

## REVIEW

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

## 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<sub>3</sub> synthesis under ambient conditions. However, the limited solubility of N<sub>2</sub> 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<sub>3</sub><sup>−</sup>), the electrochemical NO<sub>3</sub><sup>−</sup> reduction reaction (NO<sub>3</sub><sup>−</sup>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<sub>3</sub><sup>−</sup> and systematically summarizes the recent development of electrocatalysts for the NO<sub>3</sub><sup>−</sup>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><sup>−</sup>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 high-efficiency electrocatalysts for selective reduction of NO<sub>3</sub><sup>−</sup> to NH<sub>3</sub>.

Received 27th March 2023,

Accepted 27th April 2023

DOI: 10.1039/d3qi00554b

rsc.li/frontiers-inorganic

## 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 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.

Recently, electrochemical NH<sub>3</sub> 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.<sup>8,9</sup> Among them, the electrochemical N<sub>2</sub> reduction reaction (NRR) has drawn tremendous interest and achieved substantial progress. In NRR systems, the electrochemical synthesis of NH<sub>3</sub> directly originates from the reduction of N<sub>2</sub> and the

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dissociation of  $\text{H}_2\text{O}$  under ambient conditions, in which the driving force is regulated by the applied voltage.<sup>10–12</sup> Consequently, the thermodynamic energy efficiency of the NRR is about 20% higher than that of the HBP.<sup>1</sup> Meanwhile, this method can achieve the decentralized and on-site/demand production of  $\text{NH}_3$ , further supporting the fabrication of distributed fertilizers and reducing the cost of transportation. Nevertheless, the highly stable  $\text{N}\equiv\text{N}$  bond with a bond energy of  $941\text{ kJ mol}^{-1}$ , limited solubility of  $\text{N}_2$ , and the competing hydrogen evolution reaction (HER) cause the extremely low  $\text{NH}_3$  yield rate, selectivity, and faradaic efficiency (FE), which are far from meeting the practical demands, and even result in unreliable quantifications experimentally owing to the trace amounts of contaminants.<sup>13,14</sup>

Recently, the electrochemical nitrate reduction reaction ( $\text{NO}_3^-$ -RR) has been demonstrated as an alluring method for  $\text{NH}_3$  synthesis at room temperature and atmospheric pressure, and its good performance may originate from the following aspects: (i)  $\text{NO}_3^-$  is highly soluble in water, has a relatively low  $\text{N}=\text{O}$  dissociation energy of  $204\text{ kJ mol}^{-1}$ , and has a more positive potential than  $\text{N}_2$ . These characteristics are beneficial to alleviate the competing HER and attain high  $\text{NH}_3$  selectivity with only a small overpotential required, indicating that the  $\text{NO}_3^-$ -RR process is more energy-efficient than the HBP and NRR; (ii)  $\text{NO}_3^-$  is abundant in industrial wastewater and polluted groundwater, with a maximum concentration up to  $2.0\text{ mol L}^{-1}$ , and these can be considered as  $\text{NO}_3^-$  sources, providing a promising opportunity for large-scale fabrication of  $\text{NH}_3$ ; (iii) converting  $\text{NO}_3^-$  into  $\text{NH}_3$  alleviates the environmental degradation caused by excessive nitrate emission and

maintains the balance of the perturbed nitrogen cycle. The reason is attributed to the fact that the accumulation of  $\text{NO}_3^-$  in drinking water will induce illness and jeopardize human health; (iv) this process utilized water as the proton source, eliminating fossil-fuel consumption and  $\text{CO}_2$  emission. Consequently, there has been a dramatic growth in research efforts to study the ambient electrochemical reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$ .<sup>15–17</sup> However, the  $\text{NO}_3^-$ -RR is an eight-electron reaction process and generates various by-products, such as  $\text{NO}_2^-$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{NH}_2\text{OH}$ , resulting in low  $\text{NH}_3$  selectivity, FE and yield rate.<sup>18–20</sup> Such electrocatalytic performance is mainly determined by the electrocatalysts; hence, the major challenge in large-scale production of  $\text{NH}_3$  via the  $\text{NO}_3^-$ -RR lies in finding a suitable catalyst. Recently, a series of electrocatalysts, including noble metals, signal-atom catalysts, and catalysts of transition metals and their compounds have been developed and/or designed for the  $\text{NO}_3^-$ -RR under ambient conditions.<sup>21–24</sup> 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  $\text{NO}_3^-$ -RR and an analysis of corresponding materials design principles could provide a specific direction for rationally developing efficient  $\text{NO}_3^-$ -RR electrocatalysts.

Currently, several high-quality reviews focusing on the electrochemical removal of  $\text{NO}_3^-$  have been presented.<sup>18,19,25,26</sup> Nevertheless, reviews that exclusively focus on the rational design of electrocatalysts for the reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  are lacking. As a consequence, we review the recent advancements of electrocatalysts toward the  $\text{NO}_3^-$ -RR for attaining large  $\text{NH}_3$  yields, high FE, as well as high selectivity under ambient conditions. Firstly, this review briefly discusses the fundamental reaction mechanisms of the electrocatalytic  $\text{NO}_3^-$ -RR. Secondly, the most recent advancements of electrocatalysts for electrochemically converting  $\text{NO}_3^-$  to  $\text{NH}_3$  have been summarized, covering noble metals, single-atom catalysts, and catalysts of transition metals and their compounds (Fig. 1a). Meanwhile, several strategies to regulate the apparent activity or intrinsic activity of the electrocatalysts for the  $\text{NO}_3^-$ -RR to form  $\text{NH}_3$  are highlighted. Finally, the perspective and challenges in this emerging area are also presented.

## 2. Reaction pathways of electrocatalytic nitrate reduction

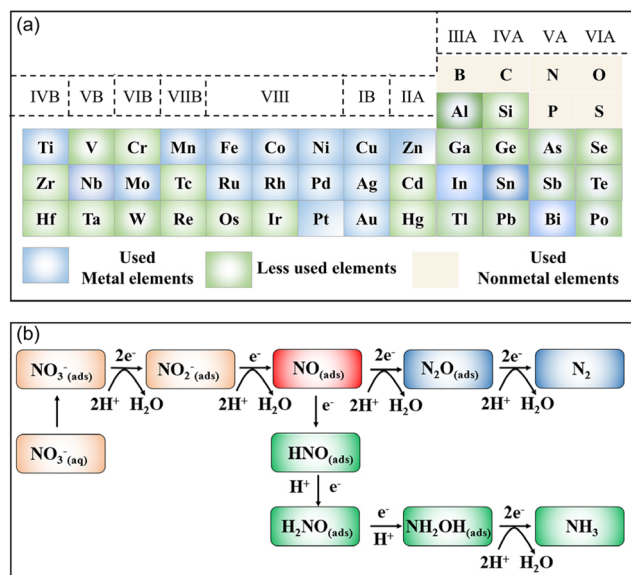
Owing to the multivalent nitrogen element, various nitrogen-containing species like  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_2\text{ON}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{H}_4$ , and  $\text{NH}_3$  will be generated during the electrochemical  $\text{NO}_3^-$  reduction procedure. Among them,  $\text{N}_2$  and  $\text{NH}_3$  feature the highest thermodynamic stability and are regarded as final products under standard conditions.<sup>27,28</sup> The corresponding reactions can be expressed through the following equations:<sup>27</sup>



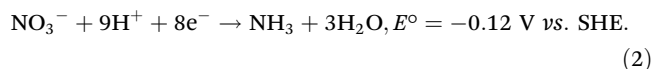
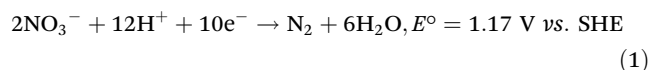
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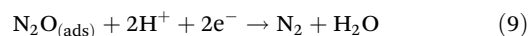
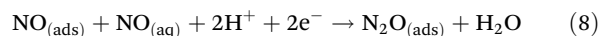
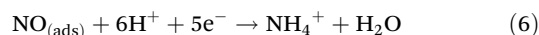
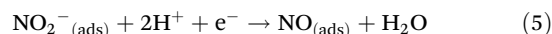
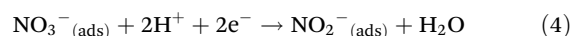


**Fig. 1** (a) Element list of reported  $\text{NO}_3^-$ -RR electrocatalysts to date. (b) The electron-mediated pathway of the electrochemical reduction of  $\text{NO}_3^-$ .



Generally, the electroreduction of  $\text{NO}_3^-$  has two different pathways, including an indirect autocatalytic reduction pathway and a direct electrocatalytic reduction pathway.<sup>29–31</sup> In terms of the former,  $\text{NO}_3^-$  does not participate in the electron-transfer process and the operating conditions are a large concentration of  $\text{NO}_3^-$  (>1 M) and high acidity (pH < 0). The latter can also be divided into two pathways: one is the regulation of active adsorbed hydrogen atoms ( $\text{H}_{\text{ads}}$ ); the second one is electron reduction at the cathode (Fig. 1b). In the adsorbed-hydrogen-mediated pathway, the first process is the generation of  $\text{H}_{\text{ads}}$  via decomposition of the adsorbed  $\text{H}_2\text{O}$  on the surface of the cathode. The second process is that  $\text{H}_{\text{ads}}$  directly reduces  $\text{NO}_3^-$  and generates intermediates to give the final-product  $\text{NH}_3$  rather than  $\text{N}_2$ , which is attributed to the fact that formation of an N–N bond is kinetically less favorable than that of an N–H bond. This process usually requires a small overpotential to promote the conversion from  $\text{NO}_3^-$  to  $\text{NH}_3$ , which can efficiently suppress the competing HER, as well as attain high  $\text{NH}_3$  selectivity and FE.<sup>32,33</sup> As for the electron-mediated pathway, electrons directly reduce  $\text{NO}_3^-$  adsorbed on the surface of the cathode to  $\text{NO}_2^-$  (eqn (3) and (4)).<sup>34</sup> Notably, converting  $\text{NO}_3^-$  to  $\text{NO}_2^-$  generally requires a high activation energy, and this process is considered as the rate-determining step to regulate the reaction kinetics of the whole  $\text{NO}_3^-$ -RR process. Then, the generated  $\text{NO}_2^-$  (ads) reduces to  $\text{NO}$  (ads), which is a decisive intermediate as a branch for the generation

of  $\text{N}_2$  or  $\text{NH}_3/\text{NH}_4^+$ . On the one hand,  $\text{NO}$  (ads) can be reduced to  $\text{HNO}$  (ads) and  $\text{H}_2\text{NO}$  (ads), and quickly followed by hydrogenation to form hydroxylamine, which finally reduces to  $\text{NH}_3$ .<sup>35</sup> On the other hand,  $\text{NO}$  (ads) can be desorbed from the electrode surface to generate  $\text{NO}$  in solution. When  $\text{NO}$  (aq) presents in the solution, a weakly adsorbed  $\text{NO}$  dimer can be formed, which is the precursor of  $\text{N}_2\text{O}$  (ads). The produced  $\text{N}_2\text{O}$  (ads) further reduces to  $\text{N}_2$  according to eqn (9), and this process plays a dominant role in the pathway of  $\text{N}_2$  evolution.<sup>36,37</sup>



### 3. Efficient $\text{NO}_3^-$ -RR electrocatalysts

Exploring advanced electrocatalysts with a high selectivity, FE, and yield rate are keenly desired for the electrosynthesis of  $\text{NH}_3$  by converting  $\text{NO}_3^-$ . Recently, a series of electrocatalysts have been investigated for the  $\text{NO}_3^-$ -RR process under ambient conditions, like noble-metal-based materials, single-atom metal catalysts, and transition-metal-based materials. In the following sections, the recent advances of those catalysts in the  $\text{NO}_3^-$ -RR toward  $\text{NH}_3$  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  $\text{NO}_3^-$ -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  $\text{NO}_3^-$ -RR electrocatalyst for the production of  $\text{NH}_3$ , in which the introduction of oxygen can increase the size of the Ru unit cell to induce tensile strains (Fig. 2c). The strains suppressed the HER but benefit  $\text{H}^*$  production by expanding the barrier of H–H coupling. As a result, this catalyst achieved a large  $\text{NH}_3$  formation rate of  $5.56 \text{ mol g}^{-1} \text{ h}^{-1}$  with a nearly 100% selectivity at  $120 \text{ mA cm}^{-2}$ . In addition, Chen *et al.*<sup>20</sup> dis-

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

| Catalyst                          | Electrolyte                                                                               | NH <sub>3</sub> yield rate                              | Faradaic efficiency | Potentials (V vs. RHE)               | Ref. |
|-----------------------------------|-------------------------------------------------------------------------------------------|---------------------------------------------------------|---------------------|--------------------------------------|------|
| Ru-dispersed Cu nanowire          | 1 M KOH + 2000 ppm KNO <sub>3</sub>                                                       | 76 500 μg h <sup>-1</sup> cm <sup>-2</sup>              | 90%                 | 0.04                                 | 20   |
| BC <sub>2</sub> N/Pd              | 0.1 M KOH + 250 mM KNO <sub>3</sub>                                                       | 1730 μg h <sup>-1</sup> cm <sup>-2</sup>                | 97.42%              | -0.7 <sup>a</sup> /-0.3 <sup>b</sup> | 40   |
| Amorphous Ru nanoclusters         | 5 mM Cs <sub>2</sub> CO <sub>3</sub> + 500 ppm NO <sub>3</sub> <sup>-</sup>               | 145.1 μg h <sup>-1</sup> mg <sup>-1</sup>               | 80.62%              | -0.2                                 | 41   |
| Strained Ru nanoclusters          | 1 M KOH + 1 M KNO <sub>3</sub>                                                            | 5.56 mol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> | 96%                 | -0.3                                 | 42   |
| Pd/Cu <sub>2</sub> O octahedra    | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 50 ppm NO <sub>3</sub> <sup>-</sup>                | 925.11 μg h <sup>-1</sup> mg <sup>-1</sup>              | 96.56%              | -0.645                               | 45   |
| Pd/Co <sub>3</sub> O <sub>4</sub> | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 200 ppm NO <sub>3</sub> <sup>-</sup>               | 0.204 mmol h <sup>-1</sup> cm <sup>-2</sup>             | 88.6%               | -0.645                               | 46   |
| CuPd aerogels                     | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 50 mg L <sup>-1</sup> NO <sub>3</sub> <sup>-</sup> | 784.37 μg h <sup>-1</sup> mg <sup>-1</sup>              | 90.02%              | -0.46                                | 47   |
| CuPd nanocubes                    | 1 M KNO <sub>3</sub> + 1 M KOH                                                            | 6.25 mol h <sup>-1</sup> g <sup>-1</sup>                | 92.5%               | -0.6 <sup>a</sup> /-0.5 <sup>b</sup> | 48   |
| PdBP nanothorn arrays             | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 100 ppm NO <sub>3</sub> <sup>-</sup>               | 0.109 mmol h <sup>-1</sup> cm <sup>-2</sup>             | 64.73%              | -0.66                                | 50   |
| RuO <sub>2</sub> nanosheets       | 0.1 M K <sub>2</sub> SO <sub>4</sub> + 200 ppm NO <sub>3</sub> <sup>-</sup>               | 0.1158 mmol h <sup>-1</sup> cm <sup>-2</sup>            | 97.46%              | -0.35                                | 52   |

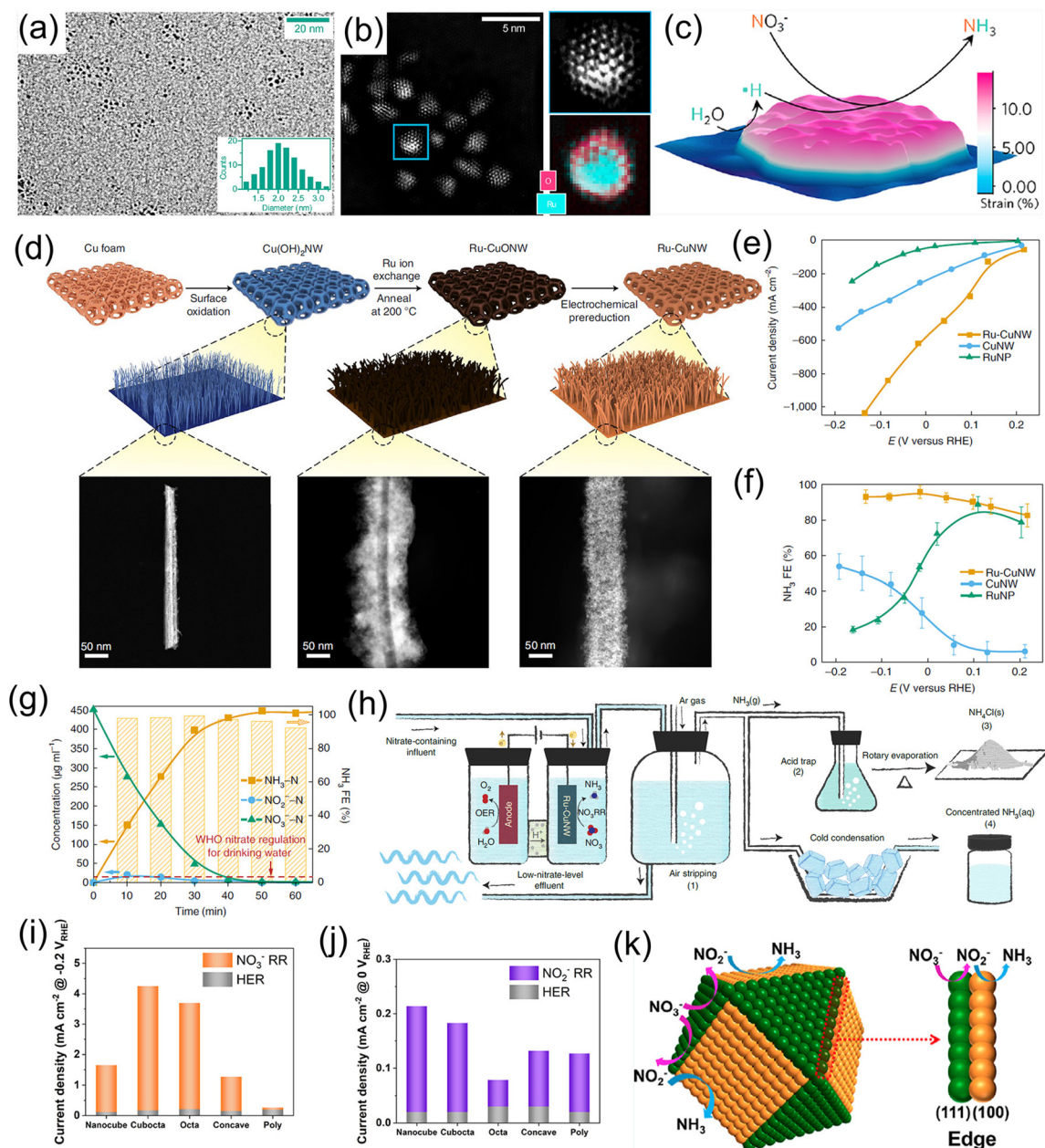
<sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

persed Ru nanoparticles into a Cu-nanowire matrix (Ru-CuNW) through a simple cation exchange method for electrochemical NH<sub>3</sub> synthesis (Fig. 2d). This catalyst presented an industrial-level NO<sub>3</sub><sup>-</sup> reduction current of ~1 A cm<sup>-2</sup> (Fig. 2e) accompanied by a maximum NH<sub>3</sub> 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><sup>-</sup> 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.*<sup>41</sup> investigated the effect of the noble-metal crystal structure on electrochemical NO<sub>3</sub><sup>-</sup>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><sup>-</sup>. The experimental results demonstrated that aRu-CNTs delivered an NH<sub>3</sub> yield of 145 μg 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><sup>-</sup>RR is essential to explore rational design strategies for electrosynthesis of NH<sub>3</sub>. Lim *et al.*<sup>43</sup> 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 (*hk*0) 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><sup>-</sup> reduction decreases in the order of Pd (111) > Pd (100) > Pd (*hk*0) and the activity for NO<sub>2</sub><sup>-</sup> reduction decreases in the order of Pd (100) > Pd (*hk*0) > 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.*<sup>40</sup> constructed a hybrid material consisting of Pd nanoparticles and a boron-carbon-nitrogen 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 μg h<sup>-1</sup> cm<sup>-2</sup> at -0.7 V vs. 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><sup>-</sup> 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.*<sup>44</sup> 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 CuO<sub>x</sub> 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<sup>-1</sup>, FE of 86.1%, and NH<sub>3</sub> selectivity of 90.06% (Fig. 3e-f). Similarly, Xu *et al.*<sup>45</sup> applied Cu<sub>2</sub>O 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-

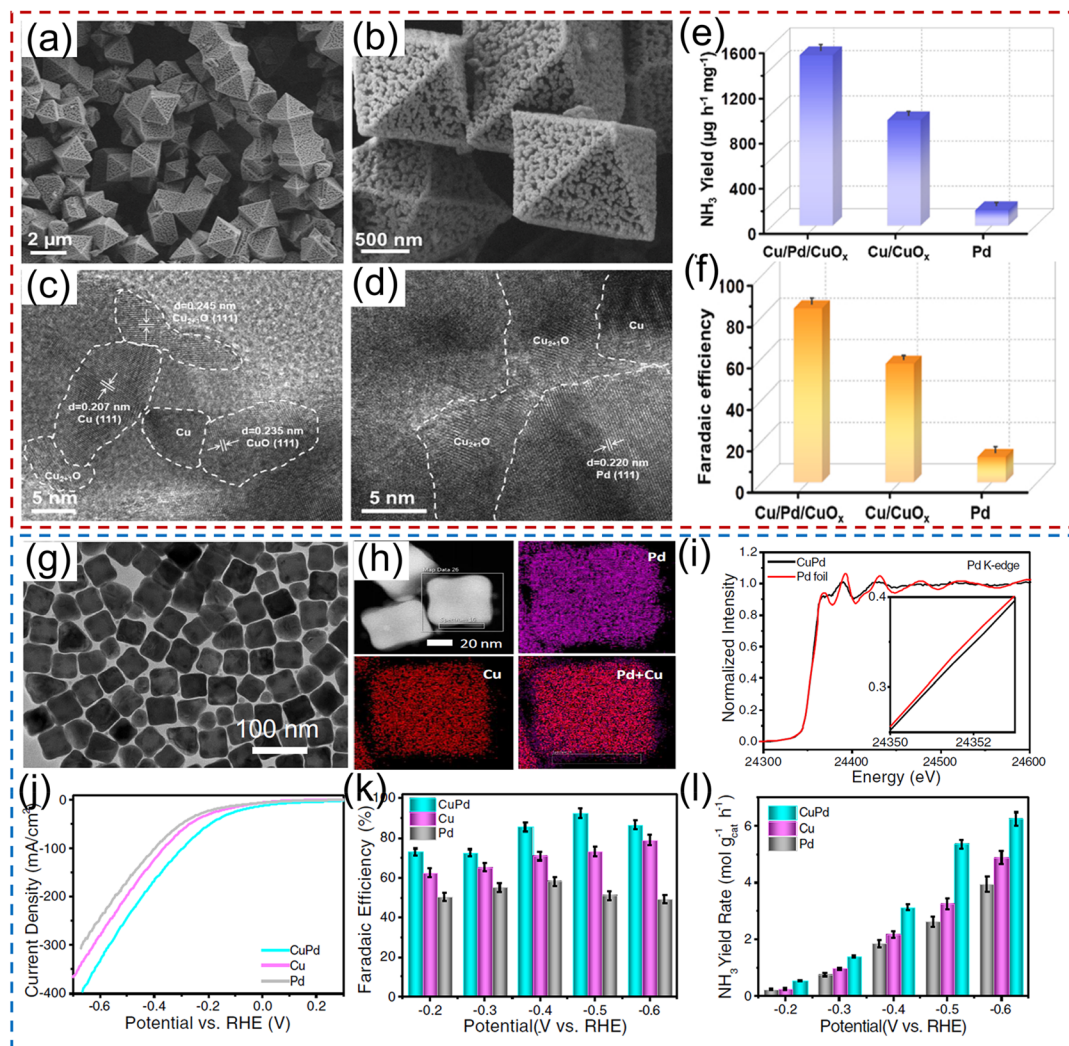


**Fig. 2** (a) TEM image and (b) aberration-corrected HAADF-STEM/EELS elemental map images of Ru/oxygen-doped Ru core/shell nanoclusters. (c) Schematic illustration of the reaction mechanism for the  $\text{NO}_3^-$ -RR on the strained Ru nanoclusters. Reproduced from ref. 42 with permission from the American Chemical Society, copyright 2020. (d) Synthesis process of the Ru-CuNW catalyst. (e) and (f)  $I$ - $V$  plots and corresponding  $\text{NH}_3$  FEs of Ru-CuNW and counterparts. (g) Complete  $\text{NO}_3^-$  removal using Ru-CuNW catalyst. (h) Schematic diagram of  $\text{NH}_4\text{Cl}_{(s)}$  and concentrated  $\text{NH}_3_{(aq)}$  products from nitrate-containing influent. Reproduced from ref. 20 with permission from the Nature Publishing Group, copyright 2022. (i) and (j) The electrocatalytic activity of Pd catalysts with various structures. (k) Schematic illustration of the reaction mechanism for the  $\text{NO}_3^-$ -RR on the different crystal facets of Pd catalysts. Reproduced from ref. 43 with permission from the American Chemical Society, copyright 2021.

trochemically reduced to  $\text{Cu}^0$  and *in situ* formed  $\text{Cu}/\text{Cu}^+$ , which could provide active sites for  $\text{NO}_3^-$  electroreduction. Meanwhile, the oxygen defects in  $\text{Cu}_2\text{O}$  were beneficial for the capture of  $\text{NO}_3^-$  and to weaken the N-O bond. As expected, Pd/ $\text{Cu}_2\text{O}$  heterostructure catalyst exhibited an excellent electrocatalytic activity of  $\text{NO}_3^-$  to  $\text{NH}_3$ , including  $\text{NH}_3$  formation rate of  $925.11 \mu\text{g h}^{-1} \text{mg}^{-1}$ , selectivity of 95.31%, and FE of

96.56%. Pd-PdO-modified  $\text{Co}_3\text{O}_4$  nanowire arrays were fabricated and applied as a catalyst to electrochemically convert  $\text{NO}_3^-$  to  $\text{NH}_3$ . In  $\text{K}_2\text{SO}_4$  solution containing  $200 \text{ mg L}^{-1}$  of  $\text{NO}_3^-$  electrolyte, such catalyst showed a high  $\text{NH}_3$  FE of 88.6% and selectivity of 95.3%.<sup>46</sup>

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>3</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.*<sup>47</sup> 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.*<sup>48</sup> employed density functional theory (DFT) calculations and machine learning to deduce that the upshifted d-band center of the Cu sites of the CuPd alloy favored the adsorption of \*NO<sub>3</sub>, and \*N was destabilized owing to the dominant role of Pauli repulsion from the subsequent Pd d orbitals, promoting the protonation of N-bonded species toward NH<sub>3</sub>. As demonstrated in Fig. 3g–l, they also experimentally synthesized CuPd

nanocube alloy catalysts, and confirmed the existence of charge transfer between Pd and Cu *via* X-ray absorption near-edge spectroscopy (XANES). In 1.0 M NaOH solution containing 1.0 M KNO<sub>3</sub>, the PdCu nanocube catalyst showed an NH<sub>3</sub> yield rate of 6.25 mol h<sup>−1</sup> 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  $\text{NO}_3^-$ . Thus, the electrochemical performance for reducing  $\text{NO}_3^-$  to  $\text{NH}_3$  was significantly enhanced after B and P doping.<sup>50</sup>

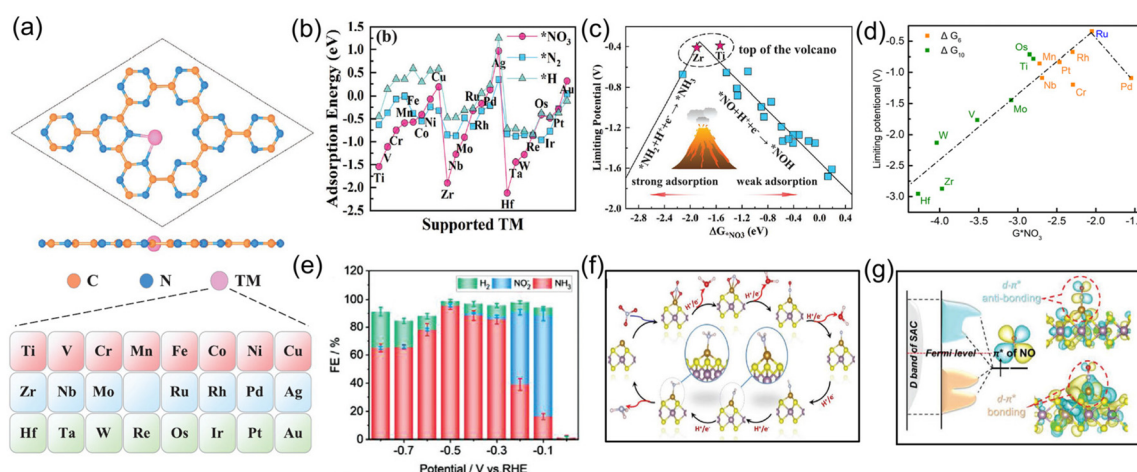
Several noble-metal oxides were also used as electrocatalysts for highly efficient  $\text{NH}_3$  formation by electrochemical conversion of  $\text{NO}_3^-$  at room temperature. Liu *et al.*<sup>51</sup> fabricated oxide-derived silver and investigated its electrochemical activity for the  $\text{NO}_3^-$ -RR. It is noted that this catalyst delivered excellent electrocatalytic activity of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  and thus promoted the reduction reaction of  $\text{NO}_2^-$  to  $\text{NH}_4^+$ , which was well controlled by the applied potential and they obtained an  $\text{NH}_4^+$  FE of 89%. Qin *et al.*<sup>52</sup> designed and synthesized  $\text{Ru}_x\text{O}_y$  clusters anchored on nickel metal-organic frameworks (MOF) for the  $\text{NO}_3^-$ -RR. Such a catalyst could provide a nearly 100%  $\text{NH}_4^+$  selectivity with an  $\text{NH}_4^+$  yield rate of  $274 \mu\text{g h}^{-1} \text{mg}^{-1}$ . Wang *et al.*<sup>53</sup> fabricated carbon-supported  $\text{RuO}_2$  nanosheets with abundant oxygen vacancies for electrochemical  $\text{NO}_3^-$  to  $\text{NH}_3$  conversion. The abundant oxygen vacancies within the  $\text{RuO}_2$  nanosheets could regulate the d-band center and improve the hydrogen affinity, thus reducing the reaction-energy barrier of the potential-determining step ( $\text{NH}_2^+ - \text{NH}_3^+$ ). As a result, this catalyst displayed a superior electrocatalytic activity for the conversion of  $\text{NO}_3^-$  to  $\text{NH}_3$  ( $\text{NH}_3$  FE of 97.46% and selectivity of 96.42%) than that of the crystalline counterparts.

### 3.2 Single-atom catalysts

Single-atom catalysts, a group of emerging frontier materials comprising isolated metal atoms dispersed into support materials, have triggered explosive research interest within the catalysis field owing to their remarkably high catalytic activity and selectivity. When applied to the  $\text{NO}_3^-$ -RR, single-atom catalysts can provide the following desirable advantages, including

(i) the specific atomic structure can expose abundant adsorption sites and homogenous catalytic active centers; (ii) the strong interactions between single atoms and the surrounding atoms enable superior long-term electrolysis; and (iii) the absence of multiple neighboring active sites required for coupling N-N bonds in their structure can efficiently suppress the generation of by-product  $\text{N}_2$ , thus enhancing  $\text{NH}_3$  selectivity. Currently, both experimental and theoretical calculations have suggested that single-atom catalysts are effective toward electroreduction of  $\text{NO}_3^-$  to  $\text{NH}_3$ .

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  $\text{NO}_3^-$  to  $\text{NH}_3$  conversion, as shown in Fig. 4a. Firstly, the adsorption energies of  $\text{NO}_3^-$ , a H proton, and an  $\text{N}_2$  molecule on TM/g-CN were systematically calculated. As revealed from Fig. 4b, the adsorption ability for  $\text{NO}_3^-$  was stronger than for H proton or  $\text{N}_2$  on TM/g-CN catalysts, except for Pt and Au, indicating that the  $\text{NO}_3^-$ -RR is more favorable than the HER and NRR. By combining with detailed pathways of  $\text{NO}_3^-$  reduction on TM/g-CN, they established a volcano plot of limiting potential selecting the adsorption energy of  $\text{NO}_3^-$  as a descriptor (Fig. 4c), where Ti and Zr appeared near the top of the volcano. Based on the above analysis, Ti/g-CN and Zr/g-CN possessed stronger adsorption abilities for  $\text{NO}_3^-$  compared with those of other TM/g-CN catalysts, making them fascinating electrocatalysts with high activity and selectivity for the  $\text{NO}_3^-$ -RR. Similarly, Lv *et al.*<sup>55</sup> explored the  $\text{NO}_3^-$ -RR performance of a set of transition-metal single-atom (Ti, Os, Ru, Cr, Mn, and Pt) catalysts supported on g- $\text{C}_3\text{N}_4$  by performing DFT calculations. The calculation results suggested that Ru/g- $\text{C}_3\text{N}_4$  featured the highest activity and selectivity for the conversion



**Fig. 4** (a) Atomic structure of TM/g-CN and corresponding element list (from Ti to Au). (b) Comparison of adsorption energies of  $\text{NO}_3^-$ ,  $\text{N}_2$ , and H proton on TM/g-CN. (c)  $\text{NO}_3^-$ -RR volcano plot of TM/g-CN using the adsorption energy of  $\text{NO}_3^-$  as the descriptor. Reproduced from ref. 54 with permission from Wiley-VCH, copyright 2021. (d) Volcano correlation curve between the limiting potential and adsorption energy of  $\text{NO}_3^-$  of TM/g- $\text{C}_3\text{N}_4$ . Reproduced from ref. 55 with permission from the American Chemical Society, copyright 2021. (e)  $\text{NH}_3$  FE of Fe-MoS<sub>2</sub> under various potentials. (f) Reaction pathway for the  $\text{NO}_3^-$ -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 M K <sub>2</sub> SO <sub>4</sub> + 0.5 M NO <sub>3</sub> <sup>-</sup>    | 0.46 mmol h <sup>-1</sup> cm <sup>-2</sup>       | 75%                 | -0.85 <sup>a</sup> /-0.66 <sup>b</sup> | 58   |
| Fe-PPy SAC                                        | 0.1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>                               | 2.75 mg h <sup>-1</sup> cm <sup>-2</sup>         | 100%                | -0.7/-0.3                              | 59   |
| Cu SAC                                            | 0.1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>                               | 4.5 mg cm <sup>-2</sup> h <sup>-1</sup>          | 84.7%               | -1.0                                   | 60   |
| Cu- <i>cis</i> -N <sub>2</sub> O <sub>2</sub> SAC | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 1000 ppm NO <sub>3</sub> <sup>-</sup> | 28.73 ± 1.25 mg h <sup>-1</sup> cm <sup>-2</sup> | 80%                 | -1.6                                   | 61   |
| FeN <sub>2</sub> O <sub>4</sub> SAC               | 0.1 M K <sub>2</sub> SO <sub>4</sub> + 0.5 M NO <sub>3</sub> <sup>-</sup>    | 46 mg h <sup>-1</sup> mg <sup>-1</sup>           | 92%                 | -0.88 <sup>a</sup> /-0.68 <sup>b</sup> | 62   |
| Ni-Cu SAC                                         | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 200 ppm NO <sub>3</sub> <sup>-</sup>  | 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 μmol cm <sup>-2</sup> h <sup>-1</sup>       | 94%                 | -0.45                                  | 64   |

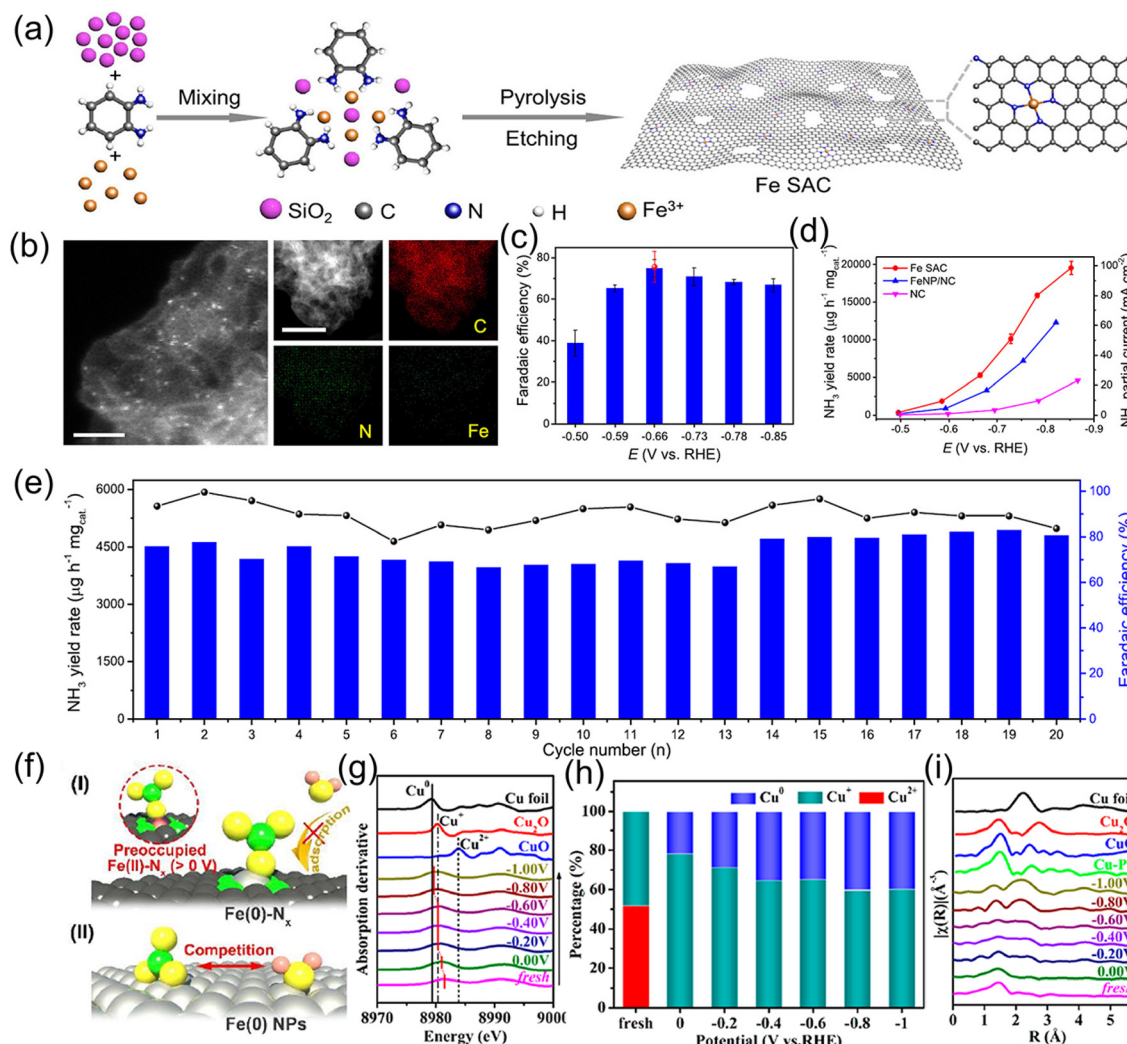
<sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

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><sup>-</sup> 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.*<sup>56</sup> 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-N<sub>2</sub>) was responsible for the good adsorption ability of the catalyst for NO<sub>3</sub><sup>-</sup> 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.*<sup>24</sup> demonstrated that Cu-N-C could effectively inhibit the generation of toxic NO<sub>2</sub><sup>-</sup> and by-product N<sub>2</sub>, as well as facilitate the reduction of HNO<sub>3</sub><sup>\*</sup> to NO<sub>2</sub><sup>\*</sup>, and NH<sub>2</sub><sup>\*</sup> to NH<sub>3</sub><sup>\*</sup>. It is well known that the nitrate reductase enzyme has a Mo(IV) atom coordinated with sulfur coordinating ligands, whereas nitrogenase is a multi-nuclear enzyme with MoFe<sub>7</sub> 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><sup>-</sup>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 NH<sub>3</sub> formation rate of 431.8 μg h<sup>-1</sup> cm<sup>-2</sup>. DFT calculations revealed that the Fe-MoS<sub>2</sub> catalyst featured a superior ability for activating NO<sub>3</sub><sup>-</sup> by virtue of the strong interaction between the d-band orbitals of the Fe atoms and the 2π\* orbitals of the NO species, lowering the energy barrier for conversion of \*NO to \*N (the rate-determining step) (Fig. 4f and g). At the same time, Wu *et al.*<sup>58</sup> chose an N-doped porous carbon matrix to anchor Fe single-atoms (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 mmol h<sup>-1</sup> cm<sup>-2</sup> at -0.85 V vs. RHE) and a high NH<sub>3</sub> FE of 75% at -0.66 V vs. RHE were achieved in K<sub>2</sub>SO<sub>4</sub> 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>x</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>x</sub> structure under operating conditions is essential to recognize the real active sites. To achieve the above-mentioned target, Li *et al.*<sup>59</sup> 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(II)-N<sub>x</sub> sites prior to the formation of Fe (0), which could effectively eliminate the competing adsorption of water under aqueous conditions. Subsequently, Yang *et al.*<sup>60</sup> discovered the restructuring of Cu-N<sub>4</sub> sites during the electrochemical production of NH<sub>3</sub> by converting NO<sub>3</sub><sup>-</sup> 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 electro-reduction 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.

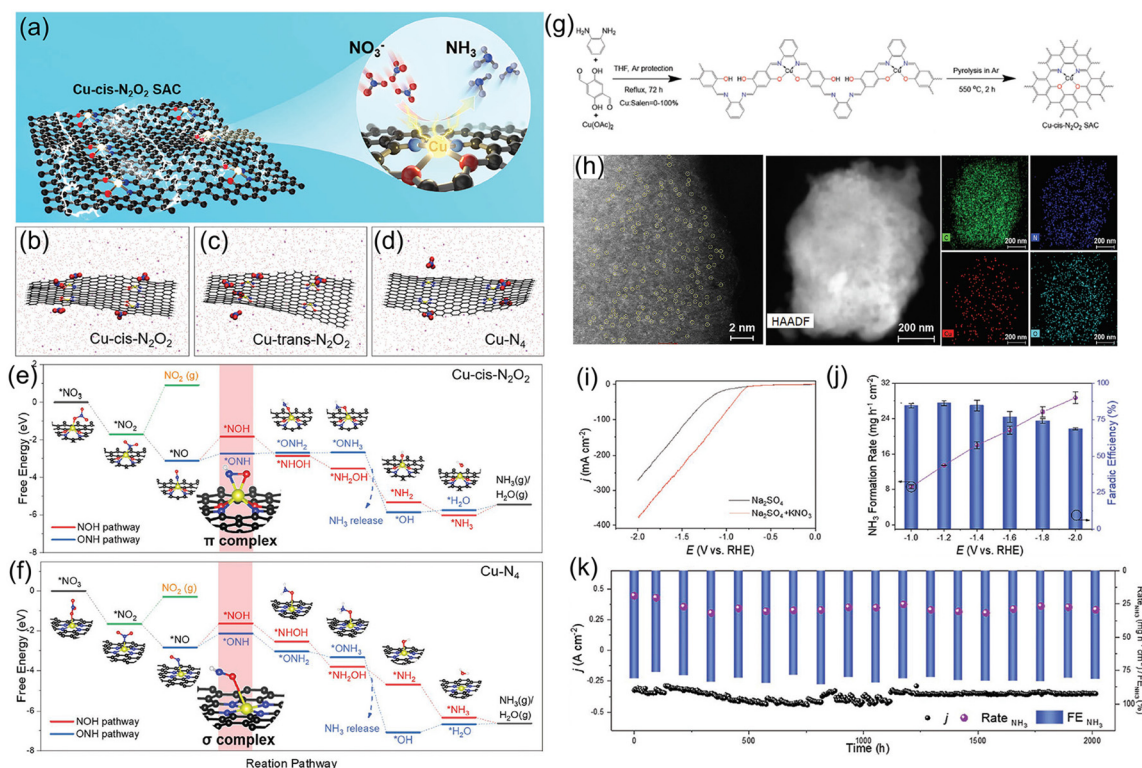
Although single-atom catalysts deliver outstanding electrocatalytic activity for the conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, the isolated metal centers usually coordinate with four N atoms in C<sub>4v</sub> symmetry. Such a coordination structure features relatively weak adsorption ability for NO<sub>3</sub><sup>-</sup>, 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><sup>-</sup>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.*<sup>61</sup> broke the coordination symmetry of Cu SAC by replacing the local coordination atoms from 4N to 2N + 2O (Cu-*cis*-N<sub>2</sub>O<sub>2</sub>). First-principle calculations were preferentially employed to reveal the coordination symmetry-breaking in Cu SAC and investigate the reaction pathways of Cu-*cis*-N<sub>2</sub>O<sub>2</sub> and Cu-N<sub>4</sub> catalysts, as indicated in Fig. 6a-e. In terms of Cu-*cis*-N<sub>2</sub>O<sub>2</sub>, 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><sup>-</sup> 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*-N<sub>2</sub>O<sub>2</sub> was well maintained after continual operation for 2000 h (Fig. 6i-k). Analogously, Zhang *et al.*<sup>62</sup> fabricated an Fe single-atom catalyst with unique FeN<sub>2</sub>O<sub>2</sub> coordination *via* direct pyrolysis of metal-organic frameworks possessing a pre-organized FeN<sub>2</sub>O<sub>4</sub> 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-N<sub>2</sub>O<sub>2</sub>. (i) LSV curves, (j) NH<sub>3</sub> formation rate and FE at each given potential. (k) Cycling stability test of Cu-cis-N<sub>2</sub>O<sub>2</sub>. 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 FeN<sub>4</sub>, FeN<sub>2</sub>O<sub>2</sub> features superior conductivity, NH<sub>3</sub> 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.*<sup>63</sup> reported a single-atom Ni-alloyed Cu catalyst that achieved an NH<sub>3</sub> yield rate of 326.7 μmol 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.*<sup>64</sup> 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 μg<sub>NH<sub>3</sub></sub> mg<sup>-1</sup> h<sup>-1</sup>) 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, non-noble transition metals, such as Cu, Co, Ni, Fe, and their alloys, have drawn extensive attention as promising alternatives in the field of electrochemical conversion of NO<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 NO<sub>3</sub><sup>-</sup>RR. In the following section, the recent advances in transition-metal-based 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 π\* molecular orbital of NO<sub>3</sub><sup>-</sup>, metallic Cu catalysts have attracted extensive

**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 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M KNO <sub>3</sub>               | 101.4 μmol h <sup>-1</sup> cm <sup>-2</sup>  | 93.91%              | -0.266                               | 71   |
| dr-Cu nanoplates                    | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 50 ppm KNO <sub>3</sub> <sup>-</sup>  | 781.25 μg h <sup>-1</sup> mg <sup>-1</sup>   | 85.47%              | -0.654                               | 72   |
| Cu with grain boundaries            | 0.1 M KOH + 10 mM NO <sub>3</sub> <sup>-</sup>                               | 487.8 mmol g <sup>-1</sup> h <sup>-1</sup>   | 94.2%               | -0.2                                 | 74   |
| Cu@C                                | 0.1 M KOH + 1 mM NO <sub>3</sub> <sup>-</sup>                                | 469.5 μg h <sup>-1</sup> cm <sup>-2</sup>    | 72.0%               | -0.9 <sup>a</sup> /-0.3 <sup>b</sup> | 77   |
| Cu/TiO <sub>2-x</sub>               | 0.5 M Na <sub>2</sub> SO <sub>4</sub> + 500 ppm NO <sub>3</sub> <sup>-</sup> | 0.1143 mmol h <sup>-1</sup> mg <sup>-1</sup> | 81.34%              | -0.75                                | 78   |
| Cu-CuO                              | 0.1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>                               | 3.17 mol h <sup>-1</sup> g <sup>-1</sup>     | 98.7%               | -0.8                                 | 79   |
| Co nanosheets                       | 1 M KOH + 0.1 M NO <sub>3</sub> <sup>-</sup>                                 | 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 mg h <sup>-1</sup> cm <sup>-2</sup>     | 90%                 | -0.5                                 | 90   |
| Ni-NCNTs                            | 0.5 M Na <sub>2</sub> SO <sub>4</sub> + 0.3 M NO <sub>3</sub> <sup>-</sup>   | 5.1 mg h <sup>-1</sup> cm <sup>-2</sup>      | 99%                 | -0.5                                 | 92   |
| CuFe alloys                         | 0.1 M Na <sub>2</sub> SO <sub>4</sub> + 100 ppm NO <sub>3</sub> <sup>-</sup> | —                                            | 81.1%               | -0.7                                 | 93   |
| CuNi@C alloy                        | 0.1 M PBS + 50 mg L <sup>-1</sup> NO <sub>3</sub> <sup>-</sup>               | —                                            | 79.6%               | -1.0                                 | 95   |
| Co <sub>0.5</sub> Cu <sub>0.5</sub> | 1 M KOH + 50 mM KNO <sub>3</sub>                                             | —                                            | 95%                 | -0.03                                | 96   |

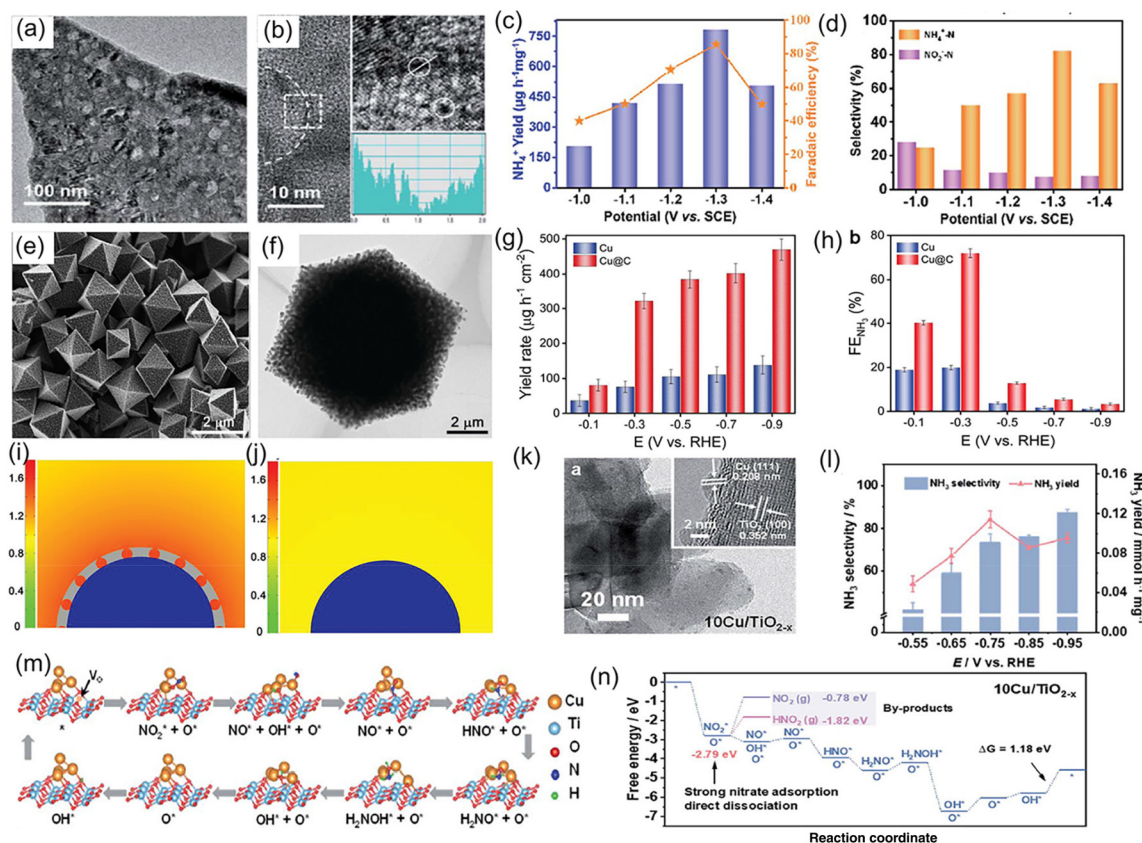
<sup>a</sup> NH<sub>3</sub> yield rate. <sup>b</sup> Faradaic efficiency.

attention toward the NO<sub>3</sub><sup>-</sup>RR.<sup>65–67</sup> 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 NO<sub>3</sub><sup>-</sup>. Previous literature indicated that rational structure design and crystal regulation could achieve the above-mentioned target.<sup>68,69</sup> For example, Fu *et al.*<sup>70</sup> 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><sup>-</sup>RR, it showed superior electrochemical activity with a large NH<sub>3</sub> 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><sup>-</sup> to NH<sub>3</sub>.<sup>71</sup>

On the other hand, interface engineering, such as defect engineering,<sup>72</sup> heteroatom doping,<sup>73</sup> coupling with carbon,<sup>65</sup> grain-boundary engineering,<sup>74</sup> and constructing heterostructures<sup>75,76</sup> has been proposed to further enhance the electrochemical NO<sub>3</sub><sup>-</sup>RR activity of metallic Cu catalysts. As presented in Fig. 7a and b, Xu *et al.*<sup>72</sup> fabricated the atomic-defect-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><sup>-</sup> conversion rate of 93.26%, favorable NH<sub>3</sub> selectivity of 81.99%, as well as a high NH<sub>3</sub> FE of 85.47%, which were superior to those of Cu nanoplates without defects (Fig. 7c and d). Song *et al.*<sup>77</sup> 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><sup>-</sup>, 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<sup>-2</sup> at -0.3 and -0.9 V vs. RHE, respectively, which were approximately 3.6 times larger than those of Cu nanoparticles (Fig. 7g and h). To reveal such impressive electrocatalytic activity, they adopted the finite-element method to simulate the enrichment effect of NO<sub>3</sub><sup>-</sup> 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><sup>-</sup> 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 the 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 NH<sub>3</sub> yield rate of 487.8 mmol g<sup>-1</sup> h<sup>-1</sup> 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 TiO<sub>2-x</sub>, in which the Cu nanoparticles were homogeneously anchored on TiO<sub>2-x</sub> nanosheets (Fig. 7k). As a catalyst for the NO<sub>3</sub><sup>-</sup>RR, the designed heterostructure electrode exhibited an NH<sub>3</sub> formation rate of 0.1143 mmol h<sup>-1</sup> mg<sup>-1</sup> along with a high FE of

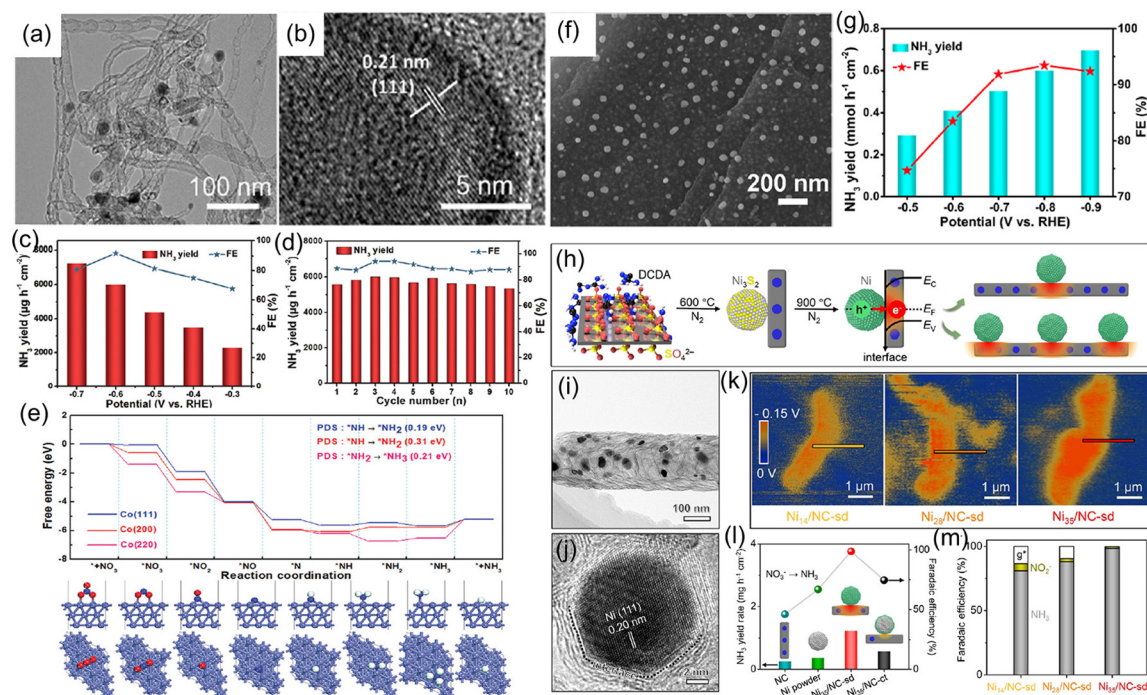


**Fig. 7** (a) TEM and (b) HRTEM images of a dr-Cu nanoplate. (c)  $\text{NH}_4^+$  yield rate and FE, and (d)  $\text{NH}_4^+$  selectivity of dr-Cu nanoplates at various potentials. Reproduced from ref. 72 with permission from The Royal Society of Chemistry, copyright 2021. (e) SEM and (f) TEM images of Cu@C. (g)  $\text{NH}_3$  yield rate and (h) FE of Cu@C under different potentials. Simulated concentrations and distribution of local  $\text{NO}_3^-$  on the surface of (i) Cu@C and (j) Cu at the diffusion time of 7  $\mu\text{s}$ . 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<sub>2-x</sub>. (l)  $\text{NH}_3$  selectivity and yield rate of Cu/TiO<sub>2-x</sub> at each applied potential. (m) Reaction mechanism and (n) corresponding calculated free energy changes of the  $\text{NO}_3^-$ 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<sub>2-x</sub> counterparts (Fig. 7l). Such excellent electrocatalytic activity could be ascribed to the introduction of oxygen defects and metallic Cu clusters, which not only modified the electronic conductivity of the heterostructure electrode, but also optimized the adsorption energy of  $\text{NO}_3^-$  and hydrogenation manner that suppressed the generation of by-products (Fig. 7m and n). Similarly, Zhao *et al.*<sup>79</sup> designed and fabricated a Cu-CuO heterostructure as an electrocatalyst for the  $\text{NO}_3^-$ RR, where the heterointerface between Cu and CuO was favorable for promoting the hydrogenation of  $^*\text{NO}$  to  $^*\text{NOH}$  and inhibiting the HER during the reduction process of  $\text{NO}_3^-$ . Thus, this heterostructure catalyst showed a molar-level  $\text{NH}_3$  yield rate of 3.17 mol h<sup>-1</sup> g<sup>-1</sup> 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  $\text{NO}_3^-$ , which controls the proton transfer rate and further leads to sluggish reaction kinetics for  $\text{NH}_3$  synthesis.<sup>80</sup> To address the above-mentioned issue, Yu *et al.*<sup>81</sup> 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  $\text{NO}_3^-$ . They experimentally encapsulated Cu nanoparticles into the uncoordinated carboxylate-ligand-rich MOF matrix through a particle decomposition route. As expected, the designed Cu-based catalyst achieved an alluring electrochemical performance for the reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  in alkaline media, including a high  $\text{NH}_3$  yield rate of 496.4 mmol h<sup>-1</sup> g<sup>-1</sup> 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  $\text{NO}_3^-$  to  $\text{NH}_3$ .<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  $\text{NO}_3^-$ RR. In 0.1 M NaOH with 0.1 M  $\text{NO}_3^-$ , the Co-NCNTs delivered a high activity for the  $\text{NO}_3^-$ RR with an  $\text{NH}_3$  production rate of 5996  $\mu\text{g h}^{-1}\text{cm}^{-2}$  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)  $\text{NH}_3$  yield rate and FE of Co-NCNTs under various potentials. (d) Recycling test of Co-NCNTs at  $-0.6$  V. (e) Free-energy profiles of the  $\text{NO}_3^-$  RR on different crystal facets of metallic Co. Reproduced from ref. 88 with permission from The Royal Society of Chemistry, copyright 2022. (f) SEM image, (g)  $\text{NH}_3$  yield rate and FE at different potentials of Co-carbon derived from corncob. Reproduced from ref. 89 with permission from the American Chemical Society, copyright 2022. (h) Fabrication process of Ni-NCNTs catalyst. (i and j) TEM and HRTEM images of Ni-NCNTs. (k) Surface electric field distribution of Ni-NCNTs sample. (l and m)  $\text{NH}_3$  yield rate and FE of Ni-NCNTs catalyst. Reproduced from ref. 92 with permission from Wiley-VCH, copyright 2021.

(Fig. 8e) revealed that the Co (111) facet is more favorable for the  $\text{NO}_3^-$  RR than the Co (200) and Co (220) facets, in which the rate-determining step is the hydrogenation of  $^*\text{NH}$  to  $^*\text{NH}_2$ . The corresponding energy barrier was only 0.19 eV, indicating the impressive  $\text{NO}_3^-$  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  $\text{NO}_3^-$  RR to  $\text{NH}_3$ , which achieved a large  $\text{NH}_3$  production rate of  $0.6 \text{ mmol h}^{-1} \text{ cm}^{-2}$  with a FE of 93.4%, as depicted in Fig. 8f and g.<sup>89</sup> Fang and coworkers<sup>90</sup> reported that metallic Fe anchored on cyano-coordination polymer porous nanosheets (Fe-cyano NSs) displayed an outstanding electrochemical  $\text{NH}_3$  synthesis through the reduction of  $\text{NO}_3^-$  in an alkaline electrolyte. Bi has also been employed as a highly efficient catalyst for electrochemical reduction of  $\text{NO}_3^-$  due to its unique atomic structure, in which the interlayer lattice compression shortens the Bi-Bi bond to broaden the 6p bandwidth for electronic delocalization, enhancing the adsorption energy for nitrogen intermediates.<sup>84</sup> Iarchuk *et al.*<sup>91</sup> synthesized Ni foam catalysts through a dynamic hydrogen-bubble-template-assisted electrodeposition process. An  $\text{NH}_3$  FE of more than 95% was obtained under the relatively low potential range from  $-0.1$  to  $-0.3$  V vs. RHE. Gao *et al.*<sup>92</sup> constructed a Schottky heterostructure composed of metallic Ni and nitrogen-doped carbon nanotubes (Ni-NCNTs) for converting  $\text{NO}_3^-$  to  $\text{NH}_3$  at room temperature (Fig. 8h–j). In terms of

heterostructure catalyst, the heterointerface between Ni nanoparticles and NCNTs could induce the formation of a built-in electric field (Fig. 8k), which facilitated the accumulation and fixation of  $\text{NO}_3^-$  on the surface of the catalyst and consequently promoting the reaction kinetics during the electrochemical process. As a result, the designed Ni-NCNTs enabled a high FE of 99% for the electrocatalytic reduction of  $\text{NO}_3^-$ , and a large  $\text{NH}_3$  formation rate of  $5.1 \text{ mg h}^{-1} \text{ cm}^{-2}$  in the electrochemical conversion of  $\text{NO}_3^-$  (Fig. 8l and m).

**3.3.2 Metal alloys.** Coupling with a secondary metal has been regarded as a fascinating route to enhance the electrochemical activity of transition-metal catalysts *via* regulating the electronic structure of the metal and exerting a synergistic effect of two different metals. Table 3 summarizes the electrochemical performance of metal alloy catalysts for the  $\text{NO}_3^-$  RR. For instance, Tang *et al.*<sup>93</sup> demonstrated that Cu-Fe bimetallic nanoalloys with a Cu/Fe molar ratio of 3 : 1 presented a high  $\text{NH}_3$  FE of 81.1% at  $-0.7$  V vs. RHE within 6 h in 0.1 M  $\text{Na}_2\text{SO}_4$  containing 100 ppm  $\text{NO}_3^-$ . Similarly, Sargent and coauthors<sup>94</sup> indicated that  $\text{Cu}_{50}\text{Ni}_{50}$  alloy catalysts only required an overpotential of 0.2 V to obtain the maximum  $\text{NH}_3$  FE under various concentrations of  $\text{NO}_3^-$ , and produced a 6-times increment in the  $\text{NO}_3^-$  RR activity compared to the case of pure Cu at 0 V vs. RHE. DFT calculations revealed that the introduction of Ni atoms led to the upshifting of the d-band center toward the Fermi level, which improved the adsorption energies of the

intermediates and enhanced the selectivity for  $\text{NH}_3$ . Recently, Liu *et al.*<sup>95</sup> incorporated CuNi alloy nanoparticles into a nitrogen-doped carbon matrix with hierarchical pores by pyrolysis of bimetallic MOFs. A high  $\text{NH}_3$  selectivity of 94.4% and FE of 79.6% were achieved when utilizing the designed CuNi@C as a catalyst for the  $\text{NO}_3^-$  RR. Jeon *et al.*<sup>96</sup> designed cobalt-copper ( $\text{Co}_{1-x}\text{Cu}_x$ ) nanoparticles supported on a three-dimensional substrate for efficient and selective  $\text{NH}_3$  synthesis via an electrocatalytic  $\text{NO}_3^-$  reduction. Typically, the optimized  $\text{Co}_{0.5}\text{Cu}_{0.5}$  catalyst performed at a high  $\text{NH}_3$  FE of over 95% at  $-0.03$  V with an  $\text{NH}_3$  partial current density of  $\sim 176$   $\text{mA cm}^{-2}$  at 50 mM nitrate, which is 7.3- and 1.7-fold higher than those of the pure Co and Cu counterparts, respectively. Importantly, replacing Co with Cu enabled tuning of the onset potential on the Co catalyst and maintained a high selectivity toward  $\text{NH}_3$ .

### 3.4 Transition-metal compound catalysts

#### 3.4.1 Metal oxides

**3.4.1.1 Copper-based oxides.** Transition-metal oxides have been widely investigated as electrocatalysts for  $\text{NH}_3$  synthesis via converting  $\text{NO}_3^-$  under ambient conditions (Table 4). As summarized in the above section, metallic Cu has been intensively studied for the electroreduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  owing to its favorable adsorption ability for  $\text{NO}_3^-$  and various intermediates (*e.g.*,  $\text{NO}_2^-$  and NO). However, pure Cu catalysts still suffer from serious catalytic instability. For the purpose of overcoming this issue, substantial efforts have

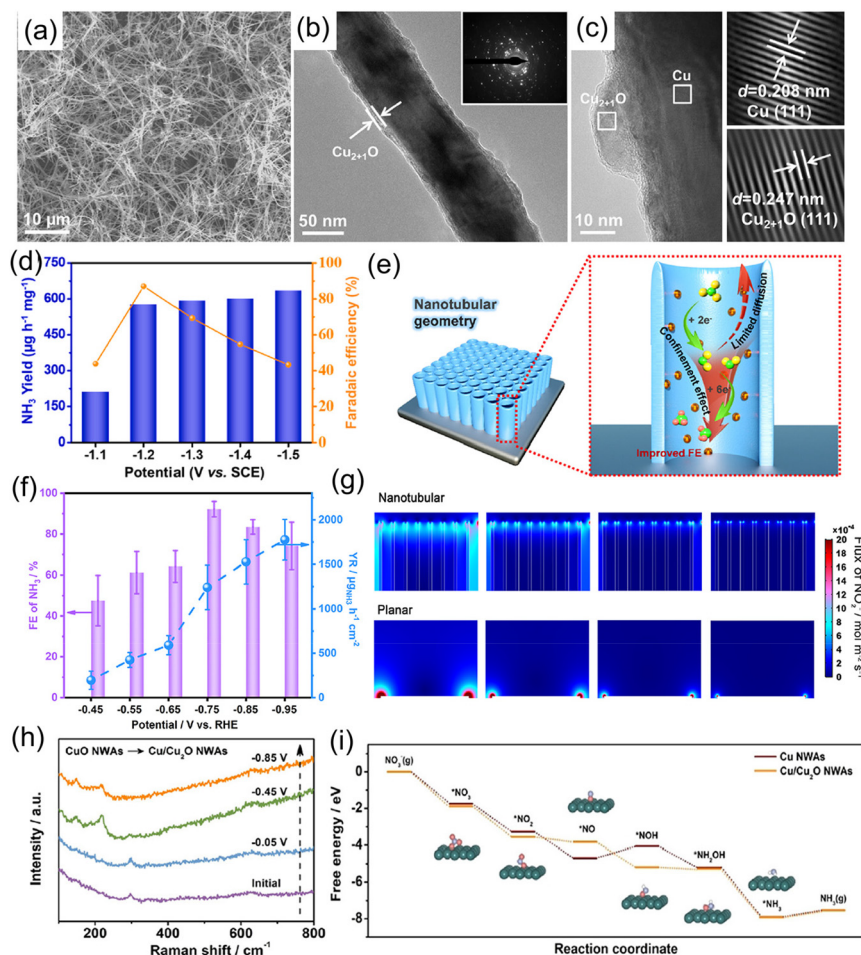
recently been made into the study of Cu-based oxide catalysts for highly-efficient electrochemical  $\text{NO}_3^-$  to  $\text{NH}_3$  conversion.

For example, Yuan *et al.*<sup>97</sup> explored the influence of Cu oxidation state on the electrochemical reduction of  $\text{NO}_3^-$ , and found that the  $\text{NH}_3$  formation rate and FE of a Cu electrode could be significantly boosted after surface oxidation. After that, Ren *et al.*<sup>98</sup> designed and fabricated core-shell structural  $\text{Cu@Cu}_{2+1}\text{O}$  nanowires (Fig. 9a–c) for electrochemical conversion of  $\text{NO}_3^-$  to  $\text{NH}_3$ . In terms of the  $\text{Cu@Cu}_{2+1}\text{O}$  catalyst, the interior metallic Cu components could provide pathways for fast electron transfer due to the one-dimensional nanowire structure, while the exterior  $\text{Cu}_{2+1}\text{O}$  layer affords a massive amount of catalytically active sites. Furthermore, DFT calculation results suggested that the introduction of a surface oxidation layer regulated the Cu d-band center and modulated the adsorption energies of various intermediates. Therefore, the constructed  $\text{Cu@Cu}_{2+1}\text{O}$  catalyst exhibited a high  $\text{NH}_3$  yield rate of  $576.53$   $\mu\text{g h}^{-1} \text{mg}^{-1}$  associated with a FE of 87.7% at  $-0.564$  V vs. RHE, and  $\text{NH}_3$  selectivity of 76% (Fig. 9d). Qin *et al.*<sup>99</sup> further illustrated the effects of the surface structure of  $\text{Cu}_2\text{O}$  (exposing facets) on  $\text{NO}_3^-$  reduction to  $\text{NH}_3$ . Both experimental and theoretical calculation results illustrated that the  $\text{Cu}_2\text{O}$  (100) facet featured a relatively smaller energy barrier for  $\text{NH}_3$  formation than the  $\text{Cu}_2\text{O}$  (111) facet, leading to a large  $\text{NH}_3$  formation rate ( $743$   $\mu\text{g h}^{-1} \text{mg}^{-1}$ ) and high FE (82.3%) at  $-0.6$  V vs. RHE.

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

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

<sup>a</sup>  $\text{NH}_3$  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<sub>3</sub> FE and yield rate of CuO<sub>x</sub>/TiO<sub>2</sub> at varying potentials. (g) Simulated NO<sub>2</sub><sup>-</sup> 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><sup>-</sup>RR over Cu nanowires. Reproduced from ref. 106 with permission from Wiley-VCH, copyright 2020.

To further enhance the electrocatalytic activity of Cu<sub>2</sub>O toward the NO<sub>3</sub><sup>-</sup>RR, various strategies have been employed, such as introducing oxygen defects<sup>100,101</sup> and constructing heterostructures.<sup>79,102,103</sup> For example, Xu *et al.*<sup>104</sup> designed core-shell structural CuO@MnO<sub>2</sub> hierarchical nanoarrays grown on Cu foam (CuO@MnO<sub>2</sub>/CF) for the NO<sub>3</sub><sup>-</sup>RR. The heterointerface between the CuO nanowires and MnO<sub>2</sub> 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 NH<sub>3</sub> yield rate and FE after 5 consecutive recycling tests. Qiu *et al.*<sup>105</sup> 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>/TiO<sub>2</sub> catalyst system, TiO<sub>2</sub> nanotubes could efficiently hinder the diffusion of NO<sub>2</sub><sup>-</sup> 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.

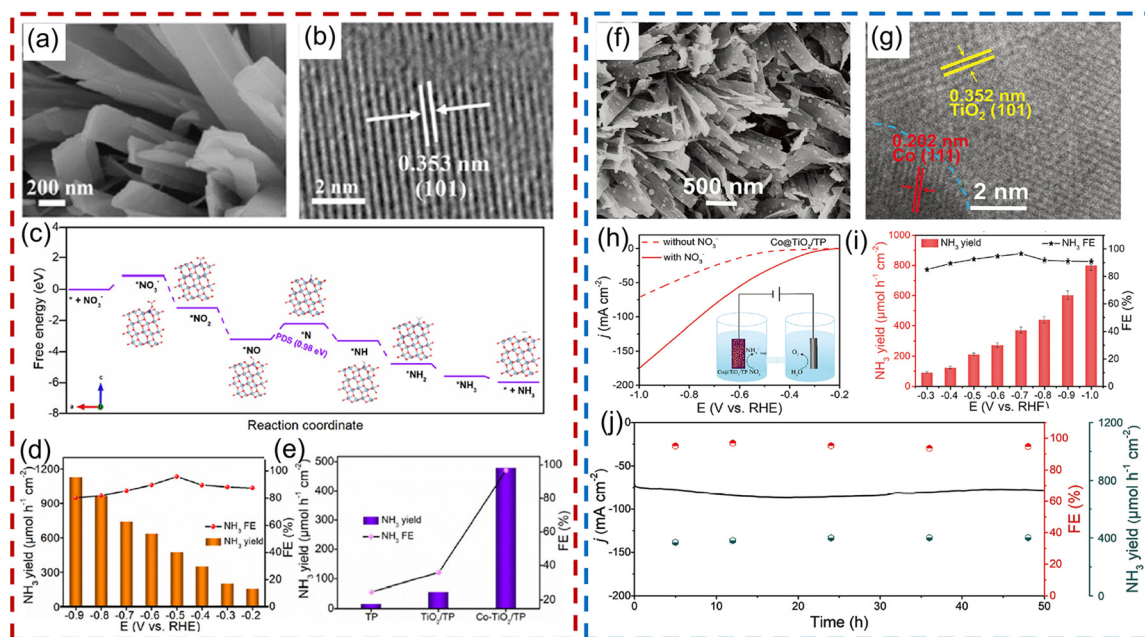
Cu-based oxidation catalysts present outstanding electrochemical activity toward selective reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, but the origin of their activity and the structural evolution that occurs during the electrochemical reaction process were still experimentally unclear. In this regard, Zhang and his co-workers applied *in situ* characterization techniques to unveil the active phase of the CuO electrocatalyst. Experimental results suggested that CuO was transformed to Cu/Cu<sub>2</sub>O during the reduction process of NO<sub>3</sub><sup>-</sup>, 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.  $\text{NO}_3^-$  adsorbed on the surface of electrode was firstly reduced to  $^*\text{NO}_2$  and  $^*\text{NO}$ , in which  $^*\text{NO}$  was hydrogenated to give  $^*\text{NHON}$  and  $^*\text{NH}_2\text{OH}$ . Subsequently,  $^*\text{NH}_2\text{OH}$  was converted to  $^*\text{NH}_3$  and further desorbed from the surface of the electrode generating  $\text{NH}_3$ . DFT calculations also discovered that the origin of the activity enhancement was attributed to the reconstructed structure, in which electron transfer from  $\text{Cu}_2\text{O}$  to Cu at the interface could promote the generation of the  $^*\text{NOH}$  intermediate and limit the competing HER (Fig. 9i).<sup>106</sup>

**3.4.1.2 Titanium-based oxides.** Titanium oxide ( $\text{TiO}_2$ ) is a promising electrocatalyst candidate for the electrochemical reduction of  $\text{NO}_3^-$  owing to its advantages in terms of cost and robustness.<sup>107,108</sup> For example, Jia *et al.*<sup>109</sup> fabricated  $\text{TiO}_2$  nanotubes rich in oxygen vacancies as an electrocatalyst for the  $\text{NO}_3^-$ -RR. An outstanding conversion rate of 95.2% for  $\text{NH}_3$  production from  $\text{NO}_3^-$  electroreduction associated with a FE of 85% was achieved. DFT calculations revealed that  $\text{NO}_3^-$  was adsorbed on the surface of the electrode and preferentially filled the oxygen defects existing in the  $\text{TiO}_2$  nanotubes, which weakened the N–O bonding, modulated the adsorption energies of the intermediates, and limited the generation of by-products. Analogously, oxygen-vacancy- $\text{TiO}_2$  nanomaterials composed of rutile and anatase phases were fabricated as a catalyst for  $\text{NH}_3$  synthesis from the electroreduction of  $\text{NO}_3^-$ , which could deliver an  $\text{NH}_3$  FE of 78.0% and selectivity of 81.9%. Online differential electrochemical mass spectrometry and first-principle calculations revealed that the existence of

oxygen vacancies ( $\text{Ti}^{3+}$ ) and the heterointerface between the rutile and anatase phases were favorable for modulating the adsorption energy of  $\text{NO}_3^-$  and facilitating the hydrogenation reaction to form  $^*\text{NOH}$ , which led to a relatively high  $\text{NH}_3$  selectivity and FE.<sup>110</sup> However, the limited selectivity for  $\text{NH}_3$  and sluggish reaction kinetics hinder their further application for  $\text{NH}_3$  electrosynthesis.

In this regard, our group proposed a series of modification strategies for improving the above-mentioned issues, such as heteroatom doping, and constructing Schottky junctions and p–n heterojunctions. For example, taking a Co-based catalyst with high catalytic activity into consideration, we introduced Co heteroatoms into a  $\text{TiO}_2$  nanoribbon array supported on Ti foil for electroreduction of  $\text{NO}_3^-$  (Fig. 10a and b). Co-doping can effectively improve the intrinsic electronic conductivity of  $\text{TiO}_2$  and increase the content of oxygen defects in  $\text{TiO}_2$ , which further facilitates the adsorption of  $\text{NO}_3^-$  and transportation of charge at the interface, as well as decreasing the energy barrier of the potential-determining step (Fig. 10c). As a result, Co-doped  $\text{TiO}_2$  nanoribbon arrays delivered a large  $\text{NH}_3$  production rate of  $1127 \mu\text{mol h}^{-1} \text{cm}^{-2}$  and a high FE of 98.2%, which was remarkably superior to that of its counterpart in alkaline media ( $88.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$ ; 35.1%), as presented in Fig. 10d and e.<sup>111</sup> Inspired by this, we further constructed a Schottky junction by integrating metallic Co nanoparticles into  $\text{TiO}_2$  nanobelt arrays ( $\text{Co@TiO}_2$ ) (Fig. 10f and g). A built-in electric field formed at the heterointerface between Co and  $\text{TiO}_2$ , which was beneficial for the capture of  $\text{NO}_3^-$  on the

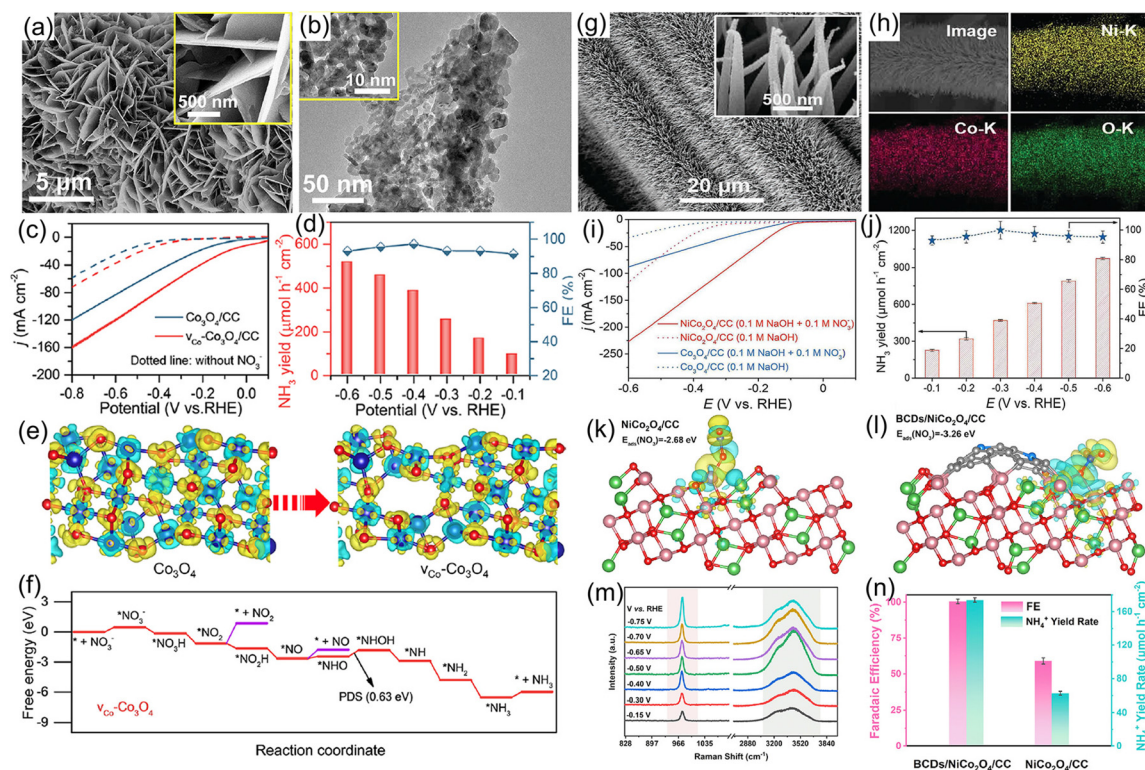


**Fig. 10** (a) SEM and (b) HRTEM images of Co-doped  $\text{TiO}_2$ . (c) Calculated free-energy changes of the  $\text{NO}_3^-$ -RR on the Co-doped  $\text{TiO}_2$ . (d)  $\text{NH}_3$  yield rate and FE of Co-doped  $\text{TiO}_2$  under given potentials. (e) Comparison of  $\text{NH}_3$  yield rate and FE between  $\text{TiO}_2$  and Co-doped  $\text{TiO}_2$ . Reproduced from ref. 111 with permission from The Royal Society of Chemistry, copyright 2022. (f) SEM and (g) HRTEM images of  $\text{Co@TiO}_2$  heterojunction catalyst. (h) LSV curves and (i)  $\text{NH}_3$  formation rate and FE at given potentials for  $\text{Co@TiO}_2$ . (j) The long-term electrocatalytic performance of the  $\text{Co@TiO}_2$  catalyst. Reproduced from ref. 112 with permission from Wiley-VCH, copyright 2023.

surface of the electrocatalyst and thus facilitated mass transfer during the electroreduction process of  $\text{NO}_3^-$ . Consequently, in a neutral medium containing 0.1 M  $\text{NO}_3^-$ , the as-designed  $\text{Co@TiO}_2$  catalyst enabled a high  $\text{NH}_3$  FE of 96.7% at  $-0.7$  V vs. RHE and a competitive  $\text{NH}_3$  formation rate of  $800 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at  $-1.0$  V (Fig. 10h and i). Meanwhile, this catalyst also showed impressive durability during recycling tests and 50 h of bulk electrolysis (Fig. 10j).<sup>112</sup> Following this,  $\text{Fe}_3\text{O}_4@\text{TiO}_2$ ,<sup>113</sup>  $\text{CoP}@\text{TiO}_2$ <sup>114</sup> and  $\text{FeS}_2@\text{TiO}_2$ <sup>115</sup> p-n heterojunctions were constructed by our team and utilized as electrocatalysts to convert  $\text{NO}_3^-$  to  $\text{NH}_3$ , where the selectivity and efficiency of bare  $\text{TiO}_2$  for the  $\text{NO}_3^-$ RR were significantly enhanced.

**3.4.1.3 Spinel oxide.** Spinel-type oxides feature unique advantages in terms of versatility, flexible ion arrangement, multivalence structure, and superior electronic conductivity, making them promising electrocatalysts for the  $\text{NO}_3^-$ RR.<sup>116</sup> For example,  $\text{Co}_3\text{O}_4$  has been extensively utilized as a catalyst for the electroreduction of  $\text{NO}_3^-$ , but its yield rate and selectivity of the target product  $\text{NH}_3$  are relatively low.<sup>117</sup> To enhance the electrocatalytic activity of  $\text{Co}_3\text{O}_4$ , our group<sup>118</sup> designed  $\text{Co}_3\text{O}_4$  nanosheet arrays with Co vacancies on carbon cloth for converting  $\text{NO}_3^-$  to  $\text{NH}_3$  (Fig. 11a and b). As presented in

Fig. 11c and d,  $\text{Co}_3\text{O}_4$  with Co vacancies delivered a high  $\text{NH}_3$  yield rate of  $517.5 \mu\text{mol h}^{-1} \text{g}^{-1}$  and a maximum FE of 97.2% at  $-0.6$  and  $-0.4$  V vs. RHE in alkaline electrolyte, respectively, which were higher than those of bare  $\text{Co}_3\text{O}_4$  nanosheets ( $183.8 \mu\text{mol h}^{-1} \text{g}^{-1}$  with a FE of 85.9%). Furthermore, DFT calculations demonstrated that the introduction of Co vacancies regulated the electron structure of  $\text{Co}_3\text{O}_4$ , optimized the adsorption energy of  $\text{NO}_3^-$  and reduced the energy barrier of the potential-determining step ( $^*\text{NHO}$  to  $^*\text{NHOH}$ ), leading to the high electrocatalytic activity (Fig. 11e and f). Similarly, we adopted Fe as a dopant to modulate the electron structure of  $\text{Co}_3\text{O}_4$ , further elevating its selectivity and  $\text{NH}_3$  yield rate during the electroreduction of  $\text{NO}_3^-$ .<sup>119</sup> In line with the above-mentioned viewpoint, many bimetal spinel oxides, such as  $\text{FeCo}_2\text{O}_4$ ,<sup>120</sup>  $\text{NiCo}_2\text{O}_4$ ,<sup>121</sup>  $\text{ZnCo}_2\text{O}_4$ ,<sup>122</sup>  $\text{AlCo}_2\text{O}_4$ ,<sup>77</sup> and  $\text{NiFe}_2\text{O}_4$ ,<sup>123</sup> have been synthesized and investigated as electrocatalysts for a highly efficient  $\text{NO}_3^-$ RR by our team. As demonstrated in Fig. 11g and h,  $\text{NiCo}_2\text{O}_4$  nanowire arrays grown on carbon cloth were synthesized for electrochemical  $\text{NH}_3$  production by conversion of  $\text{NO}_3^-$ . Owing to the synergistic effects of the two metal sites,  $\text{NiCo}_2\text{O}_4$  nanowire arrays attained a large  $\text{NH}_3$  formation rate of  $973.2 \mu\text{mol h}^{-1} \text{cm}^{-2}$  and large FE of 99.0% (Fig. 11i and j) in 0.1 M KOH with 0.1 M  $\text{NaNO}_3$ .



**Fig. 11** (a) SEM and (b) TEM images of  $\text{Co}_3\text{O}_4$  nanosheets with Co vacancies. (c) LSV curves and (d)  $\text{NH}_3$  yield rate, FE under different potentials for  $\text{Co}_3\text{O}_4$  nanosheets with Co vacancies. (e) Charge density distribution of  $\text{Co}_3\text{O}_4$  with/without Co vacancies. (f) Free-energy diagrams for the  $\text{NO}_3^-$ RR on  $\text{Co}_3\text{O}_4$  with Co vacancies. Reproduced from ref. 118 with permission from the American Chemical Society, copyright 2022. (g and h) SEM and mapping images of  $\text{NiCo}_2\text{O}_4$ . (i) LSV curves and (j) yield rate and FE of  $\text{NH}_3$  under given potentials. Reproduced from ref. 121 with permission from the Wiley-VCH, copyright 2022. Charge-density difference for  $\text{NO}_3^-$  adsorption on  $\text{NiCo}_2\text{O}_4$  (k) and BCDs/ $\text{NiCo}_2\text{O}_4$  (l). (m) *In situ* Raman spectra of  $\text{NO}_3^-$ RR over BCDs/ $\text{NiCo}_2\text{O}_4$  at different applied potentials. (n) Comparison of  $\text{NH}_3$  FEs and yield rate of BCDs/ $\text{NiCo}_2\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$ . Reproduced from ref. 124 with permission from the Elsevier, copyright 2022.

Impressively, the as-designed  $\text{NiCo}_2\text{O}_4$  nanowires displayed exceptional durability with no significant fluctuations in both  $\text{NH}_3$  production rate and FE after 16 successive electrolysis experiments. After that, taking the Lewis-base property of  $\text{NO}_3^-$  into consideration, Lu *et al.*<sup>124</sup> further introduced abundant Lewis acid sites on the surface of  $\text{NiCo}_2\text{O}_4$  nanowire arrays for increasing the adsorption energy of  $\text{NO}_3^-$  by coupling with boron-doped carbon dots (BCDs/ $\text{NiCo}_2\text{O}_4$ ). As revealed in Fig. 11k and l, the incorporation of BCDs enhanced the adsorption energy of  $\text{NO}_3^-$  on the surface of the BCDs/ $\text{NiCo}_2\text{O}_4$  electrode. Meanwhile, *in situ* Raman spectra shown in Fig. 11m suggested that the intensity of the peak at  $975\text{ cm}^{-1}$  associated with the N–O stretching vibration was boosted under the applied potentials, indicating that the Lewis acid sites induced by BCD doping were critically important for enhancing the adsorption ability of  $\text{NO}_3^-$ . As expected, the BCDs/ $\text{NiCo}_2\text{O}_4$  catalyst provided a nearly  $\sim 100\%$  FE and a large  $\text{NH}_3$  production rate of  $173.9\text{ }\mu\text{mol h}^{-1}\text{ cm}^{-2}$  at  $-0.55\text{ V}$  vs. RHE (Fig. 11n).

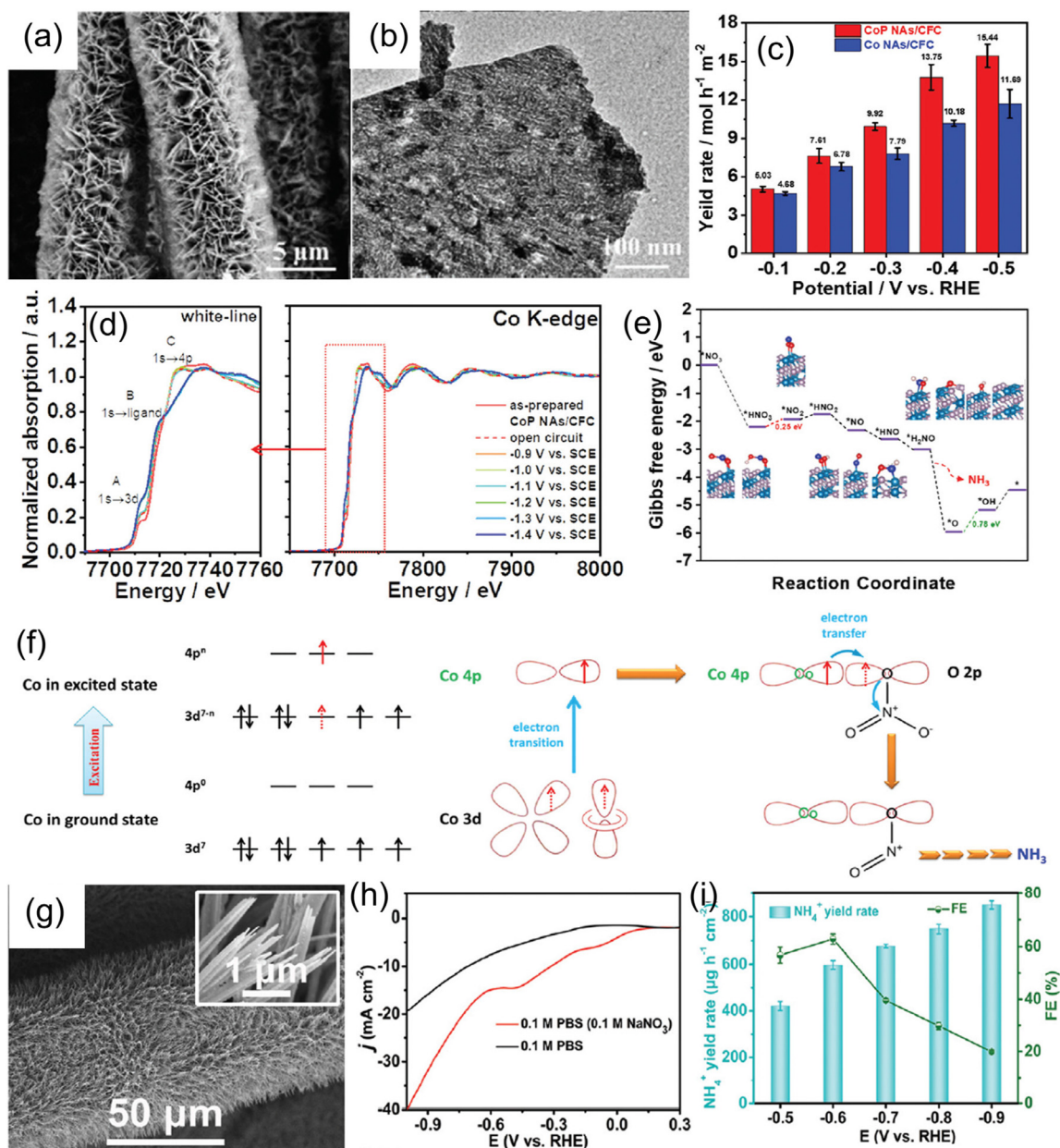
$\text{Co}_3\text{O}_4$  as an electrocatalyst for the  $\text{NO}_3^-$ RR still suffers from the critical issue that it is difficult to electrochemically reduce  $\text{NO}_3^-$  to  $\text{NO}_2^-$  using this catalyst. As mentioned above, Cu-based materials possess excellent electrocatalytic activity for  $\text{NO}_3^-$  to  $\text{NO}_2^-$ , and thus constructing a  $\text{Co}_3\text{O}_4$ -based heterostructure with Cu-based materials could achieve promising electrochemical performance. Liu *et al.*<sup>125</sup> fabricated  $\text{Co}_3\text{O}_4$  grown on CuO nanowire arrays to construct a hierarchical heterostructure for an efficient  $\text{NO}_3^-$ RR. At  $-0.23\text{ V}$  vs. RHE,  $\text{CuO@Co}_3\text{O}_4$  provided an  $\text{NH}_3$  yield rate of  $1.915\text{ mmol h}^{-1}\text{ cm}^{-2}$ , which was higher than those of CuO and  $\text{Co}_3\text{O}_4$ . Fu *et al.*<sup>126</sup> built dual active sites on a  $\text{Co}_3\text{O}_4/\text{Cu}$  electrode, in which Cu focused on the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$ , and then  $\text{Co}_3\text{O}_4$  generated  $\text{H}^*$  (active hydrogen) as a strong reducing agent to further convert  $\text{NO}_2^-$  to  $\text{NH}_3$ . As a result, the  $\text{Co}_3\text{O}_4/\text{Cu}$  catalyst presented a large  $\text{NH}_3$  yield rate of  $684\text{ }\mu\text{g mg}^{-1}\text{ h}^{-1}$  with 94.6% FE. Recently, Fan *et al.*<sup>127</sup> fabricated a  $\text{Co}_3\text{O}_4$  nanosheet grown *in situ* on  $\text{TiO}_2$  nanosheet arrays for the  $\text{NO}_3^-$ RR, which gave a large  $\text{NH}_3$  yield rate of  $875\text{ }\mu\text{mol mg}^{-1}\text{ h}^{-1}$  and a high FE of 93.1% in alkaline electrolyte.

**3.4.1.4 Other metal oxides.** Other types of transition-metal oxides have also been investigated for the  $\text{NO}_3^-$ RR, such as  $\text{Bi}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{BiFeO}_3$ , and  $\text{La}_2\text{CuO}_4$ .<sup>128–131</sup> 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.<sup>132,133</sup> For instance, Wang *et al.*<sup>134</sup> fabricated ultrathin  $\text{CoO}_x$  nanosheets with abundant surface oxygen as an  $\text{NO}_3^-$ RR catalyst, attaining a large  $\text{NH}_3$  yield of  $82.4 \pm 4.8\text{ mg h}^{-1}\text{ mg}^{-1}$  with a FE of  $93.4 \pm 3.8\%$  at  $-0.3\text{ V}$  vs. RHE. The surface oxygen on the Co sites was prone to stabilize the adsorbed hydrogen on  $\text{CoO}_x$ , and thus efficiently suppressed the formation of  $\text{H}_2$  and achieved a high selectivity for  $\text{NH}_3$  synthesis. Zhang *et al.*<sup>135</sup> reported a Co-doped  $\text{Fe}/\text{Fe}_2\text{O}_3$  catalyst for electrochemical  $\text{NH}_3$  synthesis by reducing  $\text{NO}_3^-$  under ambient conditions. This catalyst afforded an  $\text{NH}_3$  production rate of

$1505.9\text{ }\mu\text{g h}^{-1}\text{ cm}^{-2}$  with a FE of 85.2% and a high  $\text{NH}_3$  selectivity of 99.0%. Recently, our group reported that  $\text{CoTiO}_{3-x}$  nanofibers with oxygen vacancies showed an  $\text{NH}_3$  formation rate of  $30.4\text{ mg h}^{-1}\text{ mg}^{-1}$  and a large FE of 92.6% in 0.1 M NaOH solution containing 0.1 M  $\text{NO}_3^-$ .<sup>136</sup> The  $\text{CuWO}_4$  hollow nanospheres with oxygen vacancies showed a high  $\text{NH}_3$  FE of 94.6% and yield rate of  $5.84\text{ mg h}^{-1}\text{ mg}^{-1}$  at  $-0.7\text{ V}$  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  $\text{NO}_3^-$  to  $\text{NH}_3$ , which is attributed to the fact that they can afford hydrogen at a small overpotential during the electroreduction process. So far, many transition-metal phosphides, such as CoP,  $\text{Ni}_2\text{P}$ , and  $\text{Cu}_3\text{P}$ , have been used as catalysts for  $\text{NH}_3$  electrosynthesis.<sup>138–142</sup> For example, Ye *et al.*<sup>143</sup> reported that CoP nanosheet arrays supported on carbon cloth exhibited a molar level  $\text{NH}_3$  formation rate of  $9.56\text{ mol h}^{-1}\text{ m}^{-2}$  at  $-0.3\text{ V}$  vs. RHE with a FE of  $\sim 100\%$  under alkaline conditions (Fig. 12a–c). Furthermore, the reaction mechanism of the  $\text{NO}_3^-$ RR on the surface of CoP was investigated by coupling *in situ* characterization technology and theoretical calculations (Fig. 12d and e). As presented in Fig. 12f, Co 4p orbitals directly participated in the adsorption of  $\text{NO}_3^-$  via Co–O–N bonds and the electron-transfer step of the  $\text{NO}_3^-$ RR, while phosphorus within CoP could stabilize the active phase and reduce the reaction-energy barrier of the rate-determining step during the electroreduction of  $\text{NO}_3^-$ , thus leading to a highly selective electrosynthesis of  $\text{NH}_3$  from  $\text{NO}_3^-$ .  $\text{Ni}_2\text{P}$  nanoparticles supported on Ni foam were synthesized and regarded as an electrocatalyst for electrochemically converting  $\text{NO}_3^-$  to  $\text{NH}_3$  in neutral media with 50 mM  $\text{NO}_3^-$ . A high  $\text{NH}_3$  evolving rate of  $0.056\text{ mmol h}^{-1}\text{ cm}^{-2}$  with a FE of 99.23%, and a selectivity of 89.1% were obtained.<sup>144</sup> As shown in Fig. 12g, our group<sup>141</sup> synthesized  $\text{Cu}_3\text{P}$  nanowire arrays anchored on copper foam for electrochemical conversion of  $\text{NO}_3^-$  to  $\text{NH}_3$  in neutral media. In 0.1 M phosphate-buffered saline (PBS) containing 0.1 M  $\text{NaNO}_3$ , a  $\text{Cu}_3\text{P}$  nanowire catalyst delivered a large  $\text{NH}_3$  formation rate of  $848.7 \pm 18.0\text{ }\mu\text{g h}^{-1}\text{ cm}^{-2}$  and a high FE of  $62.9 \pm 2.0\%$  at  $-0.6\text{ V}$  vs. RHE (Fig. 12h and i).

**3.4.3 Other metal compounds.** Recently, other metal compounds have also been applied as electrocatalysts for  $\text{NO}_3^-$  to  $\text{NH}_3$  conversion at room temperature.<sup>145–147</sup> Zhang *et al.*<sup>148</sup> fabricated  $\text{Ni}_3\text{N}$  nanoparticles embedded on a carbon skeleton and investigated its electrochemical performance as a catalyst for the  $\text{NO}_3^-$ RR. This catalyst provided a high  $\text{NH}_3$  selectivity of 89.5% and large yield rate of  $9.185\text{ mmol h}^{-1}\text{ mg}^{-1}$  at  $-0.795\text{ V}$  vs. RHE in neutral media. Amorphous  $\text{CoB}_x$  nanoparticles anchored on carbon paper were synthesized *via* a simple wet chemical reduction method. When used for electroreduction of  $\text{NO}_3^-$  to  $\text{NH}_3$ ,  $\text{CoB}_x$  afforded a maximum FE of 94.0% and a yield rate of up to  $0.787\text{ mmol h}^{-1}\text{ cm}^{-2}$ .<sup>149</sup> Wang *et al.*<sup>150</sup> reported that  $\text{Fe}_3\text{C}$  nanoflakes embedded on N-doped carbon nanosheets displayed an  $\text{NH}_3$  yield rate of  $1.19\text{ mmol h}^{-1}\text{ mg}^{-1}$ ,  $\text{NH}_3$  FE of 96.7%, and selectivity of 79.0% at  $-0.5\text{ V}$  vs. RHE.



**Fig. 12** (a) SEM and (b) TEM images of CoP. (c) NH<sub>3</sub> yield rate of CoP at given potentials. (d) *In situ* XANES of the Co K-edge of CoP. (e) Gibbs free-energy diagram of the NO<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><sup>-</sup>RR has opened up a green and sustainable route for NH<sub>3</sub> synthesis under ambient conditions, which is associated with two advantages: (i) the electrochemical NH<sub>3</sub> synthesis from NO<sub>3</sub><sup>-</sup> 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 NH<sub>3</sub> 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 NH<sub>3</sub> 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  $\text{NO}_3^-$  to  $\text{NH}_3$ . Although considerable progress has been achieved so far, the following points should also be considered in this field:

(i) As mentioned in the discussion above, ongoing research into electrochemical  $\text{NH}_3$  synthesis from  $\text{NO}_3^-$  mainly focuses on the design and investigation of metal-based materials; less attention has been given to the exploration of metal-free electrocatalysts. From the energy-saving and emission-reduction points of view, it is of great significance to explore metal-free electrocatalysts with high activity, large selectivity and excellent stability for enabling the electrocatalytic  $\text{NO}_3^-$ RR under ambient conditions. As a consequence, more attention should be given to elaborately developing carbon-based electrocatalysts for the  $\text{NO}_3^-$ RR, providing an alluring strategy for large-scale  $\text{NH}_3$  production.

(ii) The electrochemical  $\text{NO}_3^-$ RR, as an emerging strategy for  $\text{NH}_3$  production under ambient conditions, has attained a dramatic growth in interest and various catalysts have been investigated in this field. However, none of the suitable catalysts can be regarded as a benchmark catalyst for electrocatalytic  $\text{NO}_3^-$ RR research. Besides, the variety of experimental details, such as the pH value of the electrolyte and the concentration of the nitrogen resource, play a critical role in catalytic activity and selectivity, and their effects on the electrochemical performance remain to be thoroughly studied. Such issues lead to incomparable results and thus limit the mutual communication and promotion in the community. Therefore, finding a standard catalyst and unification of experimental parameters are urgently required in the field of the electrochemical  $\text{NO}_3^-$ RR.

(iii) Many catalysts have exhibited superior catalytic activity and high  $\text{NH}_3$  selectivity during the electrochemical  $\text{NO}_3^-$ RR process, but their catalytic mechanisms and reaction processes were only revealed by theoretical calculations and remain unclear experimentally. For this reason, *in situ* characterization to scrutinize the pristine catalyst surface evolution (surface structure, element valence state, and exposed active sites) and adsorbed intermediates should be elaborately developed to uncover the real catalytic sites and reaction pathways upon the electrochemical reaction process for the rational design of electrocatalysts for the  $\text{NO}_3^-$ RR.

(iv) From the point of view of practical application, besides the fact that the electrochemical  $\text{NO}_3^-$ RR to  $\text{NH}_3$  process is still developing and lacks a catalyst with excellent durability and performance for supporting long-term electrolysis at the moment, another challenge is that this process will generate a tremendous amount of  $\text{H}_2$  as a side-product during the electrolysis, which is directly vented off into the atmosphere, forming a safety issue. Therefore, tremendous efforts are required before the electrochemical  $\text{NO}_3^-$ RR to  $\text{NH}_3$  can be put into practical operation.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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

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