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

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Ammonia (NH<sub>3</sub>) 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<sub>2</sub> 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≡N bonds result in a low NH<sub>3</sub> 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<sub>3</sub>, 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<sub>3</sub>-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<sub>3</sub>-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<sub>3</sub> 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 highefficiency electrocatalysts for selective reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>.

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#### 1. Introduction

Ammonia (NH<sub>3</sub>) 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.<sup>1–3</sup> At present, the synthesis of NH<sub>3</sub> in industry mainly hinges on the traditional Haber–Bosch process (HBP). Such a reaction process is accomplished under tough operating con-

ditions, including high temperature (400-550 °C) and high

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. 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

pressure (15–30 MPa), which is extremely energy-consuming.<sup>4,5</sup> 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<sub>2</sub> emissions.<sup>6</sup> Furthermore, the extensive centralized infrastructures involved in the HBP have to spend substantial capital, leading to a large innovation barrier and uneven regional distribution.<sup>7</sup> In this regard, exploring a clean and sustainable strategy for highly-efficient NH<sub>3</sub> production is highly desired, and presents great challenges in both fundamental science and engineering.

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dissociation of H<sub>2</sub>O 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. Meanwhile, this method can achieve the decentralized and on-site/demand production of NH<sub>3</sub>, further supporting the fabrication of distributed fertilizers and reducing the cost of transportation. Nevertheless, the highly stable N≡N bond with a bond energy of 941 kJ mol<sup>-1</sup>, limited solubility of N<sub>2</sub>, and the competing hydrogen evolution reaction (HER) cause the extremely low NH<sub>3</sub> 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<sub>3</sub>-RR) has been demonstrated as an alluring method for NH<sub>3</sub> synthesis at room temperature and atmospheric pressure, and its good performance may originate from the following aspects: (i) NO<sub>3</sub><sup>-</sup> is highly soluble in water, has a relatively low N=O dissociation energy of 204 kJ mol<sup>-1</sup>, and has a more positive potential than N2. These characteristics are beneficial to alleviate the competing HER and attain high NH3 selectivity with only a small overpotential required, indicating that the NO<sub>3</sub> RR process is more energy-efficient than the HBP and NRR; (ii) NO<sub>3</sub><sup>-</sup> is abundant in industrial wastewater and polluted groundwater, with a maximum concentration up to 2.0 mol L<sup>-1</sup>, and these can be considered as NO<sub>3</sub> sources, providing a promising opportunity for large-scale fabrication of NH<sub>3</sub>; (iii) converting NO<sub>3</sub><sup>-</sup> into NH<sub>3</sub> alleviates the environmental degradation caused by excessive nitrate emission and



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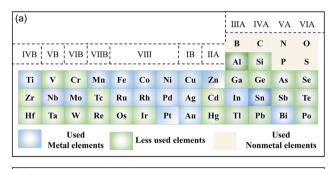
University of Electronic Science and Technology of China where he founded the Research Center of Nanocatalysis & Sensing. He was recognized as a highly cited researcher (2018-2020) in both areas of chemistry and materials science by Clarivate Analytics. He has published over 600 papers with total citations 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.

maintains the balance of the perturbed nitrogen cycle. The reason is attributed to the fact that the accumulation of NO<sub>3</sub> in drinking water will induce illness and jeopardize human health; (iv) this process utilized water as the proton source, eliminating fossil-fuel consumption and CO2 emission. Consequently, there has been a dramatic growth in research efforts to study the ambient electrochemical reduction of NO<sub>3</sub> to NH<sub>3</sub>. 15-17 However, the NO<sub>3</sub> RR is an eight-electron reaction process and generates various by-products, such as NO<sub>2</sub>, NO, N2O, N2, and NH2OH, resulting in low NH3 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 NH3 via the NO3 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 designed for the NO<sub>3</sub>-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<sub>3</sub><sup>-</sup>RR and an analysis of corresponding materials design principles could provide a specific direction for rationally developing efficient NO<sub>3</sub><sup>-</sup>RR electrocatalysts.

Currently, several high-quality reviews focusing on the electrochemical removal of NO<sub>3</sub><sup>-</sup> have been presented. 18,19,25,26 Nevertheless, reviews that exclusively focus on the rational design of electrocatalysts for the reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> are lacking. As a consequence, we review the recent advancements of electrocatalysts toward the NO<sub>3</sub><sup>-</sup>RR for attaining large NH<sub>3</sub> yields, high FE, as well as high selectivity under ambient conditions. Firstly, this review briefly discusses the fundamental reaction mechanisms of the electrocatalytic NO<sub>3</sub><sup>-</sup>RR. Secondly, the most recent advancements of electrocatalysts for electrochemically converting NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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<sub>3</sub><sup>-</sup>RR to form NH<sub>3</sub> are highlighted. Finally, the perspective and challenges in this emerging area are also presented.

### Reaction pathways of electrocatalytic nitrate reduction

Owing to the multivalent nitrogen element, various nitrogencontaining species like NO2-, N2O, NH2ON, N2, N2H4, and NH<sub>3</sub> will be generated during the electrochemical NO<sub>3</sub><sup>-</sup> reduction procedure. Among them, N2 and NH3 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:<sup>27</sup>



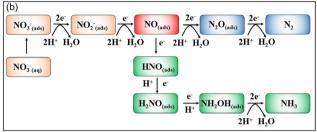


Fig. 1 (a) Element list of reported  ${\rm NO_3}^-{\rm RR}$  electrocatalysts to date. (b) The electron-mediated pathway of the electrochemical reduction of  ${\rm NO_3}^-$ .

$$2N{O_3}^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O, E^\circ = 1.17 \text{ V Vs. SHE}$$
 (1)

$${
m NO_3}^- + 9{
m H}^+ + 8{
m e}^- o {
m NH_3} + 3{
m H_2O}, E^{
m o} = -0.12 {
m \ V} {
m \ vs. \ SHE}.$$
 (2

Generally, the electroreduction of NO3- has two different pathways, including an indirect autocatalytic reduction pathway and a direct electrocatalytic reduction pathway. 29-31 In terms of the former, NO<sub>3</sub> does not participate in the electrontransfer process and the operating conditions are a large concentration of NO<sub>3</sub><sup>-</sup> (>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 (Hads); 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<sub>ads</sub> via decomposition of the adsorbed H<sub>2</sub>O on the surface of the cathode. The second process is that Hads directly reduces NO<sub>3</sub><sup>-</sup> and generates intermediates to give the final-product NH<sub>3</sub> rather than N<sub>2</sub>, 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, which can efficiently suppress the competing HER, as well as attain high NH<sub>3</sub> selectivity and FE. 32,33 As for the electron-mediated pathway, electrons directly reduce NO<sub>3</sub> adsorbed on the surface of the cathode to NO<sub>2</sub><sup>-</sup> (eqn (3) and (4)).<sup>34</sup> Notably, converting NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup>RR process. Then, the generated NO<sub>2 (ads)</sub> reduces to NO<sub>(ads)</sub>, 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  $NH_3$ . 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.  $^{36,37}$ 

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

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

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

$$NO_{(ads)} + 6H^{+} + 5e^{-} \rightarrow NH_{4}^{+} + H_{2}O$$
 (6)

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

$$NO_{(ads)} + NO_{(aq)} + 2H^{+} + 2e^{-} \rightarrow N_{2}O_{(ads)} + H_{2}O$$
 (8)

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

## Efficient NO<sub>3</sub><sup>-</sup>RR electrocatalysts

Exploring advanced electrocatalysts with a high selectivity, FE, and yield rate are keenly desired for the electrosynthesis of  $\mathrm{NH_3}$  by converting  $\mathrm{NO_3}^-$ . Recently, a series of electrocatalysts have been investigated for the  $\mathrm{NO_3}^-\mathrm{RR}$  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  $\mathrm{NO_3}^-\mathrm{RR}$  toward  $\mathrm{NH_3}$  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<sub>3</sub><sup>-</sup>RR under ambient conditions, as listed in Table 1.<sup>20,38-42,45-48,50,52</sup> For example, Li et al.<sup>42</sup> designed Ru/oxygen-doped Ru core/shell nanoclusters (Fig. 2a and b) as an NO<sub>3</sub><sup>-</sup>RR electrocatalyst for the production of NH<sub>3</sub>, 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<sup>-2</sup>. In addition, Chen et al.<sup>20</sup> dis<sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

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

	NH <sub>3</sub> yield rate	Faradaic efficiency	Potentials (V vs. RHE)	Ref.
M KOH + 2000 ppm KNO <sub>3</sub>	76 500 μg h <sup>-1</sup> cm <sup>-2</sup>	90%	0.04	20
1 M KOH + 250 mM KNO <sub>3</sub>	1730 μg h <sup>-1</sup> cm <sup>-2</sup>	97.42%	$-0.7^a/-0.3^b$	40
$mM Cs_2CO_3 + 500 ppm NO_3^-$	145.1 μg h <sup>-1</sup> mg <sup>-1</sup>	80.62%	-0.2	41
M KOH + 1 M KNO <sub>3</sub>		96%	-0.3	42
$5 \text{ M K}_2 \text{SO}_4 + 50 \text{ ppm NO}_3^-$	925.11 μg h <sup>-1</sup> mg <sup>-1</sup>	96.56%	-0.645	45
$5 \text{ M K}_2 \text{SO}_4 + 200 \text{ ppm NO}_3^-$	$0.204 \text{ mmol h}^{-1} \text{ cm}^{-2}$	88.6%	-0.645	46
$5 \text{ M K}_2 \text{SO}_4 + 50 \text{ mg L}^{-1} \text{ NO}_3^{-1}$	$784.37 \mu g h^{-1} m g^{-1}$	90.02%	-0.46	47
M KNO <sub>3</sub> + 1 M KOH	$6.25 \text{ mol h}^{-1} \text{ g}^{-1}$	92.5%	$-0.6^{a}/-0.5^{b}$	48
$5 \text{ M K}_2 \text{SO}_4 + 100 \text{ ppm NO}_3^-$	0.109 mmol h <sup>-1</sup> cm <sup>-2</sup>	64.73%	-0.66	50
$1 \text{ M K}_2 \text{SO}_4 + 200 \text{ ppm NO}_3^-$	$0.1158 \text{ mmol h}^{-1} \text{ cm}^{-2}$	97.46%	-0.35	52
1 M 5 5 M	M KOH + 250 mM KNO <sub>3</sub> nM Cs <sub>2</sub> CO <sub>3</sub> + 500 ppm NO <sub>3</sub> <sup>-</sup> 1 KOH + 1 M KNO <sub>3</sub> M K <sub>2</sub> SO <sub>4</sub> + 50 ppm NO <sub>3</sub> <sup>-</sup> M K <sub>2</sub> SO <sub>4</sub> + 200 ppm NO <sub>3</sub> <sup>-</sup> M K <sub>2</sub> SO <sub>4</sub> + 50 mg L <sup>-1</sup> NO <sub>3</sub> <sup>-</sup> 1 KNO <sub>3</sub> + 1 M KOH M K <sub>2</sub> SO <sub>4</sub> + 100 ppm NO <sub>3</sub> <sup>-</sup>	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	M KOH + 250 mM KNO $_3$ 1730 μg h $^{-1}$ cm $^{-2}$ 97.42% $-0.7^a/-0.3^b$ mM Cs $_2$ CO $_3$ + 500 ppm NO $_3$ 145.1 μg h $^{-1}$ mg $^{-1}$ 80.62% $-0.2$ 1 KOH + 1 M KNO $_3$ 5.56 mol $g_{cat}^{-1}$ h $^{-1}$ 96% $-0.3$ M K $_2$ SO $_4$ + 50 ppm NO $_3$ 925.11 μg h $^{-1}$ mg $^{-1}$ 96.56% $-0.645$ M K $_2$ SO $_4$ + 200 ppm NO $_3$ 0.204 mmol h $^{-1}$ cm $^{-2}$ 88.6% $-0.645$ M K $_2$ SO $_4$ + 50 mg L $^{-1}$ NO $_3$ 784.37 μg h $^{-1}$ mg $^{-1}$ 90.02% $-0.46$ 1 KNO $_3$ + 1 M KOH 6.25 mol h $^{-1}$ g $^{-1}$ 92.5% $-0.6^a/-0.5^b$ M K $_2$ SO $_4$ + 100 ppm NO $_3$ 0.109 mmol h $^{-1}$ cm $^{-2}$ 64.73% $-0.66$

persed Ru nanoparticles into a Cu-nanowire matrix (Ru-CuNW) through a simple cation exchange method for electrochemical NH3 synthesis (Fig. 2d). This catalyst presented an industrial-level NO<sub>3</sub> reduction current of ~1 A cm<sup>-2</sup> (Fig. 2e) accompanied by a maximum NH3 FE of 96% (Fig. 2f) when operating with a low NO<sub>3</sub><sup>-</sup> 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<sup>-2</sup>, with a high NH<sub>3</sub> FE of 90% maintained, indicating that such a catalyst features excellent durability. More importantly, it showed an ultrahigh NO<sub>3</sub> conversion ratio of 99% for NH<sub>3</sub> production, making industrial wastewater reach a drinkable water level (concentration of NO<sub>3</sub><sup>-</sup> < 50 ppm) (Fig. 2g), and the solid NH<sub>4</sub>Cl and liquid NH<sub>3</sub> solution products were collected by coupling the NO<sub>3</sub><sup>-</sup>-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<sub>3</sub> RR activity. They chose Ru as the model material and fabricated amorphous Ru nanoclusters anchored on carbon nanotubes (aRu-CNTs) for electrochemical NH<sub>3</sub> production from NO<sub>3</sub>-. The experimental results demonstrated that aRu-CNTs delivered an NH3 yield of 145  $\mu$ g h<sup>-1</sup> mg<sup>-1</sup> 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<sub>3</sub>-RR is essential to explore rational design strategies for electrosynthesis of NH3. Lim et al. 43 employed Pd as a model catalyst to understand the structure-sensitivity of NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub> 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 (hk0) facets. Based on the experimental results, the Pd (111) facet is favorable to catalyze the reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup>, while the (100) facet is inclined to catalyze the reduction of NO<sub>2</sub><sup>-</sup> to NH<sub>3</sub> (Fig. 2i-k). Hence, the

activity for NO<sub>3</sub> reduction decreases in the order of Pd (111) > Pd (100) > Pd (hk0) and the activity for  $NO_2$  reduction decreases in the order of Pd (100) > Pd (hk0) > Pd (111) under the alkaline electrolyte. As a consequence, NH<sub>3</sub> 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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-carbonnitrogen material (BC<sub>2</sub>N/Pd) for the NO<sub>3</sub><sup>-</sup>RR, which showed a superior NH<sub>3</sub> production rate of 1730  $\mu$ g h<sup>-1</sup> cm<sup>-2</sup> at -0.7 V  $\nu$ s. RHE using 250 mM KNO<sub>3</sub> solution as the nitrogen source. Theoretical calculations revealed that the free energy accumulation of the NO<sub>3</sub><sup>-</sup>RR on BC<sub>2</sub>N/Pd was higher than that of individual Pd or BC<sub>2</sub>N, and the corresponding value from NO<sub>3</sub> to \*NH could conquer the reaction energy barriers from \*NH to \*NH<sub>2</sub> and \*NH<sub>2</sub> to NH<sub>3</sub>. As exhibited in Fig. 3a-d, Ren et al. 44 constructed Cu/Pd/CuO<sub>x</sub> heterostructures with abundant pores for electrochemical conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. In terms of the Cu/Pd/CuO<sub>x</sub> heterostructure, the electronic interactions between the Cu, Pd, and CuOx 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<sub>x</sub> heterostructure afforded a superior NH<sub>3</sub> production rate of 1510.3 μg h<sup>-1</sup>  $mg^{-1}$ , FE of 86.1%, and NH<sub>3</sub> selectivity of 90.06% (Fig. 3e-f). Similarly, Xu et al. 45 applied Cu2O corner-etched octahedra with cavities and oxygen defects as the substrate to support Pd nanoparticles (Pd-Cu<sub>2</sub>O), in which the loading content of Pd active materials was only 2.93%. For Pd-Cu<sub>2</sub>O catalyst system, Pd sites were regarded as the active center for capturing \*H and generating Pd-H intermediate; while parts of Cu<sub>2</sub>O elec-

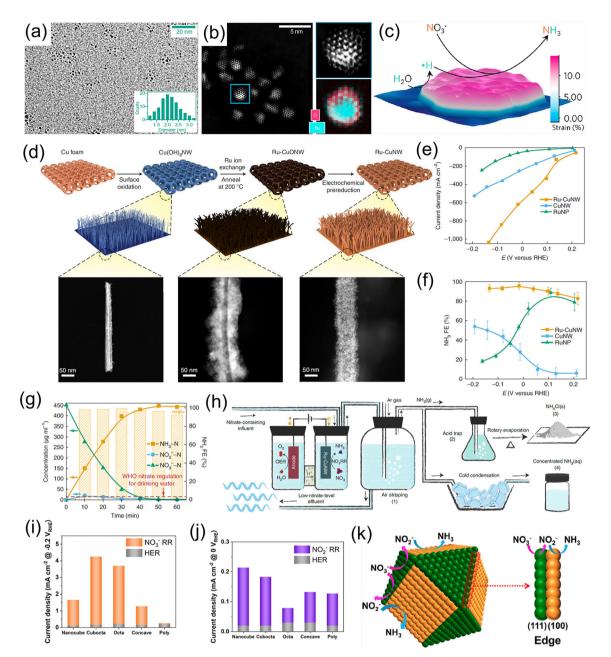


Fig. 2 (a) TEM image and (b) aberration-corrected HAADF-STEM/EELS elemental map images of Ru/oxygen-doped Ru core/shell nanoclusters. (c) Schematic illustration of the reaction mechanism for the NO<sub>3</sub><sup>-</sup>RR on the strained Ru nanoclusters. Reproduced from ref. 42 with permission from the American Chemical Society, copyright 2020. (d) Synthesis process of the Ru-CuNW catalyst. (e and f) I-V plots and corresponding NH<sub>3</sub> FEs of Ru-CuNW and counterparts. (g) Complete NO<sub>3</sub><sup>-</sup> removal using Ru-CuNW catalyst. (h) Schematic diagram of NH<sub>4</sub>Cl<sub>(s)</sub> and concentrated NH<sub>3(ad)</sub> 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<sub>3</sub><sup>-</sup>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<sup>0</sup> and in situ formed Cu/Cu<sup>+</sup>, which could provide active sites for NO<sub>3</sub><sup>-</sup> electroreduction. Meanwhile, the oxygen defects in Cu<sub>2</sub>O were beneficial for the capture of NO<sub>3</sub><sup>-</sup> and to weaken the N-O bond. As expected, Pd/Cu<sub>2</sub>O heterostructure catalyst exhibited an excellent electrocatalytic activity of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, including NH<sub>3</sub> formation rate of 925.11 µg h<sup>-1</sup> mg<sup>-1</sup>, selectivity of 95.31%, and FE of 96.56%. Pd-PdO-modified Co<sub>3</sub>O<sub>4</sub> 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<sub>3</sub> electrolyte, such catalyst showed a high NH<sub>3</sub> 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

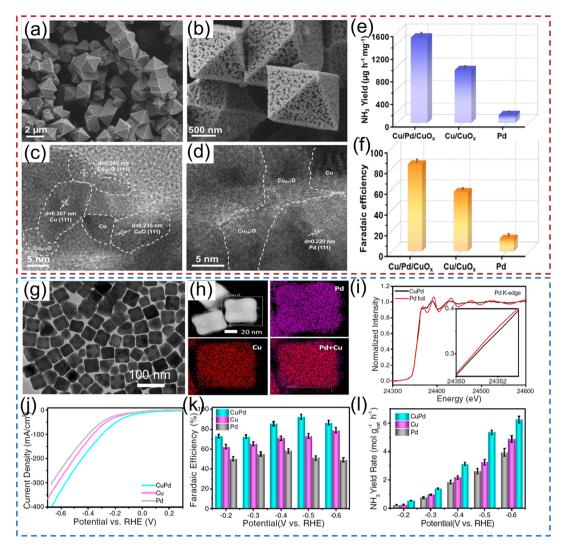


Fig. 3 (a-d) TEM and HRTEM images of Pd/CuO material. (e) NH<sub>7</sub> yield rate and (f) the corresponding FE of Pd/CuO catalyst. Reproduced from ref. 44 with permission from Elsevier, copyright 2022. (g and h) TEM and mapping images of the CuPd alloy. (i) Pd K-edge XANES spectra of CuPd and a Pd foil reference. (j) Linear scan voltammetry (LSV) curves, (k) NH<sub>3</sub> FE and (l) NH<sub>3</sub> 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<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub>. 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. In terms of the CuPd catalyst system, Pd sites serve as active centers to adsorb \*H and promote the hydrogenation reaction for NH<sub>3</sub> production. Consequently, the CuPd alloy catalyst delivered a large NH<sub>3</sub> yield rate of 784.37 μg h<sup>-1</sup> mg<sup>-1</sup>, and a high NH<sub>3</sub> 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 \*NO3, 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 NH3. 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 nearedge spectroscopy (XANES). In 1.0 M NaOH solution containing 1.0 M KNO3, the PdCu nanocube catalyst showed an NH3 yield rate of 6.25 mol  $h^{-1}$  g<sup>-1</sup> at -0.6 V vs. RHE and an NH<sub>3</sub> 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<sub>3</sub> FE of ~85.1% maintained. Similarly, Zhang and his co-authors<sup>49</sup> also employed metallic Ni as a promoter catalyst to regulate the electronic structure of Pd, and synthesized PdNi alloys for the NO<sub>3</sub><sup>-</sup>RR. PdNi nanosheets displayed an NH<sub>3</sub> formation rate of 16.7 mg h<sup>-1</sup> mg<sup>-1</sup> (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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. 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<sub>3</sub><sup>-</sup>. Thus, the electrochemical performance for reducing NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> was significantly enhanced after B and P doping.<sup>50</sup>

Several noble-metal oxides were also used as electrocatalysts for highly efficient NH3 formation by electrochemical conversion of NO<sub>3</sub><sup>-</sup> at room temperature. Liu et al.<sup>51</sup> fabricated oxidederived silver and investigated its electrochemical activity for the NO<sub>3</sub><sup>-</sup>RR. It is noted that this catalyst delivered excellent electrocatalytic activity of NO3- to NO2- and thus promoted the reduction reaction of NO<sub>2</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup>, which was well controlled by the applied potential and they obtained an NH<sub>4</sub><sup>+</sup> FE of 89%. Qin et al. 52 designed and synthesized  $Ru_xO_y$  clusters anchored on nickel metal-organic frameworks (MOF) for the NO<sub>3</sub><sup>-</sup>RR. Such a catalyst could provide a nearly 100% NH<sub>4</sub><sup>+</sup> selectivity with an NH<sub>4</sub><sup>+</sup> yield rate of 274 µg h<sup>-1</sup> mg<sup>-1</sup>. Wang et al.53 fabricated carbon-supported RuO2 nanosheets with abundant oxygen vacancies for electrochemical NO3 to NH3 conversion. The abundant oxygen vacancies within the RuO2 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<sub>3</sub> to NH<sub>3</sub> (NH<sub>3</sub> 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<sub>3</sub><sup>-</sup>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 N2, thus enhancing NH3 selectivity. Currently, both experimental and theoretical calculations have suggested that single-atom catalysts are effective toward electroreduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>.

For example, Niu and co-workers<sup>54</sup> 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> conversion, as shown in Fig. 4a. Firstly, the adsorption energies of NO<sub>3</sub>-, a H proton, and an N<sub>2</sub> molecule on TM/g-CN were systematically calculated. As revealed from Fig. 4b, the adsorption ability for NO<sub>3</sub> was stronger than for H proton or N<sub>2</sub> on TM/g-CN catalysts, except for Pt and Au, indicating that the NO3-RR is more favorable than the HER and NRR. By combining with detailed pathways of NO<sub>3</sub><sup>-</sup> reduction on TM/g-CN, they established a volcano plot of limiting potential selecting the adsorption energy of NO<sub>3</sub> 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 NO3 compared with those of other TM/g-CN catalysts, making them fascinating electrocatalysts with high activity and selectivity for the NO<sub>3</sub><sup>-</sup>RR. Similarly, Lv et al. 55 explored the NO<sub>3</sub><sup>-</sup>RR performance of a set of transition-metal single-atom (Ti, Os, Ru, Cr, Mn, and Pt) catalysts supported on g-C<sub>3</sub>N<sub>4</sub> by performing DFT calculations. The calculation results suggested that Ru/g-C3N4 featured the highest activity and selectivity for the conversion

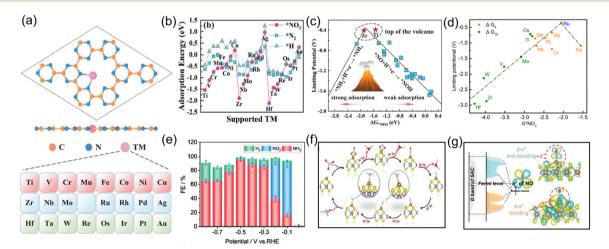


Fig. 4 (a) Atomic structure of TM/g-CN and corresponding element list (from Ti to Au). (b) Comparison of adsorption energies of NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>, and H proton on TM/g-CN. (c) NO<sub>3</sub>-RR volcano plot of TM/g-CN using the adsorption energy of NO<sub>3</sub>- as the descriptor. Reproduced from ref. 54 with permission from Wiley-VCH, copyright 2021. (d) Volcano correlation curve between the limiting potential and adsorption energy of NO<sub>3</sub><sup>-</sup> of TM/ q-C<sub>3</sub>N<sub>4</sub>. Reproduced from ref. 55 with permission from the American Chemical Society, copyright 2021. (e) NH<sub>3</sub> FE of Fe-MoS<sub>2</sub> under various potentials. (f) Reaction pathway for the NO<sub>3</sub><sup>-</sup>RR on Fe-MoS<sub>2</sub>. (g) Schematic diagram of the interaction between NO and M-MoS<sub>2</sub> 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 <sub>3</sub> yield rate	Faradaic efficiency	Potentials (V vs. RHE)	Ref.
Fe-MoS <sub>2</sub> SAC	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M NaNO <sub>3</sub>	431.8 μg h <sup>-1</sup> cm <sup>-2</sup>	98%	-0.48	57
Fe SAC	$0.1 \text{ M K}_2 \text{SO}_4 + 0.5 \text{ M NO}_3^-$	0.46 mmol h <sup>-1</sup> cm <sup>-2</sup>	75%	$-0.85^a/-0.66^b$	58
Fe-PPy SAC	$0.1 \text{ M KOH} + 0.1 \text{ M NO}_3^{-1}$	$2.75 \text{ mg h}^{-1} \text{ cm}^{-2}$	100%	-0.7/-0.3	59
Cu SAC	0.1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>	$4.5 \text{ mg cm}^{-2} \text{ h}^{-1}$	84.7%	-1.0	60
Cu-cis-N2O2 SAC	$0.5 \text{ M K}_2 \text{SO}_4 + 1000 \text{ ppm NO}_3^-$	$28.73 \pm 1.25 \text{ mg h}^{-1} \text{ cm}^{-2}$	80%	-1.6	61
FeN <sub>2</sub> O <sub>4</sub> SAC	$0.1 \text{ M K}_2\text{SO}_4 + 0.5 \text{ M NO}_3^-$	46 mg h <sup>-1</sup> mg <sup>-1</sup>	92%	$-0.88^a/-0.68^b$	62
Ni-Cu SAC	$0.5 \text{ M K}_2 \text{SO}_4 + 200 \text{ ppm NO}_3^-$	326.7 μmol h <sup>-1</sup> cm <sup>-2</sup>	100%	-0.55	63
FeMo SAC	0.05 M PBS + 0.16 M KNO <sub>3</sub>	$18.0  \mu mol  cm^{-2}  h^{-1}$	94%	-0.45	64

<sup>&</sup>lt;sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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<sub>3</sub> to NH<sub>3</sub>.

Up to now, only a few single-atom catalysts have been experimentally fabricated and employed for the electrosynthesis of NH<sub>3</sub> from NO<sub>3</sub><sup>-</sup>, 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<sub>3</sub><sup>-</sup>RR for the first time. The strong binding between Cu and N (Cu-N2) was responsible for the good adsorption ability of the catalyst for NO<sub>3</sub> adsorption, promoting the fast conversion from NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> as well as exhibiting excellent stability. Furthermore, Chen et al.24 demonstrated that Cu-N-C could effectively inhibit the generation of toxic NO<sub>2</sub> and by-product N<sub>2</sub>, as well as facilitate the reduction of HNO<sub>3</sub> to NO<sub>2</sub>, and NH<sub>2</sub> to NH<sub>3</sub>. 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 MoFe7 clusters as the active sites. Inspired by this point, Voiry's group<sup>57</sup> developed a novel heterogeneous catalyst composed of Fe single-atoms anchored on two-dimensional MoS<sub>2</sub> (Fe-MoS<sub>2</sub>) for electrochemical NH<sub>3</sub> synthesis by the reduction reaction of NO<sub>3</sub><sup>-</sup>. Fe-MoS<sub>2</sub> delivered a remarkably high FE of 98% for the NO<sub>3</sub>-RR to NH<sub>3</sub> at an onset potential of -0.48 V using 0.1 M Na<sub>2</sub>SO<sub>4</sub> containing 0.1 M NaNO<sub>3</sub> electrolyte (Fig. 4e). Under the above testing conditions, this catalyst showed a 7-hour average NH3 formation rate of 431.8  $\mu g h^{-1} cm^{-2}$ . DFT calculations revealed that the Fe-MoS<sub>2</sub> catalyst featured a superior ability for activating NO<sub>3</sub> 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 ratedetermining step) (Fig. 4f and g). At the same time, Wu et al.<sup>58</sup> chose an N-doped porous carbon matrix to anchor Fe singleatoms (Fe SAC) and applied them for electrochemical NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> conversion (Fig. 5a and b). A large NH<sub>3</sub> yield rate (up to  $0.46 \text{ mmol h}^{-1} \text{ cm}^{-2} \text{ at } -0.85 \text{ V} \text{ vs. RHE}) \text{ and a high NH}_3 \text{ FE of}$ 75% at -0.66 V vs. RHE were achieved in K2SO4 with 0.5 M KNO<sub>3</sub>, 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<sub>3</sub><sup>-</sup>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<sub>3</sub> production, but also enable the intrinsic high-efficiency active sites (Fe-N<sub>4</sub>) 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<sub>r</sub> 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<sub>r</sub> 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<sub>3</sub><sup>-</sup>RR mechanism presented in Fig. 5f that the exclusive existence of nitrate-preoccupied  $Fe(\pi)-N_r$  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<sub>4</sub> sites during the electrochemical production of NH<sub>3</sub> by converting NO3 - through in situ X-ray adsorption spectroscopy coupled with advanced electron microscopy. Specifically, as depicted in Fig. 5g-i, the Cu-N<sub>4</sub> structure experienced the sequential evolution from Cu-N<sub>3</sub> to near-free Cu<sup>0</sup> single atoms and finally to aggregated Cu<sup>0</sup> nanoparticles during the electroreduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. Moreover, the formed Cu<sup>0</sup> nanoparticles can be dismantled into single atoms and again recovered to give the Cu-N<sub>4</sub> structure upon being exposed to an ambient atmosphere after the electrolysis.

Although single-atom catalysts deliver outstanding electrocatalytic activity for the conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, the isolated metal centers usually coordinate with four N atoms in  $C_{4V}$  symmetry. Such a coordination structure features relatively weak adsorption ability for NO3-, leading to sluggish ionic

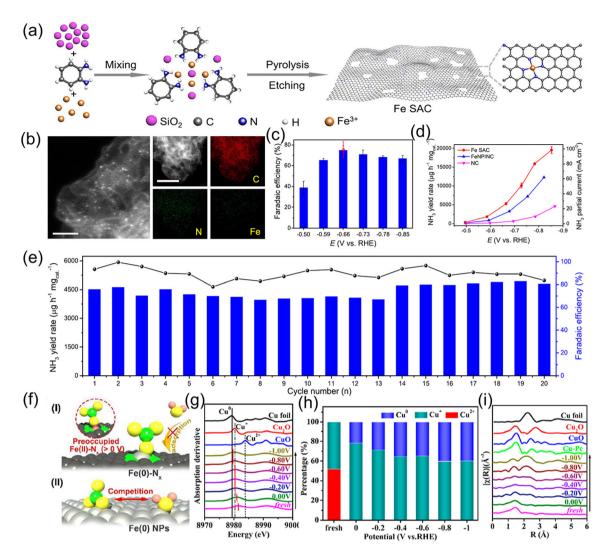


Fig. 5 (a) Schematic illustration of the preparation of Fe SAC. (b) Aberration-corrected medium-angle annular dark-field scanning TEM (HAADF STEM) and mapping images of Fe SAC. (c) NH<sub>3</sub> FE. (d) NH<sub>3</sub> yield rate and partial current density of Fe SAC under various potentials. (e) Cycling 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<sub>3</sub>-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<sub>4</sub> 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<sub>3</sub> 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<sub>3</sub><sup>-</sup> 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-N2O2). Firstprinciple calculations were preferentially employed to reveal the coordination symmetry-breaking in Cu SAC and investigate the reaction pathways of Cu-cis-N2O2 and Cu-N4 catalysts, as indicated in Fig. 6a-e. In terms of Cu-cis-N2O2, Cu is coordinated by two N and two O atoms and the catalyst possesses polar active sites, which are prone to enrich NO<sub>3</sub> on the surface of the catalyst and promote the generation of the key

reaction intermediate \*ONH, further facilitating hydrogenation to NH<sub>3</sub>. Motivated by this, a Cu-cis-N<sub>2</sub>O<sub>2</sub> catalyst was fabricated by pyrolysis of a Cu-Salen complex under an Ar atmosphere (Fig. 6g-h). When applied to the NO<sub>3</sub><sup>-</sup>RR, the NH<sub>3</sub> formation rate reached 27.84 mg h<sup>-1</sup> cm<sup>-2</sup> at an industrial-level current density of 366 mA cm<sup>-2</sup>. Moreover, the electrochemical activity of Cu-cis-N2O2 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 FeN2O2 coordination via direct pyrolysis of metal-organic frameworks possessing a preorganized FeN2O4 environment. When applying the designed Fe SAC for the NO<sub>3</sub><sup>-</sup>RR, it showed a high NH<sub>3</sub> production rate of 46 mg h<sup>-1</sup> mg<sup>-1</sup> with a FE of 92% in neutral electrolytes. Combined theoretical calculations revealed that the O atoms in FeN<sub>2</sub>O<sub>2</sub> could regulate the d-band center of Fe and conse-

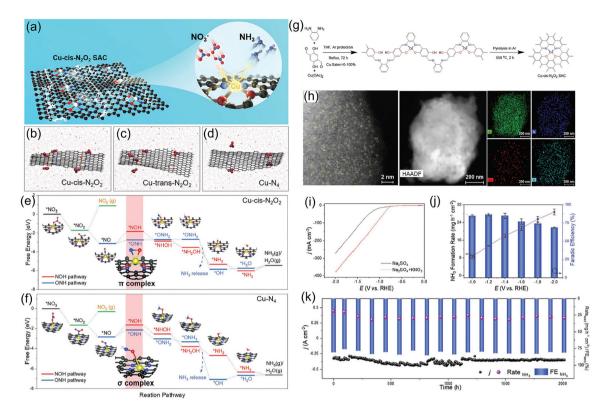


Fig. 6 (a) Illustration of the Cu-cis-N<sub>2</sub>O<sub>2</sub> catalyst. (b-d) The molecular dynamic simulation of Cu-cis-N<sub>2</sub>O<sub>2</sub> and counterparts. (e and f) Reaction pathways for the NO<sub>3</sub><sup>-</sup>RR on the surface of Cu-cis-N<sub>2</sub>O<sub>2</sub> and Cu-N<sub>4</sub>. (g) Synthesis process of Cu-cis-N<sub>2</sub>O<sub>2</sub>. (h) HAADF STEM and corresponding mapping images of Cu-cis-N2O2. (i) LSV curves, (j) NH3 formation rate and FE at each given potential. (k) Cycling stability test of Cu-cis-N2O2. Reproduced from ref. 61 with permission from Wiley-VCH, copyright 2022.

quently enhance the adsorption energies of the NO<sub>3</sub><sup>-</sup>RR intermediates. In comparison with FeN4, FeN2O2 features superior conductivity, NH3 selectivity and a lower reaction energy barrier from \*NOH to \*N, thus promoting the progress of the NO<sub>3</sub><sup>-</sup>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<sub>3</sub> production rate, selectivity and FE. For example, Cai et al. 63 reported a singleatom Ni-alloyed Cu catalyst that achieved an NH3 yield rate of 326.7  $\mu$ mol h<sup>-1</sup> cm<sup>-2</sup> at -0.55 V vs. RHE and a maximum FE of 100% in 0.5 M K<sub>2</sub>SO<sub>4</sub> with 200 ppm NO<sub>3</sub><sup>-</sup>, 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<sub>3</sub><sup>-</sup>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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, in which Mo and Fe served as the dissociative and associative sites of the initial adsorption of NO<sub>3</sub><sup>-</sup>, respectively. Benefiting from the synergistic effect of both Mo and Fe sites, this bimetallic catalyst achieved an NH<sub>3</sub> production rate of 18.0 µmol cm<sup>-2</sup> h<sup>-1</sup>

(153  $\mu g_{NH_2} mg^{-1} h^{-1}$ ) 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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, nonnoble 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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 NO3 RR. In the following section, the recent advances in transition-metalbased electrocatalysts for the NO<sub>3</sub><sup>-</sup>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  $\pi^*$  molecular orbital of NO<sub>3</sub><sup>-</sup>, metallic Cu catalysts have attracted extensive <sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

Table 3 Summary of catalytic performance of transition-metal electrocatalysts

Catalyst	Electrolyte	NH <sub>3</sub> yield rate	Faradaic efficiency	Potentials (V vs. RHE)	Ref.
Cu nanosheets	0.1 M KOH + 10 mM KNO <sub>3</sub>	390.1 μg mg <sup>-1</sup> h <sup>-1</sup>	99.7%	-0.15	70
Cu polycrystalline	$0.5 \text{ M Na}_2 \text{SO}_4 + 0.1 \text{ M KNO}_3$	101.4 μmol h <sup>-1</sup> cm <sup>-2</sup>	93.91%	-0.266	71
dr-Cu nanoplates	$0.5 \text{ M K}_2 \text{SO}_4 + 50 \text{ ppm KNO}_3^-$	$781.25 \mu g h^{-1} m g^{-1}$	85.47%	-0.654	72
Cu with grain boundaries	0.1 M KOH + 10 mM NO <sub>3</sub>	487.8 mmol $g^{-1} h^{-1}$	94.2%	-0.2	74
Cu@C	$0.1 \text{ M KOH} + 1 \text{ mM NO}_3^{-1}$	$469.5  \mu g  h^{-1}  cm^{-2}$	72.0%	$-0.9^a/-0.3^b$	77
Cu/TiO <sub>2-x</sub>	$0.5 \text{ M Na}_2 \text{SO}_4 + 500 \text{ ppm NO}_3^-$	$0.1143 \text{ mmol h}^{-1} \text{ mg}^{-1}$	81.34%	-0.75	78
Cu-CuO	0.1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>	$3.17 \text{ mol h}^{-1} \text{ g}^{-1}$	98.7%	-0.8	79
Co nanosheets	1 M KOH + 0.1 M NO <sub>3</sub>	10.4 mmol h <sup>-1</sup> cm <sup>-2</sup>	98%	-0.24	89
Fe-cyano NSs	1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>	$42.1 \text{ mg h}^{-1} \text{ cm}^{-2}$	90%	-0.5	90
Ni-NCNTs	$0.5 \text{ M Na}_2 \text{SO}_4 + 0.3 \text{ M NO}_3^-$	$5.1 \text{ mg h}^{-1} \text{ cm}^{-2}$	99%	-0.5	92
CuFe alloys	$0.1 \text{ M Na}_2 \text{SO}_4 + 100 \text{ ppm NO}_3^-$	_	81.1%	-0.7	93
CuNi@C alloy	$0.1 \text{ M PBS} + 50 \text{ mg L}^{-1} \text{ NO}_3^{-1}$	_	79.6%	-1.0	95
$Co_{0.5}Cu_{0.5}$	1 M KOH + 50 mM KNO <sub>3</sub>	_	95%	-0.03	96

attention toward the NO<sub>3</sub>-RR. 65-67 However, most metallic Cu catalysts generally convert NO<sub>3</sub><sup>-</sup> to N<sub>2</sub> instead of NH<sub>3</sub>. In terms of an electrochemical NH<sub>3</sub> synthesis system, enhancing the NH<sub>3</sub> yield rate and selectivity of metallic Cu catalysts is critical during the reduction of NO3-. 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<sub>3</sub><sup>-</sup>RR, which delivered a superior catalytic activity (NH<sub>3</sub> yield rate of 390 μg mg<sup>-1</sup> h<sup>-1</sup> 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<sub>3</sub>-RR, it showed superior electrochemical activity with a large NH3 formation rate of 101.4 µmol h<sup>-1</sup> cm<sup>-2</sup> and FE of 93.91% in neutral solution.

Meanwhile, an NH<sub>3</sub> yield rate of 82.4 μmol h<sup>-1</sup> cm<sup>-2</sup> was still achieved after six continuous cycles, with a high FE above 92.85% retained, indicating an alluring stability for electroreduction of NO<sub>3</sub> to NH<sub>3</sub>.71

On the other hand, interface engineering, such as defect engineering,<sup>72</sup> heteroatom doping,<sup>73</sup> coupling with carbon,<sup>65</sup> engineering,74 grain-boundary and heterostructures<sup>75,76</sup> has been proposed to further enhance the electrochemical NO3-RR activity of metallic Cu catalysts. As presented in Fig. 7a and b, Xu et al. 72 fabricated the atomicdefect-rich metallic Cu nanoplates (dr-Cu NPs) and investigated their catalytic activity for the NO<sub>3</sub><sup>-</sup>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<sup>-2</sup> vs. Cu NPs: 0.38 mF

cm<sup>-2</sup>), 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<sub>3</sub> conversion rate of 93.26%, favorable NH<sub>3</sub> selectivity of 81.99%, as well as a high NH3 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> conversion (Fig. 7e and f). Under an ultralow concentration of 1 mM NO<sub>3</sub>, Cu@C delivered a high NH<sub>3</sub> FE of 72.0% and a yield rate of 469.5 μg h<sup>-1</sup> 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 NO3- 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<sub>3</sub><sup>-</sup>, thereby expediting the mass transfer of NO<sub>3</sub> for efficient electroreduction into NH<sub>3</sub> 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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<sub>3</sub><sup>-</sup> for dwindling reaction barriers and enhance the reaction activity for the NO<sub>3</sub><sup>-</sup>RR. As a consequence, the constructed Cu@C catalyst exhibited a maximum FE of 94.2% and a large NH3 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<sub>3</sub><sup>-</sup>RR.<sup>74</sup> Zhang et al.<sup>78</sup> constructed a heterostructure catalyst composed of metallic Cu and oxygen-vacancy-rich TiO2-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 NH3 formation rate of 0.1143 mmol h<sup>-1</sup> mg<sup>-1</sup> along with a high FE of

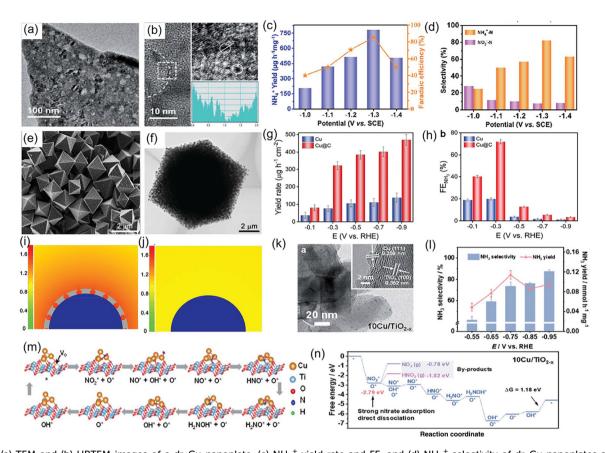


Fig. 7 (a) TEM and (b) HRTEM images of a dr-Cu nanoplate. (c) NH<sub>4</sub><sup>+</sup> yield rate and FE, and (d) NH<sub>4</sub><sup>+</sup> selectivity of dr-Cu nanoplates at various potentials. Reproduced from ref. 72 with permission from The Royal Society of Chemistry, copyright 2021. (e) SEM and (f) TEM images of Cu@C. (g) NH<sub>3</sub> yield rate and (h) FE of Cu@C under different potentials. Simulated concentrations and distribution of local NO<sub>3</sub><sup>-</sup> 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<sub>2-x</sub>. 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. 71). 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<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup>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<sub>3</sub><sup>-</sup>. Thus, this heterostructure catalyst showed a molar-level NH<sub>3</sub> 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<sub>3</sub><sup>-</sup>, which controls the proton transfer rate and further leads to sluggish reaction kinetics for NH<sub>3</sub> 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<sub>3</sub><sup>-</sup>. They experimentally encapsulated Cu nanoparticles into the uncoordinated carboxylate-ligand-rich MOF matrix through a particle decomposition route. As expected, the designed Cubased catalyst achieved an alluring electrochemical performance for the reduction of NO3 to NH3 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>.<sup>82-87</sup> 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<sub>3</sub><sup>-</sup>RR. In 0.1 M NaOH with 0.1 M NO<sub>3</sub><sup>-</sup>, the Co-NCNTs delivered a high activity for the NO3-RR with an NH3 production rate of 5996  $\mu g h^{-1} cm^{-2}$  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

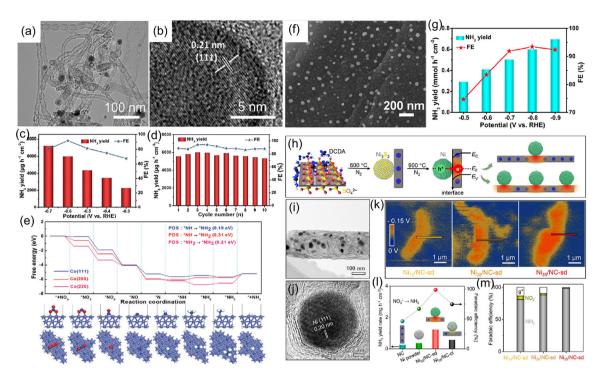


Fig. 8 (a and b) TEM images of Co-NCNTs. (c) NH<sub>3</sub> yield rate and FE of Co-NCNTs under various potentials. (d) Recycling test of Co-NCNTs at -0.6 V. (e) Free-energy profiles of the NO<sub>3</sub><sup>-</sup>RR on different crystal facets of metallic Co. Reproduced from ref. 88 with permission from The Royal Society of Chemistry, copyright 2022. (f) SEM image, (g) NH<sub>3</sub> 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) NH3 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<sub>3</sub><sup>-</sup>RR than the Co (200) and Co (220) facets, in which the rate-determining step is the hydrogenation of \*NH to \*NH2. The corresponding energy barrier was only 0.19 eV, indicating the impressive NO<sub>3</sub><sup>-</sup>RR activity of metallic Co.<sup>88</sup> Meanwhile, we also synthesized metallic Co nanoparticles embedded on carbon derived from corncob as an electrocatalyst for the NO<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub>, which achieved a large NH<sub>3</sub> production rate of 0.6 mmol h<sup>-1</sup> cm<sup>2</sup> 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<sub>3</sub> synthesis through the reduction of NO<sub>3</sub> in an alkaline electrolyte. Bi has also been employed as a highly efficient catalyst for electrochemical reduction of NO<sub>3</sub><sup>-</sup> 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 hydrogenbubble-template-assisted electrodeposition process. An NH<sub>3</sub> 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>, and a large NH<sub>3</sub> formation rate of 5.1 mg h<sup>-1</sup> cm<sup>-2</sup> in the electrochemical conversion of NO<sub>3</sub><sup>-</sup> (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<sub>3</sub><sup>-</sup>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<sub>3</sub> FE of 81.1% at -0.7 V vs. RHE within 6 h in 0.1 M Na<sub>2</sub>SO<sub>4</sub> containing 100 ppm NO<sub>3</sub><sup>-</sup>. Similarly, Sargent and coauthors<sup>94</sup> indicated that Cu50Ni50 alloy catalysts only required an overpotential of 0.2 V to obtain the maximum NH3 FE under various concentrations of NO<sub>3</sub><sup>-</sup>, and produced a 6-times increment in the NO<sub>3</sub> 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 NH3. 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 NH3 selectivity of 94.4% and FE of 79.6% were achieved when utilizing the designed CuNi@C as a catalyst for the NO<sub>3</sub><sup>-</sup>RR. Jeon et al. 96 designed cobalt-copper (Co<sub>1-x</sub>Cu<sub>x</sub>) nanoparticles supported on a three-dimensional substrate for efficient and selective NH3 synthesis via an electrocatalytic NO<sub>3</sub> reduction. Typically, the optimized Co<sub>0.5</sub>Cu<sub>0.5</sub> catalyst performed at a high NH<sub>3</sub> FE of over 95% at -0.03 V with an NH<sub>3</sub> partial current density of  $\sim 176$  mA cm<sup>-2</sup> 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<sub>3</sub>.

#### 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 NH3 synthesis via converting NO<sub>3</sub> under ambient conditions (Table 4). As summarized in the above section, metallic Cu has been intensively studied for the electroreduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> owing to its favorable adsorption ability for NO3- and various intermediates (e.g., NO<sub>2</sub> 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>

For example, Yuan et al. 97 explored the influence of Cu oxidation state on the electrochemical reduction of NO3-, and found that the NH3 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<sub>2+1</sub>O nanowires (Fig. 9a-c) for electrochemical conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. In terms of the Cu@Cu<sub>2+1</sub>O catalyst, the interior metallic Cu components could provide pathways for fast electron transfer due to the one-dimensional nanowire structure, while the exterior Cu2+1O 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@Cu2+1O catalyst exhibited a high NH3 yield rate of 576.53  $\mu g\ h^{-1}\ mg^{-1}$  associated with a FE of 87.7% at -0.564 V vs. RHE, and NH<sub>3</sub> selectivity of 76% (Fig. 9d). Qin et al. 99 further illustrated the effects of the surface structure of Cu<sub>2</sub>O (exposing facets) on NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub>. Both experimental and theoretical calculation results illustrated that the Cu<sub>2</sub>O (100) facet featured a relatively smaller energy barrier for NH<sub>3</sub> formation than the Cu<sub>2</sub>O (111) facet, leading to a large NH<sub>3</sub> formation rate (743  $\mu g h^{-1} m g^{-1}$ ) and high FE (82.3%) at −0.6 V vs. RHE.

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

Catalyst	Electrolyte	NH3 yield rate	Faradaic efficiency	Potentials (V vs. RHE)	Ref.
Cu@Cu <sub>2+1</sub> O nanowires	$0.5 \text{ M K}_2 \text{SO}_4 + 50 \text{ mg L}^{-1}$	576.53 μg h <sup>-1</sup> mg <sup>-1</sup>	87.7%	-0.545	98
0.00 0.02110 0.0000	NO <sub>3</sub>	2. 2.02 1.8 8			
$CuO@MnO_2$	0.5 M K <sub>2</sub> SO <sub>4</sub> + 100 mg L <sup>-1</sup> NO <sub>3</sub>	$0.240 \text{ mmol h}^{-1} \text{ cm}^{-2}$	94.92%	-0.645	104
CuO <sub>x</sub> /TiO <sub>2</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub> + 100 ppm NO <sub>3</sub> <sup>-</sup>	1241.81 μg h <sup>-1</sup> cm <sup>-2</sup>	92.34%	-0.75	105
TiO <sub>2-r</sub> nanotubes	$0.5 \text{ M Na}_2\text{SO}_4 + 50 \text{ ppm NO}_3^-$	0.045 mmol h <sup>-1</sup> mg <sup>-1</sup>	85%	-0.945	109
Co-doped TiO <sub>2</sub> nanosheet	0.1 M NaOH + 0.1 M NO <sub>3</sub>	1127 $\mu$ mol h <sup>-1</sup> cm <sup>-2</sup>	98.2%	$-0.9^{a}/-0.5^{b}$	111
Co@TiO <sub>2</sub>	$0.1 \text{ M PBS} + 0.1 \text{ M NO}_3^{-1}$	$800  \mu \text{mol h}^{-1}  \text{cm}^{-2}$	96.7%	$-1.0^{a}/-0.7^{b}$	112
FeS <sub>2</sub> @TiO <sub>2</sub>	0.1 M NaOH + 0.1 M NaNO <sub>3</sub>	860.3 $\mu$ mol h <sup>-1</sup> cm <sup>-2</sup>	97.0%	$-0.7^a/-0.4^b$	114
Cu-doped Co <sub>3</sub> O <sub>4</sub> nanowire	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 500 ppm NO <sub>3</sub> <sup>-</sup>	36.71 mmol h <sup>-1</sup> g <sup>-1</sup>	86.5%	-0.6	117
Co <sub>3</sub> O <sub>4</sub> nanosheets with Co vacancies	0.1 M NaOH + 0.1 M NaNO <sub>3</sub>	517.5 μmol h <sup>-1</sup> cm <sup>-2</sup>	97.2%	$-0.6^a/-0.4^b$	118
NiCo <sub>2</sub> O <sub>4</sub> nanowire	0.1 M KOH + 0.1 M NaNO <sub>3</sub>	973.2 $\mu$ mol h <sup>-1</sup> cm <sup>-2</sup>	99.0%	$-0.6^a/-0.3^b$	121
ZnCo <sub>2</sub> O <sub>4</sub> nanoarray	0.1 M KOH + 0.1 M NaNO <sub>3</sub>	634.74 mmol h <sup>-1</sup> cm <sup>-2</sup>	98.33%	$-0.8^{a}/-0.6^{b}$	122
BCDs/NiCo <sub>2</sub> O <sub>4</sub> nanowire	$0.5 \text{ M K}_2\text{SO}_4 + 200 \text{ ppm NO}_3^-$	173.9 μmol h <sup>-1</sup> cm <sup>-2</sup>	100%	-0.55	124
CuO@Co <sub>3</sub> O <sub>4</sub>	1 M KOH + 1400 ppm NO <sub>3</sub>	1.915 mmol h <sup>-1</sup> cm <sup>-2</sup>	99.17%	-0.23	125
Co-doped Fe/Fe <sub>2</sub> O <sub>3</sub>	$0.1 \text{ M Na}_2\text{SO}_4 + 50 \text{ ppm NO}_3^-$	1505.9 μg h <sup>-1</sup> cm <sup>-2</sup>	85.2%	-0.95	135
CoTiO <sub>3-x</sub> nanofibers	0.1 M NaOH + 0.1 M NaNO <sub>3</sub>	$30.4 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$	92.6%	$-1.1^a/-1.0^b$	136
CuWO <sub>4</sub> nanospheres	0.5 M Na <sub>2</sub> SO <sub>4</sub> + 0.05 M NaNO <sub>3</sub>	5.84 mg h <sup>-1</sup> mg <sup>-1</sup>	94.6%	-0.7	137
Cu <sub>3</sub> P nanowires	0.1 M PBS + 0.1 M NaNO <sub>3</sub>	$1626.6 \pm 36.1  \mu g  h^{-1}  cm^{-2}$	$91.2 \pm 2.5\%$	-0.5	141
CoP nanosheets	1.0 M NaOH + 1.0 M NaNO <sub>3</sub>	9.56 mol h <sup>-1</sup> m <sup>-2</sup>	100%	-0.3	143
$Bi_2S_3/MoS_2$	$0.1 \text{ M Na}_2\text{SO}_4 + 0.1 \text{ M NaNO}_3$	$15.04 \times 10^{-2} \text{ mmol h}^{-1} \text{ cm}^{-2}$	88.4%	-0.8	146
Ni <sub>3</sub> N nanoparticles	0.5 M Na <sub>2</sub> SO <sub>4</sub> + 0.5 M NaNO <sub>3</sub>	9.185 mmol h <sup>-1</sup> mg <sup>-1</sup>	89.5%	-0.795	148
Fe <sub>3</sub> C nanoflakes	1 M KOH + 75 mM KNO <sub>3</sub>	$1.19 \text{ mmol h}^{-1} \text{ mg}^{-1}$	96.7%	-0.5	150

<sup>&</sup>lt;sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

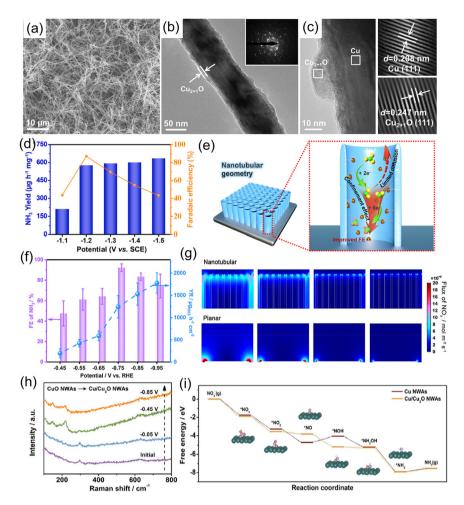


Fig. 9 (a) SEM, (b) TEM and (c) HRTEM images of Cu@Cu<sub>2+1</sub>O nanowires. (d) NH<sub>3</sub> formation rate and FE of Cu@Cu<sub>2+1</sub>O nanowires under the applied potentials. Reproduced from ref. 98 with permission from Elsevier, copyright 2021. (e) Schematic illustration of NO<sub>3</sub><sup>-</sup>-to-NH<sub>3</sub> 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<sub>3</sub>-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<sub>3</sub><sup>-</sup>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@MnO2 hierarchical nanoarrays grown on Cu foam (CuO@MnO2/CF) for the NO3 RR. The heterointerface between the CuO nanowires and MnO2 nanosheets enabled abundant catalytically active sites and induced the formation of a built-in electric field, which were beneficial to the capture of NO<sub>3</sub><sup>-</sup> and various intermediates during the electrochemical reactions, as well as accelerate ionic/electronic transfer at the interface. With these properties, CuO@MnO<sub>2</sub>/CF achieved an impressive electrochemical performance including a very-high NO<sub>3</sub><sup>-</sup> conversion of 99.38%, NH<sub>3</sub> FE of 94.92%, and selectivity of 96.67%. Meanwhile, this catalyst exhibits excellent stability, maintaining the NH3 yield rate and FE after 5 consecutive recycling tests. Qiu et al. 105 incorporated CuO<sub>x</sub> nanoparticles into a TiO<sub>2</sub>-nanotube reactor

for highly selective conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. In this CuO<sub>x</sub>/ TiO2 catalyst system, TiO2 nanotubes could efficiently hinder the diffusion of NO2 intermediate and promote the conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> (Fig. 9e and g). The constructed CuO<sub>x</sub>/ TiO<sub>2</sub> heterostructure achieved a yield rate of 1241.81 μg h<sup>-1</sup> cm<sup>-2</sup>, 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, 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 coworkers applied in situ characterization techniques to unveil the active phase of the CuO electrocatalyst. Experimental results suggested that CuO was transformed to Cu/Cu2O during the reduction process of NO<sub>3</sub>-, and served as an active phase for NO<sub>3</sub><sup>-</sup> conversion (Fig. 9h). Then, online differential electrochemical mass spectrometry was adopted to analyze the

reaction pathway. NO<sub>3</sub> adsorbed on the surface of electrode was firstly reduced to \*NO2 and \*NO, in which \*NO was hydrogenated to give \*NHON and \*NH2OH. Subsequently, \*NH2OH was converted to \*NH3 and further desorbed from the surface of the electrode generating NH3. DFT calculations also discovered that the origin of the activity enhancement was attributed to the reconstructed structure, in which electron transfer from Cu<sub>2</sub>O 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 (TiO2) is a promising electrocatalyst candidate for the electrochemical reduction of NO<sub>3</sub><sup>-</sup> owing to its advantages in terms of cost and robustness. 107,108 For example, Jia et al. 109 fabricated TiO2 nanotubes rich in oxygen vacancies as an electrocatalyst for the NO<sub>3</sub><sup>-</sup>RR. An outstanding conversion rate of 95.2% for NH<sub>3</sub> production from NO<sub>3</sub> 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 TiO2 nanotubes, which weakened the N-O bonding, modulated the adsorption energies of the intermediates, and limited the generation of by-products. Analogously, oxygen-vacancy-TiO2 nanomaterials composed of rutile and anatase phases were fabricated as a catalyst for NH<sub>3</sub> synthesis from the electroreduction of NO<sub>3</sub><sup>-</sup>, which could deliver an NH3 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 (Ti3+) and the heterointerface between the rutile and anatase phases were favorable for modulating the adsorption energy of NO<sub>3</sub><sup>-</sup> and facilitating the hydrogenation reaction to form \*NOH, which led to a relatively high NH3 selectivity and FE. 110 However, the limited selectivity for NH3 and sluggish reaction kinetics hinder their further application for NH<sub>3</sub> 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<sub>2</sub> nanoribbon array supported on Ti foil for electroreduction of NO<sub>3</sub><sup>-</sup> (Fig. 10a and b). Co-doping can effectively improve the intrinsic electronic conductivity of TiO<sub>2</sub> and increase the content of oxygen defects in TiO<sub>2</sub>, which further facilitates the adsorption of NO<sub>3</sub><sup>-</sup> 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 TiO2 nanoribbon arrays delivered a large NH3 production rate of 1127  $\mu$ mol h<sup>-1</sup> cm<sup>-2</sup> and a high FE of 98.2%, which was remarkably superior to that of its counterpart in alkaline media (88.5 µmol h<sup>-1</sup> cm<sup>-2</sup>; 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<sub>2</sub> nanobelt arrays (Co@TiO<sub>2</sub>) (Fig. 10f and g). A built-in electric field formed at the heterointerface between Co and TiO<sub>2</sub>, which was beneficial for the capture of NO<sub>3</sub> on the

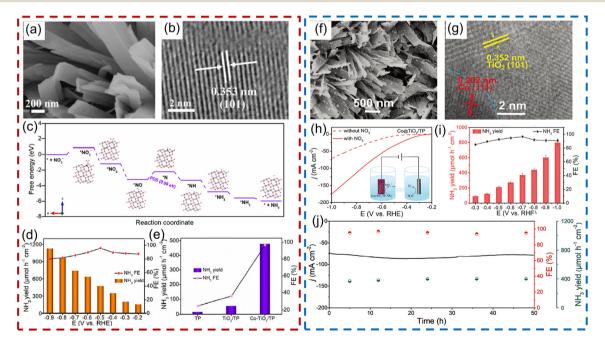


Fig. 10 (a) SEM and (b) HRTEM images of Co-doped TiO<sub>2</sub>. (c) Calculated free-energy changes of the NO<sub>3</sub><sup>-</sup>RR on the Co-doped TiO<sub>2</sub>. (d) NH<sub>3</sub> yield rate and FE of Co-doped TiO<sub>2</sub> under given potentials. (e) Comparison of NH<sub>3</sub> yield rate and FE between TiO<sub>2</sub> and Co-doped TiO<sub>2</sub>. Reproduced from ref. 111 with permission from The Royal Society of Chemistry, copyright 2022. (f) SEM and (g) HRTEM images of Co@TiO2 heterojunction catalyst. (h) LSV curves and (i) NH<sub>3</sub> formation rate and FE at given potentials for Co@TiO<sub>2</sub>. (j) The long-term electrocatalytic performance of the Co@TiO<sub>2</sub> 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<sub>3</sub><sup>-</sup>. Consequently, in a neutral medium containing 0.1 M NO<sub>3</sub>-, the as-designed Co@TiO2 catalyst enabled a high NH3 FE of 96.7% at -0.7 V vs. RHE and a competitive NH<sub>3</sub> formation rate of 800 µmol h<sup>-1</sup> cm<sup>-2</sup> at -1.0 V (Fig. 10h and i). Meanwhile, this catalyst also showed impressive durability during recycling tests and 50 h bulk electrolysis (Fig. 10j). Following this,  $Fe_3O_4@TiO_2$ , <sup>113</sup>  $CoP@TiO_2$  <sup>114</sup> and  $FeS_2@TiO_2$  <sup>115</sup> p-n heterojunctions were constructed by our team and utilized as electrocatalysts to convert NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, where the selectivity and efficiency of bare TiO<sub>2</sub> for the NO<sub>3</sub> 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<sub>3</sub><sup>-</sup>RR. 116 For example, Co<sub>3</sub>O<sub>4</sub> has been extensively utilized as a catalyst for the electroreduction of NO<sub>3</sub>-, but its yield rate and selectivity of the target product NH3 are relatively low. 117 To enhance the electrocatalytic activity of Co<sub>3</sub>O<sub>4</sub>, our group<sup>118</sup> designed Co<sub>3</sub>O<sub>4</sub> nanosheet arrays with Co vacancies on carbon cloth for converting NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> (Fig. 11a and b). As presented in

Fig. 11c and d, Co<sub>3</sub>O<sub>4</sub> with Co vacancies delivered a high NH<sub>3</sub> yield rate of 517.5 μmol h<sup>-1</sup> g<sup>-1</sup> 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 Co3O4 nanosheets (183.8  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> with a FE of 85.9%). Furthermore, DFT calculations demonstrated that the introduction of Co vacancies regulated the electron structure of Co<sub>3</sub>O<sub>4</sub>, optimized the adsorption energy of NO<sub>3</sub> 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<sub>3</sub>O<sub>4</sub>, further elevating its selectivity and NH<sub>3</sub> yield rate during the electroreduction of NO<sub>3</sub><sup>-.119</sup> In line with the abovementioned viewpoint, many bimetal spinel oxides, such as  $FeCo_2O_4$ , <sup>120</sup>  $NiCo_2O_4$ , <sup>121</sup>  $ZnCo_2O_4$ , <sup>122</sup>  $AlCo_2O_4$ , <sup>77</sup> NiFe<sub>2</sub>O<sub>4</sub>, <sup>123</sup> have been synthesized and investigated as electrocatalysts for a highly efficient NO<sub>3</sub><sup>-</sup>RR by our team. As demonstrated in Fig. 11g and h, NiCo2O4 nanowire arrays grown on carbon cloth were synthesized for electrochemical NH3 production by conversion of NO<sub>3</sub><sup>-</sup>. Owing to the synergistic effects of the two metal sites, NiCo2O4 nanowire arrays attained a large NH<sub>3</sub> formation rate of 973.2 μmol h<sup>-1</sup> cm<sup>-2</sup> and large FE of 99.0% (Fig. 11i and j) in 0.1 M KOH with 0.1 M NaNO<sub>3</sub>.

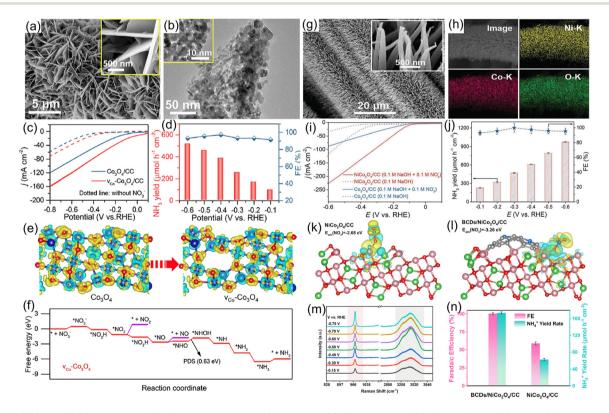


Fig. 11 (a) SEM and (b) TEM images of Co<sub>3</sub>O<sub>4</sub> nanosheets with Co vacancies. (c) LSV curves and (d) NH<sub>3</sub> yield rate, FE under different potentials for Co<sub>3</sub>O<sub>4</sub> nanosheets with Co vacancies. (e) Charge density distribution of Co<sub>3</sub>O<sub>4</sub> with/without Co vacancies. (f) Free-energy diagrams for the NO<sub>3</sub><sup>-</sup>RR on Co<sub>3</sub>O<sub>4</sub> 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<sub>2</sub>O<sub>4</sub>. (i) LSV curves and (j) yield rate and FE of NH<sub>3</sub> under given potentials. Reproduced from ref. 121 with permission from the Wiley-VCH, copyright 2022. Charge-density difference for NO<sub>3</sub><sup>-</sup> adsorption on NiCo<sub>2</sub>O<sub>4</sub> (k) and BCDs/NiCo<sub>2</sub>O<sub>4</sub> (l). (m) In situ Raman spectra of NO<sub>3</sub><sup>-</sup>RR over BCDs/NiCo<sub>2</sub>O<sub>4</sub> at different applied potentials. (n) Comparison of NH<sub>3</sub> FEs and yield rate of BCDs/NiCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>. Reproduced from ref. 124 with permission from the Elsevier, copyright 2022.

Impressively, the as-designed NiCo2O4 nanowires displayed exceptional durability with no significant fluctuations in both NH<sub>3</sub> production rate and FE after 16 successive electrolysis experiments. After that, taking the Lewis-base property of NO<sub>3</sub> into consideration, Lu et al. 124 further introduced abundant Lewis acid sites on the surface of NiCo2O4 nanowire arrays for increasing the adsorption energy of NO<sub>3</sub><sup>-</sup> by coupling with boron-doped carbon dots (BCDs/NiCo2O4). As revealed in Fig. 11k and l, the incorporation of BCDs enhanced the adsorption energy of NO<sub>3</sub> on the surface of the BCDs/ NiCo<sub>2</sub>O<sub>4</sub> electrode. Meanwhile, in situ Raman spectra shown in Fig. 11m suggested that the intensity of the peak at 975 cm<sup>-1</sup> 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<sub>3</sub>-. As expected, the BCDs/NiCo2O4 catalyst provided a nearly ~100% FE and a large NH<sub>3</sub> production rate of 173.9 μmol h<sup>-1</sup> cm<sup>-2</sup> at -0.55 V vs. RHE (Fig. 11n).

Co<sub>3</sub>O<sub>4</sub> as an electrocatalyst for the NO<sub>3</sub><sup>-</sup>RR still suffers from the critical issue that it is difficult to electrochemically reduce NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> using this catalyst. As mentioned above, Cu-based materials possess excellent electrocatalytic activity for NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup>, and thus constructing a Co<sub>3</sub>O<sub>4</sub>based heterostructure with Cu-based materials could achieve promising electrochemical performance. Liu et al. 125 fabricated Co<sub>3</sub>O<sub>4</sub> grown on CuO nanowire arrays to construct a hierarchical heterostructure for an efficient NO3-RR. At -0.23 V vs. RHE, CuO@Co<sub>3</sub>O<sub>4</sub> provided an NH<sub>3</sub> yield rate of 1.915 mmol h<sup>-1</sup> cm<sup>-2</sup>, which was higher than those of CuO and Co<sub>3</sub>O<sub>4</sub>. Fu et al. 126 built dual active sites on a Co<sub>3</sub>O<sub>4</sub>/Cu electrode, in which Cu focused on the reduction of NO<sub>3</sub><sup>-</sup> to NO2-, and then Co3O4 generated H\* (active hydrogen) as a strong reducing agent to further convert NO<sub>2</sub><sup>-</sup> to NH<sub>3</sub>. As a result, the Co<sub>3</sub>O<sub>4</sub>/Cu catalyst presented a large NH<sub>3</sub> yield rate of 684  $\mu g m g^{-1} h^{-1}$  with 94.6% FE. Recently, Fan et al. 127 fabricated a Co<sub>3</sub>O<sub>4</sub> nanosheet grown in situ on TiO<sub>2</sub> nanosheet arrays for the NO<sub>3</sub>-RR, which gave a large NH<sub>3</sub> yield rate of 875 μmol mg<sup>-1</sup> h<sup>-1</sup> 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<sub>3</sub>-RR, such as Bi<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, BiFeO<sub>3</sub>, and La<sub>2</sub>CuO<sub>4</sub>. 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<sub>x</sub> nanosheets with abundant surface oxygen as an NO<sub>3</sub><sup>-</sup>RR catalyst, attaining a large NH<sub>3</sub> yield of 82.4 ± 4.8 mg h<sup>-1</sup> mg<sup>-1</sup> with a FE of 93.4  $\pm$  3.8% at -0.3 V  $\nu s$ . RHE. The surface oxygen on the Co sites was prone to stabilize the adsorbed hydrogen on CoOx, and thus efficiently suppressed the formation of H2 and achieved a high selectivity for NH<sub>3</sub> synthesis. Zhang et al. 135 reported a Co-doped Fe/Fe<sub>2</sub>O<sub>3</sub> catalyst for electrochemical NH3 synthesis by reducing NO3 under ambient conditions. This catalyst afforded an NH<sub>3</sub> production rate of 1505.9 µg h<sup>-1</sup> cm<sup>-2</sup> with a FE of 85.2% and a high NH<sub>3</sub> selectivity of 99.0%. Recently, our group reported that CoTiO<sub>3-x</sub> nanofibers with oxygen vacancies showed an NH3 formation rate of 30.4 mg  $h^{-1}$  mg<sup>-1</sup> and a large FE of 92.6% in 0.1 M NaOH solution containing 0.1 M NO<sub>3</sub><sup>-.136</sup> The CuWO<sub>4</sub> hollow nanospheres with oxygen vacancies showed a high NH<sub>3</sub> FE of 94.6% and yield rate of 5.84 mg  $h^{-1}$  mg<sup>-1</sup> at -0.7 V vs. RHE. <sup>137</sup>

3.4.2 Metal phosphides. Metal phosphides featuring metallic characteristics and high catalytic activities for the HER have become fascinating electrocatalysts for converting NO<sub>3</sub> to NH<sub>3</sub>, 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<sub>2</sub>P, and Cu<sub>3</sub>P, have been used as catalysts for NH<sub>3</sub> electrosynthesis. 138-142 For example, Ye et al. 143 reported that CoP nanosheet arrays supported on carbon cloth exhibited a molar level NH<sub>3</sub> formation rate of 9.56 mol h<sup>-1</sup> m<sup>-2</sup> at -0.3 V vs. RHE with a FE of  $\sim 100\%$  under alkaline conditions (Fig. 12a-c). Furthermore, the reaction mechanism of the NO<sub>3</sub> 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<sub>3</sub> via Co-O-N bonds and the electron-transfer step of the NO<sub>3</sub>-RR, while phosphorus within CoP could stabilize the active phase and reduce the reaction-energy barrier of the ratedetermining step during the electroreduction of NO<sub>3</sub><sup>-</sup>, thus leading to a highly selective electrosynthesis of NH3 from NO<sub>3</sub>-. Ni<sub>2</sub>P nanoparticles supported on Ni foam were synthesized and regarded as an electrocatalyst for electrochemically converting NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> in neutral media with 50 mM  $NO_3^-$ . A high  $NH_3$  evolving rate of 0.056 mmol  $h^{-1}$  cm<sup>-2</sup> 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<sub>3</sub>P nanowire arrays anchored on copper foam for electrochemical conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> in neutral media. In 0.1 M phosphate-buffered saline (PBS) containing 0.1 M NaNO<sub>3</sub>, a Cu<sub>3</sub>P nanowire catalyst delivered a large NH<sub>3</sub> formation rate of 848.7  $\pm$  18.0  $\mu g\ h^{-1}\ cm^{-2}$  and a high FE of  $62.9 \pm 2.0\%$  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<sub>3</sub><sup>-</sup> to NH<sub>3</sub> conversion at room temperature. Thang et al. 48 fabricated Ni<sub>3</sub>N nanoparticles embedded on a carbon skeleton and investigated its electrochemical performance as a catalyst for the NO<sub>3</sub><sup>-</sup>RR. This catalyst provided a high NH<sub>3</sub> selectivity of 89.5% and large yield rate of 9.185 mmol h<sup>-1</sup> mg<sup>-1</sup> at -0.795 V vs. RHE in neutral media. Amorphous CoB<sub>x</sub> nanoparticles anchored on carbon paper were synthesized via a simple wet chemical reduction method. When used for electroreduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, CoB<sub>x</sub> afforded a maximum FE of 94.0% and a yield rate of up to 0.787 mmol h<sup>-1</sup> cm<sup>-2</sup>.<sup>149</sup> Wang et al. 150 reported that Fe<sub>3</sub>C nanoflakes embedded on N-doped carbon nanosheets displayed an NH3 yield rate of 1.19 mmol  $h^{-1} mg^{-1}$ , NH<sub>3</sub> FE of 96.7%, and selectivity of 79.0% at -0.5 Vvs. RHE.

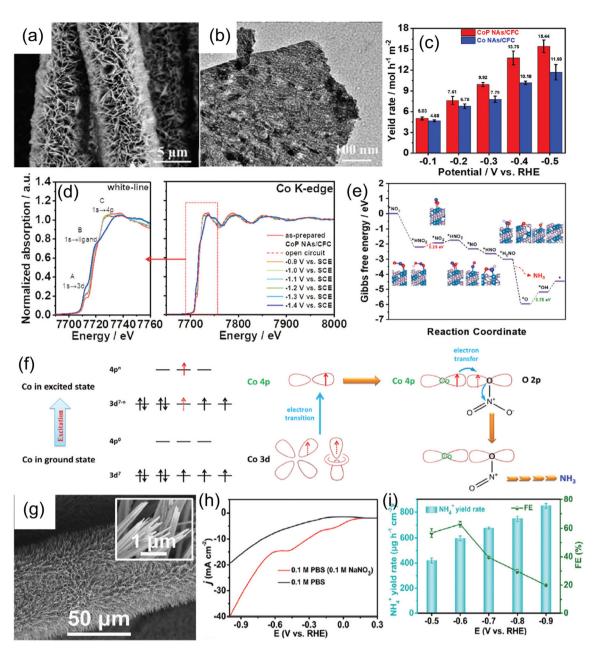


Fig. 12 (a) SEM and (b) TEM images of CoP. (c) NH3 yield rate of CoP at given potentials. (d) In situ XANES of the Co K-edge of CoP. (e) Gibbs freeenergy diagram of the NO<sub>3</sub><sup>-</sup>RR on CoP. (f) Mechanism of the NO<sub>3</sub><sup>-</sup>RR on CoP. Reproduced from ref. 143 with permission from The Royal Society of Chemistry, copyright 2022. (g) SEM image of Cu<sub>3</sub>P. (h) LSV curve, (i) NH<sub>3</sub> yield rate and FE of Cu<sub>3</sub>P in NaNO<sub>3</sub>. Reproduced from ref. 141 with permission from The Royal Society of Chemistry, copyright 2021.

#### 4. Conclusions

The electrochemical NO<sub>3</sub> RR has opened up a green and sustainable route for NH3 synthesis under ambient conditions, which is associated with two advantages: (i) the electrochemical NH3 synthesis from NO3 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<sub>3</sub> production cost; (ii) the benign reaction conditions of the conversion of NO<sub>3</sub><sup>-</sup> would enable distribu-

ted NH<sub>3</sub> production in smaller-scale devices, which facilitates the production of fertilizer on demand and realizes a neutral carbon footprint. The important electrochemical characteristics of NH3 yield rate, Faradaic efficiency and selectivity largely depend on the electrocatalysts. Therefore, this review briefly describes the electroreduction mechanism from NO<sub>3</sub><sup>-</sup> to NH3 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<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. 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<sub>3</sub> synthesis from NO<sub>3</sub><sup>-</sup> 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<sub>3</sub>-RR under ambient conditions. As a consequence, more attention should be given to elaborately developing carbon-based electrocatalysts for the NO<sub>3</sub><sup>-</sup>RR, providing an alluring strategy for largescale NH<sub>3</sub> production.
- (ii) The electrochemical NO3 RR, as an emerging strategy for NH<sub>3</sub> 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<sub>3</sub><sup>-</sup>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<sub>3</sub><sup>-</sup>RR.
- (iii) Many catalysts have exhibited superior catalytic activity and high NH<sub>3</sub> selectivity during the electrochemical NO<sub>3</sub><sup>-</sup>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<sub>3</sub><sup>-</sup>RR.
- (iv) From the point of view of practical application, besides the fact that the electrochemical NO<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub> 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 H2 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<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub> can be put into practical operation.

#### Conflicts of interest

There are no conflicts to declare.

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