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# Review

# Copper-based electro-catalytic nitrate reduction to ammonia from water: Mechanism, preparation, and research directions



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#### ABSTRACT

Global water bodies are increasingly imperiled by nitrate pollution, primarily originating from industrial waste, agricultural runoffs, and urban sewage. This escalating environmental crisis challenges traditional water treatment paradigms and necessitates innovative solutions. Electro-catalysis, especially utilizing copper-based catalysts, known for their efficiency, cost-effectiveness, and eco-friendliness, offer a promising avenue for the electro-catalytic reduction of nitrate to ammonia. In this review, we systematically consolidate current research on diverse copper-based catalysts, including pure Cu, Cu alloys, oxides, single-atom entities, and composites. Furthermore, we assess their catalytic performance, operational mechanisms, and future research directions to find effective, long-term solutions to water purification and ammonia synthesis. Electro-catalysis technology shows the potential in mitigating nitrate pollution and has strategic importance in sustainable environmental management. As to the application, challenges regarding complexity of the real water, the scale-up of the commerical catalysts, and the efficient collection of produced NH<sub>3</sub> are still exist. Following reseraches of catalyst specially on long term stability and *in situ* mechanisms are proposed.

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# 1. Introduction

Nitrate (NO<sub>3</sub><sup>-</sup>) contamination is a widespread problem affecting both surface water and groundwater, resulting from the leaching of various sources into the soil and eventually entering the water supply [1–3]. This contamination leads to eutrophication and disruption of the natural nitrogen cycle and poses significant risks to human health [4]. The removal of NO<sub>3</sub><sup>-</sup> from wastewater proves to be particularly challenging due to its stability, high solubility, and poor adsorption properties [5,6]. Traditional biochemical denitrification methods often prove ineffective, requiring harsh conditions and generating excessive amounts of sludge [7]. Subsequently, researchers have been investigating alternative approaches, and the electrocatalytic water treatment process has attracted much attention [8–10].

Figure. 1 illustrates the nitrogen cycle in the ecological system,

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highlighting the main forms of nitrogen and its circulation within the ecosystem. There are two primary pathways for nitrogen fixation: industrial synthetic NH<sub>3</sub> and biological nitrogen fixation (primarily involving nitrogen-fixing microorganisms) [11,12]. However, excessive  $NO_3^-$  in water bodies has been on the rise due to human activities, such as the discharge of industrial wastewater, livestock wastewater, and municipal sewage [13]. NH<sub>3</sub> can be converted into NO<sub>3</sub><sup>-</sup> through nitrifying bacteria, a process known as nitrification [14]. Denitrification, which involves the conversion of  $\mathrm{NO}_3^-$  into harmless nitrogen, can be achieved through anaerobic bacteria and physicochemical methods, such as electro-catalytic  $NO_3^-$  reduction (NO<sub>3</sub>RR) [15,16]. The NO<sub>3</sub>RR has the potential to play a crucial role in new technologies for NO<sub>3</sub>-containing water pollution control [17-19]. In addition, the recent development of electrocatalysts capable of selectively reducing NO<sub>3</sub> waste to NH<sub>3</sub> opens up new possibilities for  $NO_3^-$  treatment, with both environmental and economic impacts on sustainable NH<sub>3</sub> synthesis [20,21].

Generally, the electrochemical reduction of  $NO_3^-$  to  $NH_3$  concluding reactions of eight electrons and nine protons  $(NO_3^- + 9H^+ + 8e^- \rightarrow 3H_2O + NH_3)$ , resulting in many reaction

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Fig. 1. The simplified nitrogen cycle diagram and concept of electrocatalytic  $NO_3^-$  reduction for the sustainable nitrogen cycle.

intermediates, like  $*NO_2^-$ ,  $*NO_2H$ , \*NO, \*NOH, \*N, \*NH, and  $*NH_2$ , among others [22,23]. However, due to the multiple reactions among these intermediates. NO<sub>3</sub>RR are not exclusively NH<sub>3</sub> and N<sub>2</sub>. The intermediate  $*NH_2$  generally favors NH<sub>3</sub> formation, while the intermediate  $*N_2O$  tends to N<sub>2</sub> generation. Additionally, NO<sub>3</sub>RR typically occurs at negative potentials ranging from -0.1 to -0.6 V vs. RHE, where the competitive hydrogen evolution reaction (HER) occurs [24]. During NO<sub>3</sub>RR to NH<sub>3</sub>, the undesired generation of N<sub>2</sub> and H<sub>2</sub> consumes many electrons, resulting in a low Faradaic efficiency (FE) of NH<sub>3</sub>, especially at high overpotentials [25,26]. Therefore, developing efficient electrocatalysts with specific structures that can suppress the H–H and N–N coupling reactions is crucial, thus improving the NH<sub>3</sub> FE.

Recently, Cu-based catalysts have emerged as highly promising candidates for NO<sub>3</sub>RR owing to their excellent performances, abundance, and cost-effectiveness [27,28]. However, the practical application of Cu-based catalysts in NO<sub>3</sub>RR necessitates addressing critical challenges, such as the inadequate FE at high current densities and strong adsorption energies on intermediates, hampering the transformation of  $NO_3^-$  to  $NH_3$  [29]. To address these issues, researchers have developed several strategies, including crystal facet engineering, alloying, oxidizing, doping modifications, single atom dispersion strategy, etc., to enhance the FE of NH<sub>3</sub> and the intrinsic activity of Cu-based catalysts. Electrochemical measurement techniques, like cyclic voltammetry (CV) and linear sweep voltammetry (LSV), were employed to evaluate the electrocatalytic activity by measuring the current density and potential of the reaction [30]. In addition, the overall conversion rate of NO<sub>3</sub>, selectivity towards NH<sub>3</sub>, and catalyst stability were considerations when tailoring Cu-based catalysts for NO<sub>3</sub>RR. All these parameters contribute to the optimization of catalyst design and performance during NO<sub>3</sub>RR.

This review thoroughly examines the advancements in four series of Cu-based catalysts, including Cu, Cu alloys, Cu oxides, Cu single-atom catalysts (SACs), and other Cu compounds for NO<sub>3</sub>RR, encompassing essential aspects such as reaction activity, stability, reaction mechanisms, and performance evaluation. Additionally, the review emphasizes the recent developments and strategies employed in Cu-based catalyst construction and explores potential applications.

# 2. Mechanism study of Cu-based NO<sub>3</sub>RR

The electrocatalysis of NO3RR on Cu-based catalysts typically

involves multiple consecutive steps, comprising a nine-proton and eight-electron process, including electrotransfer, mass transfer, and the formation of a chemical adsorption intermediate on the electrode surface [22]. The initial step entails the adsorption of  $NO_{\overline{3}}$ anion on the active site, followed by successive reduction to  $NO_2^$ and subsequently to NH<sub>4</sub><sup>+</sup>. Cu-based catalysts effectively promote these reactions by providing a suitable surface for  $NO_{3}^{-}$  adsorption and facilitating electron transfer between the catalyst and  $NO_{3}$ species [28]. Therefore, the surface properties play a great role in determining the performances and mechanisms. Based on density functional theory (DFT) calculations of Gibbs free energies on intermediates, the most common reaction pathways for NO<sub>3</sub>RR can be deduced [31,32]. And DFT calculations were widely used in the NO<sub>3</sub>RR-related mechanism study [33–35]. Researchers also used software such as VASP, Gaussian, and Materials Studio et al. to conduct the calculation. Calculations on  $NO_3^-$  adsorption energy showed the binding affinity of  $NO_3^-$  on the active site. The real reaction pathway on different catalyst surfaces may vary, depending on the Gibbs free energy. Meanwhile, calculations on differential charge density can reflect the charge transfer and activity of the site.

Achieving a high FE in the NO<sub>3</sub>RR requires proper suppression of the competing HER. The NO<sub>3</sub>RR process typically involves two distinct pathways. Firstly, the adsorbed active \*H pathway is named the Volmer process [31]. The other pathway involves electron transfer and H<sup>+</sup> [32]. The mechanisms commence with NO<sub>3</sub> adsorption on the Cu-based catalyst surface through an oxygen atom in a chelating O–Cu configuration [36].

As shown in Fig. S1, mechanisms in NO<sub>3</sub>RR were summarized as four pathways. Some metals (Pt, Rh, Ni, etc.) showed high affinities for adsorbing active atomic hydrogen, and Pathway I is more likely to occur [32,36-38]. Here, the \*H acting as a reactant, undergoes stepwise deoxygenation from NO<sub>3</sub><sup>-</sup> to \*N subsequently. Afterward, the \*N is hydrogenated, producing the desorbed NH<sub>3</sub> [39,40]. Hence, the enhanced affinity of catalyst surfaces for \*H facilitates NH<sub>3</sub> production. Regarding the electron transfer pathway, it is more likely to occur on surfaces with strong NO<sub>3</sub><sup>-</sup> affinity but low affinity to \*H [21].

In Pathway II, \*NH<sub>2</sub>OH is initially formed through the stepwise hydrogenation of \*NO  $\rightarrow$  \*NOH  $\rightarrow$  \*NH<sub>2</sub>OH, followed by deoxygenation and hydrogenation reactions to produce \*NH<sub>3</sub> [41,42]. Notably, the \*NH<sub>2</sub>OH intermediate readily desorbs from the catalyst surfaces, forming hydroxylamine as a byproduct. Reports confirm the detection of hydroxylamine during the NO<sub>3</sub>RR process catalyzed by various Cu-based catalysts [43]. In Pathway III, the \*NO undergoes direct deoxygenation by electrons and H<sup>+</sup> to generate \*N, which is subsequently electrocatalytically hydrogenated stepby-step to \*NH<sub>3</sub> [44,45]. Recently, a novel electrochemical reduction pathway from  $NO_3^-$  to  $NH_3$  was reported, which is called Pathway IV [46]. The intermediate \*NHOH is formed through a two-step hydrogenation of the intermediate \*NO. However, in Pathway IV, \*NHOH is directly deoxygenated to \*NH, following hydrogenation to NH<sub>3</sub> along the same path as Pathway III. Actually, the choice of pathways depends on the type of catalyst element; one or more pathways may co-exist on the catalyst surface.

The solution pH potentially affects the NO<sub>3</sub>RR pathways. Fig. 2 illustrates the free energy calculations of different intermediates at pH 0, 7, and 14 [47] when the calculation considers the rate-determining step (RDS) during the reaction of NO<sub>3</sub> reduced to NH<sub>3</sub> (NRA). The results show that the desorption of NH<sub>3</sub> is NRA1, which requires 0.37 eV. Similarly, it is also the RDS for NRA2 and NRA3 in Fig. 2a. The activated energy of \*NO to \*N is 1.62 eV, larger than \*NO to \*NOH. As a result, pathway NRA3 is considered the most favorable pathway. At the solution of pH 7, the RDS of NRA3 is \*NO  $\rightarrow$  \*NOH, rather than the desorption of \*NH<sub>3</sub> (Fig. 2b).



**Fig. 2.** Reaction-free energies for different intermediates on Cu(111). Three kinds of  $NO_3RR$  pathways using Cu(111) at electrolyte pH of pH 0 (**a**), pH 7 (**b**), and pH 14 (**c**). Reproduced with permission from Ref. [47]. Copyright 2022, ACS.

Conversely, at the solution pH 14, the RDS shifts to the hydrogenation of \*NO in Fig. 2c [48]. Above all, the mechanism of Cu-based catalysts on NO<sub>3</sub>RR varied, resulting from different catalyst surfaces and electrolytes. Thus, the targeted catalyst design and regulation should be tailored to specific materials and strategies, such as tuning the oxidation state of Cu [49].

#### 3. Cu and Cu alloys catalysts

In recent years, monometallic Cu catalysts have garnered significant attention in various reactions, especially the studies in electrocatalysis [50–54]. For example, Cu metal, has been extensively investigated for its involvement in the electrocatalytic oxygen reduction reaction (ORR) [55,56], electrocatalytic carbon dioxide reduction reaction (CO<sub>2</sub>RR) [57,58], and HER [59,60]. As to NO<sub>3</sub>RR, researchers have explored the Cu or Cu alloy catalysts with diverse morphologies and unique electronic structures to exploit their reactivity in electrocatalytic NO<sub>3</sub>RR. The performances and mechanisms of NO<sub>3</sub>RR using Cu or Cu alloys were specially presented. Strategies on Cu modifications and Cu alloys for better NO<sub>3</sub>RR performance were also elaborated.

# 3.1. Typical Cu

Recent studies comparing the electrocatalysis activity of late transition and noble metals through volcano plots have demonstrated that Cu outperforms Pd, Ag, and Au [50] (Fig. 3a). This reflects the potential of Cu as a commercial catalyst. To evaluate the performance of an electrocatalyst, a three-electrode system is commonly used. The structure of a three-electrode system electrolytic cell is depicted in Fig. 3b; the working electrode holds the Cu-based catalysts, the Pt plate usually serves as the counter electrode, and Hg/HgO or Ag/AgCl works as the reference electrode for electrolysis of  $NO_3^-$ -containing electrolyte. In research focused on  $NO_3RR$ , alkaline electrolytes primarily composed of  $KNO_3$ , KOH, and  $K_2SO_4$  are commonly utilized. The inclusion of  $SO_4^{2-}$  helps enhance the electrolyte's conductivity of the electrolyte, while  $NO_3^-$  serves as the main target for electrolysis.

CV or LSV are commonly employed during electrochemical measurements using three-electrode systems. For instance, Dima et al. [61] discovered that Cu foil exhibits higher electrocatalytic activity than noble metals like gold and silver (Fig. 3c), providing valuable insights for NO<sub>3</sub>RR research. CV studies on Cu single crystals [62-64] often exhibit oxidation and reduction peaks, highlighting the microscopic processes involved in NO3RR and requiring a thorough explanation. Fortunately, Gabriel et al. [62] conducted two sets of experiments that skillfully elucidated the formation of different oxidation and reduction peaks, supporting the identification of intermediate products in NO<sub>3</sub>RR. R<sub>1</sub> and R2 peaks generated from Cu reduction during LSV on Cu foam are depicted in Fig. 3d and e. The positions of R<sub>1</sub> and R<sub>2</sub> peaks remain consistent at different NaNO<sub>3</sub> concentrations, suggesting that NO<sub>3</sub> does not play a role in their formation. Expanding the sweeping potential range (Fig. 3f) revealed an additional reducing peak (RNO<sub>2</sub>) when LSV was performed on a NaNO<sub>2</sub> electrolyte. However, when LSV was conducted on a NaNO<sub>3</sub> electrolyte, two new reducing peaks (RNO<sub>3</sub><sup>-</sup> and RNO<sub>2</sub><sup>-</sup>) emerged. Comparing the LSV curves of these two electrolytes enabled clear identification of reduction peaks influenced by  $NO_3^-$  or  $NO_2^-$ .

Cu foam has also emerged as a promising catalyst for NO<sub>3</sub>RR due to its unique properties. Its three-dimensional (3D) structure provides a large surface area, which exposes more activated sites. Furthermore, Cu foam can be easily modified with different coatings or dopants to improve its performance. However, Cu foams suffer from surface defects and low intrinsic reactivity, limiting their applications. To overcome these limitations, various processes have been employed to adjust and control the morphology and structure of Cu single-crystal electrocatalysts to further increase their specific surface area and improve NO<sub>3</sub>RR performance. In recent years, various nanostructures that outperform Cu foams and Cu foils have been developed. Examples include Cu nanosheets [64], Cu nanobelts [65,66], Cu nanowires [67], and Cu nanoparticles [68,69]. For instance, Wang et al. [66] introduced a 3D Cu nanobelt that demonstrated nearly 100% NO<sub>3</sub><sup>-</sup> removal, compared to merely 2.6% using pristine Cu foam. Importantly, the 3D Cu nanobelt exhibited no reaction with dissolved oxygen or production of H<sub>2</sub>O<sub>2</sub>, thus highlighting the advantages of nanostructures in NO<sub>3</sub>RR. In another study, Zhao et al. [63] focused on morphological regulation and synthesized Cu catalysts with flower-like structures. These catalysts achieved a high FE of 93.91% and an impressive NH<sub>3</sub> yield of 101.4  $\mu$ mol h<sup>-1</sup> cm<sup>-2</sup>, showcasing their excellent performance. Overall, utilizing nanostructures and tailored morphologies in Cu catalysts holds great promise for enhancing NO<sub>3</sub>RR efficiency and improving the practical applications of Cu-based catalysts.

Catalysts that possess open reaction environments and heterogeneous synergistic polycrystalline surfaces have been found to enhance the mass transfer in the liquid phase. Additionally, adjusting the morphology and structure of Cu single-crystal catalysts can expose more active crystal planes. For example, Gao et al. [50] discovered that both Cu(100) and Cu(111) crystal planes are thermodynamically favorable through DFT calculations (Fig. 3g). Similarly, Hu et al. [47] employed DFT calculations to confirm that Cu(100) and Cu(111) planes exhibit enhanced catalytic activity compared to Cu(100). Notably, Cu(111) displays superior electrocatalytic performance for NO $_3$  to NH $_3$  reduction in neutral or alkaline electrolytes, while Cu(100) demonstrates stronger catalytic performance in strongly acidic electrolytes.

To facilitate NO<sub>3</sub>RR using Cu, it is meaningful to expose more

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**Fig. 3. a**, The electrocatalysis activity volcano plot of metals. Reproduced with permission from Ref. [50]. Copyright 2022, Nature Publishing Group. **b**, Scheme of the commonly used electrochemical workstation. **c**, The CV curves of Au, Ag, and Cu. Reproduced from Ref. [61]. Copyright 2003, Elsevier. **d**, NO<sub>3</sub>R using Cu foam in the absence and presence of NaNO<sub>3</sub>. **e**, NO<sub>3</sub>R using Cu foam at different concentrations of NaNO<sub>3</sub>. **f**, LSV of Cu foam in Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>. Reproduced with permission from Ref. [62]. Copyright 2022, Elsevier. **g**, Free energy calculation of NO<sub>3</sub>RR on Cu(100) and Cu(111) at 0 V vs. RHE from grand-canonical DFT calculations. Reproduced with permission from Ref. [50]. Copyright 2022, Nature Publishing Group. **h**, df-Cu NPs and dr-Cu NPs. **i**, The NO<sub>3</sub> conversion (C(NO<sub>3</sub>-N)), NO<sub>2</sub> selectivity (S (NO<sub>2</sub>-N)), NH<sub>3</sub> selectivity (S(NH<sub>4</sub><sup>+</sup>-N)) and NH<sub>3</sub> FE over dr-Cu NPs and df-Cu NPs. Reproduced with permission from Ref. [65]. Copyright 2022, RSC.

active crystal planes. Xu et al. [65] utilized the electroreduction method to produce defect-rich Cu nanoplates. These nanoplates exposed active crystal planes, providing additional active sites for intermediate adsorption (Fig. 3h). Consequently, the electrocatalyst demonstrated improved conversion of NH<sub>3</sub>, and FE compared to Cu nanoplates, achieving values of 781.25  $\mu$ g h<sup>-1</sup> mg<sup>-1</sup>, 93.26%, and 81.99%, respectively (Fig. 3i). In a similar manner, Fu et al. [64] synthesized (111) facet exposed Cu nanosheets using the liquid phase method, which exhibited a FE of 99.7% at -0.15 V vs. RHE and an impressive NH<sub>3</sub> yield of 390.1  $\mu$ g mg<sup>-1</sup> Cu h<sup>-1</sup>. The performance of Cu(111) crystal planes can be further enhanced through defect reconstruction. Such as Wu et al. reported the fabrication of uniform Cu nanodisks with increased Cu(111) crystal planes formed by surface-reconstructed triatomic Cu clusters [70]. These nanodisks demonstrated enhanced activity during cathodic deoxygenation and exhibited a higher affinity for  $NO_3^-$  adsorption. Consequently, the NH<sub>3</sub> FE and yield improved, reaching 81.1% at -0.5 V vs. RHE and 2.16 mg mgcat<sup>-1</sup> h<sup>-1</sup>, respectively.

# 3.2. Strategies on Cu

Morphology control alone is not sufficient to meet the performance requirements of electrocatalysts. Porous carbon or porous carbon frameworks can be combined with Cu single crystals of various shapes and sizes to enhance electron transfer capacity and stability, as previously discussed. For instance, Song et al. [71] developed a structured octahedral morphology Cu nanoparticle electrocatalyst (Cu@C) by encapsulating it within a porous carbon framework through the thermal decomposition of Cu-BTC MOF. High-angle annular dark-field (HAADF) imaging revealed that the Cu nanoparticles were uniformly incorporated into the porous carbon framework (Fig. S2a). In situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) spectra of Cu@C exhibited an infrared adsorption peak corresponding to  $NO_2^-$  at 1239 cm<sup>-1</sup> (Fig. S2b), indicating more  $NO_2^-$  on the Cu@C surface compared to the Cu nanoparticle surface (Fig. S2c). This suggests that Cu@C attracted more NO<sub>3</sub><sup>-</sup> for reduction to NO<sub>2</sub>, leading to enhanced NO<sub>3</sub> reducing activity compared

to Cu nanoparticles. Finite element analysis (FEA) demonstrated that more NO<sub>3</sub> on the Cu@C surface facilitated efficient medium transport, effectively reducing energy barrier of NO<sub>3</sub> to NH<sub>3</sub> (Fig. S2d). Cu@C achieved a maximum FE of NH<sub>3</sub> generation of 72.0% at -0.3 V vs. RHE, which was 3.6 times higher than using Cu nanoparticles (19.9%). Furthermore, Zhao et al. [68] synthesized a composite of Cu nanoparticle-modified nitrogen-doped porous carbon (16Cu-NPC). They achieved 100% NO<sub>3</sub> removal and 67.1% N<sub>2</sub> selectivity with the assistance of Cl anodic oxidation in 9 h at -2.1 V. The synergy between Cu nanoparticles and the NPC carrier promoted NO<sub>3</sub> conversion to NO<sub>2</sub>- and accelerated subsequent hydrogenation, resulting in a total nitrogen removal of 64%, nearly 3 times higher than the commercial Cu sheet and 17 times higher than the graphite sheet.

Furthermore, incorporating boron (B) can be employed to modify the electronic state of Cu, thereby enhancing NO<sub>3</sub>RR efficiency. For instance, Zhang et al. [72] and their colleagues reported doping boron elements into Cu catalysts to modulate the electronic state of Cu. Importantly, as the amount of doped boron increases, the concentration of Cu<sup>+</sup> also increases, resulting in enhanced NO<sub>3</sub> to NH<sub>3</sub> conversion activity (Fig. S2e). Additionally, the results regarding the adsorption energy of  $NO_3^-$  on the catalyst surface indicate that the adsorption of the Cu(B) catalysts onto  $NO_{\overline{3}}$  is strengthened. The current density achieved using the Cu(B) catalyst is nearly 11 times that of Cu at -0.6 V vs. RHE (Fig. S2f). This leads to elongation of the N–O bond, indicating an asymmetric bond length and increasing the likelihood of N-O bond breakage, thus promoting NO<sub>3</sub> activation (Fig. S2g). Under 100 ppm  $NO_3^-$  electrolyte, the catalysts exhibit a remarkable 100% conversion of  $NO_{3}$ , and a high NH<sub>3</sub> yield of 309 mmol  $h^{-1}$  gcat<sup>-1</sup>.

Recently, Gou et al. [73] also reported efficiently utilizing Bdoped Cu nanowires as an electrocatalyst, denoted as B–Cu NWs/ CF (Fig. S2h). The successful incorporation of B into Cu nanowires effectively inhibited hydrogen evolution and the formation of undesired by-products.

#### 3.3. Strategies on Cu alloys

Compared to pure Cu catalysts, Cu alloys have a regulated electronic structure after introducing another metal, thus emerging as a promising class of electrocatalysts for NO<sub>3</sub>RR. One effective strategy to enhance their catalytic activity involves adjusting their adsorption capacity towards reactant intermediates, resulting in a substantial reduction in the energy barrier of the reaction.

Despite the relatively good electrocatalytic performance of Cu single crystals, their ability to adsorb \*H is weak. Consequently,  $NO_3^-$  often undergoes conversion to  $NO_2^-$ , while the hydrogenation reaction is hindered due to insufficient \*H availability. This results in the accumulation of  $NO_3^-$  on the Cu surface, negatively impacting NH<sub>3</sub> selectivity and FE [74]. However, incorporating other metals holds promise for regulating the affinity of different intermediates, reducing the reaction barrier, lowering onset potential, and enhancing activity during the NO<sub>3</sub>RR. These factors are crucial for developing efficient Cu alloys [75–77].

Transition metals, such as Cu, Fe, Co, and Ni, have garnered significant attention due to their favorable electrocatalytic activity and cost-effectiveness. To further enhance their catalytic performance, researchers have explored using bimetallic catalysts, where different metals collaborate to improve NO<sub>3</sub>RR efficiency. Zhao et al. [78] studied the properties of bimetallic metals with different ratios of Cu–Fe, Cu–Co, and Cu–Ni, utilizing ordered mesoporous carbon (OMC) as the support (Fig. 4a,b). Their findings revealed that Cu<sub>5</sub>Fe<sub>5</sub>/OMC showed the optimal NH<sub>3</sub> yield among various CuM/OMC catalysts at 0.8 V vs. RHE. This suggests that the synergistic effects arising from the combination of different metals effectively

enhance catalytic performance. However, it is worth noting that factors such as the choice of support material and the distance between active sites can also impact the synergistic effect.

Another example using Cu–Fe alloys can be found in research conducted by Tang et al. [79]. They reported a Cu<sub>3</sub>Fe bimetallic catalyst achieving NO<sub>3</sub> conversion efficiencies of 81.1% and NH<sub>3</sub> selectivity of 70.3% at -0.7 V vs. RHE. The incorporation of Fe shifted the d-band center and facilitated stepwise hydrogenation during NO<sub>3</sub>RR. This promoted NO<sub>3</sub> adsorption on Cu<sub>3</sub>Fe, thereby improving NH<sup>‡</sup> selectivity. Moreover, the synergy between Fe and Cu atoms can be enhanced by controlling the distance between active sites. He et al. [80] employed N-doped graphitized carbon to immobilize Cu and Fe nanoparticles on nickel foam (CuFe NPs@NAC/NF) to regulate the proximity of Fe and Cu. Furthermore, Wang et al. [81] conducted atomic-level investigations on the Fe–Cu active site. They precisely controlled the spacing between multiple Fe and Cu atoms by arranging clusters of Fe–Cu within regular surface sites.

Furthermore, the inclusion of noble metals such as Pd [81–83], Pt [62], Au [84], Ru [85,86], and Rh [87] has been implemented to enhance the adsorption capabilities of Cu-based catalysts for hydrogen atoms. For instance, Wang et al. [82] utilized a one-step solution-processed method to create Cu–Pd alloys by uniformly loading Cu and Pd nanoclusters onto carbon nanobelts (Fig. 4c). The resulting catalyst, consisting of Cu nanoparticles and Pd clusters, served as nitrogen and hydrogen sources, respectively. With the assistance of carbon nanoribbons, the electron transport capacity was improved, leading to increased production of NH<sub>3</sub> and Faraday efficiency (Fig. 4d). Gabriel et al. [62] constructed a Cu–Pt nanointerface on a bimetallic Cu-Pt foam electrode, which exhibited a synergistic effect that accelerated the hydrogenation reduction process. Moreover, bimetallic catalyst synergy can adjust the energy barrier of intermediate species involved in NO<sub>3</sub>RR. Lim et al. [83] employed DFT calculations to investigate Cu-Pd alloy electrocatalysts and observed that while Cu(100) readily adsorbed  $NO_3^$ and NO<sub>2</sub>, the NO intermediates were more effectively adsorbed on Pd (100). This suggests that Pd can enhance the adsorption capacity of intermediates during the reaction. Besides, Zhang et al. [84] prepared an Au<sub>1</sub>Cu(111) single-atom catalyst with a Cu vacancy, which not only utilized \*H inhibiting hydrogen-hydrogen coupling as the hydrogen source to reduce the energy barrier of hydrogenation but also ready to \*NH<sub>3</sub> desorption (Fig. 4e). As a result, the yield of NH<sub>3</sub> and FE reached 555  $\mu g$   $h^{-1}$   $cm^{-2}$  and 98.7%, respectively.

Optimizing the catalyst's adsorption capacity for reactant intermediates is a crucial strategy to reduce the barrier and enhance catalyst performance. Wang et al. [88] synthesized the CuNi alloys with varying proportions to investigate their properties. It was found that the Cu<sub>50</sub>Ni<sub>50</sub> catalyst exhibited a current density six times higher than pure Cu at 0 V vs. RHE and achieved an NH<sub>3</sub> FE of  $99 \pm 1\%$  at -0.15 V vs. RHE (Fig. 4f). Ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy revealed that the Cu d-band center shifted towards the Fermi level, indicating improved adsorption energies of intermediate species (Fig. 4g). Additionally, DFT simulations indicated that the introduction of Ni shifted the potential-dependent step (PDS) of the electrocatalyst from  $NO_3^-$  adsorption to  $*NH_2$  hydrogenation. However, when the Cu-Ni ratio exceeded 1:1, the exposure of Cu active sites decreased, leading to a PDS shift of Cu<sub>30</sub>Ni<sub>70</sub> to 0.6 eV, which resulted in decreased activity and selectivity of the electrocatalyst (Fig. 4h).

Similarly, Fang et al. [89] studied the influence of different Ni contents on NO<sub>3</sub>RR using Cu catalysts. They encapsulated  $Cu_xNi_y$  nanoparticles in an N-doped carbon film and found that  $Cu_{0.43}Ni_{0.57}/NC$  exhibited a superior NO<sub>3</sub>–N removal of 89%, surpassing reference catalysts. Experimental results and DFT

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**Fig. 4. a**, Schematic for CuM/OMC catalysts. **b**, NH<sub>3</sub> yield rates and FE of Cu<sub>7</sub>Ni<sub>3</sub>/OMC catalyst. Reproduced with permission from Ref. [78]. Copyright 2023, ACS. **c**, Diagram of Pd–Cu/ C NBs for NO<sub>3</sub>RR. **d**, NH<sub>3</sub> yield of Cu–Pd/C NBs and Cu/C NBs. Reproduced with permission from Ref. [82]. Copyright 2022, ACS. **e**, Mechanism illustration of VCu–Au1Cu SAAs. Reproduced with permission from Ref. [84]. Copyright 2022, Elsevier. **f**, LSV curves of Au<sub>1</sub>Cu SAAs tested in KNO<sub>3</sub>/KOH electrolyte. **g**, DFT calculations of CuNi alloy. Reproduced with permission from Ref. [88]. Copyright 2020, ACS.

calculations suggested that appropriate Ni atoms lowered the energy barriers for  $*NO_2$  to \*NO conversion, enhancing the catalytic activity. The synergistic effects of a Cu–Co alloy in catalyzing NO<sub>3</sub>RR have been observed, where Cu can adsorb and reduce NO<sub>3</sub>, while the Co-active site facilitates hydrogenation. In their study, Fang et al. [90] developed a Cu–Co bimetallic nanosheet catalyst that achieved an approximately 100% faradaic efficiency at -0.2 V vs. RHE, with an NH<sub>3</sub> production rate of 4.8 mmol cm<sup>-2</sup> h<sup>-1</sup>. A mechanistic investigation revealed a significant synergy effect of Cu and Co, where the Co sites facilitated the hydrogenation of NO<sub>3</sub> to NH<sub>3</sub> through adsorbed \*H species, where the coverages of adsorbed \*H and \*NO<sub>3</sub> were ideally controlled.

In addition, combining noble metals exhibit higher electrocatalytic activity than pure Cu, and even small amounts of them can greatly enhance catalyst performance. For instance, Chen et al. [85] employed a cation exchange method to disperse a single Ru atom onto Cu nanowires (Ru–Cu NW). They achieved a current density of 1 A cm<sup>-2</sup> at –0.13 V vs. RHE, along with a remarkable FE of 96% for NH<sub>3</sub> production at 0.04 V. These values were significantly higher compared to those of Cu NW and Ru NP (Figs. S3a–b). In practical applications, the composition of the electrolyte can be complex and diverse, particularly at low NO<sub>3</sub> concentrations, which can substantially impact the electrocatalyst's activity. Nonetheless, Ru–Cu NW maintained an FE of over 90% and a NO<sub>3</sub> to NH<sub>3</sub> conversion rate exceeding 99% across a wide range of NO<sub>3</sub> concentrations, ranging from 2000 to 50 ppm. DFT calculations revealed that the highly dispersed Ru atoms served as active sites for NO<sub>3</sub>RR, while the presence of Cu inhibited by-product and hydrogen evolution reactions (Fig. S3c).

Moreover, Tran et al. [86] reported on the dispersion of single-

atom Ru on a Cu nanowire array, which exhibited an NH<sub>3</sub> FE of 94.1% and an NH<sub>3</sub> yield of up to 211.73 mg h<sup>-1</sup> cm<sup>-2</sup>. Liu et al. [91] demonstrated a catalyst consisting of single-atom Rh dispersed onto Cu nanowires via a galvanic replacement reaction (Rh@Cu-0.6%). Rh facilitated the transfer of adsorbed \*H to the Cu-adsorbed \*NO intermediate, promoting hydrogenation and NH<sub>3</sub> formation (Fig. S3d). The \*H signal observed around the Rh nanoparticles and the Rh@Cu-0.6% catalyst in the NO<sub>3</sub> electrolyte indicated their involvement in the hydrogenation reaction (Figs. S3e and f). Since Cu is well-known for its excellent catalytic activity and ability to inhibit the HER, by combining Cu with Rh, an electrocatalyst with remarkable performance can be achieved.

#### 4. Cu oxide catalysts

Cu oxides (CuO and Cu<sub>2</sub>O, CuO<sub>x</sub>) have been extensively studied as effective catalyst materials, exhibiting excellent electrocatalytic performance for various applications [92–96]. Among them, Cu oxides are particularly promising electrocatalysts for NO<sub>3</sub>RR due to their high selectivity towards NH<sub>3</sub> production and costeffectiveness. The composition and morphology of Cu differ from metallic Cu, and these distinctions profoundly impact its performance. Consequently, Cu oxide catalysts have seen significant development in electrochemical NO<sub>3</sub>RR.

# 4.1. Typical Cu oxide catalysts

As a typical example, Wang et al. reported the synthesis of CuO nanowire arrays (NWAs) by heat-treating Cu(OH)<sub>2</sub> NWAs in an oxygen atmosphere at 300 °C [97]. The CuO NWAs underwent in situ conversion to Cu/Cu<sub>2</sub>O NWAs during the electrochemical reduction reaction (Fig. 5a). In their study, the in situ Raman spectroscopy results revealed a gradual disappearance of the characteristic peak of CuO with an increase in applied voltage, accompanied by the appearance of the characteristic peak of  $Cu_2O$ , indicating that CuO underwent conversion to a Cu/Cu<sub>2</sub>O heterostructure (Fig. 5b). The strong electronic interaction occurring at the interface of Cu and Cu<sub>2</sub>O was the source of the true catalytic activity of the material, leading to the high selectivity and current density for NO<sub>3</sub>RR (Fig. 5c). Online differential electrochemistry mass spectrometry (DEMS) and DFT calculations suggested that Cu/ Cu<sub>2</sub>O NWAs were more effective than Cu NWAs in suppressing HER and reducing the energy barrier of intermediates, thereby promoting NO<sub>3</sub>RR to NH<sub>3</sub> (Fig. 5d,f). Inspired by this work, Zhao et al. [98] fabricated a Cu-cube material with a Cu–CuO heterostructure skin and compared its performance with pure Cu cube and CuO cube catalysts. The results indicated that all three materials exhibited high selectivity, but the Cu@Cu-CuO cube demonstrated the highest positive starting potential and current density (Fig. 5e).

Recently, Li et al. [99] demonstrated the growth of Cu oxide nanosheets on nickel foam for efficient  $NO_3^-$  reduction to N<sub>2</sub>. The catalyst exhibited an impressive N<sub>2</sub> selectivity of 99.53% under an applied current of -50 mA and rapidly reduced NO<sub>3</sub> within 100 min, producing almost no N<sub>2</sub>H<sub>4</sub> or other by-products. Jiang et al. synthesized a 3D porous Cu@Cu2O microspheric material derived from the fine Cu@Cu<sub>2</sub>O nanoparticles, which displayed an ultra-high NH<sub>3</sub> yield of 327.6 mmol h<sup>-1</sup> gcat<sup>-1</sup> and a high reaction selectivity of 84.63% [100]. This catalyst showcased excellent performance in NO<sub>3</sub>RR. Furthermore, Fu et al. [101] conducted DFT calculations and find the Cu<sub>2</sub>O/Cu interface decreased NO<sub>2</sub> adsorption energy from -2.02 eV (for pure Cu) to -1.59 eV, thereby promoting the diffusion of  $NO_2^-$  intermediates and accelerating the NO<sub>3</sub>RR (Fig. 5g). According to these findings, copper oxides showed high current density, high selectivity, and fast reaction kinetics in NO<sub>3</sub>RR, which have showed great application potential.

#### 4.2. Crystal facet regulation and modifications on Cu oxide catalysts

It is well-established that different crystal surfaces can display distinct catalytic properties [102-105]. Numerous studies have investigated the impact of exposed crystal surfaces of Cu-O on catalyst performance [106]. Cu<sub>2</sub>O materials attract more attention to the crystal plane regulation of Cu–O. For instance, Zhong et al. [107] examined the influence of various exposed crystal surfaces of Cu<sub>2</sub>O on the catalytic NO<sub>3</sub>RR (Fig. S4a). They observed that the  $Cu_2O(111)$  surface exhibited superior catalytic activity for  $NO_3^$ reduction, characterized by a lower onset potential, higher current density, and faster charge transfer rate compared to the (100) surface and the mixture of (100) and (111) surfaces (Fig. S4b). The Cu<sub>2</sub>O(111) facet exhibited a higher oxygen vacancies concentration in comparison to the (100) facet, thereby effectively promoting the adsorption of intermediates. Moreover, the Cu<sub>2</sub>O(111) facet exhibited a higher concentration of hydroxyl groups, facilitating water cracking to produce \*H species while preventing H-H coupling from generating H<sub>2</sub>. As a result, the Cu<sub>2</sub>O(111) facet displayed superior comprehensive catalytic performance compared to the Cu<sub>2</sub>O(100) facet, offering enhanced efficiency in various aspects.

In contrast, Qin et al. [108] synthesized Cu<sub>2</sub>O cubes surrounded by six (100) facets and Cu<sub>2</sub>O octahedra with eight (111) facets (Fig. S4c). They discovered that the Cu<sub>2</sub>O with (100) facets achieved a FE of 82.3% and exhibited a higher current density and NH<sup>+</sup><sub>4</sub> yield than the counterpart with (111) facets. This observation was further supported by DFT calculations, which verified that the (100) facets possessed a lower energy barrier for NH<sub>3</sub> formation due to their partially unfilled Cu 3d state. Consequently, the authors concluded that Cu<sub>2</sub>O(100) facets demonstrated greater NH<sub>3</sub> selectivity and NO<sub>3</sub>RR catalytic activity than the (111) facets.

Furthermore, numerous studies have concentrated on modifying Cu oxide materials using various methods to enhance their catalytic activity [109–115]. For instance, Wang et al. developed an *in situ* approach to load Cu<sub>2</sub>O active sites onto island Cu and utilized it for NO<sub>3</sub><sup>-</sup> reduction (Fig. S4d) [116]. The incorporation of Cu<sub>2</sub>O significantly augmented the reaction current density raised the FE to 98.28%, and improved the selectivity towards NH<sub>3</sub> to 96.6% (Fig. S4e). In another study, Ren et al. fabricated Cu nanowires coated with concave and convex surface Cu<sub>2+1</sub>O layers (Cu@Cu<sub>2+1</sub>O NWs) (Fig. S4f) [117]. The metallic Cu within the nanowires facilitated efficient electron transport along the nanowire structure, while the Cu<sub>2+1</sub>O layer on the outer surface provided abundant active sites (Fig. S4g).

Besides, Niu et al. [118] reported the synthesis of surface oxygen-modified Cu nanoparticles enclosed in layered graphite carbon (Cu@C). The presence of Cu<sub>2</sub>O on the surface of Cu nanoparticles significantly suppressed the competitive HER, facilitated electron transfer between the \*NOH intermediate and the catalyst surface, and lowered the energy barrier for hydrogenation from \*NO to \*NOH. These advantageous features rendered it an excellent catalyst for NO<sub>3</sub>RR. Likewise, Du et al. designed a mixed-valence dual-net Cu metal-organic framework using MOF material [119]. This framework readily formed Cu<sub>2</sub>O/CuO@C heterojunctions, resulting in a remarkable Faraday efficiency of 93.05% and a selectivity of 93.11%.

Modifying Cu oxides is an attractive strategy to improve the catalytic performance of Cu oxide materials, which not only overcomes the inherent shortcomings but also generates new properties based on the synergistic effects. As shown above, many studies have modified Cu–O using interaction regulation between Cu and other elements.



**Fig. 5.** The typical Cu oxide catalysts and its various applications. **a**, A schematic diagram of the *in situ* conversion of CuO NWAs to Cu/Cu<sub>2</sub>O NWAs. **b**, *In situ* electrochemical Raman spectroscopy of CuO NWAs. **c**, LSV curves of Cu/Cu<sub>2</sub>O NWAs in different electrolytes. **d**, The free energy of H<sub>2</sub> formation on Cu/Cu<sub>2</sub>O NWAs and Cu NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, LSV curves of Cu/Cu<sub>2</sub>O NWAs. Reproduced with permission from Ref. [97]. Copyright 2020, Wiley-VCH. **e**, The configuration of Cu<sub>2</sub>O/Cu interface and Cu adsorbed NO<sub>2</sub>. Reproduced with permission from Ref. [101]. Copyright 2022, Elsevier.

# 4.3. Organics regulation of Cu oxide catalysts

Among the various methods of modifying Cu oxide catalysts, utilizing organic polymers has emerged as a promising approach for regulation. Xu et al. [120] synthesized CuO nanowires that vertically grew on a Cu foam substrate modified with a polyaniline (PANI) surface (Fig. 6a). They investigated the potential of the prepared CuO@PANI/CF catalyst for selective electrocatalytic conversion of NO<sub>3</sub> to NH<sub>3</sub> and observed remarkable performance, including high current density, NH<sub>3</sub> selectivity, and NH<sub>3</sub> production, all reaching their maximum at an applied potential of -1.3V (vs. SCE) (Fig. 6 b–d). The PANI coating on CuO nanowires not only regulated the chemical microenvironment of the catalyst surface but also improved its conductivity. This facilitated the enrichment of reactants and hydrides on the catalyst surface while maintaining the structural integrity of the nanowire array.

In contrast, Gao et al. [121] incorporated hydrophobic polytetrafluoroethylene (PTFE) nanoparticles into CuO catalyst layers (Fig. 6e–g). The hybrid catalyst not only exhibited no adverse effect on the intrinsic catalytic performance of CuO but also improved its catalytic performance in various aspects (Fig. 6e,g). The presence of PTFE nanoparticles facilitated the adsorption and subsequent desorption of gas products, thus preventing blockages in the ion conduction pathway and active sites on the electrocatalyst surface (Fig. 6f). As a result, the hybrid catalyst demonstrated superior catalytic activity compared to pure CuO catalysts. Additionally, Li et al. reported the *in situ* electrochemical reconstruction of a nanofiber-like polypyrrole Cu (PPy-Cu-E) 3D network, which achieved a FE of approximately 91.95% in a fluid electrolyte [122].

#### 4.4. Oxygen vacancy regulation of Cu oxide catalysts

Vacancy engineering has emerged as a promising strategy for catalyst modification [123–126]. In particular, introducing an appropriate concentration of oxygen vacancies to Cu-O can significantly enhance its catalytic activity. The procedure for plasma-treated catalyst preparation for electrocatalysis is illustrated in Fig. S5a [127]. Gong et al. employed plasma treatment to generate Cu<sub>2</sub>O materials, denoted as Ar-20, Ar-40, and Ar-60, with varying concentrations of defective oxygen vacancies on their surfaces [127]. It was found that Ar-40 exhibited the highest current density, Faraday efficiency (85.26%), NH<sub>3</sub> selectivity (85.78%), and NH<sub>3</sub> yield among the tested samples (Fig. S5b). However, the excessive concentration of defective oxygen vacancies in A-60 resulted in a severe etching effect, leading to inferior catalytic performance compared to Ar-40. The DFT calculations indicated that defective oxygen vacancies lowered the adsorption energy of adsorbed intermediates (Fig. S5c). These theoretical calculations,



**Fig. 6.** Organics regulation of Cu oxide catalysts. **a**, Schematic of CuO@PANI/CF. **b**, LSV properties of CuO@PANI/CF in different electrolytes. **c**, Selectivity of CuO@PANI/CF **d**, Plot of NO<sub>3</sub>, NO<sub>2</sub> and NH<sub>3</sub> concentrations using CuO@PANI/CF at -1.3V (vs. SCE). Reproduced with permission from Ref. [120]. Copyright 2023, Elsevier. **e**, Schematic diagram of PTFE-CuO/C. **f**, NO<sub>3</sub>RR CV diagrams of CuO/C and PTFE-CuO/C electrodes in different electrolytes. **g**, Comparison of FE, NO<sub>3</sub> reduction kinetic constant (K), NH<sub>3</sub> yield, partial current density, and NH<sub>3</sub> selectivity of CuO/C and PTFE-CuO/C electrodes on NH<sub>3</sub>. Reproduced with permission from Ref. [121]. Copyright 2023, Wiley-VCH.

along with experimental results, demonstrated that an appropriate concentration of oxygen vacancies markedly improves the NO<sub>3</sub>RR catalytic performance of Cu<sub>2</sub>O.

As to CuO materials, Rahman et al. conducted theoretical calculations on CuO (Fig. S5d) [128]. Subsequently, CuO nano-catalysts with oxygen vacancy defects were synthesized using flame spray pyrolysis technology and subjected to plasma treatment for experimental verification. The DFT calculations revealed that an appropriate concentration of oxygen vacancies (greater than 1 OV) in CuO material could reduce the adsorption of  $NO_{\overline{3}}$  and inhibit the competitive adsorption from many other anions while suppressing HER (Figs. S5e-f). Experimental results demonstrated a noticeable improvement in the catalytic performance of CuO catalysts after 5 min of plasma treatment. However, excessive defects caused a decrease in the surface crystallinity of the CuO material after 10 min of treatment, resulting in significant changes in the surface chemical state and electrical conductivity. The observed effect of oxygen vacancy concentration on the catalytic properties of both Cu<sub>2</sub>O and CuO materials exhibited the same trend.

Additionally, Wang et al. [129] synthesized hollow  $Cu_2O$  nanocubes with abundant oxygen vacancies, achieving an impressive Faraday efficiency of 92.9% at -0.85 V (vs. RHE). Oxygen vacancies in the catalyst greatly enhanced selectivity, FE, and NH<sub>3</sub> yield. Similarly, another study by Wang et al. [130] investigated the catalytic performance of Cu/CuO<sub>x</sub> planar heterogeneous nanosheet arrays with abundant oxygen vacancies for the reduction of NO<sub>3</sub> to NH<sub>3</sub>. Additionally, Geng et al. [131] also found the enhanced catalytic activity of CuO<sub>x</sub> nanoparticles enriched with oxygen vacancies for NO<sub>3</sub> reduction in a fluidic electrocatalytic system.

# 4.5. Synergistic effect of Cu oxides with other metals or metal oxides

Materials incorporating Cu oxides with other metal elements can possess more than two active sites, resulting in a synergistic effect between Cu and these elements. This synergistic effect influences the interaction between the reactant and the catalyst, reducing the reaction's energy barrier and promoting its progress.

Studies have also demonstrated the enhanced performance of Cu–O in NO<sub>3</sub>RR when combined with other metal oxides to form heterostructures. For instance, Xu et al. [132] synthesized CuO 1D nanowire arrays decorated with MnO<sub>2</sub> 2D nanosheets on a Cu foam substrate, referred to as CuO@MnO<sub>2</sub>/CF, as illustrated in Fig. S6a. Transmission electron microscopy (TEM) images revealed the presence of heterogeneous structures between CuO and MnO<sub>2</sub> in

CuO@MnO<sub>2</sub>/CF (Fig. S6b). Research has confirmed that CuO@MnO<sub>2</sub>/ CF exhibited excellent catalytic activity for NO<sub>3</sub>RR, achieving a current density exceeding 100 mA cm<sup>-2</sup>, a NO<sub>3</sub> conversion rate of 99.38%, an NH<sub>3</sub> FE of 94.92%, and an NH<sub>3</sub> selectivity of 96.67%. These performances surpassed those of comparative materials such as CuO/CF (Fig. S6c). The heterogeneous interface between CuO and MnO<sub>2</sub> provided a favorable built-in electric field that optimized the adsorption of reactants or reaction intermediates on the catalyst surface, thereby accelerating selective NO<sub>3</sub>RR.

Meanwhile, Liu et al. [133] assembled CuO nanowire arrays modified with Co<sub>3</sub>O<sub>4</sub> flocs on a Cu foam substrate, as depicted in Fig. S6d. In an alkaline electrolyte, the CuO NWAs@Co<sub>3</sub>O<sub>4</sub> catalyst demonstrated superior current density, electrocatalytic activity, and stability compared to CuO NWAs and Co<sub>3</sub>O<sub>4</sub> flocs. The catalyst exhibited a FE of 99.17%, NH<sub>3</sub> selectivity of 82.28%, and NO<sub>3</sub><sup>-</sup> conversion of 96.96% (Figs. S6e–f). Recently, Co-based oxide catalysts with moderate modification for NO<sub>3</sub>RR were also widely studied in NO<sub>3</sub>RR [134–136]. The significant enhancement in catalytic performance was mainly attributed to the synergistic effect between the catalytic performance of CuO NWAs and the \*H adsorption function promoted by the Co<sub>3</sub>O<sub>4</sub> flocs.

Another example is the TiO<sub>2</sub> NTs/CuO<sub>x</sub> system [137], where a TiO<sub>2</sub> carbon nanotube reactor with CuO<sub>x</sub> active nanoparticles (Fig. S6g) displayed a more positive initial potential, higher current density, greater FE, and increased NH<sub>3</sub> yield compared to TiO<sub>2</sub> NTs (Figs. S6h–i). This improvement is attributed to the synergistic effect of TiO<sub>2</sub>/Cu<sub>2</sub>O/Cu and the steric limiting effect of the nanotube structure on the reaction intermediates. Other metal oxides have also been investigated for their synergistic interactions with Cu oxides [138–145], such as the Co-CuO<sub>x</sub> electrochemical filter composed of vertically aligned CuO<sub>x</sub> nanowalls embedded with CoO<sub>x</sub> nanoclusters [140]. This filter exhibited a N<sub>2</sub> selectivity of 96.0% and low energy consumption during NO<sub>3</sub>RR. The incorporation of CoO<sub>x</sub> increased the number of oxygen vacancies, facilitating the adsorption of intermediates and electron transfer between active centers.

Moreover, researchers also explored the strategy of doping Cu oxides using other metals [146–149]. For example, Xu et al. [146] synthesized ultralow-content Pd (2.93 at%) incorporated Cu<sub>2</sub>O corner-etched octahedra (Fig. S7a). The resulting Pd–Cu<sub>2</sub>O CEO catalyst exhibited a more positive initial potential and higher current density than pure Cu<sub>2</sub>O (Fig. S7b). It achieved an NH<sub>3</sub> FE of 96.56% and an NH<sub>3</sub> selectivity of 95.31% at the optimal operating potential of -1.3 V vs. SCE (Fig. S7c). The incorporation of Pd provided active sites for hydride aggregation, while the synergistic effect of the cavity and oxygen vacancies weakened the N–O bond in NO<sub>3</sub>. These factors combined to greatly enhance the catalytic activity of Pd–Cu<sub>2</sub>O (Fig. S7d).

Similarly, Du et al. [147] fabricated a self-supported Zn–CuO nanosheet array doped with Zn (Fig. S7e), which exhibited high NH<sub>3</sub> yield, electrochemical stability, and a Faraday efficiency of up to 95.6%. Zn–CuO NAs displayed significantly higher NH<sub>3</sub> yield and FE than pure CuO NAs (Fig. S7f). The doped Zn regulated CuO electronic structure, thus effectively promoting interfacial charge transfer and internal electron transfer.

In contrast, Gong et al. [148] conducted a study using a series of layered La<sub>2</sub>CuO<sub>4</sub> as a model system to investigate the impact of B-site cationic doping on the regulation of NO<sub>3</sub>RR activity (Fig. S7g). The findings revealed that Co doping significantly enhanced the NO<sub>3</sub>RR activity, whereas Zn doping only exhibited a marginal enhancement effect (Fig. S7h). Interestingly, the incorporation of Ni had a slight inhibitory effect on the performance of the NO<sub>3</sub>RR process.

In addition to the aforementioned interactions, Cu has been found to interact with other metallic elements as well [150-153]. Chen et al. reported the synthesis of a PdCu/Cu<sub>2</sub>O hybrid with a

mesoporous hollow sphere structure [154]. Incorporating Pd in the hybrid resulted in the formation of highly dispersed PdCu alloy, which created new NO<sub>3</sub><sup>-</sup> adsorption sites and adjusted the NH<sub>3</sub> synthesis pathway of the catalyst, leading to improved catalytic performance in NO<sub>3</sub>RR. The PdCu/Cu<sub>2</sub>O hybrid exhibited a selectivity of 96.70% and an FE of 94.32%, representing significant enhancements compared to pure Cu<sub>2</sub>O.

Yin et al. [155] constructed an Ag/Cu<sub>2</sub>O hybrid by inducing oxygen vacancies. The interface between Ag nanoparticles and Cu<sub>2</sub>O served as new active sites, and their strong interaction significantly enhanced the catalytic activity of NO<sub>3</sub>RR. The Ag/Cu<sub>2</sub>O hybrid demonstrated a high selectivity of 96.85% and an FE of 96.45%. Furthermore, Wang et al. [156] deposited a graphene oxide (GO) layer on a titanium plate. They facilitated the aggregation of Cu, Cu<sub>2</sub>O, and CuO on the GO layer, forming the Cu/GO/Ti electrode. Compared to the Cu/Ti electrode, the Cu/GO/Ti electrode exhibited a substantially increased NO<sub>3</sub><sup>-</sup> removal rate while reducing energy consumption.

In summary, due to its low cost, unique electronic structure, and great catalytic potential, Cu oxides have been widely used as anode catalytic materials in electrocatalytic NO<sub>3</sub>RR reactions. Many modification methods, such as crystal facet regulation, organics regulation, oxygen vacancy regulation, etc., have also been employed, demonstrating high current density, FE, and NH<sub>3</sub> yield. These strategies are hoped to spire the following attempts in materials development.

#### 5. Cu single-atom catalysts

Theoretically, Cu-based catalysts with isolated active sites, such as Cu SACs, hold even greater promise for achieving specific reaction pathways and high NH<sub>3</sub> selectivity, thanks to their well-defined and uniform coordination structures. In recent years, significant advancements have been made in the field of SACs [157–164]. The concept of SACs has found widespread applications in various electrocatalytic processes, including ORR [165–167], HER [168–170], and CO<sub>2</sub>RR [171–173]. Among these SACs, Cu SACs have attracted increasing attention [174–178]. Cu-based SACs and their derivatives are typically synthesized by doping Cu ions into porous nitrogen-doped carbon, forming Cu-NC SACs. Moreover, Cu-based SACs have also demonstrated promising performance in the electrocatalytic NO<sub>3</sub>RR. The activity of these Cu-based SACs depends on the loading capacity of Cu atoms and the coordination environment between the nitrogen-carbon matrix and the Cu atoms.

# 5.1. Typical Cu SAC

Cu monatomic catalysts, known for their precise controlled synthesis procedure [179–183], have been discovered to exhibit high activity and selectivity in electrocatalytic NO<sub>3</sub>RR. These catalysts offer convenience in exploring and understanding the mechanism of this process due to their clear coordination structure. In Fig. 7a, the schematic diagram illustrates the synthesis process of Cu SACs, where a precursor containing Cu, N, and C was synthesized, followed by the formation of the Cu SACs catalyst through high-temperature pyrolysis [184]. Yang et al. [185] utilized operando X-ray absorption spectroscopy and advanced electron microscopy to reveal a Cu–N<sub>4</sub> monatomic catalyst that recombines the Cu site into 5 nm nanoparticles in NO<sub>3</sub>RR, as shown in Fig. 7b. The evenly dispersed bright spots in Fig. 7c indicate the uniform distribution of Cu on the nitrogen-carbon doped carrier.

The polarization LSV curve in Fig. 7d demonstrates that Cu-NC exhibits a significantly lower overpotential for  $NO_3RR$  than NC. Additionally, this study employed operando XAS to investigate the



Fig. 7. a, The synthetic procedure, morphology, and microstructure of Cu–HNCS. Reproduced with permission from Ref. [184]. Copyright 2022, Wiley-VCH. b, Changes in Cu sites at different potentials. c, HAADF image of Cu–N–C SAC. d, LSV polarization curves using N–C and Cu–N–C SAC. e, Cu K-edge XANES spectra. f, Cu K-edge FT-EXAFS spectra. g, proposed mechanisms of CuNC in NO<sub>3</sub>RR. Reproduced with permission from Ref. [185]. Copyright 2022, ACS.

electrochemical process (Fig. 7e). As depicted in Fig. 7f. It was observed that as the voltage increases,  $Cu^{2+}$  is successively reduced to  $Cu^+$  and then to  $Cu^0$ , resulting in the aggregation of Cu nanoparticles. The simultaneous changes in the percentage of  $Cu^0$  and the FE of NH<sub>3</sub> suggest that these Cu nanoparticles serve as the active sites for NO<sub>3</sub>RR at this specific potential. Interestingly, upon exposure to air, the Cu clusters revert back to their original Cu $-N_4$ state, as shown in Fig. 7g. In another study conducted by Wang et al. [186], a monoatomic catalyst was synthesized by incorporating 3,4,9,10-perylene tetracarboxylate dihydride (PTCDA) into Cu.

The Cu-PTCDA catalyst exhibited remarkable yield and selectivity for NH<sub>3</sub> production. To explore the formation energy of \*H and \*NO<sub>3</sub>, this study anchored a structurally optimized Cu atom onto PTCDA, as illustrated in Figs. S8a-d [186]. The energy difference was utilized to assess the likelihood of the respective reactions (Fig. S8e). Notably, Fig. S8f demonstrates that the high energy potential barrier observed during the desorption of \*NO2 and adsorption of \*NO, combined with the subsequent dissociation of  $NO_2^-$  to form  $*N_2O_3$  (highlighted with orange shading), may be the primary factor driving NH<sub>3</sub> formation through direct eight-electron transfer facilitated by the Cu-PTCDA catalyst. Conversely, the higher energy barrier observed during Cu-NC desorption of \*NO2 indicates that  $NO_2^-$  is not involved in  $NO_3RR$ . Moreover, the presence of the Cu site favors the protonation of \*NO to \*NOH instead of  $NO_2^-$  ions to N<sub>2</sub>O<sub>3</sub>, which further indicates the selective reduction of NO $\overline{3}$  to NH<sub>3</sub> rather than N<sub>2</sub> (Figs. S8f-h).

The results revealed a limited HER activity of the catalyst. Systematic theoretical calculations demonstrated a significant adsorption effect of the catalyst on  $NO_3^-$ , enabling its subsequent co-reduction with H<sup>+</sup>. This observation highlights the crucial role of PTCDA as the substrate, which not only suppresses HER but also provides electron and proton storage and supply capabilities. Furthermore, the distinct electronic structure of Cu allows for the simultaneous inhibition of HER and the promotion of N–H binding. To gain deeper insights into the actual electrocatalytic NO<sub>3</sub>RR mechanism, further studies investigating the real state of the Cu SACs in NO<sub>3</sub>RR are proposed.

# 5.2. Strategies of surrounding atom manipulation on Cu SACs

Modulating the coordination environment of Cu represents an impressive strategy for enhancing the performance of Cu monatomic catalysts, offering significant potential in single-atom electrocatalysis [187–191]. In this regard, Cheng et al. designed symmetry-broken Cu SACs by preparing a precursor with a N<sub>2</sub>O<sub>2</sub> coordination environment of Cu, followed by sintering at 550 °C with Ar to get the Cu–N<sub>2</sub>O<sub>2</sub> coordination monatomic catalyst (Fig. 8a–c) [187]. The XANES spectra reveal that the energy absorption threshold of Cu-Cis-N<sub>2</sub>O<sub>2</sub> SAC lies between Cu<sub>2</sub>O and CuO, indicating that the valence state of Cu-Cis-N<sub>2</sub>O<sub>2</sub> SAC is an intermediary between Cu<sup>+</sup> and Cu<sup>2+</sup>. The fitted oxidation valence of Cu in Cu-Cis-N<sub>2</sub>O<sub>2</sub> is determined to be 1.84 (Fig. 8d), which aligns with



**Fig. 8. a**–**c**, Molecular dynamics simulation of Cu-cis-N<sub>2</sub>O<sub>2</sub> (**a**), Cu-trans-N<sub>2</sub>O<sub>2</sub> (**b**), and CuN<sub>4</sub> SAC (**c**). **d**, Correlation between the Cu oxidation state and the energy position of the XANES spectrum. **e**, Long-term stability of Cu-cis-N<sub>2</sub>O<sub>2</sub>. Reproduced with permission from Ref. [187]. Copyright 2022, Wiley-VCH. **f**, Preparation of Cu/Ni–NC. **g**, LSV curves of Cu/Ni–NC, cu–NC, and Ni–NC. **h**, Performances of Cu/Ni–NC in NO<sub>3</sub>RR. **i**, Charge transfer on Cu/Ni–NC. **j**, PDOS plots of NO<sub>3</sub>\*O adsorption on Cu–NC, Ni–NC, and Cu/Ni–NC. Reproduced with permission from Ref. [191]. Copyright 2023, Wiley-VCH.

previous findings. Remarkably, the catalyst's activity remained consistent after 2000 h of operation (Fig. 8e), with the NH<sub>3</sub> production rate reaching 27.84 mg h<sup>-1</sup> cm<sup>-2</sup> at 366 mA cm<sup>-2</sup>. By breaking the symmetry of the coordination environment, the active site becomes more polar, effectively reducing the coordination symmetry.

Furthermore, it has been demonstrated that Cu-based diatomic sites offer more advantages in electrocatalysis compared to simple Cu single-atomic sites, as evidenced by studies on Cu diatomic NO<sub>3</sub>RR [192–194]. Wang et al. [191] synthesized CuNi diatomic catalysts by incorporating Cu and Ni sources into the synthesis process of ZIF-8, trapping the Cu and Ni precursors within the framework, followed by high-temperature pyrolysis (Fig. 8f). Notably, CuNi–NC exhibited superior catalytic activity compared to Ni–NC (34.66 mA cm<sup>-2</sup>) and Cu–NC (88.2 mA cm<sup>-2</sup>), with a current density of 158.9 mA cm<sup>-2</sup> at -1.7V vs. RHE (Fig. 8g). The polarization curve LSV indicated that CuNi–NC achieved higher current

density than Cu–NC and Ni–NC at the same potential. The FE of the catalyst reached 97.28%, and the conversion rate reached 98.5% at –0.7V (vs. RHE) (Fig. 8h), highlighting the effective promotion of NH<sub>3</sub> synthesis by the CuNi double monatomic catalyst. Additionally, based on DFT theory calculations (Fig. 8i,j), it was observed that the hybridization between CuNi–NC and NO<sub>3</sub> is stronger compared to that between Cu-NC and Ni-NC, facilitating the effective combination of \*NO<sub>3</sub> and promoting electron transfer from CuNi–NC to NO<sub>3</sub>.

# 5.3. Strategies of Cu SAC carriers

The performance of Cu SACs can be influenced not only by changes in the Cu coordination environment but also by alterations in the matrix, as demonstrated in previous studies [195–197]. Hu et al. [195] synthesized a monatomic catalyst with a Cu atom supported on BCN (Fig. S9a). It was observed that the catalytic

activity of CN–Cu doped with B was higher than that without B, which may be attributed to the improved stability of the Cu monatomic dispersion achieved through nitrogen and carbon doping with B. Similarly, Li et al. [197] developed a highly dispersed zero-valent Cu atom catalyst on two-dimensional graphene (Figs. S9b-c). Auger spectra and XANES analysis confirmed that the Cu metal atom existed in a zero-valence state. The graphdivne nanoarray enriched the active site of the zero-valent Cu atom. It exhibited exceptional electrocatalytic performance in  $NO_3^-$  to  $NH_3$ conversion, achieving an NH<sub>3</sub> yield of 15.45 mmol  $h^{-1}$  cm<sup>-2</sup> and the highest FE of 81.25%. Furthermore, the catalyst maintained its activity over 36 cycles without any degradation. Besides, monatomic catalysts have also been utilized to convert NO3 to urea. For example, Daiyan et al. [198] designed a Cu monatomic catalyst with a Cu- $N_xC_y$  coordination environment for the simultaneous electrocatalytic reduction of  $CO_2$  and  $NO_3^-$ , leading to urea synthesis.

# 6. Other Cu-based composite catalysts

In addition, Cu can also be combined with other compounds for NO<sub>3</sub>RR. Compared to other Cu-based catalysts, catalysts that integrate Cu metal with other compounds offer the advantage of achieving synergistic effects among multiple components, opening up new avenues for developing catalysts with enhanced performance. For example, He et al. [199] proposed a design concept for a tandem catalyst, where  $NO_{\overline{3}}$  is preferentially reduced to  $NO_{\overline{2}}$  on the  $Cu/CuO_x$  phase, followed by the reduction of  $NO_2^-$  on the  $Co/CoO_x$ phase (Fig. 9a and b). This division of labor, coupling active sites of different transition metal compounds, enables the catalyst to rapidly produce NH<sub>3</sub> at low overpotential. The FE and yield of NH<sub>3</sub> in 0.1 M NO3 at 0.175 V vs. RHE reached 93.32% and 1.17 mmol  $h^{-1}$  cm<sup>-2</sup>, respectively. Furthermore, the incorporation of non-metallic elements can enhance the ability of Cu to provide atomic \*H and facilitate electron transfer. For instance, Yao et al. [200] reported a binder-free composite electrode (Cu<sub>3</sub>P/CF), which served as a bifunctional catalyst, enabling efficient electron transfer and stable production of atomic \*H for NO<sub>2</sub> conversion.

The synergistic effects of Cu and other compounds play a crucial role in enhancing NO<sub>3</sub>RR by facilitating electron transfer and creating an interfacial electric field. For instance, Fu et al. [201] employed electrodeposition and calcination techniques to establish an interfacial electric field between Cu and CoO (Fig. 9c). The high Fermi level of Cu facilitated electron transfer from Cu to CoO, as confirmed by XPS measurements (Fig. 9d). The unique configuration of NO<sub>3</sub> adsorption on CoO, with one oxygen atom adsorbed on Cu and the other on Co, resulted in stronger adsorption and improved FE, and the interfacial electric field between CoO and Cu also enhanced the charge transfer (Fig. 9e,f). Similarly, Sun et al. [202] stacked CuCl(111) and rutile TiO<sub>2</sub>(110) layers to create an interfacial electric field that enhanced electron transfer and lowered the barrier by elevating the energy of key intermediate \*NO. Besides, Cu carbonate, such as Co-doped Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, was also applied in the electrocatalytic NO<sub>3</sub><sup>-</sup> reduction, while the product was N<sub>2</sub> [203].

Adding a small amount of Cu through doping can introduce more defects and metal active sites, increasing the charge transfer ability in electrocatalysts. For example, Song et al. [204] demonstrated that Cu doping could activate oxygen vacancies in TiO<sub>2</sub> nanotube arrays, leading to enhanced charge transfer and a lower energy barrier for NO<sub>3</sub>RR. Additionally, Li et al. [205] synthesized Cu-doped SnS<sub>2-x</sub> electrocatalysts via a hydrothermal method, which exhibited nearly twice the NH<sub>3</sub> yield (0.63 mmol h<sup>-1</sup> mgcat<sup>-1</sup>) and FE (93.8%) compared to pristine SnS<sub>2</sub> at -0.7 V vs. RHE (Fig. 9g). Interestingly, the adsorption energy of Cu–SnS<sub>2-x</sub> was lower than that of SnS<sub>2</sub> but higher than that of pristine SnS<sub>2</sub>. DFT calculations revealed that the adsorption energy of  $SnS_{2-x}$  was greater than that of Cu–SnS<sub>2-x</sub>, hindering the reaction process due to the excessive adsorption energy of \*NO<sub>2</sub>. Therefore, the design of electrocatalysts with appropriate adsorption capacity is crucial for optimizing their catalytic performance.

# 7. Challenges for large-scale sewage treatment and industrialization

Although some high-performance catalysts for NO<sub>3</sub>RR have emerged, overcoming the challenges of utilizing these catalysts for large-scale sewage treatment and establishing industrial-scale production remains a substantial barrier. One challenge is the complexity of the polluted water in practical applications, where factors such as electrolyte composition and pH may influence the selectivity and stability of the catalysts. Another challenge is the scale-up of the commerical catalysts for NO<sub>3</sub> containing water treatment and the efficient collection of NH<sub>3</sub> produced in the solution.

It is known that the  $NO_3^-$  concentrations in drinking water and industrial wastewater range from 50 to 2000 ppm. The water treatment should also be explored to evaluate the value of highperformance catalysts in environmental applications. Song et al. [71] designed a catalyst of Cu@C with high FE in the electrolyte NO<sub>3</sub> concentrations of 5-100 mM NO<sub>3</sub> (equal to 70-1400 ppm). Besides, there is a lack of further comparison on the catalyst's performance in actual and simulated polluted water. Liu et al. [91] paid attention to the performance of catalysts at low NO<sub>3</sub> concentrations, but they did not include the performance in polluted water. Hence, evaluating the practical application value of these catalysts remains challenging. Fortunately, researchers have begun to pay attention to this issue gradually. Liu et al. [206] extend their study of catalysts to test their performance in natural water, proposing a system based on TiO<sub>2</sub>-Cu for NO<sub>3</sub>RR and NH<sub>3</sub> collection (Fig. 10a and b). The efficiency of  $NO_3^-$  conversion to  $NH_3$  in polluted water was 95.5% and 96.7%, respectively, with  $NO_3^-$  concentrations of 22.5 and 112.5 ppm. (Fig. 10c). Additionally, Liu et al. [207] reported that using CuCN/NHCSs as a catalyst could reduce the concentration of  $NO_3^-$  from 50.0 to 5.7 ppm within 10 h. These satisfactory results provide valuable experience and confidence for future environmental applications. However, there is still limited research on NO<sub>3</sub>RR when tackling complex natural water containing more coexisting ions.

Compared to the mentioned challenges, scaling up these denitrifying electrocatalysts for application and attaining efficient NH<sub>3</sub> recovery seems to be a bigger, more substantial barrier. In contrast, for the previously mentioned issues, we can use an extra pretreatment method, such as adjusting the pH of the electrolyte to improve the catalyst's adaptability to various polluted waters. However, an unavoidable consequence of scaling up catalysts is an increase in electrolyte resistance. Additionally, most of the electrocatalysts currently studied require mixing with Nafion solution and dropping onto a substrate for drying and film formation. As a result, using catalysts in large-scale sewage treatment is still quite difficult, given present approaches. Zhou et al. [208] reported a circulation-coupled device that consisted of a denitrifying electrocatalytic cell and an ammonia separation unit (Fig. 10d). The cost of  $NO_3^-$  reduction was lowered by 21%–33% when compared to the uncoupled system, offering valuable information for future practical application budgets (Fig. 10e). Furthermore, Chen et al. [85] combined the electrocatalytic NO3RR system with air stripping methods, thoroughly exploring NO<sub>3</sub>RR and NH<sub>3</sub> collection processes and comparing the efficiency of different NH<sub>3</sub> collection methods (Fig. 10f). The air stripping approach yielded the ammonia conversion rate of 99.7%. The collected methods of collecting

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**Fig. 9. a**, Mechanism illustration of tandem catalysts. **b**, The LSV-derived potentials a and the reaction constants (k, k<sub>1</sub> for NO<sub>3</sub><sup>-</sup>-to-NO<sub>2</sub>, and k<sub>2</sub> for NO<sub>2</sub><sup>-</sup>-to-NO conversion) for NO<sub>3</sub> and NO<sub>2</sub><sup>-</sup> reduction on CuSP, CoSP, and CuCoSP catalysts. Reproduced with permission from Ref. [199]. Copyright 2022, Nature Publishing Group. **c**, Co, Cu, and O elements mapping of CoO/Cu foam electrodes. **d**, XPS of Cu 2p orbital of CoO/Cu foam and Cu foam electrodes, respectively. **e**, Modeling CoO/Cu foam with adsorbed NO<sub>3</sub><sup>-</sup>. **f**, Schematic illusion of interfacial electric field (Criterion was fermi level of CoO). Reproduced with permission from Ref. [201]. Copyright 2023, Elsevier. **g**, Calculated free energy changes of the NO<sub>3</sub>RR on Cu–SnS<sub>2-x</sub> and SnS<sub>2-x</sub>. Reproduced with permission from Ref. [205]. Copyright 2023, RSC.

NH<sub>4</sub>Cl(s) from aqueous and condensing NH<sub>3</sub>(aq) are all beyond a 90% conversion rate. Based on these explorations, the authors proposed a continuous and efficient scheme for collecting high-purity NH<sub>3</sub>, in which NH<sub>3</sub>-containing gas is pumped into a hydrochloric acid solution and cold concentrated devices, producing different NH<sub>3</sub> products (Fig. 10g). This encouraging outcome shows infinite NO<sub>3</sub>RR possibilities for energy conversion and environmental management. However, there are presently few reports on technologies or strategies for scale-up the catalysts to sewage treatment. It is still extremely challenging to implement industrial production and large-scale sewage treatment.

# 8. Comparison, perspective, and implications of Cu-based catalysts on NO<sub>3</sub>RR

Cu-based catalysts have emerged as highly promising candidates for NO<sub>3</sub>RR due to their exceptional catalytic properties and cost-effectiveness. Significant progress has been made in developing Cu-based catalysts for NO<sub>3</sub>RR in recent years, especially in the last three years. This review tried to support a systematic classification and investigation of various types of Cu-based catalysts, such as Cu, Cu alloys, Cu oxides, Cu SACs, and other Cu compounds in NO<sub>3</sub>RR. These diverse Cu-based catalysts exhibit unique properties and mechanisms during NO<sub>3</sub>RR, and their performances have been extensively studied and optimized. Cu SACs are particularly notable for their high selectivity and activity towards NO<sub>3</sub>RR, stemming from the strong interaction between Cu atoms and the supporting materials. Furthermore, Cu oxide-based catalysts have demonstrated excellent stability and high catalytic activity for NO<sub>3</sub>RR. As shown in Tables S1–S3, the comparison of different Cu-based catalysts is listed. Among these results, we can see that most Cu-based catalysts exhibit an FE of around 90% on  $NO_3RR$ , while the  $NO_3^-$  conversion rate and  $NH_3$  selectivity. Most catalysts were tested in a relatively shorter time or even several cycles for stability validation; therefore, a longer experimental procedure is expected. Factors that affect each kind of Cu catalyst may be varied. Such as, Cu and Cu alloys hold superior electronic conductivity, Cu oxides supply rich content oxygen vacancies, and Cu SAC constructs the high dispersity of Cu atoms and improves the atom utilization rate. Besides, the electrolyte, temperature, electrode structure, conductivity of the circuit, etc., may also affect the activity of the catalyst.

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**Fig. 10. a**, Water quality of Cuihu Lake located in Chongqing Technology and Business University, Chongqing, China. **b**, Schematic illustration of the sequential NO<sub>3</sub>RR and NH<sub>3</sub>–N collection system. **c**, The efficiency of NO<sub>3</sub> conversion to NH<sub>3</sub> in different nitrate concentrations. Reproduced with permission from Ref. [206]. Copyright 2023, ACS. **d**, Optical image of the solar-driven coupled device. **e**, The expenditure analysis with or without considering ammonia profits. Reproduced with permission from Ref. [207]. Copyright 2023, Elsevier. **f**, The conversion efficiency of different steps for the ammonia product synthesis process. **g**, Schematic of the ammonia product synthesis process. Reproduced with permission from Ref. [85]. Copyright 2023, Nature Publishing Group.

However, there is limited research on the *in situ* chemical environment of the catalysts, owing to the catalyst may display reconstruction under the different applied potential or electrolytes. The *in situ* XAS techniques should also be employed to unveil the *in situ* local coordination states of active Cu sites during NO<sub>3</sub>RR. Other *in situ* SRD, and *in situ* Oprando, etc., are suggested to elucidate the reaction intermediates and provide evidence for the proposed reaction mechanism. As to the DFT mechanism explorations, calculations under the applied potential voltage and simulations at the real electrolyte are proposed. Importantly, to assess the NO<sub>3</sub>RR performance for future practical applications, it is essential to employ real NO<sub>3</sub><sup>-</sup>-containing wastewater instead of simulated NO<sub>3</sub><sup>-</sup> electrolytes (e.g., KOH + NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> + NaNO<sub>3</sub>).

Above all, the recent research on Cu-based catalysts for NO<sub>3</sub>RR showed an active and rapidly advancing research field, holding immense potential for practical applications in NO<sub>3</sub><sup>-</sup>-contaminated water treatment and NH<sub>3</sub> synthesis. Future endeavors should prioritize optimizing catalyst design, fabrication, and testing methods to achieve superior catalytic performances. Furthermore, there is a

need to investigate the feasibility of these catalysts in large-scale wastewater treatment applications.

#### **CRediT authorship contribution statement**

**Jinshan Wei:** Conceptualization, Methodology, Formal Analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Funding Acquisition. Yi Li: Writing - Original Draft, Writing - Review & Editing. Hexing Lin: Writing - Original Draft, Writing - Review & Editing. Xihui Lu: Writing - Original Draft, Chucheng Zhou: Formal Analysis. Ya-yun Li: Visualization, Supervision, Funding Acquisition.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

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