2 emission. Consequently, there has been a dramatic growth in research efforts to study the ambient electrochemical reduction of NO_3^- to NH_3.[15–17] However, the NO_3^-RR is an eight-electron reaction process and generates various by-products, such as NO_2^-, NO, N_2O, N_2, and NH_2OH, resulting in low NH_3 selectivity, FE and yield rate.[18–20] Such electrocatalytic performance is mainly determined by the electrocatalysts; hence, the major challenge in large-scale production of NH_3 *via* the NO_3^-RR lies in finding a suitable catalyst. Recently, a series of electrocatalysts, including noble metals, signal-atom catalysts, and catalysts of transition metals and their compounds have been developed and/or designed for the NO_3^-RR under ambient conditions.[21–24] Meanwhile, extensive research efforts have pointed out that their electrocatalytic activities can be significantly ameliorated by elaborate structural design, defect engineering (oxygen vacancies and heteroatom doping), strain engineering, and constructing heterostructures. Thus, a systematic discussion on the recent progress of electrocatalysts for the NO_3^-RR and an analysis of corresponding materials design principles could provide a specific direction for rationally developing efficient NO_3^-RR electrocatalysts.

Currently, several high-quality reviews focusing on the electrochemical removal of NO_3^- have been presented.[18,19,25,26] Nevertheless, reviews that exclusively focus on the rational design of electrocatalysts for the reduction of NO_3^- to NH_3 are lacking. As a consequence, we review the recent advancements of electrocatalysts toward the NO_3^-RR for attaining large NH_3 yields, high FE, as well as high selectivity under ambient conditions. Firstly, this review briefly discusses the fundamental reaction mechanisms of the electrocatalytic NO_3^-RR. Secondly, the most recent advancements of electrocatalysts for electrochemically converting NO_3^- to NH_3 have been summarized, covering noble metals, single-atom catalysts, and catalysts of transition metals and their compounds (Fig. 1a). Meanwhile, several strategies to regulate the apparent activity or intrinsic activity of the electrocatalysts for the NO_3^-RR to form NH_3 are highlighted. Finally, the perspective and challenges in this emerging area are also presented.

Xuping Sun

Xuping Sun received his PhD degree from the Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences, in 2006. From 2006 to 2009, he carried out postdoctoral research at Konstanz University, the University of Toronto, and Purdue University. In 2010, he started his independent research career as a Full Professor at CIAC and then moved to Sichuan University in 2015. In 2018, he joined the University of Electronic Science and Technology of China where he founded the Research Center of Nanocatalysis & Sensing. He was recognized as a highly cited researcher (2018–2020) in both areas of chemistry and materials science by Clarivate Analytics. He has published over 600 papers with total citations of over 63 000 and has a h-*index of 130. His research mainly focuses on the rational design of nanocatalysts toward applications in electrosynthesis of green hydrogen and ammonia, as well as electrochemical denitration of vehicle exhaust emissions and industrial wastewater.*

2. Reaction pathways of electrocatalytic nitrate reduction

Owing to the multivalent nitrogen element, various nitrogen-containing species like NO_2^-, N_2O, NH_2ON, N_2, N_2H_4, and NH_3 will be generated during the electrochemical NO_3^- reduction procedure. Among them, N_2 and NH_3 feature the highest thermodynamic stability and are regarded as final products under standard conditions.[27,28] The corresponding reactions can be expressed through the following equations:[27]

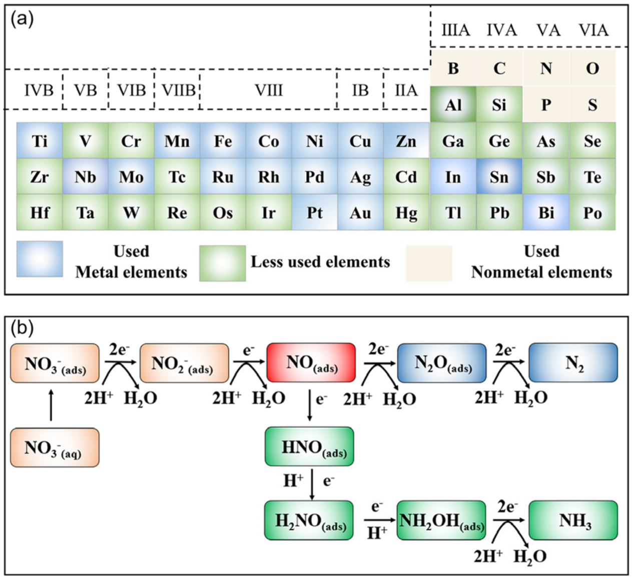

Fig. 1 (a) Element list of reported NO_3^-RR electrocatalysts to date. (b) The electron-mediated pathway of the electrochemical reduction of NO_3^-.

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O, E^\circ = 1.17 \text{ V } vs. \text{ SHE} \quad (1)$$

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O, E^\circ = -0.12 \text{ V } vs. \text{ SHE}. \quad (2)$$

Generally, the electroreduction of NO_3^- has two different pathways, including an indirect autocatalytic reduction pathway and a direct electrocatalytic reduction pathway.[29–31] In terms of the former, NO_3^- does not participate in the electron-transfer process and the operating conditions are a large concentration of NO_3^- (>1 M) and high acidity (pH < 0). The latter can also be divided into two pathways: one is the regulation of active adsorbed hydrogen atoms (H_{ads}); the second one is electron reduction at the cathode (Fig. 1b). In the adsorbed-hydrogen-mediated pathway, the first process is the generation of H_{ads} *via* decomposition of the adsorbed H_2O on the surface of the cathode. The second process is that H_{ads} directly reduces NO_3^- and generates intermediates to give the final-product NH_3 rather than N_2, which is attributed to the fact that formation of an N–N bond is kinetically less favorable than that of an N–H bond. This process usually requires a small overpotential to promote the conversion from NO_3^- to NH_3, which can efficiently suppress the competing HER, as well as attain high NH_3 selectivity and FE.[32,33] As for the electron-mediated pathway, electrons directly reduce NO_3^- adsorbed on the surface of the cathode to NO_2^- (eqn (3) and (4)).[34] Notably, converting NO_3^- to NO_2^- generally requires a high activation energy, and this process is considered as the rate-determining step to regulate the reaction kinetics of the whole NO_3^-RR process. Then, the generated $NO_2^-{}_{(ads)}$ reduces to $NO_{(ads)}$, which is a decisive intermediate as a branch for the generation of N_2 or NH_3/NH_4^+. On the one hand, $NO_{(ads)}$ can be reduced to $HNO_{(ads)}$ and $H_2NO_{(ads)}$, and quickly followed by hydrogenation to form hydroxylamine, which finally reduces to NH_3.[35] On the other hand, $NO_{(ads)}$ can be desorbed from the electrode surface to generate NO in solution. When $NO_{(aq)}$ presents in the solution, a weakly adsorbed NO dimer can be formed, which is the precursor of $N_2O_{(ads)}$. The produced $N_2O_{(ads)}$ further reduces to N_2 according to eqn (9), and this process plays a dominant role in the pathway of N_2 evolution.[36,37]

$$NO_3^-{}_{(aq)} \rightarrow NO_3^-{}_{(ads)} \quad (3)$$

$$NO_3^-{}_{(ads)} + 2H^+ + 2e^- \rightarrow NO_2^-{}_{(ads)} + H_2O \quad (4)$$

$$NO_2^-{}_{(ads)} + 2H^+ + e^- \rightarrow NO_{(ads)} + H_2O \quad (5)$$

$$NO_{(ads)} + 6H^+ + 5e^- \rightarrow NH_4^+ + H_2O \quad (6)$$

$$NO_{(ads)} \rightarrow NO_{(aq)} \quad (7)$$

$$NO_{(ads)} + NO_{(aq)} + 2H^+ + 2e^- \rightarrow N_2O_{(ads)} + H_2O \quad (8)$$

$$N_2O_{(ads)} + 2H^+ + 2e^- \rightarrow N_2 + H_2O \quad (9)$$

3. Efficient NO_3^-RR electrocatalysts

Exploring advanced electrocatalysts with a high selectivity, FE, and yield rate are keenly desired for the electrosynthesis of NH_3 by converting NO_3^-. Recently, a series of electrocatalysts have been investigated for the NO_3^-RR process under ambient conditions, like noble-metal-based materials, single-atom metal catalysts, and transition-metal-based materials. In the following sections, the recent advances of those catalysts in the NO_3^-RR toward NH_3 and the corresponding optimization strategies for electrocatalytic activity will be systematically discussed.

3.1 Noble-metal catalysts

Noble metals have been widely utilized as electrocatalysts for diverse electrochemical conversion reactions including the HER, the oxygen evolution reaction, the oxygen reduction reaction, and the NRR, owing to their alluring electronic conductivity, moderate capturing ability for various reactants, and high density of under-coordinated surface atoms. Recently, both experiments and theoretical calculations have suggested that noble-metal materials (Pt, Pd, Ru, and Rh) are promising electrocatalysts for the NO_3^-RR under ambient conditions, as listed in Table 1.[20,38–42,45–48,50,52] For example, Li *et al.*[42] designed Ru/oxygen-doped Ru core/shell nanoclusters (Fig. 2a and b) as an NO_3^-RR electrocatalyst for the production of NH_3, in which the introduction of oxygen can increase the size of the Ru unit cell to induce tensile strains (Fig. 2c). The strains suppressed the HER but benefit H* production by expanding the barrier of H–H coupling. As a result, this catalyst achieved a large NH_3 formation rate of 5.56 mol g^{-1} h^{-1} with a nearly 100% selectivity at 120 mA cm^{-2}. In addition, Chen *et al.*[20] dis-

Table 1 Summary of catalytic performance of noble-metal-based electrocatalysts

Catalyst	Electrolyte	NH_3 yield rate	Faradaic efficiency	Potentials (V *vs.* RHE)	Ref.
Ru-dispersed Cu nanowire	1 M KOH + 2000 ppm KNO_3	76 500 μg h^{-1} cm^{-2}	90%	0.04	20
BC_2N/Pd	0.1 M KOH + 250 mM KNO_3	1730 μg h^{-1} cm^{-2}	97.42%	$-0.7^a/-0.3^b$	40
Amorphous Ru nanoclusters	5 mM Cs_2CO_3 + 500 ppm NO_3^-	145.1 μg h^{-1} mg^{-1}	80.62%	−0.2	41
Strained Ru nanoclusters	1 M KOH + 1 M KNO_3	5.56 mol g_{cat}^{-1} h^{-1}	96%	−0.3	42
Pd/Cu_2O octahedra	0.5 M K_2SO_4 + 50 ppm NO_3^-	925.11 μg h^{-1} mg^{-1}	96.56%	−0.645	45
Pd/Co_3O_4	0.5 M K_2SO_4 + 200 ppm NO_3^-	0.204 mmol h^{-1} cm^{-2}	88.6%	−0.645	46
CuPd aerogels	0.5 M K_2SO_4 + 50 mg L^{-1} NO_3^-	784.37 μg h^{-1} mg^{-1}	90.02%	−0.46	47
CuPd nanocubes	1 M KNO_3 + 1 M KOH	6.25 mol h^{-1} g^{-1}	92.5%	$-0.6^a/-0.5^b$	48
PdBP nanothorn arrays	0.5 M K_2SO_4 + 100 ppm NO_3^-	0.109 mmol h^{-1} cm^{-2}	64.73%	−0.66	50
RuO_2 nanosheets	0.1 M K_2SO_4 + 200 ppm NO_3^-	0.1158 mmol h^{-1} cm^{-2}	97.46%	−0.35	52

[a] NH_3 yield rate. [b] Faradaic efficiency.

persed Ru nanoparticles into a Cu-nanowire matrix (Ru-CuNW) through a simple cation exchange method for electrochemical NH_3 synthesis (Fig. 2d). This catalyst presented an industrial-level NO_3^- reduction current of ∼1 A cm^{-2} (Fig. 2e) accompanied by a maximum NH_3 FE of 96% (Fig. 2f) when operating with a low NO_3^- concentration of 2000 ppm (typical industrial wastewater). Meanwhile, the voltage of Ru-CuNW does not significantly change during the long-term electrolysis of 100 h under the current density of 400 mA cm^{-2}, with a high NH_3 FE of 90% maintained, indicating that such a catalyst features excellent durability. More importantly, it showed an ultrahigh NO_3^- conversion ratio of 99% for NH_3 production, making industrial wastewater reach a drinkable water level (concentration of $NO_3^- < 50$ ppm) (Fig. 2g), and the solid NH_4Cl and liquid NH_3 solution products were collected by coupling the NO_3^--reduction effluent stream with the air-stripping process, as displayed in Fig. 2h. In another study, Jiang *et al.*[41] investigated the effect of the noble-metal crystal structure on electrochemical NO_3^-RR activity. They chose Ru as the model material and fabricated amorphous Ru nanoclusters anchored on carbon nanotubes (aRu-CNTs) for electrochemical NH_3 production from NO_3^-. The experimental results demonstrated that aRu-CNTs delivered an NH_3 yield of 145 μg h^{-1} mg^{-1} with a FE of 80.62% at −0.2 V *vs.* RHE, and the achieved yield was 3.1 times larger than that of crystalline Ru. Therefore, the amorphization of noble metals can be recognized as a promising route for increasing the amount of active sites on the catalysts to a certain degree.

Besides, revealing the electrocatalytic behaviors on noble metals with different facets for the NO_3^-RR is essential to explore rational design strategies for electrosynthesis of NH_3. Lim *et al.*[43] employed Pd as a model catalyst to understand the structure-sensitivity of NO_3^- reduction to NH_3 on a Pd catalyst. Specifically, they fabricated Pd nanoparticles with diverse morphologies, such as nanocubes containing six (100) facets, cuboctahedrons containing six (100) and eight (111) facets, octahedrons containing eight (111) facets, and concave nanocubes containing (100) and (*hk*0) facets. Based on the experimental results, the Pd (111) facet is favorable to catalyze the reduction of NO_3^- to NO_2^-, while the (100) facet is inclined to catalyze the reduction of NO_2^- to NH_3 (Fig. 2i–k). Hence, the activity for NO_3^- reduction decreases in the order of Pd (111) > Pd (100) > Pd (*hk*0) and the activity for NO_2^- reduction decreases in the order of Pd (100) > Pd (*hk*0) > Pd (111) under the alkaline electrolyte. As a consequence, NH_3 production using noble-metal catalysts can be enhanced through controlling their structure and facets.

Numerous research studies have demonstrated that the electrochemical performance of noble metals for converting NO_3^- to NH_3 can be significantly modified by constructing a heterostructure with two materials, with the modified performance originating from the unique physical properties induced by the charge distribution and energy-band bending at the heterointerface. For instance, Li *et al.*[40] constructed a hybrid material consisting of Pd nanoparticles and a boron–carbon–nitrogen material (BC_2N/Pd) for the NO_3^-RR, which showed a superior NH_3 production rate of 1730 μg h^{-1} cm^{-2} at −0.7 V *vs.* RHE using 250 mM KNO_3 solution as the nitrogen source. Theoretical calculations revealed that the free energy accumulation of the NO_3^-RR on BC_2N/Pd was higher than that of individual Pd or BC_2N, and the corresponding value from NO_3^- to $^*NH$ could conquer the reaction energy barriers from $^*NH$ to $^*NH_2$ and $^*NH_2$ to NH_3. As exhibited in Fig. 3a–d, Ren *et al.*[44] constructed Cu/Pd/CuO_x heterostructures with abundant pores for electrochemical conversion of NO_3^- to NH_3. In terms of the Cu/Pd/CuO_x heterostructure, the electronic interactions between the Cu, Pd, and CuO_x components lead to electron transfer from Pd to Cu, which can increase the number of reactive sites and thus modulate the adsorption ability for intermediates, meanwhile suppressing the competitive hydrogen evolution reaction process. Moreover, the abundant channels provided sufficient contact area between electrolyte and catalyst. Benefiting from interfacial engineering and a unique porous structure, the designed Cu/Pd/CuO_x heterostructure afforded a superior NH_3 production rate of 1510.3 μg h^{-1} mg^{-1}, FE of 86.1%, and NH_3 selectivity of 90.06% (Fig. 3e–f). Similarly, Xu *et al.*[45] applied Cu_2O corner-etched octahedra with cavities and oxygen defects as the substrate to support Pd nanoparticles (Pd-Cu_2O), in which the loading content of Pd active materials was only 2.93%. For Pd-Cu_2O catalyst system, Pd sites were regarded as the active center for capturing $^*H$ and generating Pd–H intermediate; while parts of Cu_2O elec-

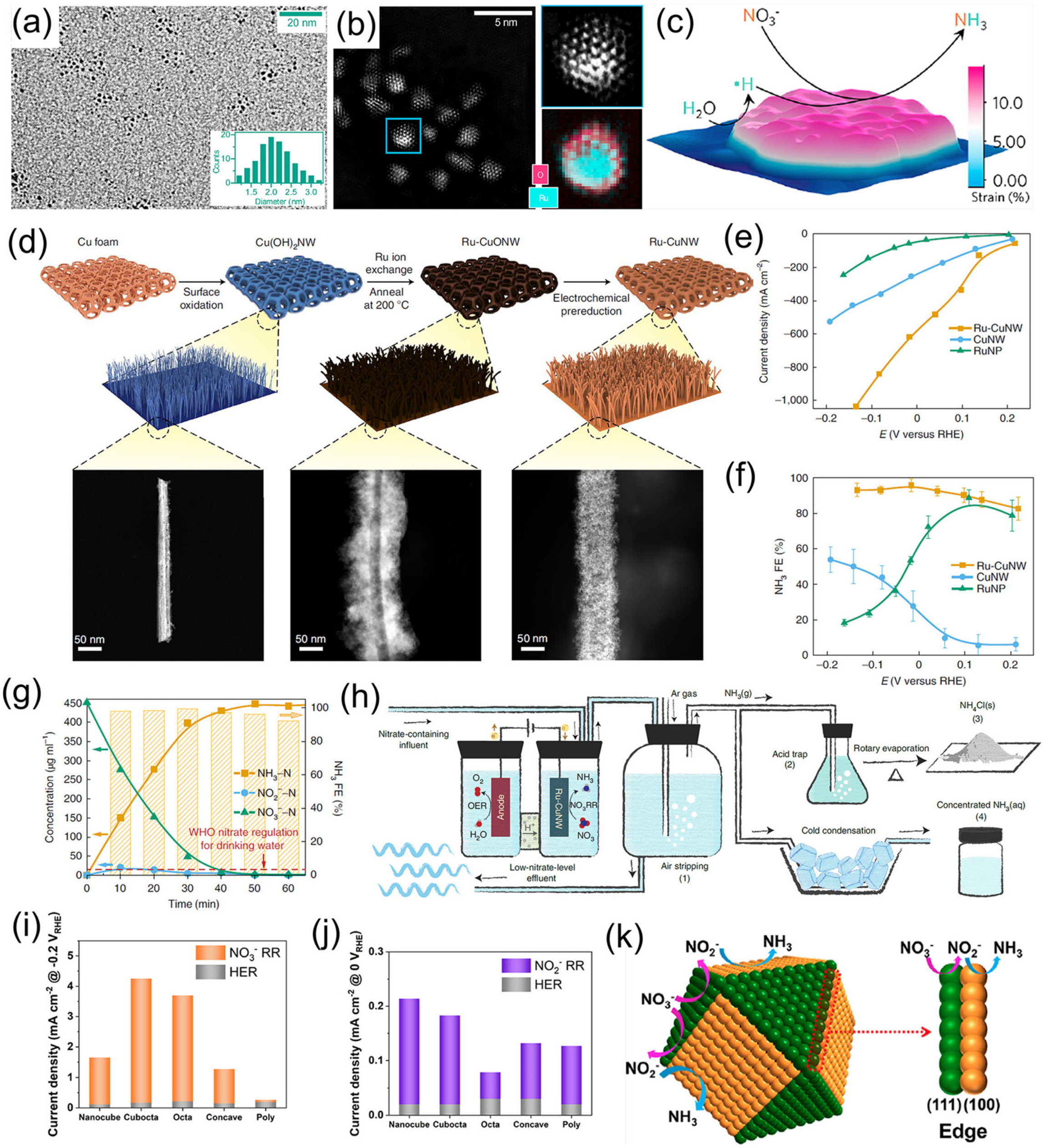

Fig. 2 (a) TEM image and (b) aberration-corrected HAADF-STEM/EELS elemental map images of Ru/oxygen-doped Ru core/shell nanoclusters. (c) Schematic illustration of the reaction mechanism for the NO_3^-RR on the strained Ru nanoclusters. Reproduced from ref. 42 with permission from the American Chemical Society, copyright 2020. (d) Synthesis process of the Ru-CuNW catalyst. (e and f) *I*–*V* plots and corresponding NH_3 FEs of Ru-CuNW and counterparts. (g) Complete NO_3^- removal using Ru-CuNW catalyst. (h) Schematic diagram of $NH_4Cl_{(s)}$ and concentrated $NH_{3(aq)}$ products from nitrate-containing influent. Reproduced from ref. 20 with permission from the Nature Publishing Group, copyright 2022. (i and j) The electrocatalytic activity of Pd catalysts with various structures. (k) Schematic illustration of the reaction mechanism for the NO_3^-RR on the different crystal facets of Pd catalysts. Reproduced from ref. 43 with permission from the American Chemical Society, copyright 2021.

trochemically reduced to Cu^0 and *in situ* formed Cu/Cu^+, which could provide active sites for NO_3^- electroreduction. Meanwhile, the oxygen defects in Cu_2O were beneficial for the capture of NO_3^- and to weaken the N–O bond. As expected, Pd/Cu_2O heterostructure catalyst exhibited an excellent electrocatalytic activity of NO_3^- to NH_3, including NH_3 formation rate of 925.11 μg h^{-1} mg^{-1}, selectivity of 95.31%, and FE of 96.56%. Pd-PdO-modified Co_3O_4 nanowire arrays were fabricated and applied as a catalyst to electrochemically convert NO_3^- to NH_3. In K_2SO_4 solution containing 200 mg L^{-1} of NO_3^- electrolyte, such catalyst showed a high NH_3 FE of 88.6% and selectivity of 95.3%.[46]

Tailoring the catalytic sites of noble-metal materials by alloying with another metal is another fascinating strategy to

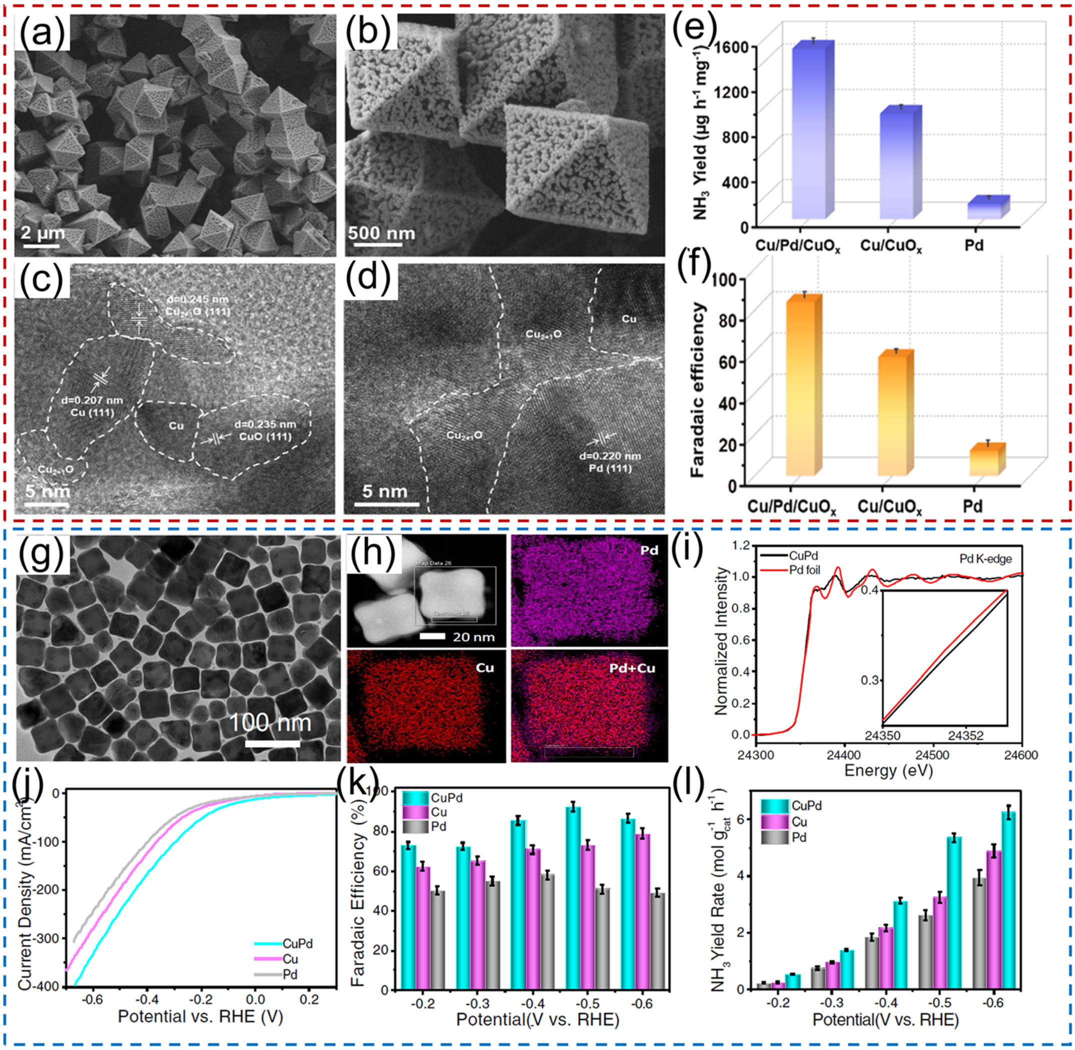

Fig. 3 (a–d) TEM and HRTEM images of Pd/CuO material. (e) NH_3 yield rate and (f) the corresponding FE of Pd/CuO catalyst. Reproduced from ref. 44 with permission from Elsevier, copyright 2022. (g and h) TEM and mapping images of the CuPd alloy. (i) Pd K-edge XANES spectra of CuPd and a Pd foil reference. (j) Linear scan voltammetry (LSV) curves, (k) NH_3 FE and (l) NH_3 yield rate under different potentials for CuPd, Cu, and Pd. Reproduced from ref. 48 with permission from the Nature Publishing Group, copyright 2022.

further improve their catalytic activity for the NO_3^-RR to NH_3. For example, Xu *et al.*[47] rationally chose Pd as an active metal and Cu as a promoting metal to construct a CuPd bimetallic catalyst for electrochemical conversion of NO_3^- to NH_3. In terms of the CuPd catalyst system, Pd sites serve as active centers to adsorb *H and promote the hydrogenation reaction for NH_3 production. Consequently, the CuPd alloy catalyst delivered a large NH_3 yield rate of 784.37 μg h^{-1} mg^{-1}, and a high NH_3 FE of 90.02% at −0.46 V *vs.* RHE, which was superior to those of pure Cu and Pd catalysts. Furthermore, Gao *et al.*[48] employed density functional theory (DFT) calculations and machine learning to deduce that the upshifted d-band center of the Cu sites of the CuPd alloy favored the adsorption of $*NO_3$, and *N was destabilized owing to the dominant role of Pauli repulsion from the subsequent Pd d orbitals, promoting the protonation of N-bonded species toward NH_3. As demonstrated in Fig. 3g–l, they also experimentally synthesized CuPd nanocube alloy catalysts, and confirmed the existence of charge transfer between Pd and Cu *via* X-ray absorption near-edge spectroscopy (XANES). In 1.0 M NaOH solution containing 1.0 M KNO_3, the PdCu nanocube catalyst showed an NH_3 yield rate of 6.25 mol h^{-1} g^{-1} at −0.6 V *vs.* RHE and an NH_3 FE of 92.5% at −0.5 V *vs.* RHE, respectively. Furthermore, the current density remained stable over 12 h of continuous operation, with a high NH_3 FE of ∼85.1% maintained. Similarly, Zhang and his co-authors[49] also employed metallic Ni as a promoter catalyst to regulate the electronic structure of Pd, and synthesized PdNi alloys for the NO_3^-RR. PdNi nanosheets displayed an NH_3 formation rate of 16.7 mg h^{-1} mg^{-1} (at −1.2 V *vs.* RHE) and a FE of 87.9% (at −0.6 V *vs.* RHE). After that, a ternary PdBP nanothorn-array catalyst was also designed and utilized for converting NO_3^- to NH_3. In terms of the ternary system, B and P doping could induce the lattice strain, thus regulating the electronic structure and increasing the number of active sites of Pd; in addition, the doping sites also served as the Lewis acid to improve the adsorption ability for NO_3^-. Thus, the electrochemical performance for reducing NO_3^- to NH_3 was significantly enhanced after B and P doping.[50]

Several noble-metal oxides were also used as electrocatalysts for highly efficient NH_3 formation by electrochemical conversion of NO_3^- at room temperature. Liu *et al.*[51] fabricated oxide-derived silver and investigated its electrochemical activity for the NO_3^-RR. It is noted that this catalyst delivered excellent electrocatalytic activity of NO_3^- to NO_2^- and thus promoted the reduction reaction of NO_2^- to NH_4^+, which was well controlled by the applied potential and they obtained an NH_4^+ FE of 89%. Qin *et al.*[52] designed and synthesized Ru_xO_y clusters anchored on nickel metal–organic frameworks (MOF) for the NO_3^-RR. Such a catalyst could provide a nearly 100% NH_4^+ selectivity with an NH_4^+ yield rate of 274 μg h^{-1} mg^{-1}. Wang *et al.*[53] fabricated carbon-supported RuO_2 nanosheets with abundant oxygen vacancies for electrochemical NO_3^- to NH_3 conversion. The abundant oxygen vacancies within the RuO_2 nanosheets could regulate the d-band center and improve the hydrogen affinity, thus reducing the reaction-energy barrier of the potential-determining step ($NH_2^* - NH_3^*$). As a result, this catalyst displayed a superior electrocatalytic activity for the conversion of $NO_3^-$to NH_3 (NH_3 FE of 97.46% and selectivity of 96.42%) than that of the crystalline counterparts.

3.2 Single-atom catalysts

Single-atom catalysts, a group of emerging frontier materials comprising isolated metal atoms dispersed into support materials, have triggered explosive research interest within the catalysis field owing to their remarkably high catalytic activity and selectivity. When applied to the NO_3^-RR, single-atom catalysts can provide the following desirable advantages, including (i) the specific atomic structure can expose abundant adsorption sites and homogenous catalytic active centers; (ii) the strong interactions between single atoms and the surrounding atoms enable superior long-term electrolysis; and (iii) the absence of multiple neighboring active sites required for coupling N–N bonds in their structure can efficiently suppress the generation of by-product N_2, thus enhancing NH_3 selectivity. Currently, both experimental and theoretical calculations have suggested that single-atom catalysts are effective toward electroreduction of NO_3^- to NH_3.

For example, Niu and co-workers[54] used first-principle calculations to systematically investigate the electrocatalytic activity of various transition-metal single-atoms (from Ti to Au) anchored on carbon nitride (TM/g-CN) for electrochemical NO_3^- to NH_3 conversion, as shown in Fig. 4a. Firstly, the adsorption energies of NO_3^-, a H proton, and an N_2 molecule on TM/g-CN were systematically calculated. As revealed from Fig. 4b, the adsorption ability for NO_3^- was stronger than for H proton or N_2 on TM/g-CN catalysts, except for Pt and Au, indicating that the NO_3^-RR is more favorable than the HER and NRR. By combining with detailed pathways of NO_3^- reduction on TM/g-CN, they established a volcano plot of limiting potential selecting the adsorption energy of NO_3^- as a descriptor (Fig. 4c), where Ti and Zr appeared near the top of the volcano. Based on the above analysis, Ti/g-CN and Zr/g-CN possessed stronger adsorption abilities for NO_3^- compared with those of other TM/g-CN catalysts, making them fascinating electrocatalysts with high activity and selectivity for the NO_3^-RR. Similarly, Lv *et al.*[55] explored the NO_3^-RR performance of a set of transition-metal single-atom (Ti, Os, Ru, Cr, Mn, and Pt) catalysts supported on g-C_3N_4 by performing DFT calculations. The calculation results suggested that Ru/g-C_3N_4 featured the highest activity and selectivity for the conversion

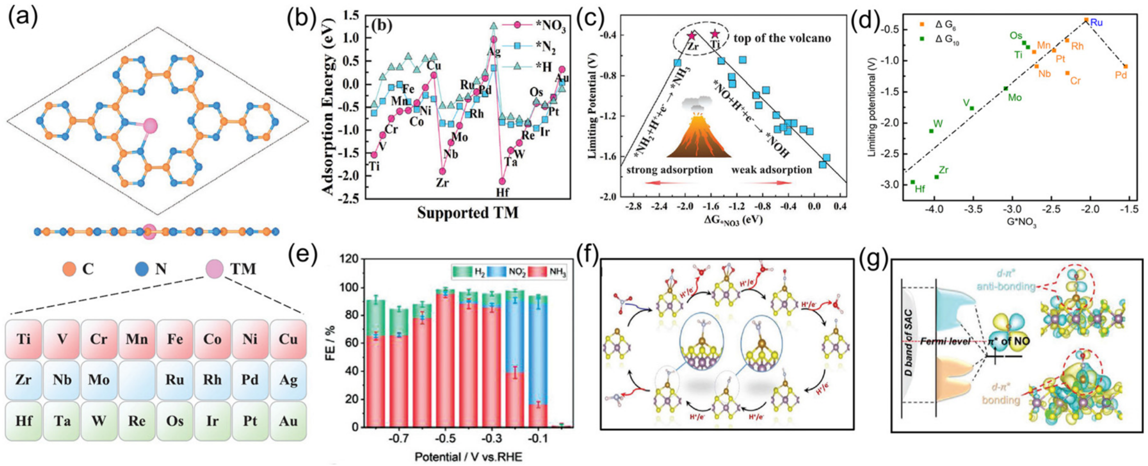

Fig. 4 (a) Atomic structure of TM/g-CN and corresponding element list (from Ti to Au). (b) Comparison of adsorption energies of NO_3^-, N_2, and H proton on TM/g-CN. (c) NO_3^-RR volcano plot of TM/g-CN using the adsorption energy of NO_3^- as the descriptor. Reproduced from ref. 54 with permission from Wiley-VCH, copyright 2021. (d) Volcano correlation curve between the limiting potential and adsorption energy of NO_3^- of TM/g-C_3N_4. Reproduced from ref. 55 with permission from the American Chemical Society, copyright 2021. (e) NH_3 FE of Fe-MoS_2 under various potentials. (f) Reaction pathway for the NO_3^-RR on Fe-MoS_2. (g) Schematic diagram of the interaction between NO and M-MoS_2 nanosheets. Reproduced from ref. 57 with permission from Wiley-VCH, copyright 2022.

Table 2 Summary of catalytic performance of single-atom metal electrocatalysts

Catalyst	Electrolyte	NH_3 yield rate	Faradaic efficiency	Potentials (V *vs.* RHE)	Ref.
Fe-MoS_2 SAC	0.1 M Na_2SO_4 + 0.1 M $NaNO_3$	431.8 μg h^{-1} cm^{-2}	98%	−0.48	57
Fe SAC	0.1 M K_2SO_4 + 0.5 M NO_3^-	0.46 mmol h^{-1} cm^{-2}	75%	$-0.85^a/-0.66^b$	58
Fe-PPy SAC	0.1 M KOH + 0.1 M NO_3^-	2.75 mg h^{-1} cm^{-2}	100%	−0.7/−0.3	59
Cu SAC	0.1 M KOH + 0.1 M NO_3^-	4.5 mg cm^{-2} h^{-1}	84.7%	−1.0	60
Cu-*cis*-N_2O_2 SAC	0.5 M K_2SO_4 + 1000 ppm NO_3^-	28.73 ± 1.25 mg h^{-1} cm^{-2}	80%	−1.6	61
FeN_2O_4 SAC	0.1 M K_2SO_4 + 0.5 M NO_3^-	46 mg h^{-1} mg^{-1}	92%	$-0.88^a/-0.68^b$	62
Ni-Cu SAC	0.5 M K_2SO_4 + 200 ppm NO_3^-	326.7 μmol h^{-1} cm^{-2}	100%	−0.55	63
FeMo SAC	0.05 M PBS + 0.16 M KNO_3	18.0 μmol cm^{-2} h^{-1}	94%	−0.45	64

[a] NH_3 yield rate. [b] Faradaic efficiency.

of NO_3^- to NH_3 with a limiting potential of −0.34 V, as presented in Fig. 4d. Thus, theoretical calculations have provided an advanced direction for the application of single-atom catalysts and paved the way for the electrochemical conversion of NO_3^- to NH_3.

Up to now, only a few single-atom catalysts have been experimentally fabricated and employed for the electrosynthesis of NH_3 from NO_3^-, including Fe, Cu, Ni, Mo, and their alloys, as listed in Table 2. For example, Zhu *et al.*[56] prepared a single-atom Cu-catalyst supported on nitrogenated carbon nanosheets (Cu–N–C) and investigated its catalytic performance for the NO_3^-RR for the first time. The strong binding between Cu and N (Cu–N_2) was responsible for the good adsorption ability of the catalyst for NO_3^- adsorption, promoting the fast conversion from NO_3^- to NH_3 as well as exhibiting excellent stability. Furthermore, Chen *et al.*[24] demonstrated that Cu–N–C could effectively inhibit the generation of toxic NO_2^- and by-product N_2, as well as facilitate the reduction of HNO_3^* to NO_2^*, and NH_2^* to NH_3^*. It is well known that the nitrate reductase enzyme has a Mo(IV) atom coordinated with sulfur coordinating ligands, whereas nitrogenase is a multinuclear enzyme with $MoFe_7$ clusters as the active sites. Inspired by this point, Voiry's group[57] developed a novel heterogeneous catalyst composed of Fe single-atoms anchored on two-dimensional MoS_2 (Fe-MoS_2) for electrochemical NH_3 synthesis by the reduction reaction of NO_3^-. Fe-MoS_2 delivered a remarkably high FE of 98% for the NO_3^-RR to NH_3 at an onset potential of −0.48 V using 0.1 M Na_2SO_4 containing 0.1 M $NaNO_3$ electrolyte (Fig. 4e). Under the above testing conditions, this catalyst showed a 7-hour average NH_3 formation rate of 431.8 μg h^{-1} cm^{-2}. DFT calculations revealed that the Fe-MoS_2 catalyst featured a superior ability for activating NO_3^- by virtue of the strong interaction between the d-band orbitals of the Fe atoms and the $2\pi^*$ orbitals of the NO species, lowering the energy barrier for conversion of *NO to *N (the rate-determining step) (Fig. 4f and g). At the same time, Wu *et al.*[58] chose an N-doped porous carbon matrix to anchor Fe single-atoms (Fe SAC) and applied them for electrochemical NO_3^- to NH_3 conversion (Fig. 5a and b). A large NH_3 yield rate (up to 0.46 mmol h^{-1} cm^{-2} at −0.85 V *vs.* RHE) and a high NH_3 FE of 75% at −0.66 V *vs.* RHE were achieved in K_2SO_4 with 0.5 M KNO_3, and remained stable during 20 consecutive electrolysis cycles (Fig. 5c–e). These results indicated that Fe SAC featured superior electrocatalytic activity and outstanding durability for the NO_3^-RR. The favorable catalytic activity of the as-designed Fe SAC originated from the unique structure, which can not only effectively suppress the N–N coupling and enhance the selectivity of NH_3 production, but also enable the intrinsic high-efficiency active sites (Fe–N_4) to possess lower thermodynamic barriers. However, the detailed reaction mechanism of Fe SAC was only revealed through theoretical modeling. During the electrocatalytic reaction process, the M (metal)–N_x catalyst may experience structural evolution induced by the applied potential and/or the interaction with reactants or electrolytes, which complicates the comprehension of the structure–performance relationship and seriously blocks the rational design of efficient catalysts. Consequently, revealing the dynamic transformation of the M–N_x structure under operating conditions is essential to recognize the real active sites. To achieve the above-mentioned target, Li *et al.*[59] employed *in situ* characterisation techniques to establish the reaction pathway and evolution mechanism of the catalysts, selecting a catalyst of Fe single atoms anchored on carbon derived from polypyrrole as an example. They proposed the preoccupied NO_3^-RR mechanism presented in Fig. 5f that the exclusive existence of nitrate-preoccupied Fe(II)–N_x sites prior to the formation of Fe (0), which could effectively eliminate the competing adsorption of water under aqueous conditions. Subsequently, Yang *et al.*[60] discovered the restructuring of Cu–N_4 sites during the electrochemical production of NH_3 by converting NO_3^- through *in situ* X-ray adsorption spectroscopy coupled with advanced electron microscopy. Specifically, as depicted in Fig. 5g–i, the Cu–N_4 structure experienced the sequential evolution from Cu–N_3 to near-free Cu^0 single atoms and finally to aggregated Cu^0 nanoparticles during the electroreduction of NO_3^- to NH_3. Moreover, the formed Cu^0 nanoparticles can be dismantled into single atoms and again recovered to give the Cu–N_4 structure upon being exposed to an ambient atmosphere after the electrolysis.

Although single-atom catalysts deliver outstanding electrocatalytic activity for the conversion of NO_3^- to NH_3, the isolated metal centers usually coordinate with four N atoms in C_{4V} symmetry. Such a coordination structure features relatively weak adsorption ability for NO_3^-, leading to sluggish ionic

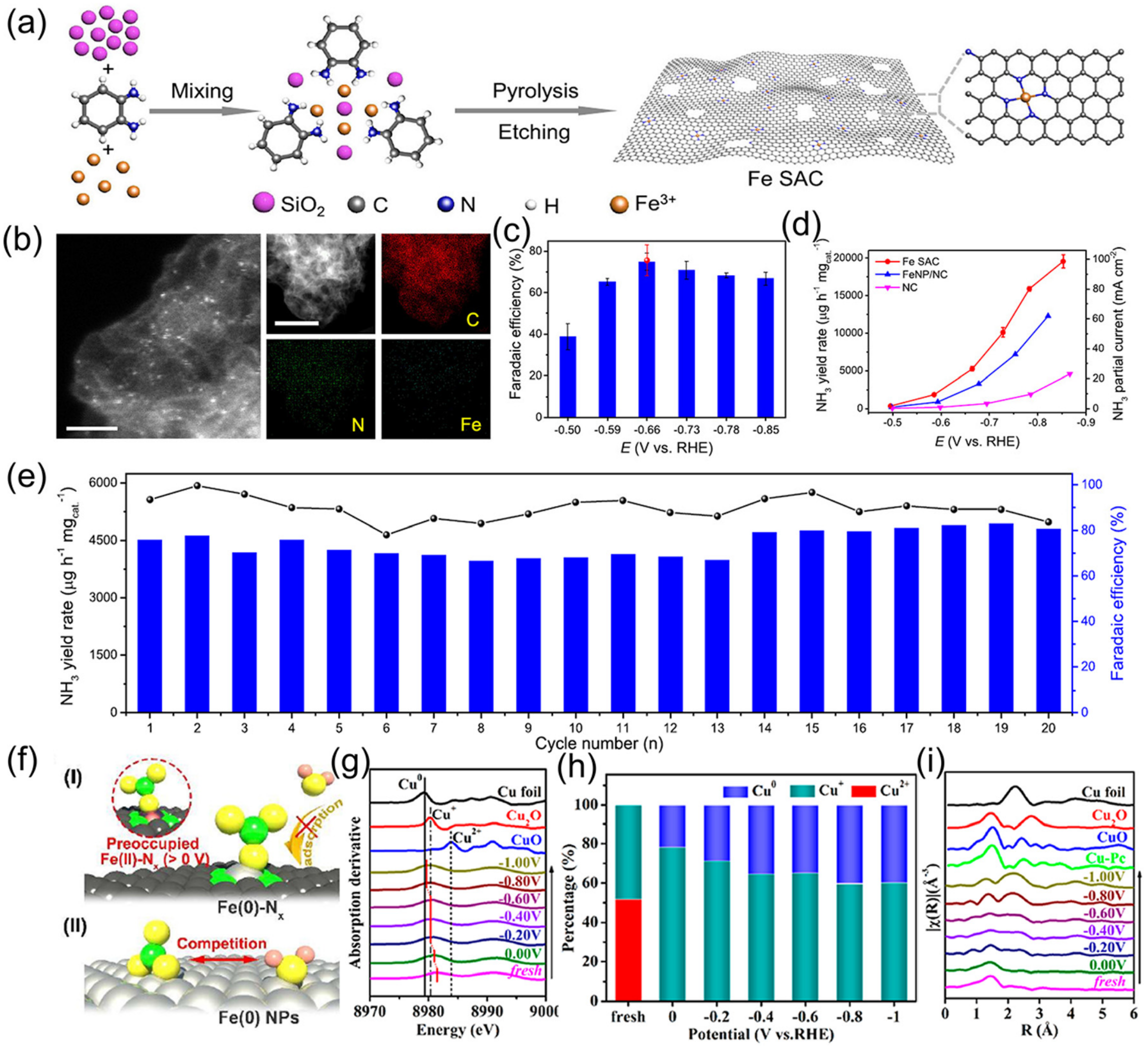

Fig. 5 (a) Schematic illustration of the preparation of Fe SAC. (b) Aberration-corrected medium-angle annular dark-field scanning TEM (HAADF STEM) and mapping images of Fe SAC. (c) NH_3 FE. (d) NH_3 yield rate and partial current density of Fe SAC under various potentials. (e) Cycling durability of Fe SAC at −0.66 V *vs.* RHE. Reproduced from ref. 58 with permission from the Nature Publishing Group, copyright 2021. (f) The proposed preoccupied NO_3^-RR mechanism for Fe SAC. Reproduced from ref. 59 with permission from The Royal Society of Chemistry, copyright 2021. (g) *In situ* XANES spectra of Cu–N_4 at each given potential. (h) Linear combination fitting result of the Cu K-edge XANES spectra and (i) corresponding Cu K-edge FT-EXAFS spectra at different potentials. Reproduced from ref. 60 with permission from the American Chemical Society, copyright 2022.

migration and low NH_3 production rate. Related literature has demonstrated that introducing weakly coordinated heteroatoms to substitute some of the coordinated N is an admirable strategy for breaking the coordination symmetry of the metal centers, consequently increasing the site polarity and improving NO_3^- accumulation. For instance, Cheng *et al.*[61] broke the coordination symmetry of Cu SAC by replacing the local coordination atoms from 4N to 2N + 2O (Cu-*cis*-N_2O_2). First-principle calculations were preferentially employed to reveal the coordination symmetry-breaking in Cu SAC and investigate the reaction pathways of Cu-*cis*-N_2O_2 and Cu–N_4 catalysts, as indicated in Fig. 6a–e. In terms of Cu-*cis*-N_2O_2, Cu is coordinated by two N and two O atoms and the catalyst possesses polar active sites, which are prone to enrich NO_3^- on the surface of the catalyst and promote the generation of the key reaction intermediate *ONH, further facilitating hydrogenation to NH_3. Motivated by this, a Cu-*cis*-N_2O_2 catalyst was fabricated by pyrolysis of a Cu–Salen complex under an Ar atmosphere (Fig. 6g–h). When applied to the NO_3^-RR, the NH_3 formation rate reached 27.84 mg h^{-1} cm^{-2} at an industrial-level current density of 366 mA cm^{-2}. Moreover, the electrochemical activity of Cu-*cis*-N_2O_2 was well maintained after continual operation for 2000 h (Fig. 6i–k). Analogously, Zhang *et al.*[62] fabricated an Fe single-atom catalyst with unique FeN_2O_2 coordination *via* direct pyrolysis of metal–organic frameworks possessing a pre-organized FeN_2O_4 environment. When applying the designed Fe SAC for the NO_3^-RR, it showed a high NH_3 production rate of 46 mg h^{-1} mg^{-1} with a FE of 92% in neutral electrolytes. Combined theoretical calculations revealed that the O atoms in FeN_2O_2 could regulate the d-band center of Fe and conse-

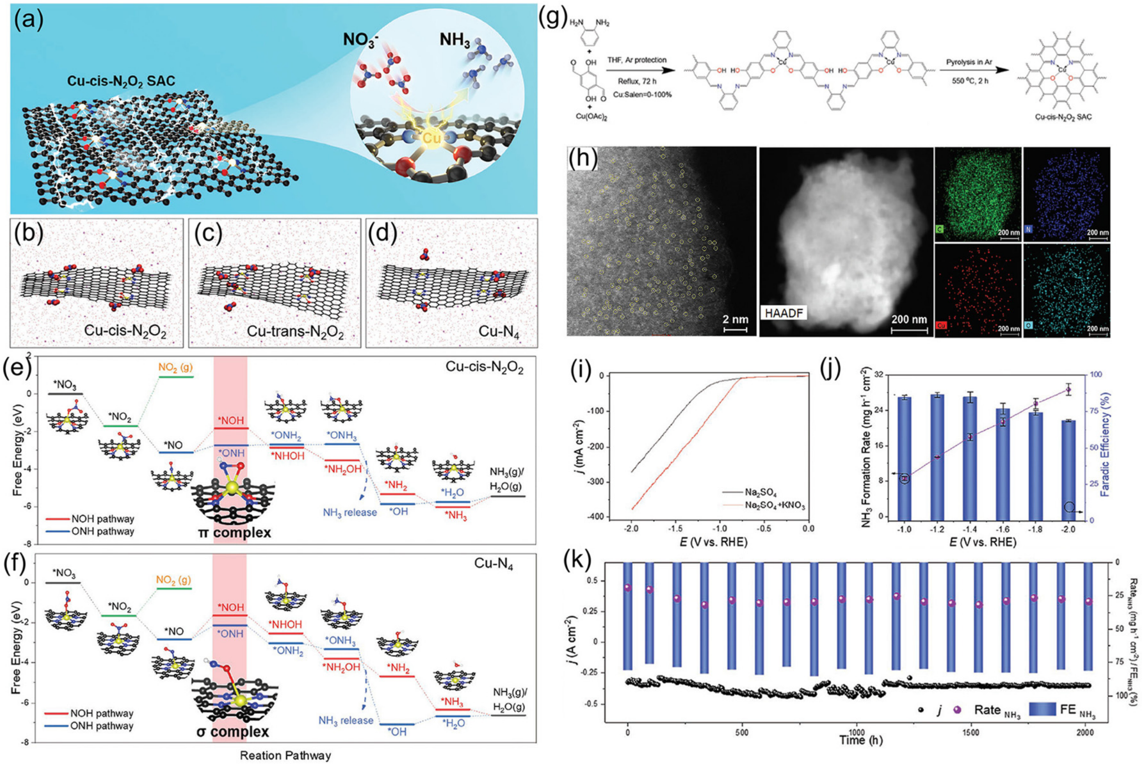

Fig. 6 (a) Illustration of the Cu-*cis*-N_2O_2 catalyst. (b–d) The molecular dynamic simulation of Cu-*cis*-N_2O_2 and counterparts. (e and f) Reaction pathways for the NO_3^-RR on the surface of Cu-*cis*-N_2O_2 and Cu-N_4. (g) Synthesis process of Cu-*cis*-N_2O_2. (h) HAADF STEM and corresponding mapping images of Cu-*cis*-N_2O_2. (i) LSV curves, (j) NH_3 formation rate and FE at each given potential. (k) Cycling stability test of Cu-*cis*-N_2O_2. Reproduced from ref. 61 with permission from Wiley-VCH, copyright 2022.

quently enhance the adsorption energies of the NO_3^-RR intermediates. In comparison with FeN_4, FeN_2O_2 features superior conductivity, NH_3 selectivity and a lower reaction energy barrier from *NOH to *N, thus promoting the progress of the NO_3^-RR.

To further enhance the catalytic activity of single-atom catalysts, tuning the electronic structures of active sites through introducing foreign atoms in the metal matrix can be regarded as an alluring approach to increase the NH_3 production rate, selectivity and FE. For example, Cai *et al.*[63] reported a single-atom Ni-alloyed Cu catalyst that achieved an NH_3 yield rate of 326.7 μmol h^{-1} cm^{-2} at −0.55 V *vs.* RHE and a maximum FE of 100% in 0.5 M K_2SO_4 with 200 ppm NO_3^-, in which the yield rate was nearly 10.7 times superior to that of a bare Cu catalyst. Theoretical calculations suggested that the single Ni atom on the Cu catalyst regulated the third protonation reaction of the electrocatalytic NO_3^-RR and increased the adsorption energy of the crucial NOOH* intermediate, thus decreasing the limiting potential and inhibiting the formation of by-product. Murphy *et al.*[64] reported a bimetallic FeMo-based single-atom catalyst for electroreduction of NO_3^- to NH_3, in which Mo and Fe served as the dissociative and associative sites of the initial adsorption of NO_3^-, respectively. Benefiting from the synergistic effect of both Mo and Fe sites, this bimetallic catalyst achieved an NH_3 production rate of 18.0 μmol cm^{-2} h^{-1} (153 μg_{NH_3} mg^{-1} h^{-1}) with a FE of 94%, as well as outstanding long-term durability with a well-maintained FE above 90% for over 60 h of electrolysis.

In the above-mentioned two parts, we have discussed noble-metal and single-atom metal catalysts for conversion of NO_3^- to NH_3 under ambient conditions. Although an extensive number of electrocatalysts deliver desirable activity, high FE and superior selectivity, their large-scale practical application is still impeded by their expensive cost, rare resources (noble metals) and low yield (single-atom catalysts). In contrast, non-noble transition metals, such as Cu, Co, Ni, Fe, and their alloys, have drawn extensive attention as promising alternatives in the field of electrochemical conversion of NO_3^- to NH_3 by virtue of their abundant resources and favorable catalytic activity. Transition-metal-based materials including metals, metal oxides, metal phosphides, and so on, have been widely investigated as highly efficient catalysts for the NO_3^-RR. In the following section, the recent advances in transition-metal-based electrocatalysts for the NO_3^-RR will be systematically discussed.

3.3 Transition-metal catalysts

3.3.1 Zero-metal catalysts. Owing to the similar energy levels between the d orbitals of Cu and the LUMO π* molecular orbital of NO_3^-, metallic Cu catalysts have attracted extensive

Table 3 Summary of catalytic performance of transition-metal electrocatalysts

Catalyst	Electrolyte	NH_3 yield rate	Faradaic efficiency	Potentials (V *vs.* RHE)	Ref.
Cu nanosheets	0.1 M KOH + 10 mM KNO_3	390.1 μg mg^{-1} h^{-1}	99.7%	−0.15	70
Cu polycrystalline	0.5 M Na_2SO_4 + 0.1 M KNO_3	101.4 μmol h^{-1} cm^{-2}	93.91%	−0.266	71
dr-Cu nanoplates	0.5 M K_2SO_4 + 50 ppm KNO_3^-	781.25 μg h^{-1} mg^{-1}	85.47%	−0.654	72
Cu with grain boundaries	0.1 M KOH + 10 mM NO_3^-	487.8 mmol g^{-1} h^{-1}	94.2%	−0.2	74
Cu@C	0.1 M KOH + 1 mM NO_3^-	469.5 μg h^{-1} cm^{-2}	72.0%	$-0.9^a/-0.3^b$	77
Cu/TiO_{2-x}	0.5 M Na_2SO_4 + 500 ppm NO_3^-	0.1143 mmol h^{-1} mg^{-1}	81.34%	−0.75	78
Cu-CuO	0.1 M KOH + 0.1 M NO_3^-	3.17 mol h^{-1} g^{-1}	98.7%	−0.8	79
Co nanosheets	1 M KOH + 0.1 M NO_3^-	10.4 mmol h^{-1} cm^{-2}	98%	−0.24	89
Fe-cyano NSs	1 M KOH + 0.1 M NO_3^-	42.1 mg h^{-1} cm^{-2}	90%	−0.5	90
Ni-NCNTs	0.5 M Na_2SO_4 + 0.3 M NO_3^-	5.1 mg h^{-1} cm^{-2}	99%	−0.5	92
CuFe alloys	0.1 M Na_2SO_4 + 100 ppm NO_3^-	—	81.1%	−0.7	93
CuNi@C alloy	0.1 M PBS + 50 mg L^{-1} NO_3^-	—	79.6%	−1.0	95
$Co_{0.5}Cu_{0.5}$	1 M KOH + 50 mM KNO_3	—	95%	−0.03	96

[a] NH_3 yield rate. [b] Faradaic efficiency.

attention toward the NO_3^-RR.[65–67] However, most metallic Cu catalysts generally convert NO_3^- to N_2 instead of NH_3. In terms of an electrochemical NH_3 synthesis system, enhancing the NH_3 yield rate and selectivity of metallic Cu catalysts is critical during the reduction of NO_3^-. Previous literature indicated that rational structure design and crystal regulation could achieve the above-mentioned target.[68,69] For example, Fu *et al.*[70] designed Cu nanosheets as electrocatalysts for the NO_3^-RR, which delivered a superior catalytic activity (NH_3 yield rate of 390 μg mg^{-1} h^{-1} and FE of 99.7%) to Cu foil and Cu nanoparticles (with the yield rate being about 400 times that of Cu foil and 1.7 times that of Cu nanoparticles) (Table 3). Such excellent performance might be ascribed to the large surface areas of Cu nanosheets, which could expose abundant active sites. In a recent study, flower-like polycrystalline Cu grown *in situ* on carbon paper was fabricated by an electrodeposition technique. The unique structure provided an open reaction environment beneficial to the permeation of electrolyte, and thus enhanced the liquid-phase mass-transfer process. When regarded as a catalyst for the NO_3^-RR, it showed superior electrochemical activity with a large NH_3 formation rate of 101.4 μmol h^{-1} cm^{-2} and FE of 93.91% in neutral solution.

Meanwhile, an NH_3 yield rate of 82.4 μmol h^{-1} cm^{-2} was still achieved after six continuous cycles, with a high FE above 92.85% retained, indicating an alluring stability for electroreduction of NO_3^- to NH_3.[71]

On the other hand, interface engineering, such as defect engineering,[72] heteroatom doping,[73] coupling with carbon,[65] grain-boundary engineering,[74] and constructing heterostructures[75,76] has been proposed to further enhance the electrochemical NO_3^-RR activity of metallic Cu catalysts. As presented in Fig. 7a and b, Xu *et al.*[72] fabricated the atomic-defect-rich metallic Cu nanoplates (dr-Cu NPs) and investigated their catalytic activity for the NO_3^-RR. After the introduction of a large number of defects in the lattice, the electrochemically active surface area of the Cu nanoplates was remarkably enhanced (dr-Cu NPs: 1.28 mF cm^{-2} *vs.* Cu NPs: 0.38 mF cm^{-2}), thus increasing the surface-active sites and facilitating the adsorption of various intermediates during the electrochemical process. As expected, dr-Cu NPs displayed a large NO_3^- conversion rate of 93.26%, favorable NH_3 selectivity of 81.99%, as well as a high NH_3 FE of 85.47%, which were superior to those of Cu nanoplates without defects (Fig. 7c and d). Song *et al.*[77] designed Cu nanoparticles encapsulated in a porous carbon matrix for NO_3^- to NH_3 conversion (Fig. 7e and f). Under an ultralow concentration of 1 mM NO_3^-, Cu@C delivered a high NH_3 FE of 72.0% and a yield rate of 469.5 μg h^{-1} cm^{-2} at −0.3 and −0.9 V *vs.* RHE, respectively, which were approximately 3.6 times larger than those of Cu nanoparticles (Fig. 7g and h). To reveal such impressive electrocatalytic activity, they adopted the finite-element method to simulate the enrichment effect of NO_3^- on the surface of Cu@C and Cu. The structure model of a Cu slab coated with or without porous carbon shown in Fig. 7i and j suggested that the porous carbon skeleton within Cu@C was beneficial to the concentration of NO_3^-, thereby expediting the mass transfer of NO_3^- for efficient electroreduction into NH_3 at ultralow concentrations. In addition, Cu nanoparticles with abundant grain boundaries encapsulated by hollow carbon (Cu@C) were constructed and regarded as an electrocatalyst for thee conversion of NO_3^- to NH_3 in alkaline media. In terms of this catalyst system, apart from the enrichment effect of carbon, the grain boundaries within the Cu nanoparticles could appropriately regulate the adsorption energy of NO_3^- for dwindling reaction barriers and enhance the reaction activity for the NO_3^-RR. As a consequence, the constructed Cu@C catalyst exhibited a maximum FE of 94.2% and a large NH_3 yield rate of 487.8 mmol g^{-1} h^{-1} at a low potential of −0.2 V *vs.* RHE in alkaline media, achieving an exceptional performance for the NO_3^-RR.[74] Zhang *et al.*[78] constructed a heterostructure catalyst composed of metallic Cu and oxygen-vacancy-rich TiO_{2-x}, in which the Cu nanoparticles were homogenously anchored on TiO_{2-x} nanosheets (Fig. 7k). As a catalyst for the NO_3^-RR, the designed heterostructure electrode exhibited an NH_3 formation rate of 0.1143 mmol h^{-1} mg^{-1} along with a high FE of

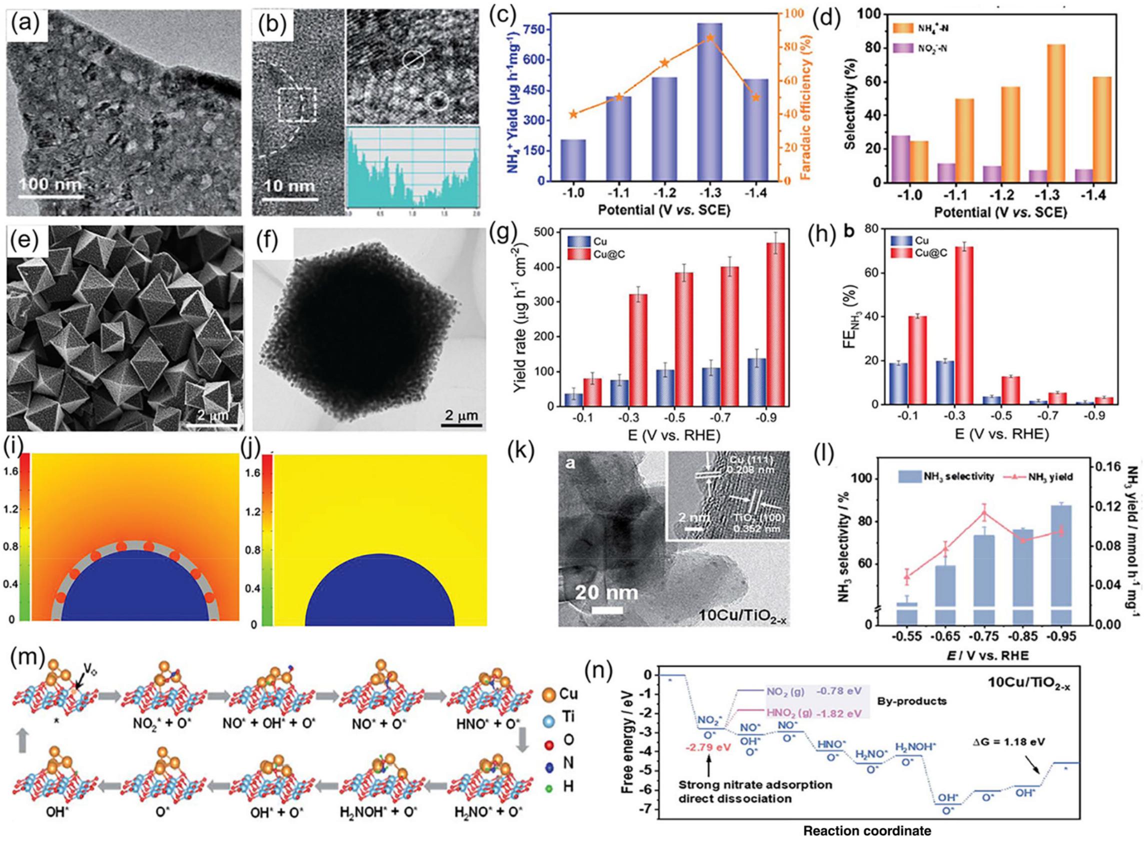

Fig. 7 (a) TEM and (b) HRTEM images of a dr-Cu nanoplate. (c) NH_4^+ yield rate and FE, and (d) NH_4^+ selectivity of dr-Cu nanoplates at various potentials. Reproduced from ref. 72 with permission from The Royal Society of Chemistry, copyright 2021. (e) SEM and (f) TEM images of Cu@C. (g) NH_3 yield rate and (h) FE of Cu@C under different potentials. Simulated concentrations and distribution of local NO_3^- on the surface of (i) Cu@C and (j) Cu at the diffusion time of 7 μs. The blue semicircle and the gray shell represent Cu and porous carbon, respectively. Reproduced from ref. 77 with permission from Wiley-VCH, copyright 2022. (k) TEM image of Cu/TiO_{2-x}. (l) NH_3 selectivity and yield rate of Cu/TiO_{2-x} at each applied potential. (m) Reaction mechanism and (n) corresponding calculated free energy changes of the NO_3^-RR on the surface of Cu/TiO_{2-x}. Reproduced from ref. 72 with permission from The Royal Society of Chemistry, copyright 2021.

81.34%, which obviously outperformed the individual Cu and TiO_{2-x} counterparts (Fig. 7l). Such excellent electrocatalytic activity could be ascribed to the introduction of oxygen defects and metallic Cu clusters, which not only modified the electronic conductivity of the heterostructure electrode, but also optimized the adsorption energy of NO_3^- and hydrogenation manner that suppressed the generation of by-products (Fig. 7m and n). Similarly, Zhao *et al.*[79] designed and fabricated a Cu-CuO heterostructure as an electrocatalyst for the NO_3^-RR, where the heterointerface between Cu and CuO was favorable for promoting the hydrogenation of *NO to *NOH and inhibiting the HER during the reduction process of NO_3^-. Thus, this heterostructure catalyst showed a molar-level NH_3 yield rate of 3.17 mol h^{-1} g^{-1} and an ultrahigh FE of 98.7%. In addition, metallic Cu exhibits substantially high energy barriers to the dissociation of water in both neutral and alkaline electrolytes during electroreduction of NO_3^-, which controls the proton transfer rate and further leads to sluggish reaction kinetics for NH_3 synthesis.[80] To address the above-mentioned issue, Yu *et al.*[81] employed DFT calculations to seek applicable ligands and confirmed that the uncoordinated carboxylate ligands could considerably promote water dissociation on Cu, accelerating the proton transfer and reaction kinetics of NO_3^-. They experimentally encapsulated Cu nanoparticles into the uncoordinated carboxylate-ligand-rich MOF matrix through a particle decomposition route. As expected, the designed Cu-based catalyst achieved an alluring electrochemical performance for the reduction of NO_3^- to NH_3 in alkaline media, including a high NH_3 yield rate of 496.4 mmol h^{-1} g^{-1} at an ultralow potential of −0.2 V *vs.* RHE and an outstanding stability of 20 h.

In addition to metallic Cu, other metal catalysts like Co, Fe, Ni, and Bi have been applied to highly effective reduction of NO_3^- to NH_3.[82–87] For instance, our group synthesized metallic Co–nitrogen-doped carbon nanotubes hybrid (Co–NCNTs) (Fig. 8a and b) and investigated their electrocatalytic activity for the NO_3^-RR. In 0.1 M NaOH with 0.1 M NO_3^-, the Co–NCNTs delivered a high activity for the NO_3^-RR with an NH_3 production rate of 5996 μg h^{-1} cm^{-2} and FE of 92% at 0.6 V *vs.* RHE (Fig. 8c and d), and exhibited excellent durability with ~8.7% attenuation of current density and well-maintained FE during the 12-h electrolysis. Furthermore, DFT calculations

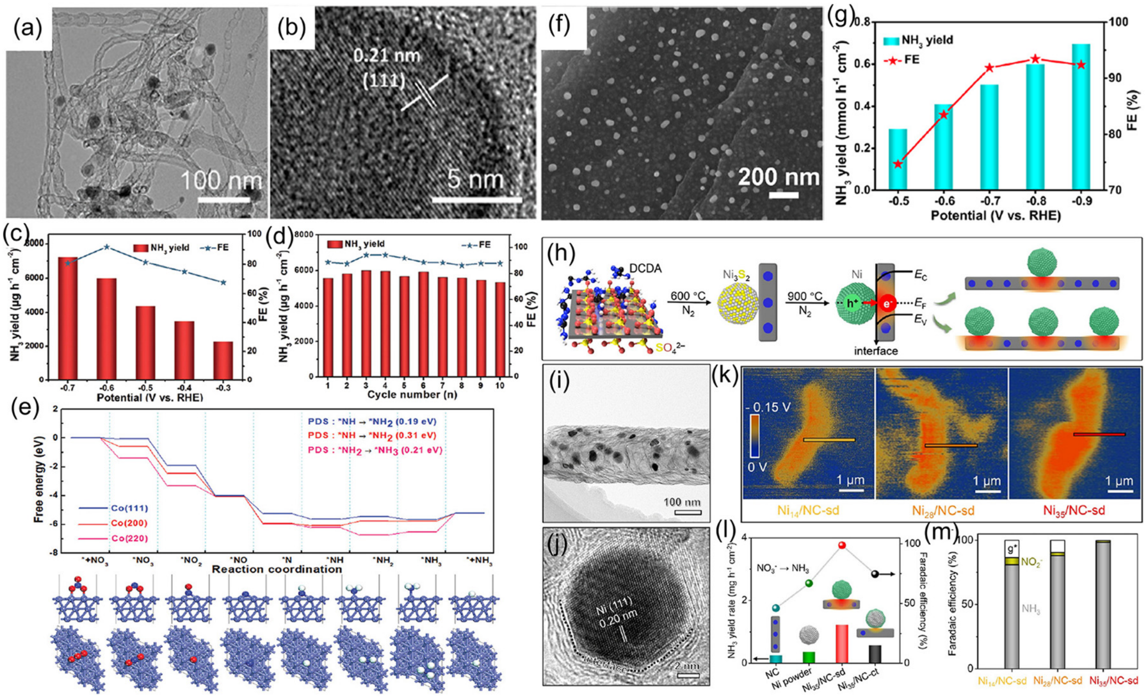

Fig. 8 (a and b) TEM images of Co-NCNTs. (c) NH_3 yield rate and FE of Co-NCNTs under various potentials. (d) Recycling test of Co-NCNTs at −0.6 V. (e) Free-energy profiles of the NO_3^-RR on different crystal facets of metallic Co. Reproduced from ref. 88 with permission from The Royal Society of Chemistry, copyright 2022. (f) SEM image, (g) NH_3 yield rate and FE at different potentials of Co-carbon derived from corncob. Reproduced from ref. 89 with permission from the American Chemical Society, copyright 2022. (h) Fabrication process of Ni-NCNTs catalyst. (i and j) TEM and HRTEM images of Ni-NCNTs. (k) Surface electric field distribution of Ni-NCNTs sample. (l and m) NH_3 yield rate and FE of Ni-NCNTs catalyst. Reproduced from ref. 92 with permission from Wiley-VCH, copyright 2021.

(Fig. 8e) revealed that the Co (111) facet is more favorable for the NO_3^-RR than the Co (200) and Co (220) facets, in which the rate-determining step is the hydrogenation of *NH to *NH_2. The corresponding energy barrier was only 0.19 eV, indicating the impressive NO_3^-RR activity of metallic Co.[88] Meanwhile, we also synthesized metallic Co nanoparticles embedded on carbon derived from corncob as an electrocatalyst for the NO_3^-RR to NH_3, which achieved a large NH_3 production rate of 0.6 mmol h^{-1} cm^2 with a FE of 93.4%, as depicted in Fig. 8f and g.[89] Fang and coworkers[90] reported that metallic Fe anchored on cyano-coordination polymer porous nanosheets (Fe-cyano NSs) displayed an outstanding electrochemical NH_3 synthesis through the reduction of NO_3^- in an alkaline electrolyte. Bi has also been employed as a highly efficient catalyst for electrochemical reduction of NO_3^- due to its unique atomic structure, in which the interlayer lattice compression shortens the Bi–Bi bond to broaden the 6p bandwidth for electronic delocalization, enhancing the adsorption energy for nitrogen intermediates.[84] Iarchuk *et al.*[91] synthesized Ni foam catalysts through a dynamic hydrogen-bubble-template-assisted electrodeposition process. An NH_3 FE of more than 95% was obtained under the relatively low potential range from −0.1 to −0.3 V *vs.* RHE. Gao *et al.*[92] constructed a Schottky heterostructure composed of metallic Ni and nitrogen-doped carbon nanotubes (Ni-NCNTs) for converting NO_3^- to NH_3 at room temperature (Fig. 8h–j). In terms of heterostructure catalyst, the heterointerface between Ni nanoparticles and NCNTs could induce the formation of a built-in electric field (Fig. 8k), which facilitated the accumulation and fixation of NO_3^- on the surface of the catalyst and consequently promoting the reaction kinetics during the electrochemical process. As a result, the designed Ni-NCNTs enabled a high FE of 99% for the electrocatalytic reduction of NO_3^-, and a large NH_3 formation rate of 5.1 mg h^{-1} cm^{-2} in the electrochemical conversion of NO_3^- (Fig. 8l and m).

3.3.2 Metal alloys.

Coupling with a secondary metal has been regarded as a fascinating route to enhance the electrochemical activity of transition-metal catalysts *via* regulating the electronic structure of the metal and exerting a synergistic effect of two different metals. Table 3 summarizes the electrochemical performance of metal alloy catalysts for the NO_3^-RR. For instance, Tang *et al.*[93] demonstrated that Cu–Fe bimetallic nanoalloys with a Cu/Fe molar ratio of 3 : 1 presented a high NH_3 FE of 81.1% at −0.7 V *vs.* RHE within 6 h in 0.1 M Na_2SO_4 containing 100 ppm NO_3^-. Similarly, Sargent and coauthors[94] indicated that $Cu_{50}Ni_{50}$ alloy catalysts only required an overpotential of 0.2 V to obtain the maximum NH_3 FE under various concentrations of NO_3^-, and produced a 6-times increment in the NO_3^-RR activity compared to the case of pure Cu at 0 V *vs.* RHE. DFT calculations revealed that the introduction of Ni atoms led to the upshifting of the d-band center toward the Fermi level, which improved the adsorption energies of the intermediates and enhanced the selectivity for NH_3. Recently, Liu *et al.*[95] incorporated CuNi alloy nanoparticles into a nitrogen-doped carbon matrix with hierarchical pores by pyrolysis of bimetallic MOFs. A high NH_3 selectivity of 94.4% and FE of 79.6% were achieved when utilizing the designed CuNi@C as a catalyst for the NO_3^-RR. Jeon *et al.*[96] designed cobalt–copper ($Co_{1-x}Cu_x$) nanoparticles supported on a three-dimensional substrate for efficient and selective NH_3 synthesis *via* an electrocatalytic NO_3^- reduction. Typically, the optimized $Co_{0.5}Cu_{0.5}$ catalyst performed at a high NH_3 FE of over 95% at −0.03 V with an NH_3 partial current density of ~176 mA cm^{-2} at 50 mM nitrate, which is 7.3- and 1.7-fold higher than those of the pure Co and Cu counterparts, respectively. Importantly, replacing Co with Cu enabled tuning of the onset potential on the Co catalyst and maintained a high selectivity toward NH_3.

3.4 Transition-metal compound catalysts

3.4.1 Metal oxides

3.4.1.1 Copper-based oxides. Transition-metal oxides have been widely investigated as electrocatalysts for NH_3 synthesis *via* converting NO_3^- under ambient conditions (Table 4). As summarized in the above section, metallic Cu has been intensively studied for the electroreduction of NO_3^- to NH_3 owing to its favorable adsorption ability for NO_3^- and various intermediates (*e.g.*, NO_2^- and NO). However, pure Cu catalysts still suffer from serious catalytic instability. For the purpose of overcoming this issue, substantial efforts have recently been made into the study of Cu-based oxide catalysts for highly-efficient electrochemical NO_3^- to NH_3 conversion.

For example, Yuan *et al.*[97] explored the influence of Cu oxidation state on the electrochemical reduction of NO_3^-, and found that the NH_3 formation rate and FE of a Cu electrode could be significantly boosted after surface oxidation. After that, Ren *et al.*[98] designed and fabricated core–shell structural $Cu@Cu_{2+1}O$ nanowires (Fig. 9a–c) for electrochemical conversion of NO_3^- to NH_3. In terms of the $Cu@Cu_{2+1}O$ catalyst, the interior metallic Cu components could provide pathways for fast electron transfer due to the one-dimensional nanowire structure, while the exterior $Cu_{2+1}O$ layer affords a massive amount of catalytically active sites. Furthermore, DFT calculation results suggested that the introduction of a surface oxidation layer regulated the Cu d-band center and modulated the adsorption energies of various intermediates. Therefore, the constructed $Cu@Cu_{2+1}O$ catalyst exhibited a high NH_3 yield rate of 576.53 μg h^{-1} mg^{-1} associated with a FE of 87.7% at −0.564 V *vs.* RHE, and NH_3 selectivity of 76% (Fig. 9d). Qin *et al.*[99] further illustrated the effects of the surface structure of Cu_2O (exposing facets) on NO_3^- reduction to NH_3. Both experimental and theoretical calculation results illustrated that the Cu_2O (100) facet featured a relatively smaller energy barrier for NH_3 formation than the Cu_2O (111) facet, leading to a large NH_3 formation rate (743 μg h^{-1} mg^{-1}) and high FE (82.3%) at −0.6 V *vs.* RHE.

Table 4 Summary of catalytic performance of transition-metal compound electrocatalysts

Catalyst	Electrolyte	NH_3 yield rate	Faradaic efficiency	Potentials (V *vs.* RHE)	Ref.
$Cu@Cu_{2+1}O$ nanowires	0.5 M K_2SO_4 + 50 mg L^{-1} NO_3^-	576.53 μg h^{-1} mg^{-1}	87.7%	−0.545	98
$CuO@MnO_2$	0.5 M K_2SO_4 + 100 mg L^{-1} NO_3^-	0.240 mmol h^{-1} cm^{-2}	94.92%	−0.645	104
CuO_x/TiO_2	0.5 M Na_2SO_4 + 100 ppm NO_3^-	1241.81 μg h^{-1} cm^{-2}	92.34%	−0.75	105
TiO_{2-x} nanotubes	0.5 M Na_2SO_4 + 50 ppm NO_3^-	0.045 mmol h^{-1} mg^{-1}	85%	−0.945	109
Co-doped TiO_2 nanosheet	0.1 M NaOH + 0.1 M NO_3^-	1127 μmol h^{-1} cm^{-2}	98.2%	$-0.9^a/-0.5^b$	111
$Co@TiO_2$	0.1 M PBS + 0.1 M NO_3^-	800 μmol h^{-1} cm^{-2}	96.7%	$-1.0^a/-0.7^b$	112
$FeS_2@TiO_2$	0.1 M NaOH + 0.1 M $NaNO_3$	860.3 μmol h^{-1} cm^{-2}	97.0%	$-0.7^a/-0.4^b$	114
Cu-doped Co_3O_4 nanowire	0.1 M Na_2SO_4 + 500 ppm NO_3^-	36.71 mmol h^{-1} g^{-1}	86.5%	−0.6	117
Co_3O_4 nanosheets with Co vacancies	0.1 M NaOH + 0.1 M $NaNO_3$	517.5 μmol h^{-1} cm^{-2}	97.2%	$-0.6^a/-0.4^b$	118
$NiCo_2O_4$ nanowire	0.1 M KOH + 0.1 M $NaNO_3$	973.2 μmol h^{-1} cm^{-2}	99.0%	$-0.6^a/-0.3^b$	121
$ZnCo_2O_4$ nanoarray	0.1 M KOH + 0.1 M $NaNO_3$	634.74 mmol h^{-1} cm^{-2}	98.33%	$-0.8^a/-0.6^b$	122
BCDs/$NiCo_2O_4$ nanowire	0.5 M K_2SO_4 + 200 ppm NO_3^-	173.9 μmol h^{-1} cm^{-2}	100%	−0.55	124
$CuO@Co_3O_4$	1 M KOH + 1400 ppm NO_3^-	1.915 mmol h^{-1} cm^{-2}	99.17%	−0.23	125
Co-doped Fe/Fe_2O_3	0.1 M Na_2SO_4 + 50 ppm NO_3^-	1505.9 μg h^{-1} cm^{-2}	85.2%	−0.95	135
$CoTiO_{3-x}$ nanofibers	0.1 M NaOH + 0.1 M $NaNO_3$	30.4 mg h^{-1} mg_{cat}^{-1}	92.6%	$-1.1^a/-1.0^b$	136
$CuWO_4$ nanospheres	0.5 M Na_2SO_4 + 0.05 M $NaNO_3$	5.84 mg h^{-1} mg^{-1}	94.6%	−0.7	137
Cu_3P nanowires	0.1 M PBS + 0.1 M $NaNO_3$	1626.6 ± 36.1 μg h^{-1} cm^{-2}	91.2 ± 2.5%	−0.5	141
CoP nanosheets	1.0 M NaOH + 1.0 M $NaNO_3$	9.56 mol h^{-1} m^{-2}	100%	−0.3	143
Bi_2S_3/MoS_2	0.1 M Na_2SO_4 + 0.1 M $NaNO_3$	15.04×10^{-2} mmol h^{-1} cm^{-2}	88.4%	−0.8	146
Ni_3N nanoparticles	0.5 M Na_2SO_4 + 0.5 M $NaNO_3$	9.185 mmol h^{-1} mg^{-1}	89.5%	−0.795	148
Fe_3C nanoflakes	1 M KOH + 75 mM KNO_3	1.19 mmol h^{-1} mg^{-1}	96.7%	−0.5	150

[a] NH_3 yield rate. [b] Faradaic efficiency.

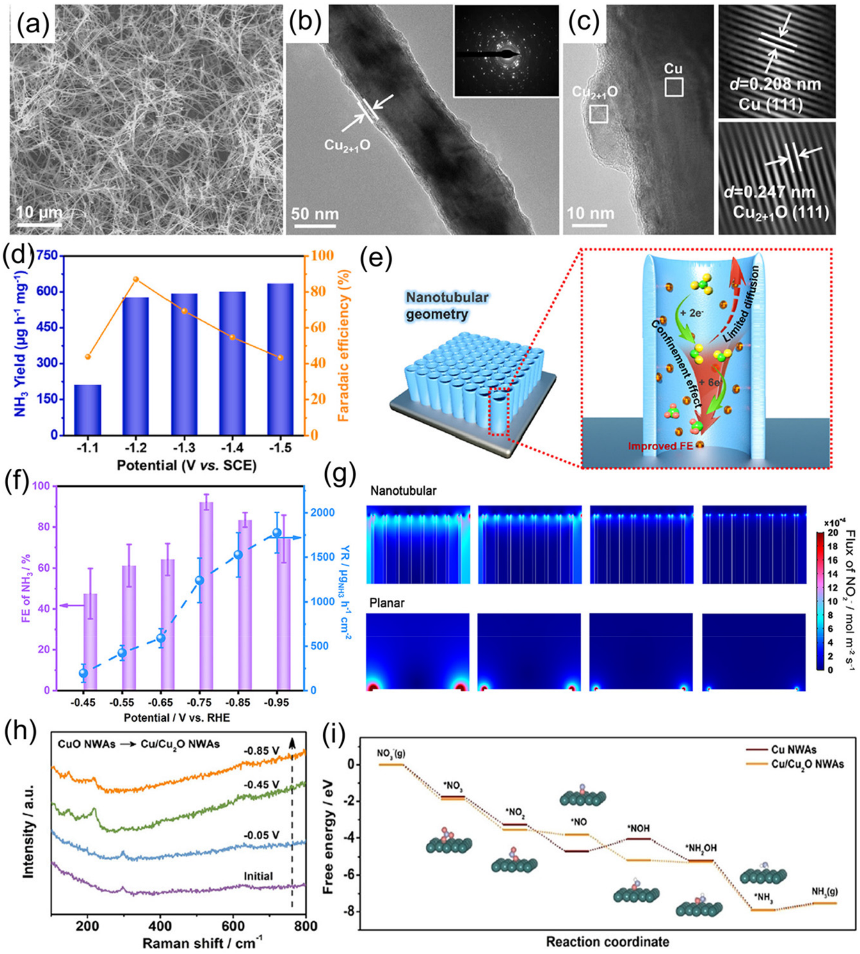

Fig. 9 (a) SEM, (b) TEM and (c) HRTEM images of Cu@$Cu_{2+1}O$ nanowires. (d) NH_3 formation rate and FE of Cu@$Cu_{2+1}O$ nanowires under the applied potentials. Reproduced from ref. 98 with permission from Elsevier, copyright 2021. (e) Schematic illustration of NO_3^--to-NH_3 reduction over electrodes with nanotubular geometries. (f) NH_3 FE and yield rate of CuO_x/TiO_2 at varying potentials. (g) Simulated NO_2^- concentration distribution on nanotubular and planar geometries. Reproduced from ref. 105 with permission from Elsevier, copyright 2022. (h) *In situ* electrochemical Raman spectra of CuO nanowires at given potentials. (i) Free-energy diagram for the NO_3^-RR over Cu nanowires. Reproduced from ref. 106 with permission from Wiley-VCH, copyright 2020.

To further enhance the electrocatalytic activity of Cu_2O toward the NO_3^-RR, various strategies have been employed, such as introducing oxygen defects[100,101] and constructing heterostructures.[79,102,103] For example, Xu *et al.*[104] designed core–shell structural CuO@MnO_2 hierarchical nanoarrays grown on Cu foam (CuO@MnO_2/CF) for the NO_3^-RR. The heterointerface between the CuO nanowires and MnO_2 nanosheets enabled abundant catalytically active sites and induced the formation of a built-in electric field, which were beneficial to the capture of NO_3^- and various intermediates during the electrochemical reactions, as well as accelerate ionic/electronic transfer at the interface. With these properties, CuO@MnO_2/CF achieved an impressive electrochemical performance including a very-high NO_3^- conversion of 99.38%, NH_3 FE of 94.92%, and selectivity of 96.67%. Meanwhile, this catalyst exhibits excellent stability, maintaining the NH_3 yield rate and FE after 5 consecutive recycling tests. Qiu *et al.*[105] incorporated CuO_x nanoparticles into a TiO_2-nanotube reactor for highly selective conversion of NO_3^- to NH_3. In this CuO_x/TiO_2 catalyst system, TiO_2 nanotubes could efficiently hinder the diffusion of NO_2^- intermediate and promote the conversion of NO_3^- to NH_3 (Fig. 9e and g). The constructed CuO_x/TiO_2 heterostructure achieved a yield rate of 1241.81 μg h^{-1} cm^{-2}, a high FE of 92.93% (Fig. 9f), and outstanding durability with a stable FE during the ten successive cycles of electrolysis.

Cu-based oxidation catalysts present outstanding electrochemical activity toward selective reduction of NO_3^- to NH_3, but the origin of their activity and the structural evolution that occurs during the electrochemical reaction process were still experimentally unclear. In this regard, Zhang and his co-workers applied *in situ* characterization techniques to unveil the active phase of the CuO electrocatalyst. Experimental results suggested that CuO was transformed to Cu/Cu_2O during the reduction process of NO_3^-, and served as an active phase for NO_3^- conversion (Fig. 9h). Then, online differential electrochemical mass spectrometry was adopted to analyze the reaction pathway. NO_3^- adsorbed on the surface of electrode was firstly reduced to $*NO_2$ and *NO, in which *NO was hydrogenated to give *NHON and $*NH_2OH$. Subsequently, $*NH_2OH$ was converted to $*NH_3$ and further desorbed from the surface of the electrode generating NH_3. DFT calculations also discovered that the origin of the activity enhancement was attributed to the reconstructed structure, in which electron transfer from Cu_2O to Cu at the interface could promote the generation of the *NOH intermediate and limit the competing HER (Fig. 9i).[106]

3.4.1.2 Titanium-based oxides. Titanium oxide (TiO_2) is a promising electrocatalyst candidate for the electrochemical reduction of NO_3^- owing to its advantages in terms of cost and robustness.[107,108] For example, Jia *et al.*[109] fabricated TiO_2 nanotubes rich in oxygen vacancies as an electrocatalyst for the NO_3^-RR. An outstanding conversion rate of 95.2% for NH_3 production from NO_3^- electroreduction associated with a FE of 85% was achieved. DFT calculations revealed that NO_3^- was adsorbed on the surface of the electrode and preferentially filled the oxygen defects existing in the TiO_2 nanotubes, which weakened the N–O bonding, modulated the adsorption energies of the intermediates, and limited the generation of by-products. Analogously, oxygen-vacancy-TiO_2 nanomaterials composed of rutile and anatase phases were fabricated as a catalyst for NH_3 synthesis from the electroreduction of NO_3^-, which could deliver an NH_3 FE of 78.0% and selectivity of 81.9%. Online differential electrochemical mass spectrometry and first-principle calculations revealed that the existence of oxygen vacancies (Ti^{3+}) and the heterointerface between the rutile and anatase phases were favorable for modulating the adsorption energy of NO_3^- and facilitating the hydrogenation reaction to form *NOH, which led to a relatively high NH_3 selectivity and FE.[110] However, the limited selectivity for NH_3 and sluggish reaction kinetics hinder their further application for NH_3 electrosynthesis.

In this regard, our group proposed a series of modification strategies for improving the above-mentioned issues, such as heteroatom doping, and constructing Schottky junctions and p–n heterojunctions. For example, taking a Co-based catalyst with high catalytic activity into consideration, we introduced Co heteroatoms into a TiO_2 nanoribbon array supported on Ti foil for electroreduction of NO_3^- (Fig. 10a and b). Co-doping can effectively improve the intrinsic electronic conductivity of TiO_2 and increase the content of oxygen defects in TiO_2, which further facilitates the adsorption of NO_3^- and transportation of charge at the interface, as well as decreasing the energy barrier of the potential-determining step (Fig. 10c). As a result, Co-doped TiO_2 nanoribbon arrays delivered a large NH_3 production rate of 1127 μmol h^{-1} cm^{-2} and a high FE of 98.2%, which was remarkably superior to that of its counterpart in alkaline media (88.5 μmol h^{-1} cm^{-2}; 35.1%), as presented in Fig. 10d and e.[111] Inspired by this, we further constructed a Schottky junction by integrating metallic Co nanoparticles into TiO_2 nanobelt arrays (Co@TiO_2) (Fig. 10f and g). A built-in electric field formed at the heterointerface between Co and TiO_2, which was beneficial for the capture of NO_3^- on the

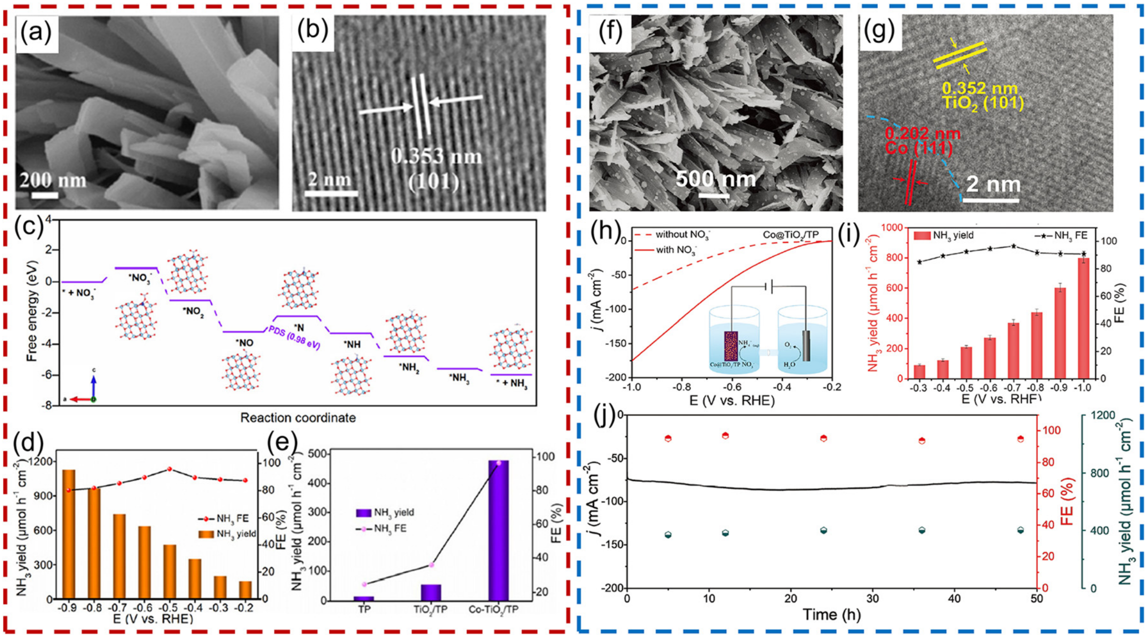

Fig. 10 (a) SEM and (b) HRTEM images of Co-doped TiO_2. (c) Calculated free-energy changes of the NO_3^-RR on the Co-doped TiO_2. (d) NH_3 yield rate and FE of Co-doped TiO_2 under given potentials. (e) Comparison of NH_3 yield rate and FE between TiO_2 and Co-doped TiO_2. Reproduced from ref. 111 with permission from The Royal Society of Chemistry, copyright 2022. (f) SEM and (g) HRTEM images of Co@TiO_2 heterojunction catalyst. (h) LSV curves and (i) NH_3 formation rate and FE at given potentials for Co@TiO_2. (j) The long-term electrocatalytic performance of the Co@TiO_2 catalyst. Reproduced from ref. 112 with permission from Wiley-VCH, copyright 2023.

surface of the electrocatalyst and thus facilitated mass transfer during the electroreduction process of NO_3^-. Consequently, in a neutral medium containing 0.1 M NO_3^-, the as-designed Co@TiO_2 catalyst enabled a high NH_3 FE of 96.7% at −0.7 V *vs.* RHE and a competitive NH_3 formation rate of 800 μmol h^{-1} cm^{-2} at −1.0 V (Fig. 10h and i). Meanwhile, this catalyst also showed impressive durability during recycling tests and 50 h of bulk electrolysis (Fig. 10j).[112] Following this, Fe_3O_4@TiO_2,[113] CoP@TiO_2 [114] and FeS_2@TiO_2 [115] p–n heterojunctions were constructed by our team and utilized as electrocatalysts to convert NO_3^- to NH_3, where the selectivity and efficiency of bare TiO_2 for the NO_3^-RR were significantly enhanced.

3.4.1.3 Spinel oxide. Spinel-type oxides feature unique advantages in terms of versatility, flexible ion arrangement, multivalence structure, and superior electronic conductivity, making them promising electrocatalysts for the NO_3^-RR.[116] For example, Co_3O_4 has been extensively utilized as a catalyst for the electroreduction of NO_3^-, but its yield rate and selectivity of the target product NH_3 are relatively low.[117] To enhance the electrocatalytic activity of Co_3O_4, our group[118] designed Co_3O_4 nanosheet arrays with Co vacancies on carbon cloth for converting NO_3^- to NH_3 (Fig. 11a and b). As presented in Fig. 11c and d, Co_3O_4 with Co vacancies delivered a high NH_3 yield rate of 517.5 μmol h^{-1} g^{-1} and a maximum FE of 97.2% at −0.6 and −0.4 V *vs.* RHE in alkaline electrolyte, respectively, which were higher than those of bare Co_3O_4 nanosheets (183.8 μmol h^{-1} g^{-1} with a FE of 85.9%). Furthermore, DFT calculations demonstrated that the introduction of Co vacancies regulated the electron structure of Co_3O_4, optimized the adsorption energy of NO_3^- and reduced the energy barrier of the potential-determining step (*NHO to *NHOH), leading to the high electrocatalytic activity (Fig. 11e and f). Similarly, we adopted Fe as a dopant to modulate the electron structure of Co_3O_4, further elevating its selectivity and NH_3 yield rate during the electroreduction of NO_3^-.[119] In line with the above-mentioned viewpoint, many bimetal spinel oxides, such as $FeCo_2O_4$,[120] $NiCo_2O_4$,[121] $ZnCo_2O_4$,[122] $AlCo_2O_4$,[77] and $NiFe_2O_4$,[123] have been synthesized and investigated as electrocatalysts for a highly efficient NO_3^-RR by our team. As demonstrated in Fig. 11g and h, $NiCo_2O_4$ nanowire arrays grown on carbon cloth were synthesized for electrochemical NH_3 production by conversion of NO_3^-. Owing to the synergistic effects of the two metal sites, $NiCo_2O_4$ nanowire arrays attained a large NH_3 formation rate of 973.2 μmol h^{-1} cm^{-2} and large FE of 99.0% (Fig. 11i and j) in 0.1 M KOH with 0.1 M $NaNO_3$.

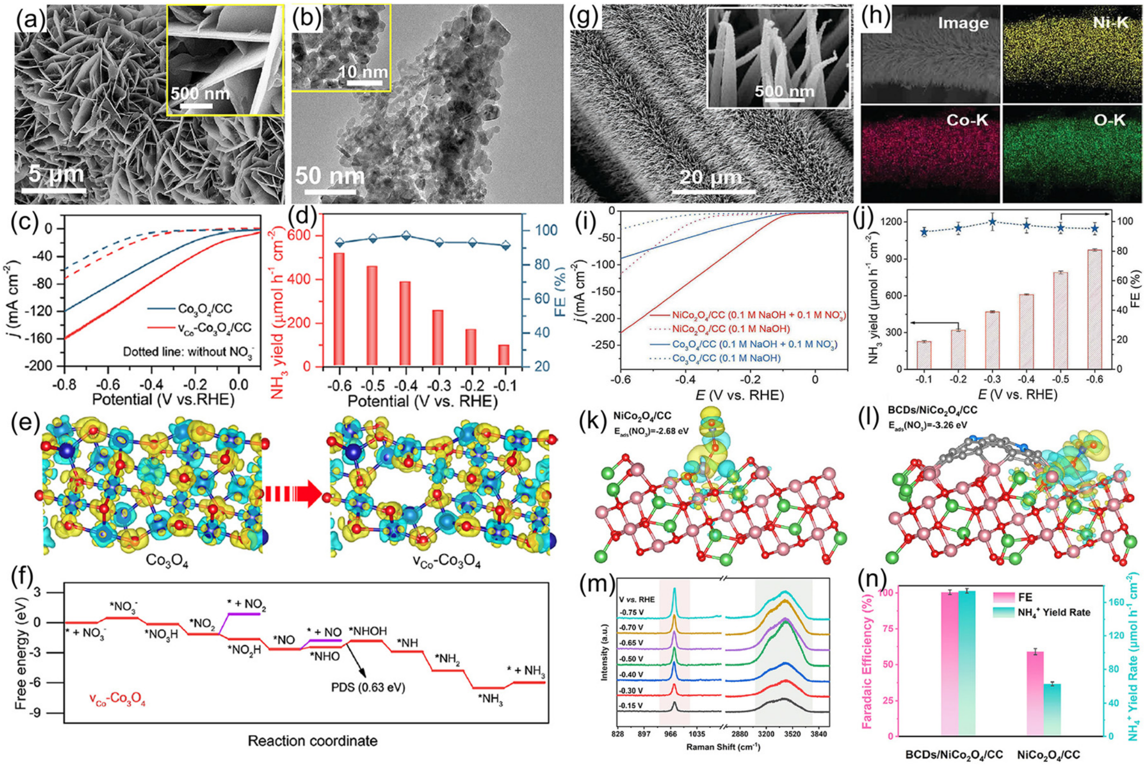

Fig. 11 (a) SEM and (b) TEM images of Co_3O_4 nanosheets with Co vacancies. (c) LSV curves and (d) NH_3 yield rate, FE under different potentials for Co_3O_4 nanosheets with Co vacancies. (e) Charge density distribution of Co_3O_4 with/without Co vacancies. (f) Free-energy diagrams for the NO_3^-RR on Co_3O_4 with Co vacancies. Reproduced from ref. 118 with permission from the American Chemical Society, copyright 2022. (g and h) SEM and mapping images of $NiCo_2O_4$. (i) LSV curves and (j) yield rate and FE of NH_3 under given potentials. Reproduced from ref. 121 with permission from the Wiley-VCH, copyright 2022. Charge-density difference for NO_3^- adsorption on $NiCo_2O_4$ (k) and BCDs/$NiCo_2O_4$ (l). (m) *In situ* Raman spectra of NO_3^-RR over BCDs/$NiCo_2O_4$ at different applied potentials. (n) Comparison of NH_3 FEs and yield rate of BCDs/$NiCo_2O_4$ and $NiCo_2O_4$. Reproduced from ref. 124 with permission from the Elsevier, copyright 2022.

Impressively, the as-designed $NiCo_2O_4$ nanowires displayed exceptional durability with no significant fluctuations in both NH_3 production rate and FE after 16 successive electrolysis experiments. After that, taking the Lewis-base property of NO_3^- into consideration, Lu *et al.*[124] further introduced abundant Lewis acid sites on the surface of $NiCo_2O_4$ nanowire arrays for increasing the adsorption energy of NO_3^- by coupling with boron-doped carbon dots (BCDs/$NiCo_2O_4$). As revealed in Fig. 11k and l, the incorporation of BCDs enhanced the adsorption energy of NO_3^- on the surface of the BCDs/$NiCo_2O_4$ electrode. Meanwhile, *in situ* Raman spectra shown in Fig. 11m suggested that the intensity of the peak at 975 cm^{-1} associated with the N–O stretching vibration was boosted under the applied potentials, indicating that the Lewis acid sites induced by BCD doping were critically important for enhancing the adsorption ability of NO_3^-. As expected, the BCDs/$NiCo_2O_4$ catalyst provided a nearly ~100% FE and a large NH_3 production rate of 173.9 μmol h^{-1} cm^{-2} at −0.55 V *vs.* RHE (Fig. 11n).

Co_3O_4 as an electrocatalyst for the NO_3^-RR still suffers from the critical issue that it is difficult to electrochemically reduce NO_3^- to NO_2^- using this catalyst. As mentioned above, Cu-based materials possess excellent electrocatalytic activity for NO_3^- to NO_2^-, and thus constructing a Co_3O_4-based heterostructure with Cu-based materials could achieve promising electrochemical performance. Liu *et al.*[125] fabricated Co_3O_4 grown on CuO nanowire arrays to construct a hierarchical heterostructure for an efficient NO_3^-RR. At −0.23 V *vs.* RHE, CuO@Co_3O_4 provided an NH_3 yield rate of 1.915 mmol h^{-1} cm^{-2}, which was higher than those of CuO and Co_3O_4. Fu *et al.*[126] built dual active sites on a Co_3O_4/Cu electrode, in which Cu focused on the reduction of NO_3^- to NO_2^-, and then Co_3O_4 generated H* (active hydrogen) as a strong reducing agent to further convert NO_2^- to NH_3. As a result, the Co_3O_4/Cu catalyst presented a large NH_3 yield rate of 684 μg mg^{-1} h^{-1} with 94.6% FE. Recently, Fan *et al.*[127] fabricated a Co_3O_4 nanosheet grown *in situ* on TiO_2 nanosheet arrays for the NO_3^-RR, which gave a large NH_3 yield rate of 875 μmol mg^{-1} h^{-1} and a high FE of 93.1% in alkaline electrolyte.

3.4.1.4 Other metal oxides. Other types of transition-metal oxides have also been investigated for the NO_3^-RR, such as Bi_2O_3, Mn_3O_4, $BiFeO_3$, and La_2CuO_4.[128–131] However, the inferior electronic conductivity of metal oxides hinders their electrocatalytic activity. Currently, regulating their electronic structure through oxygen-defect engineering is a promising strategy.[132,133] For instance, Wang *et al.*[134] fabricated ultrathin CoO_x nanosheets with abundant surface oxygen as an NO_3^-RR catalyst, attaining a large NH_3 yield of 82.4 ± 4.8 mg h^{-1} mg^{-1} with a FE of 93.4 ± 3.8% at −0.3 V *vs.* RHE. The surface oxygen on the Co sites was prone to stabilize the adsorbed hydrogen on CoO_x, and thus efficiently suppressed the formation of H_2 and achieved a high selectivity for NH_3 synthesis. Zhang *et al.*[135] reported a Co-doped Fe/Fe_2O_3 catalyst for electrochemical NH_3 synthesis by reducing NO_3^- under ambient conditions. This catalyst afforded an NH_3 production rate of 1505.9 μg h^{-1} cm^{-2} with a FE of 85.2% and a high NH_3 selectivity of 99.0%. Recently, our group reported that $CoTiO_{3-x}$ nanofibers with oxygen vacancies showed an NH_3 formation rate of 30.4 mg h^{-1} mg^{-1} and a large FE of 92.6% in 0.1 M NaOH solution containing 0.1 M NO_3^-.[136] The $CuWO_4$ hollow nanospheres with oxygen vacancies showed a high NH_3 FE of 94.6% and yield rate of 5.84 mg h^{-1} mg^{-1} at −0.7 V *vs.* RHE.[137]

3.4.2 Metal phosphides. Metal phosphides featuring metallic characteristics and high catalytic activities for the HER have become fascinating electrocatalysts for converting NO_3^- to NH_3, which is attributed to the fact that they can afford hydrogen at a small overpotential during the electroreduction process. So far, many transition-metal phosphides, such as CoP, Ni_2P, and Cu_3P, have been used as catalysts for NH_3 electrosynthesis.[138–142] For example, Ye *et al.*[143] reported that CoP nanosheet arrays supported on carbon cloth exhibited a molar level NH_3 formation rate of 9.56 mol h^{-1} m^{-2} at −0.3 V *vs.* RHE with a FE of ~100% under alkaline conditions (Fig. 12a–c). Furthermore, the reaction mechanism of the NO_3^-RR on the surface of CoP was investigated by coupling *in situ* characterization technology and theoretical calculations (Fig. 12d and e). As presented in Fig. 12f, Co 4p orbitals directly participated in the adsorption of NO_3^- *via* Co–O–N bonds and the electron-transfer step of the NO_3^-RR, while phosphorus within CoP could stabilize the active phase and reduce the reaction-energy barrier of the rate-determining step during the electroreduction of NO_3^-, thus leading to a highly selective electrosynthesis of NH_3 from NO_3^-. Ni_2P nanoparticles supported on Ni foam were synthesized and regarded as an electrocatalyst for electrochemically converting NO_3^- to NH_3 in neutral media with 50 mM NO_3^-. A high NH_3 evolving rate of 0.056 mmol h^{-1} cm^{-2} with a FE of 99.23%, and a selectivity of 89.1% were obtained.[144] As shown in Fig. 12g, our group[141] synthesized Cu_3P nanowire arrays anchored on copper foam for electrochemical conversion of NO_3^- to NH_3 in neutral media. In 0.1 M phosphate-buffered saline (PBS) containing 0.1 M $NaNO_3$, a Cu_3P nanowire catalyst delivered a large NH_3 formation rate of 848.7 ± 18.0 μg h^{-1} cm^{-2} and a high FE of 62.9 ± 2.0% at −0.6 V *vs.* RHE (Fig. 12h and i).

3.4.3 Other metal compounds. Recently, other metal compounds have also been applied as electrocatalysts for NO_3^- to NH_3 conversion at room temperature.[145–147] Zhang *et al.*[148] fabricated Ni_3N nanoparticles embedded on a carbon skeleton and investigated its electrochemical performance as a catalyst for the NO_3^-RR. This catalyst provided a high NH_3 selectivity of 89.5% and large yield rate of 9.185 mmol h^{-1} mg^{-1} at −0.795 V *vs.* RHE in neutral media. Amorphous CoB_x nanoparticles anchored on carbon paper were synthesized *via* a simple wet chemical reduction method. When used for electroreduction of NO_3^- to NH_3, CoB_x afforded a maximum FE of 94.0% and a yield rate of up to 0.787 mmol h^{-1} cm^{-2}.[149] Wang *et al.*[150] reported that Fe_3C nanoflakes embedded on N-doped carbon nanosheets displayed an NH_3 yield rate of 1.19 mmol h^{-1} mg^{-1}, NH_3 FE of 96.7%, and selectivity of 79.0% at −0.5 V *vs.* RHE.

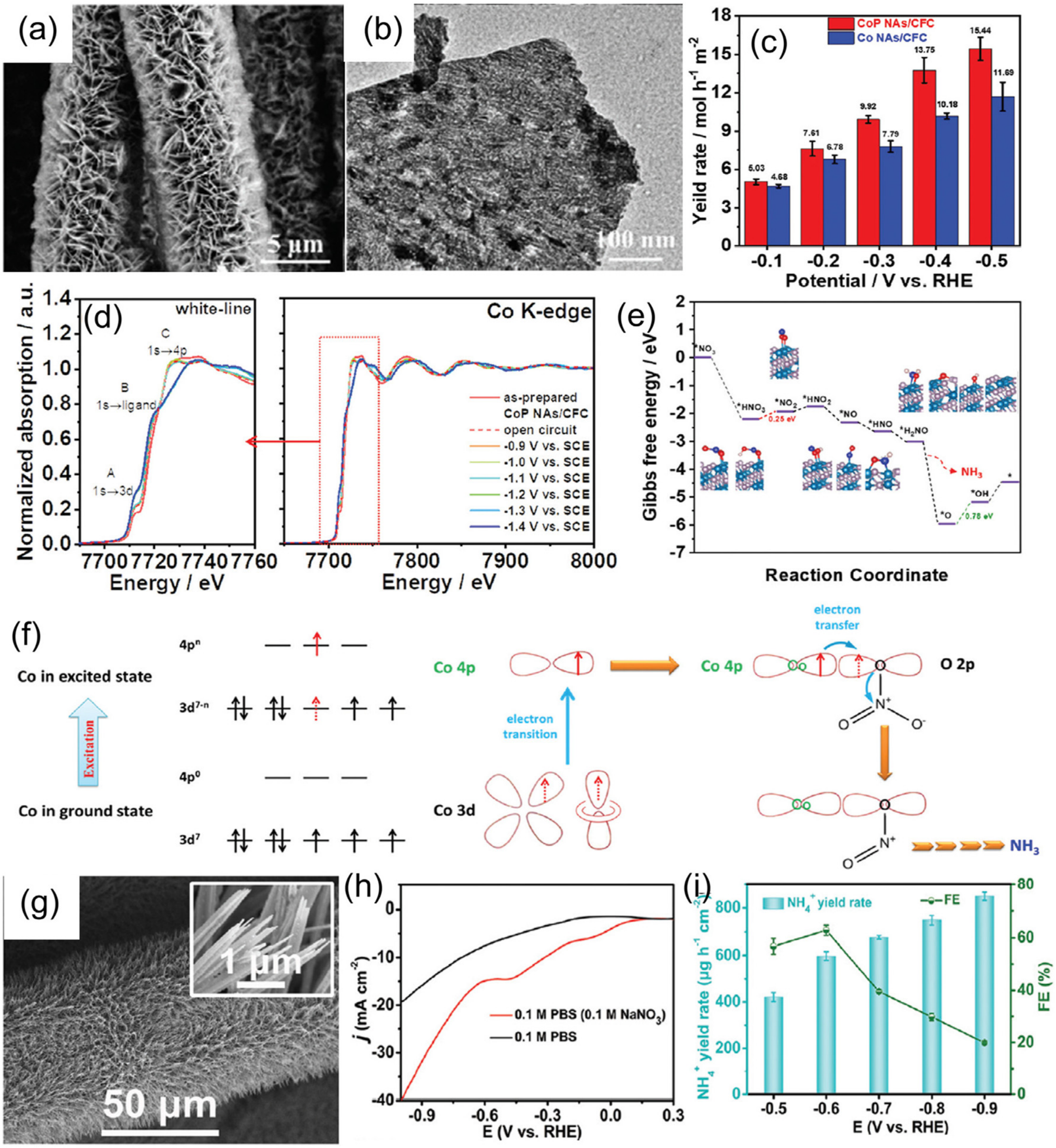

Fig. 12 (a) SEM and (b) TEM images of CoP. (c) NH_3 yield rate of CoP at given potentials. (d) *In situ* XANES of the Co K-edge of CoP. (e) Gibbs free-energy diagram of the NO_3^-RR on CoP. (f) Mechanism of the NO_3^-RR on CoP. Reproduced from ref. 143 with permission from The Royal Society of Chemistry, copyright 2022. (g) SEM image of Cu_3P. (h) LSV curve, (i) NH_3 yield rate and FE of Cu_3P in $NaNO_3$. Reproduced from ref. 141 with permission from The Royal Society of Chemistry, copyright 2021.

4. Conclusions

The electrochemical NO_3^-RR has opened up a green and sustainable route for NH_3 synthesis under ambient conditions, which is associated with two advantages: (i) the electrochemical NH_3 synthesis from NO_3^- utilizes water as a proton source and is powered by renewable energy, which means that this process avoids the utilization of fossil fuels and reduces the NH_3 production cost; (ii) the benign reaction conditions of the conversion of NO_3^- would enable distributed NH_3 production in smaller-scale devices, which facilitates the production of fertilizer on demand and realizes a neutral carbon footprint. The important electrochemical characteristics of NH_3 yield rate, Faradaic efficiency and selectivity largely depend on the electrocatalysts. Therefore, this review briefly describes the electroreduction mechanism from NO_3^- to NH_3 under mild environmental conditions and summarizes the recent development of various electrocatalysts including noble-metal-based materials, single-atom metal catalysts, and transition-metal-based materials. Meanwhile, various effective design strategies for enhancing the electrocatalytic activity are outlined. Furthermore, it provides profound insights into the knowledge behind various optimization strategies, which are imperative for the development of highly-efficient electrocatalysts for the electrochemical conversion of NO_3^- to NH_3. Although considerable progress has been achieved so far, the following points should also be considered in this field:

(i) As mentioned in the discussion above, ongoing research into electrochemical NH_3 synthesis from NO_3^- mainly focuses on the design and investigation of metal-based materials; less attention has been given to the exploration of metal-free electrocatalysts. From the energy-saving and emission-reduction points of view, it is of great significance to explore metal-free electrocatalysts with high activity, large selectivity and excellent stability for enabling the electrocatalytic NO_3^-RR under ambient conditions. As a consequence, more attention should be given to elaborately developing carbon-based electrocatalysts for the NO_3^-RR, providing an alluring strategy for large-scale NH_3 production.

(ii) The electrochemical NO_3^-RR, as an emerging strategy for NH_3 production under ambient conditions, has attained a dramatic growth in interest and various catalysts have been investigated in this field. However, none of the suitable catalysts can be regarded as a benchmark catalyst for electrocatalytic NO_3^-RR research. Besides, the variety of experimental details, such as the pH value of the electrolyte and the concentration of the nitrogen resource, play a critical role in catalytic activity and selectivity, and their effects on the electrochemical performance remain to be thoroughly studied. Such issues lead to incomparable results and thus limit the mutual communication and promotion in the community. Therefore, finding a standard catalyst and unification of experimental parameters are urgently required in the field of the electrochemical NO_3^-RR.

(iii) Many catalysts have exhibited superior catalytic activity and high NH_3 selectivity during the electrochemical NO_3^-RR process, but their catalytic mechanisms and reaction processes were only revealed by theoretical calculations and remain unclear experimentally. For this reason, *in situ* characterization to scrutinize the pristine catalyst surface evolution (surface structure, element valence state, and exposed active sites) and adsorbed intermediates should be elaborately developed to uncover the real catalytic sites and reaction pathways upon the electrochemical reaction process for the rational design of electrocatalysts for the NO_3^-RR.

(iv) From the point of view of practical application, besides the fact that the electrochemical NO_3^-RR to NH_3 process is still developing and lacks a catalyst with excellent durability and performance for supporting long-term electrolysis at the moment, another challenge is that this process will generate a tremendous amount of H_2 as a side-product during the electrolysis, which is directly vented off into the atmosphere, forming a safety issue. Therefore, tremendous efforts are required before the electrochemical NO_3^-RR to NH_3 can be put into practical operation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding support through large group Research Project under Grant No. RGP2/199/44.

References

1 S. L. Foster, S. I. P. Bakovic, R. D. Duda, S. Maheshwari, R. D. Milton, S. D. Minteer, M. J. Janik, J. N. Renner and L. F. Greenlee, Catalysts for nitrogen reduction to ammonia, *Nat. Catal.*, 2018, **1**, 490–500.

2 Y. C. Wan, J. C. Xu and R. T. Lv, Heterogeneous electrocatalysts design for nitrogen reduction reaction under ambient conditions, *Mater. Today*, 2019, **27**, 69–90.

3 J. Liang, Q. Liu, A. A. Alshehri and X. Sun, Recent advances in nanostructured heterogeneous catalysts for N-cycle electrocatalysis, *Nano Res. Energy*, 2022, **1**, e9120010.

4 J. W. S. Erisman, M. A. Sutton, J. Galloway, Z. Klimont and W. Winiwarter, How a century of ammonia synthesis changed the world. W, *Nat. Geosci.*, 2008, **1**, 636–639.

5 R. Schlogl, Catalytic synthesis of ammonia—A "never-ending story"?, *Angew. Chem., Int. Ed.*, 2003, **42**, 2004–2008.

6 C. Philibert, Renewable energy for industry: from green energy to green materials and fuels, IEA Report, 2017.

7 J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis, P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider and R. R. Schrock, Beyond fossil fuel–driven nitrogen transformations, *Science*, 2018, **360**, eaar6611.

8 L. Wang, M. Xia, H. Wang, K. Huang, C. Qian, C. T. Maravelias and G. A. Ozin, Greening ammonia toward the solar ammonia refinery, *Joule*, 2018, **2**, 1055–1074.

9 B. Ma, H. Zhao, T. Li, Q. Liu, Y. Luo, C. Li, S. Lu, A. M. Asiri, D. Ma and X. Sun, Iron-group electrocatalysts for ambient nitrogen reduction reaction in aqueous media, *Nano Res.*, 2021, **14**, 555–569.

10 X. Zhu, S. Mou, Q. Peng, Q. Liu, Y. Luo, G. Chen, S. Gao and X. Sun, Aqueous electrocatalytic N_2 reduction for ambient NH_3 synthesis: recent advances in catalyst development and performance improvement, *J. Mater. Chem. A*, 2020, **8**, 1545–1556.

11 C. Tang and S. Z. Qiao, How to explore ambient electrocatalytic nitrogen reduction reliably and insightfully, *Chem. Soc. Rev.*, 2019, **48**, 3166–3180.

12 T. Xu, B. Ma, J. Liang, L. Yue, Q. Liu, T. Li, H. Zhao, Y. Luo, S. Lu and X. Sun, Recent progress in metal-free electrocatalysts toward ambient N_2 reduction reaction, *Acta Phys.–Chim. Sin.*, 2021, **37**, 2009043.

13 Q. Liu, T. Xu, Y. Luo, Q. Kong, T. Li, S. Lu, A. A. Alshehri, K. A. Alzahrani and X. Sun, Recent advances in strategies for highly selective electrocatalytic N_2 reduction toward ambient NH_3 synthesis, *Curr. Opin. Electrochem.*, 2021, **29**, 100766.

14 D. Liu, M. Chen, X. Du, H. Ai, K. H. Lo, S. Wang, S. Chen, G. Xing, X. Wang and H. Pan, Development of electrocatalysts for efficient nitrogen reduction reaction under ambient condition, *Adv. Funct. Mater.*, 2021, **31**, 2008983.

15 P. H. van Langevelde, I. Katsounaros and M. T. M. Koper, Electrocatalytic nitrate reduction for sustainable ammonia production, *Joule*, 2021, **5**, 290–294.

16 Y. Xu, K. Shi, T. Ren, H. Yu, K. Deng, X. Wang, H. Wang and L. Wang, Electronic metal-support interaction triggering interfacial charge polarization over CuPd/N-doped-C nanohybrids drives selectively electrocatalytic conversion of nitrate to ammonia, *Small*, 2022, **18**, 2203335.

17 Y. Wang, C. Wang, M. Li, Y. Yu and B. Zhang, Nitrate electroreduction: mechanism insight, in situ characterization, performance evaluation, and challenges, *Chem. Soc. Rev.*, 2021, **50**, 6720–6733.

18 D. Anastasiadou, Y. van Beek, E. J. M. Hensen and M. C. Figueiredo, Ammonia electrocatalytic synthesis from nitrate, *Electrochem. Sci. Adv.*, 2022, DOI: **10.1002/elsa.202100220**.

19 J. Theerthagiri, J. Park, H. T. Das, N. Rahamathulla, E. S. F. Cardoso, A. P. Murthy, G. Maia, D. V. N. Vo and M. Y. Choi, Electrocatalytic conversion of nitrate waste into ammonia: a review, *Environ. Chem. Lett.*, 2022, **20**, 2929–2949.

20 H. Xu, Y. Ma, J. Chen, W. X. Zhang and J. Yang, Electrocatalytic reduction of nitrate–A step towards a sustainable nitrogen cycle, *Chem. Soc. Rev.*, 2022, **51**, 2710.

21 Z. Li, Z. Deng, L. Ouyang, X. Fan, L. Zhang, S. Sun, Q. Liu, A. A. Alshehri, Y. Luo, Q. Kong and X. Sun, CeO_2 nanoparticles with oxygen vacancies decorated N-doped carbon nanorods: A highly efficient catalyst for nitrate electroreduction to ammonia, *Nano Res.*, 2022, **15**, 8914–8921.

22 Q. Liu, Q. Liu, L. Xie, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, L. Yu and X. Sun, A 3D FeOOH nanotube array: an efficient catalyst for ammonia electrosynthesis by nitrite reduction, *Chem. Commun.*, 2022, **58**, 5160–5163.

23 Y. Arikawa, Y. Otsubo, H. Fujino, S. Horiuchi, E. Sakuda and K. Umakoshi, Nitrite reduction cycle on a dinuclear ruthenium complex producing ammonia, *J. Am. Chem. Soc.*, 2018, **140**, 842–847.

24 H. Chen, C. Zhang, L. Sheng, M. Wang, W. Fu, S. Gao, Z. Zhang, S. Chen, R. Si, L. Wang and B. Yang, Copper single-atom catalyst as a high-performance electrocatalyst for nitrate-ammonium conversion, *J. Hazard. Mater.*, 2022, **434**, 128892.

25 Y. Zeng, C. Priest, G. Wang and G. Wu, Restoring the nitrogen cycle by electrochemical reduction of nitrate: progress and prospects, *Small Methods*, 2020, **4**, 2000672.

26 X. Zhang, Y. Wang, C. Liu, Y. Yu, S. Lu and B. Zhang, Recent advances in non-noble metal electrocatalysts for nitrate reduction, *Chem. Eng. J.*, 2021, **403**, 126269.

27 S. Garcia-Segura, M. Lanzarini-Lopes, K. Hristovski and P. Westerhoff, Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications, *Appl. Catal., B*, 2018, **236**, 546–568.

28 M. D. V. Rosca, M. T. de Groot and M. T. M. Koper, Nitrogen cycle electrocatalysis, *Chem. Rev.*, 2009, **109**, 2209–2244.

29 M. T. de Groot and M. T. M. Koper, The influence of nitrate concentration and acidity on the electrocatalytic reduction of nitrate on platinum, *J. Electroanal. Chem.*, 2004, **562**, 81–94.

30 R. Lange, E. Maisonhaute, R. Robin and V. Vivier, On the kinetics of the nitrate reduction in concentrated nitric acid, *Electrochem. Commun.*, 2013, **29**, 25–28.

31 D. Sicsic, F. Balbaud-Célérier and B. Tribollet, Mechanism of nitric acid reduction and kinetic modelling, *Eur. J. Inorg. Chem.*, 2014, **2014**, 6174–6184.

32 D. Xu, Y. Li, L. Yin, Y. Ji, J. Niu and Y. Yu, Electrochemical removal of nitrate in industrial wastewater, *Front. Environ. Sci. Eng.*, 2018, **12**, 9.

33 J. Gao, B. Jiang, C. Ni, Y. Qi and X. Bi, Enhanced reduction of nitrate by noble metal-free electrocatalysis on P doped three-dimensional Co_3O_4 cathode: Mechanism exploration from both experimental and DFT studies, *Chem. Eng. J.*, 2020, **382**, 123034.

34 A. C. A. de Vooys, R. A. van Santen and J. A. R. van Veen, Electrocatalytic reduction of NO_3^- onpalladium/copper electrodes, *J. Mol. Catal. A: Chem.*, 2000, **154**, 203–215.

35 W. L. M. D. Bartberger, E. Ford, K. M. Miranda, C. Switzer, J. M. Fukuto, P. J. Farmer, D. A. Wink and K. N. Houk, The reduction potential of nitric oxide (NO) and its importance to NO biochemistry, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 10958.

36 A. C. A. de Vooys, M. T. M. Koper, R. A. van Santen and J. A. R. van Veen, Mechanistic study of the nitric oxide reduction on a polycrystalline platinum electrode, *Electrochim. Acta*, 2001, **46**, 923–930.

37 T. Yoshioka, K. Iwase, S. Nakanishi, K. Hashimoto and K. Kamiya, Electrocatalytic reduction of nitrate to nitrous oxide by a copper-modified covalent triazine framework, *J. Phys. Chem. C*, 2016, **120**, 15729–15734.

38 G. A. Cerrón-Calle, A. S. Fajardo, C. M. Sánchez-Sánchez and S. Garcia-Segura, Highly reactive Cu-Pt bimetallic 3D-electrocatalyst for selective nitrate reduction to ammonia, *Appl. Catal., B*, 2022, **302**, 120844.

39 C. A. Clark, C. P. Reddy, H. Xu, K. N. Heck, G. Luo, T. P. Senftle and M. S. Wong, Mechanistic insights into

pH-controlled nitrite reduction to ammonia and hydrazine over rhodium, *ACS Catal.*, 2020, **10**, 494–509.

40 X. Li, X. Zhao, Y. Zhou, J. Hu, H. Zhang, X. Hu and G. Hu, Pd nanocrystals embedded in BC_2N for efficient electrochemical conversion of nitrate to ammonia, *Appl. Surf. Sci.*, 2022, **584**, 152556.

41 M. Jiang, A. Tao, Y. Hu, L. Wang, K. Zhang, X. Song, W. Yan, Z. Tie and Z. Jin, Crystalline modulation engineering of Ru nanoclusters for boosting ammonia electrosynthesis from dinitrogen or nitrate, *ACS Appl. Mater. Interfaces*, 2022, **14**, 17470–17478.

42 J. Li, G. Zhan, J. Yang, F. Quan, C. Mao, Y. Liu, B. Wang, F. Lei, L. Li, A. W. M. Chan, L. Xu, Y. Shi, Y. Du, W. Hao, P. K. Wong, J. Wang, S. X. Dou, L. Zhang and J. C. Yu, Efficient ammonia electrosynthesis from nitrate on strained ruthenium nanoclusters, *J. Am. Chem. Soc.*, 2020, **142**, 7036–7046.

43 J. Lim, C. Y. Liu, J. Park, Y. H. Liu, T. P. Senftle, S. W. Lee and M. C. Hatzell, Structure sensitivity of Pd facets for enhanced electrochemical nitrate reduction to ammonia, *ACS Catal.*, 2021, **11**, 7568–7577.

44 T. Ren, Z. Yu, H. Yu, K. Deng, Z. Wang, X. Li, H. Wang, L. Wang and Y. Xu, Interfacial polarization in metal-organic framework reconstructed $Cu/Pd/CuO_x$ multi-phase heterostructures for electrocatalytic nitrate reduction to ammonia, *Appl. Catal., B*, 2022, **318**, 121805.

45 Y. Xu, K. Ren, T. Ren, M. Wang, Z. Wang, X. Li, L. Wang and H. Wang, Ultralow-content Pd in-situ incorporation mediated hierarchical defects in corner-etched Cu_2O octahedra for enhanced electrocatalytic nitrate reduction to ammonia, *Appl. Catal., B*, 2022, **306**, 121094.

46 M. Liu, Q. Mao, K. Shi, Z. Wang, Y. Xu, X. Li, L. Wang and H. Wang, Electroreduction of nitrate to ammonia on palladium–cobalt–oxygen nanowire arrays, *ACS Appl. Mater. Interfaces*, 2022, **14**, 13169–13176.

47 Y. Xu, K. Ren, T. Ren, M. Wang, M. Liu, Z. Wang, X. Li, L. Wang and H. Wang, Cooperativity of Cu and Pd active sites in CuPd aerogels enhances nitrate electroreduction to ammonia, *Chem. Commun.*, 2021, **57**, 7525–7528.

48 Q. Gao, H. S. Pillai, Y. Huang, S. Liu, Q. Mu, X. Han, Z. Yan, H. Zhou, Q. He, H. Xin and H. Zhu, Breaking adsorption-energy scaling limitations of electrocatalytic nitrate reduction on intermetallic CuPd nanocubes by machine-learned insights, *Nat. Commun.*, 2022, **13**, 2338.

49 G. Zhang, X. Li, P. Shen, Y. Luo, X. Li and K. Chu, PdNi nanosheets boost nitrate electroreduction to ammonia, *J. Environ. Chem. Eng.*, 2022, **10**, 108362.

50 Y. Xu, Y. Sheng, M. Wang, T. Liu, H. Yu, K. Deng, Z. Wang, L. Wang and H. Wang, Lattice-strain and Lewis acid sites synergistically promoted nitrate electroreduction to ammonia over PdBP nanothorn arrays, *J. Mater. Chem. A*, 2022, **10**, 16290–16296.

51 H. Liu, J. Park, Y. Chen, Y. Qiu, Y. Cheng, K. Srivastava, S. Gu, B. H. Shanks, L. T. Roling and W. Li, Electrocatalytic nitrate reduction on oxide-derived silver with tunable selectivity to nitrite and ammonia, *ACS Catal.*, 2021, **11**, 8431–8442.

52 J. Qin, K. Wu, L. Chen, X. Wang, Q. Zhao, B. Liu and Z. Ye, Achieving high selectivity for nitrate electrochemical reduction to ammonia over MOF-supported Ru_xO_y clusters, *J. Mater. Chem. A*, 2022, **10**, 3963–3969.

53 Y. Wang, H. Li, W. Zhou, X. Zhang, B. Zhang and Y. Yu, Structurally disordered RuO_2 nanosheets with rich oxygen vacancies for enhanced nitrate electroreduction to ammonia, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202604.

54 H. Niu, Z. Zhang, X. Wang, X. Wan, C. Shao and Y. Guo, Theoretical insights into the mechanism of selective nitrate-to-ammonia electroreduction on single-atom catalysts, *Adv. Funct. Mater.*, 2021, **31**, 2008533.

55 L. Lv, Y. Shen, J. Liu, X. Meng, X. Gao, M. Zhou, Y. Zhang, D. Gong, Y. Zheng and Z. Zhou, Computational screening of high activity and selectivity TM/gC_3N_4 single-atom catalysts for electrocatalytic reduction of nitrates to ammonia, *J. Phys. Chem. Lett.*, 2021, **12**, 11143–11150.

56 T. Zhu, Q. Chen, P. Liao, W. Duan, S. Liang, Z. Yan and C. Feng, Single-atom Cu catalysts for enhanced electrocatalytic nitrate reduction with significant alleviation of nitrite production, *Small*, 2020, **16**, 2004526.

57 J. Li, Y. Zhang, C. Liu, L. Zheng, E. Petit, K. Qi, Y. Zhang, H. Wu, W. Wang, A. Tiberj, X. Wang, M. Chhowalla, L. Lajaunie, R. Yu and D. Voiry, 3.4% Solar-to-ammonia efficiency from nitrate using Fe single atomic catalyst supported on MoS_2 nanosheets, *Adv. Funct. Mater.*, 2022, **32**, 2108316.

58 Z. Y. Wu, M. Karamad, X. Yong, Q. Huang, D. A. Cullen, P. Zhu, C. Xia, Q. Xiao, M. Shakouri, F. Y. Chen, J. Y. T. Kim, Y. Xia, K. Heck, Y. Hu, M. S. Wong, Q. Li, I. Gates, S. Siahrostami and H. Wang, Electrochemical ammonia synthesis via nitrate reduction on Fe single atom catalyst, *Nat. Commun.*, 2021, **12**, 2870.

59 P. Li, Z. Jin, Z. Fang and G. Yu, A single-site iron catalyst with preoccupied active centers that achieves selective ammonia electrosynthesis from nitrate, *Energy Environ. Sci.*, 2021, **14**, 3522–3531.

60 J. Yang, H. Qi, A. Li, X. Liu, X. Yang, S. Zhang, Q. Zhao, Q. Jiang, Y. Su, L. Zhang, J. F. Li, Z. Q. Tian, W. Liu, A. Wang and T. Zhang, Potential-driven restructuring of Cu single atoms to nanoparticles for boosting the electrochemical reduction of nitrate to ammonia, *J. Am. Chem. Soc.*, 2022, **144**, 12062–12071.

61 X. F. Cheng, J. H. He, H. Q. Ji, H. Y. Zhang, Q. Cao, W. J. Sun, C. L. Yan and J. M. Lu, Coordination symmetry breaking of single-atom catalysts for robust and efficient nitrate electroreduction to ammonia, *Adv. Mater.*, 2022, **34**, 2205767.

62 W. D. Zhang, H. Dong, L. Zhou, H. Xu, H. R. Wang, X. Yan, Y. Jiang, J. Zhang and Z. G. Gu, Fe single-atom catalysts with pre-organized coordination structure for efficient electrochemical nitrate reduction to ammonia, *Appl. Catal., B*, 2022, **317**, 121750.

63 J. Cai, Y. Wei, A. Cao, J. Huang, Z. Jiang, S. Lu and S. Q. Zang, Electrocatalytic nitrate-to-ammonia conversion with ∼100% Faradaic efficiency via single-atom alloying, *Appl. Catal., B*, 2022, **316**, 121683.

64 E. Murphy, Y. Liu, I. Matanovic, S. Guo, P. Tieu, Y. Huang, A. Ly, S. Das, I. Zenyuk, X. Pan, E. Spoerke and P. Atanassov, Highly durable and selective Fe- and Mo-based atomically dispersed electrocatalysts for nitrate reduction to ammonia via distinct and synergized NO_2^- pathways, *ACS Catal.*, 2022, **12**, 6651–6662.

65 D. Yin, Y. Liu, P. Song, P. Chen, X. Liu, L. Cai and L. Zhang, In situ growth of copper/reduced graphene oxide on graphite surfaces for the electrocatalytic reduction of nitrate, *Electrochim. Acta*, 2019, **324**, 134846.

66 G. F. Chen, Y. Yuan, H. Jiang, S. Y. Ren, L. X. Ding, L. Ma, T. Wu, J. Lu and H. Wang, Electrochemical reduction of nitrate to ammonia via direct eight-electron transfer using a copper–molecular solid catalyst, *Nat. Energy*, 2020, **5**, 605–613.

67 E. Pérez-Gallent, M. C. Figueiredo, I. Katsounaros and M. T. M. Koper, Electrocatalytic reduction of nitrate on copper single crystals in acidic and alkaline solutions, *Electrochim. Acta*, 2017, **227**, 77–84.

68 X. Wang, M. Zhu, G. Zeng, X. Liu, C. Fang and C. Li, A three-dimensional Cu nanobelt cathode for highly efficient electrocatalytic nitrate reduction, *Nanoscale*, 2020, **12**, 9385–9391.

69 K. Wu, C. Sun, Z. Wang, Q. Song, X. Bai, X. Yu, Q. Li, Z. Wang, H. Zhang, J. Zhang, X. Tong, Y. Liang, A. Khosla and Z. Zhao, Surface reconstruction on uniform Cu nanodisks boosted electrochemical nitrate reduction to ammonia, *ACS Mater. Lett.*, 2022, **4**, 650–656.

70 X. Fu, X. Zhao, X. Hu, K. He, Y. Yu, T. Li, Q. Tu, X. Qian, Q. Yue, M. R. Wasielewski and Y. Kang, Alternative route for electrochemical ammonia synthesis by reduction of nitrate on copper nanosheets, *Appl. Mater. Today*, 2020, **19**, 100620.

71 Y. Zhao, Y. Liu, Z. Zhang, Z. Mo, C. Wang and S. Gao, Flower-like open-structured polycrystalline copper with synergistic multi-crystal plane for efficient electrocatalytic reduction of nitrate to ammonia, *Nano Energy*, 2022, **97**, 107124.

72 Y. Xu, M. Wang, K. Ren, T. Ren, M. Liu, Z. Wang, X. Li, L. Wang and H. Wang, Atomic defects in pothole-rich two-dimensional copper nanoplates triggering enhanced electrocatalytic selective nitrate-to-ammonia transformation, *J. Mater. Chem. A*, 2021, **9**, 16411–16417.

73 L. Yang, J. Li, F. Du, J. Gao, H. Liu, S. Huang, H. Zhang, C. Li and C. Guo, Interface engineering cerium-doped copper nanocrystal for efficient electrochemical nitrate-to-ammonia production, *Electrochim. Acta*, 2022, **411**, 140095.

74 Q. Hu, Y. Qin, X. Wang, H. Zheng, K. Gao, H. Yang, P. Zhang, M. Shao and C. He, Grain boundaries engineering of hollow copper nanoparticles enables highly efficient ammonia electrosynthesis from nitrate, *CCS Chem.*, 2022, **4**, 2053–2064.

75 X. Zhao, G. Hu, F. Tan, S. Zhang, X. Wang, X. Hu, A. V. Kuklin, G. V. Baryshnikov, H. Ågren, X. Zhou and H. Zhang, Copper confined in vesicle-like BCN cavities promotes electrochemical reduction of nitrate to ammonia in water, *J. Mater. Chem. A*, 2021, **9**, 23675–23686.

76 X. Zhu, H. Huang, H. Zhang, Y. Zhang, P. Shi, K. Qu, S. B. Cheng, A. L. Wang and Q. Lu, Filling mesopores of conductive metal–organic frameworks with Cu clusters for selective nitrate reduction to ammonia, *ACS Appl. Mater. Interfaces*, 2022, **14**, 32176–32182.

77 Z. Song, Y. Liu, Y. Zhong, Q. Guo, J. Zeng and Z. Geng, Efficient Electroreduction of Nitrate into Ammonia at Ultralow Concentrations Via an Enrichment Effect, *Adv. Mater.*, 2022, **34**, 2204306.

78 X. Zhang, C. Wang, Y. Guo, B. Zhang, Y. Wang and Y. Yu, Cu clusters/TiO_{2-x} with abundant oxygen vacancies for enhanced electrocatalytic nitrate reduction to ammonia, *J. Mater. Chem. A*, 2022, **10**, 6448–6453.

79 J. Zhao, Z. Shen, J. Yu, Y. Guo, M. Mushtaq, Y. Ding, Z. Song, W. Zhang, X. Huang, Y. Li, D. Liu and X. Cai, Constructing Cu-CuO heterostructured skin on Cu cubes to promote electrocatalytic ammonia production from nitrate wastewater, *J. Hazard Mater.*, 2022, **439**, 129653.

80 M. Luo, Z. Wang, Y. C. Li, J. Li, F. Li, Y. Lum, D. H. Nam, B. Chen, J. Wicks, A. Xu, T. Zhuang, W. R. Leow, X. Wang, C. T. Dinh, Y. Wang, Y. Wang, D. Sinton and E. H. Sargent, Hydroxide promotes carbon dioxide electroreduction to ethanol on copper via tuning of adsorbed hydrogen, *Nat. Commun.*, 2019, **10**, 5814.

81 J. Yu, Y. Qin, X. Wang, H. Zheng, K. Gao, H. Yang, L. Xie, Q. Hu and C. He, Boosting electrochemical nitrate-ammonia conversion via organic ligands-tuned proton transfer, *Nano Energy*, 2022, **103**, 107705.

82 X. Deng, Y. Yang, L. Wang, X. Z. Fu and J. L. Luo, Metallic Co nanoarray catalyzes selective NH_3 production from electrochemical nitrate reduction at current densities exceeding 2 A cm^{-2}, *Adv. Sci.*, 2021, **8**, 2004523.

83 J. Wang, J. Liang, P. Liu, Z. Yan, L. Cui, L. Yue, L. Zhang, Y. Ren, T. Li, Y. Luo, Q. Liu, X. E. Zhao, N. Li, B. Tang, Y. Liu, S. Gao, A. M. Asiri, H. Hao, R. Gao and X. Sun, Biomass Juncus derived carbon decorated with cobalt nanoparticles enables high-efficiency ammonia electrosynthesis by nitrite reduction, *J. Mater. Chem. A*, 2022, **10**, 2842–2848.

84 N. Zhang, J. Shang, X. Deng, L. Cai, R. Long, Y. Xiong and Y. Chai, Governing interlayer strain in bismuth nanocrystals for efficient ammonia electrosynthesis from nitrate reduction, *ACS Nano*, 2022, **16**, 4795–4804.

85 Q. Chen, J. Liang, Q. Liu, K. Dong, L. Yue, P. Wei, Y. Luo, Q. Liu, N. Li, B. Tang, A. A. Alshehri, M. S. Hamdy, Z. Jiang and X. Sun, Co nanoparticle-decorated pomelo-peel-derived carbon enabled high-efficiency electro-

catalytic nitrate reduction to ammonia, *Chem. Commun.*, 2022, **58**, 4259–4262.

86 K. Wang, R. Mao, R. Liu, J. Zhang and X. Zhao, Sulfur-dopant-promoted electrocatalytic reduction of nitrate by a self-supported iron cathode: selectivity, stability, and underlying mechanism, *Appl. Catal., B*, 2022, **319**, 121862.

87 C. Wang, W. Zhou, Z. Sun, Y. Wang, B. Zhang and Y. Yu, Integrated selective nitrite reduction to ammonia with tetrahydroisoquinoline semi-dehydrogenation over a vacancy-rich Ni bifunctional electrode, *J. Mater. Chem. A*, 2021, **9**, 239.

88 J. Chen, Q. Zhou, L. Yue, D. Zhao, L. Zhang, Y. Luo, Q. Liu, N. Li, A. A. Alshehri, M. S. Hamdy, F. Gong and X. Sun, Co–NCNT nanohybrid as a highly active catalyst for the electroreduction of nitrate to ammonia, *Chem. Commun.*, 2022, **58**, 3787–3790.

89 T. Xie, X. Li, J. Li, J. Chen, S. Sun, Y. Luo, Q. Liu, D. Zhao, C. Xu, L. Xie and X. Sun, Co nanoparticles decorated corncob-derived biomass carbon as an efficientelectrocatalyst for nitrate reduction to ammonia, *Inorg. Chem.*, 2022, **61**, 14195–14200.

90 Z. Fang, Z. Jin, S. Tang, P. Li, P. Wu and G. Yu, Porous two-dimensional iron-cyano nanosheets for high-rate electrochemical nitrate reduction, *ACS Nano*, 2022, **16**, 1072–1081.

91 A. Iarchuk, A. Dutta and P. Broekmann, Novel Ni foam catalysts for sustainable nitrate to ammonia electroreduction, *J. Hazard. Mater.*, 2022, **439**, 129504.

92 P. Gao, Z. H. Xue, S. N. Zhang, D. Xu, G. Y. Zhai, Q. Y. Li, J. S. Chen and X. H. Li, Schottky barrier-induced surface electric field boosts universal reduction of NO_x^- in water to ammonia, *Angew. Chem., Int. Ed.*, 2021, **60**, 20711–20716.

93 Z. Tang, Z. Bai, X. Li, L. Ding, B. Zhang and X. Chang, Chloride-derived bimetallic Cu-Fe nanoparticles for high-selective nitrate-to-ammonia electrochemical catalysis, *Processes*, 2022, **10**, 751.

94 Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D. H. Nam, C. S. Tan, Y. Ding, J. Wu, Y. Lum, C. T. Dinh, D. Sinton, G. Zheng and E. H. Sargent, Enhanced nitrate-to-ammonia activity on copper-nickel alloys via tuning of intermediate adsorption, *J. Am. Chem. Soc.*, 2020, **142**, 5702–5708.

95 Y. Liu, B. Deng, K. Li, H. Wang, Y. Sun and F. Dong, Metal-organic framework derived carbon-supported bimetallic copper-nickel alloy electrocatalysts for highly selective nitrate reduction to ammonia, *J. Colloid Interface Sci.*, 2022, **614**, 405–414.

96 T. H. Jeon, Z. Y. Wu, F. Y. Chen, W. Choi, P. J. J. Alvarez and H. Wang, Cobalt-copper nanoparticles on three-dimensional substrate for efficient ammonia synthesis via electrocatalytic nitrate reduction, *J. Phys. Chem. C*, 2022, **126**, 6982–6989.

97 J. Yuan, Z. Xing, Y. Tang and C. Liu, Tuning the oxidation state of Cu Electrodes for selective electrosynthesis of ammonia from nitrate, *ACS Appl. Mater. Interfaces*, 2021, **13**, 52469–52478.

98 T. Ren, K. Ren, M. Wang, M. Liu, Z. Wang, H. Wang, X. Li, L. Wang and Y. Xu, Concave-convex surface oxide layers over copper nanowires boost electrochemical nitrate-to-ammonia conversion, *Chem. Eng. J.*, 2021, **426**, 130759.

99 Q. Hu, Y. Qin, X. Wang, Z. Wang, X. Huang, H. Zheng, K. Gao, H. Yang, P. Zhang, M. Shao and C. He, Reaction intermediate-mediated electrocatalyst synthesis favors specified facet and defect exposure for efficient nitrate–ammonia conversion, *Energy Environ. Sci.*, 2021, **14**, 4989–4997.

100 Z. Gong, W. Zhong, Z. He, Q. Liu, H. Chen, D. Zhou, N. Zhang, X. Kang and Y. Chen, Regulating surface oxygen species on copper(I) oxides via plasma treatment for effective reduction of nitrate to ammonia, *Appl. Catal., B*, 2022, **305**, 121021.

101 J. Geng, S. Ji, H. Xu, C. Zhao, S. Zhang and H. Zhang, Electrochemical reduction of nitrate to ammonia in a fluidized electrocatalysis system with oxygen vacancy-rich CuO_x nanoparticles, *Inorg. Chem. Front.*, 2021, **8**, 5209–5213.

102 H. Wang, Y. Guo, C. Li, H. Yu, K. Deng, Z. Wang, X. Li, Y. Xu and L. Wang, Cu/CuO_x in-plane heterostructured nanosheetarrays with rich oxygen vacancies enhance nitrate electroreduction to ammonia, *ACS Appl. Mater. Interfaces*, 2022, **14**, 34761–34769.

103 S. Liu, L. Cui, S. Yin, H. Ren, Z. Wang, Y. Xu, X. Li, L. Wang and H. Wang, Heterointerface-triggered electronic structure reformation: Pd/CuO nano-olives motivate nitrite electroreduction to ammonia, *Appl. Catal., B*, 2022, **319**, 121876.

104 Y. Xu, Y. Sheng, M. Wang, T. Ren, K. Shi, Z. Wang, X. Li, L. Wang and H. Wang, Interface coupling induced built-in electric fields boost electrochemical nitrate reduction to ammonia over $CuO@MnO_2$ core-shell hierarchical nanoarrays, *J. Mater. Chem. A*, 2022, **10**, 16883–16890.

105 W. Qiu, X. Chen, Y. Liu, D. Xiao, P. Wang, R. Li, K. Liu, Z. Jin and P. Li, Confining intermediates within a catalytic nanoreactor facilitates nitrate-to-ammonia electrosynthesis, *Appl. Catal., B*, 2022, **315**, 121548.

106 Y. Wang, W. Zhou, R. Jia, Y. Yu and B. Zhang, Unveiling the activity origin of a copper-based electrocatalyst for selective nitrate reduction to ammonia, *Angew. Chem., Int. Ed.*, 2020, **59**, 5350–5354.

107 Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong and C. Zhi, Pd doping-weakened intermediate adsorption to promote electrocatalytic nitrate reduction on TiO_2 nanoarrays for ammonia production and energy supply with zinc-nitrate batteries, *Energy Environ. Sci.*, 2021, **14**, 3938–3944.

108 J. Gao, B. Jiang, C. Ni, Y. Qi, Y. Zhang, N. Oturan and M. A. Oturan, Non-precious Co_3O_4-TiO_2/Ti cathode based electrocatalytic nitrate reduction: preparation, performance and mechanism, *Appl. Catal., B*, 2019, **254**, 391–402.

109 R. Jia, Y. Wang, C. Wang, Y. Ling, Y. Yu and B. Zhang, Boosting selective nitrate electroreduction to ammonium by constructing oxygen vacancies in TiO_2, *ACS Catal.*, 2020, **10**, 3533–3540.

110 Z. Wei, X. Niu, H. Yin, S. Yu and J. Li, Synergistic effect of oxygen defects and hetero-phase junctions of TiO_2 for selective nitrate electroreduction to ammonia, *Appl. Catal., A*, 2022, **636**, 118596.

111 D. Zhao, C. Ma, J. Li, R. Li, X. Fan, L. Zhang, K. Dong, Y. Luo, D. Zheng, S. Sun, Q. Liu, Q. Li, Q. Lu and X. Sun, Direct eight-electron NO_3^--to-NH_3 conversion: using a Co-doped TiO_2 nanoribbon array as a high-efficiency electrocatalyst, *Inorg. Chem. Front.*, 2022, **9**, 6412–6417.

112 X. Fan, D. Zhao, Z. Deng, L. Zhang, J. Li, Z. Li, S. Sun, Y. Luo, D. Zheng, Y. Wang, B. Ying, J. Zhang, A. Alshehri, Y. Lin, C. Tang, X. Sun and Y. Zheng, Constructing Co@TiO_2 nanoarray heterostructure with schottky contact for selective electrocatalytic nitrate reduction to ammonia, *Small*, 2023, **19**, 2208036.

113 X. He, J. Li, R. Li, D. Zhao, L. Zhang, X. Ji, X. Fan, J. Chen, Y. Wang, Y. Luo, D. Zheng, L. Xie, S. Sun, Z. Cai, Q. Liu, K. Ma and X. Sun, Ambient ammonia synthesis via nitrate electroreduction in neutral media on Fe_3O_4 nanoparticles-decorated TiO_2 nanoribbon array, *Inorg. Chem.*, 2023, **62**, 25–29.

114 H. Wang, D. Zhao, C. Liu, X. Fan, Z. Li, Y. Luo, D. Zheng, S. Sun, J. Chen, J. Zhang, Y. Liu, S. Gao, F. Gong and X. Sun, FeS_2@TiO_2 nanobelt array enabled high-efficiency electrocatalytic nitrate reduction to ammonia, *J. Mater. Chem. A*, 2022, **10**, 24462–24467.

115 Z. Deng, C. Ma, X. Fan, Z. Li, Y. Luo, S. Sun, D. Zheng, Q. Liu, J. Du, Q. Lu, B. Zheng and X. Sun, Construction of CoP/TiO_2 nanoarray for enhanced electrochemical nitrate reduction to ammonia, *Mater. Today Phys.*, 2022, **28**, 100854.

116 X. Fan, L. Xie, J. Liang, Y. Ren, L. Zhang, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, Y. Liu, S. Gao, A. A. Alshehri, Q. Liu, Q. Kong and X. Sun, In situ grown Fe_3O_4 particle on stainless steel: A highly efficient electrocatalyst for nitrate reduction to ammonia, *Nano Res.*, 2022, **15**, 3050–3055.

117 Z. Niu, S. Fan, X. Li, Z. Liu, J. Wang, J. Duan, M. O. Tade and S. Liu, Facile tailoring of the electronic structure and the d-band center of copper-doped cobaltate for efficient nitrate electrochemical hydrogenation, *ACS Appl. Mater. Interfaces*, 2022, **14**, 35477–35484.

118 Z. Deng, C. Ma, Z. Li, Y. Luo, L. Zhang, S. Sun, Q. Liu, J. Du, Q. Lu, B. Zheng and X. Sun, High-efficiency electrochemical nitrate reduction to ammonia on a Co_3O_4 nanoarray catalyst with cobalt vacancies, *ACS Appl. Mater. Interfaces*, 2022, **14**, 46595–46602.

119 P. Wei, J. Liang, Q. Liu, L. Xie, X. Tong, Y. Ren, T. Li, Y. Luo, N. Li, B. Tang, A. M. Asiri, M. S. Hamdy, Q. Kong, Z. Wang and X. Sun, Iron-doped cobalt oxide nanoarray for efficient electrocatalytic nitrate-to-ammonia conversion, *J. Colloid Interface Sci.*, 2022, **615**, 636–642.

120 J. Li, D. Zhao, L. Zhang, L. Yue, Y. Luo, Q. Liu, N. Li, A. A. Alshehri, M. S. Hamdy, Q. Li and X. Sun, A $FeCo_2O_4$ nanowire array enabled electrochemical nitrate conversion to ammonia, *Chem. Commun.*, 2022, **58**, 4480–4483.

121 Q. Liu, L. Xie, J. Liang, Y. Ren, Y. Wang, L. Zhang, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, Y. Liu, S. Gao, A. A. Alshehri, I. Shakir, P. O. Agboola, Q. Kong, Q. Wang, D. Ma and X. Sun, Ambient ammonia synthesis via electrochemical-reduction of nitrate enabled by $NiCo_2O_4$ nanowire array, *Small*, 2022, **18**, 2106961.

122 Z. Li, J. Liang, Q. Liu, L. Xie, L. Zhang, Y. Ren, L. Yue, N. Li, B. Tang, A. A. Alshehri, M. S. Hamdy, Y. Luo, Q. Kong and X. Sun, High-efficiency ammonia electrosynthesis via selective reduction of nitrate on $ZnCo_2O_4$ nanosheet array, *Mater. Today Phys.*, 2022, **23**, 100619.

123 L. Xie, L. Hu, Q. Liu, S. Sun, L. Zhang, D. Zhao, Q. Liu, J. Chen, J. Li, L. Ouyang, A. Alshehri, Q. Kong and X. Sun, High-performance electrochemical nitrate reduction to ammonia under ambient conditions using $NiFe_2O_4$ nanosheet arrays, *Inorg. Chem. Front.*, 2022, **9**, 3392–3397.

124 X. Lu, J. Yu, J. Cai, Q. Zhang, S. Yang, L. Gu, G. I. N. Waterhouse, S. Q. Zang, B. Yang and S. Lu, Exclusive nitrate to ammonia conversion via boron-doped carbon dots induced surface Lewis acid sites, *Cell Rep. Phys. Sci.*, 2022, **3**, 100961.

125 H. Liu, J. Li, F. Du, L. Yang, S. Huang, J. Gao, C. Li and C. Guo, A core-shell copper oxides-cobalt oxides heterostructure nanowire arrays for nitrate reduction to ammonia with high yield rate, *Green Energy Environ.*, 2022, DOI: **10.1016/j.gee.2022.03.003**.

126 W. Fu, Z. Hu, Y. Du, P. Su, Y. Su, Q. Zhang and M. Zhou, Building dual active sites Co_3O_4/Cu electrode to break scaling relations for enhancement of electrochemical reduction of nitrate to high-value ammonia, *J. Hazard. Mater.*, 2022, **434**, 128887.

127 X. Fan, C. Ma, D. Zhao, Z. Deng, L. Zhang, Y. Wang, Y. Luo, D. Zheng, T. Li, J. Zhang, S. Sun, Q. Lu and X. Sun, Unveiling selective nitrate reduction to ammonia with Co_3O_4 nanosheets/TiO_2 nanobelt heterostructure catalyst, *J. Colloid Interface Sci.*, 2023, **630**, 714–720.

128 M. Chen, J. Bi, X. Huang, T. Wang, Z. Wang and H. Hao, Bi_2O_3 nanosheets arrays in-situ decorated on carbon cloth for efficient electrochemical reduction of nitrate, *Chemosphere*, 2021, **278**, 130386.

129 H. Wang, Q. Mao, T. Ren, T. Zhou, K. Deng, Z. Wang, X. Li, Y. Xu and L. Wang, Synergism of interfaces and defects: Cu/oxygen vacancy-rich Cu-Mn_3O_4 heterostructured ultrathin nanosheet arrays for selective nitrate electroreduction to ammonia, *ACS Appl. Mater. Interfaces*, 2021, **13**, 44733–44741.

130 J. Wang, D. Wu, M. Li, X. Wei, X. Yang, M. Shao and M. Gu, Bismuth ferrite as an electrocatalyst for the electrochemical nitrate reduction, *Nano Lett.*, 2022, **22**, 5600–5606.

131 Z. Gong, W. Zhong, Z. He, C. Jia, D. Zhou, N. Zhang, X. Kang and Y. Chen, Improving electrochemical nitrate

reduction activity of layered perovskite oxide La_2CuO_4 via B-site doping, *Catal. Today*, 2022, **402**, 259–265.

132 F. Du, J. Li, C. Wang, J. Yao, Z. Tan, Z. Yao, C. Li and C. Guo, Active sites-rich layered double hydroxide for nitrate-to-ammonia production with high selectivity and stability, *Chem. Eng. J.*, 2022, **434**, 134641.

133 X. Wan, W. Guo, X. Dong, H. Wu, X. Sun, M. Chu, S. Han, J. Zhai, W. Xia, S. Jia, M. He and B. Han, Boosting nitrate electroreduction to ammonia on NbO_x via constructing oxygen vacancies, *Green Chem.*, 2022, **24**, 1090–1095.

134 J. Wang, C. Cai, Y. Wang, X. Yang, D. Wu, Y. Zhu, M. Li, M. Gu and M. Shao, Electrocatalytic reduction of nitrate to ammonia on low-cost ultrathin CoO_x nanosheets, *ACS Catal.*, 2021, **11**, 15135–15140.

135 S. Zhang, M. Li, J. Li, Q. Song and X. Liu, High-ammonia selective metal-organic framework–derived Co-doped Fe/Fe_2O_3 catalysts for electrochemical nitrate reduction, *Proc. Natl. Acad. Sci. U. S. A.*, 2022, **119**, e2115504119.

136 X. Fan, J. Liang, L. Zhang, D. Zhao, L. Yue, Y. Luo, Q. Liu, L. Xie, N. Li, B. Tang, Q. Kong and X. Sun, Enhanced electrocatalytic nitrate reduction to ammonia using plasma-induced oxygen vacancies in $CoTiO_{3-x}$ nanofiber, *Carbon Neutralization*, 2022, **1**, 6–13.

137 D. Chen, S. Zhang, X. Bu, R. Zhang, Q. Quan, Z. Lai, W. Wang, Y. Meng, D. Yin, S. Yip, C. Liu, C. Zhi and J. C. Ho, Synergistic modulation of local environment for electrochemical nitrate reduction via asymmetric vacancies and adjacent ion clusters, *Nano Energy*, 2022, **98**, 107338.

138 Q. L. Hong, J. Zhou, Q. G. Zhai, Y. C. Jiang, M. C. Hu, X. Xiao, S. N. Li and Y. Chen, Cobalt phosphide nanorings towards efficient electrocatalytic nitrate reduction to ammonia, *Chem. Commun.*, 2021, **57**, 11621–11624.

139 Y. Jia, Y. G. Ji, Q. Xue, F. M. Li, G. T. Zhao, P. J. Jin, S. N. Li and Y. Chen, Efficient nitrate-to-ammonia electroreduction at cobalt phosphide nanoshuttles, *ACS Appl. Mater. Interfaces*, 2021, **13**, 45521–45527.

140 Q. Yao, J. Chen, S. Xiao, Y. Zhang and X. Zhou, Selective electrocatalytic reduction of nitrate to ammonia with nickel phosphide, *ACS Appl. Mater. Interfaces*, 2021, **13**, 30458–30467.

141 J. Liang, B. Deng, Q. Liu, G. Wen, Q. Liu, T. Li, Y. Luo, A. A. Alshehri, K. A. Alzahrani, D. Ma and X. Sun, High-efficiency electrochemical nitrite reduction to ammonium using a Cu_3P nanowire array under ambient conditions, *Green Chem.*, 2021, **23**, 5487–5493.

142 G. Wen, J. Liang, Q. Liu, T. Li, X. An, F. Zhang, A. A. Alshehri, K. A. Alzahrani, Y. Luo, Q. Kong and X. Sun, Ambient ammonia production via electrocatalytic nitrite reduction catalyzed by a CoP nanoarray, *Nano Res.*, 2022, **15**, 972–977.

143 S. Ye, Z. Chen, G. Zhang, W. Chen, C. Peng, X. Yang, L. Zheng, Y. Li, X. Ren, H. Cao, D. Xue, J. Qiu, Q. Zhang and J. Liu, Elucidating the activity, mechanism and application of selective electrosynthesis of ammonia from nitrate on cobalt phosphide, *Energy Environ. Sci.*, 2022, **15**, 760–770.

144 Q. Yao, J. Chen, S. Xiao, Y. Zhang and X. Zhou, Selective electrocatalytic reduction of nitrate to ammonia with nickel phosphide, *ACS Appl. Mater. Interfaces*, 2021, **13**, 30458–30467.

145 F. Ni, Y. Ma, J. Chen, W. Luo and J. Yang, Boron-iron nanochains for selective electrocatalytic reduction of nitrate, *Chin. Chem. Lett.*, 2021, **32**, 2073–2078.

146 X. Liu, X. Xu, F. Li, J. Xu, H. Ma, X. Sun, D. Wu, C. Zhang, X. Ren and Q. Wei, Heterostructured Bi_2S_3/MoS_2 nanoarrays for efficient electrocatalytic nitrate reduction to ammonia under ambient conditions, *ACS Appl. Mater. Interfaces*, 2022, **14**, 38835–38843.

147 Z. Li, G. Wen, J. Liang, T. Li, Y. Luo, Q. Kong, X. Shi, A. M. Asiri, Q. Liu and X. Sun, High-efficiency nitrate electroreduction to ammonia on electrodeposited cobalt–phosphorus alloy film, *Chem. Commun.*, 2021, **57**, 9720.

148 X. Zhang, G. Ma, L. Shui, G. Zhou and X. Wang, Ni_3N nanoparticles on porous nitrogen-doped carbon nanorods for nitrate electroreduction, *Chem. Eng. J.*, 2022, **430**, 132666.

149 Y. Shi, S. Xu and F. Li, Electrocatalytic nitrate reduction to ammonia via amorphous cobalt boride, *Chem. Commun.*, 2022, **58**, 8714–8717.

150 Y. Wang, L. Zhang, Y. Niu, D. Fang, J. Wang, Q. Su and C. Wang, Boosting NH_3 production from nitrate electroreduction via electronic structure engineering of Fe_3C nanoflakes, *Green Chem.*, 2021, **23**, 7594–7608.