



Advanced carbon-based catalysts for efficient electrochemical nitrate upgrading

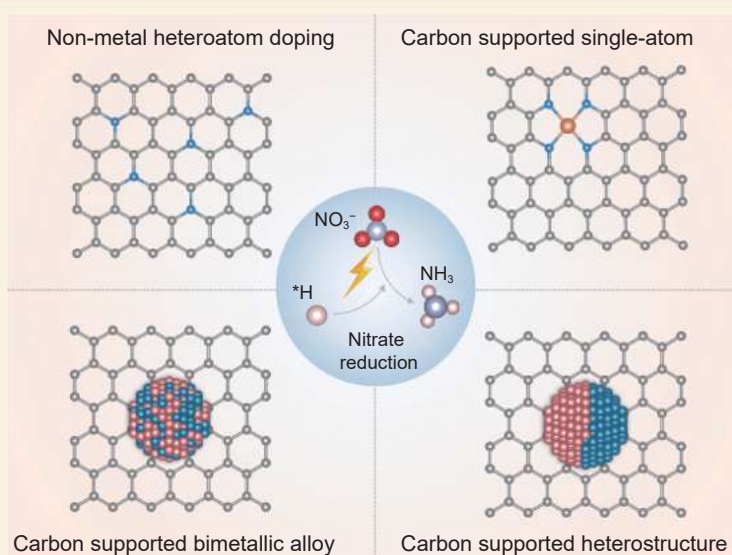
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Abstract: Electrochemical nitrate upgrading, which is the reduction of nitrate to ammonia (NO_3^- RR), has emerged as a sustainable route for both wastewater treatment and green ammonia synthesis, circumventing the energy-intensive Haber-Bosch process. However, the development of electrocatalytic NO_3^- RR is impeded by the presence of complex multi-step reaction pathways with different byproducts, which requires the design of advanced catalysts with better selectivity, activity and stability. Because of their adjustable electronic structures, carbon-based electrocatalysts with excellent electrical conductivity, a large specific surface area, and a high degree of structural diversity, have become a research focus in this field. The fundamental reaction mechanisms of

the NO_3^- RR are reviewed, including multi-step proton-electron coupled transfer pathways with their possible side reactions and byproducts. Advanced in-situ characterization techniques that enable real-time monitoring of catalyst reconstruction and the evolution of intermediates are highlighted for analyzing the reaction pathway. Furthermore, four main design strategies for carbon-based catalysts are summarized: non-metal heteroatom doping, single-atom catalysts, bimetallic alloy systems and heterostructure construction. Finally, the main challenges in using these catalysts, including higher overpotentials and inadequate stability at a high current density are addressed. This underscores the significance of controlling the metal-support interaction to facilitate advances in the practical application of carbon-based catalysts.

Key words: Electrochemical nitrate reduction; Ammonia synthesis; Carbon-based catalyst; Reaction mechanism; Design strategy



1 Introduction

Since the mid-20th century, rapid global population growth and accelerated industrialization have increased the severity of groundwater contamination, with nitrate (NO_3^-) pollution emerging as one of the most prominent concerns^[1-2]. The continued expansion of agricultural activities and the substantial rise in fertilizer use have resulted in steadily increasing nitrate concentrations in groundwater^[3]. Due to nitrate's high solubility in water and excellent mobility, nitrates can quickly infiltrate groundwater systems and spread over large areas^[4]. Once in water bodies, ni-

trates contribute to eutrophication, disrupting the balance of aquatic ecosystems, and in severe cases, may induce algal blooms that pose lethal risks to fish^[5]. Moreover, excessive nitrate pollution not only threatens water quality but also presents significant health risks, including methemoglobinemia, cancer, and endocrine disruption, thus endangering human

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drinking water safety^[6]. Consequently, the nitrate contamination in groundwater is not only a severe threat to global ecology but also a pressing challenge for public health and social stability, attracting considerable global attention^[7–8].

Conventional approaches for addressing nitrate contamination in water primarily rely on physico-chemical techniques, which include biological denitrification, ion exchange, and reverse osmosis^[9]. However, these approaches, which rely on physical processes to separate and concentrate pollutants, are typically associated with high energy consumption and significant operational costs, thus hindering their large-scale applications. More critically, these conventional techniques do not fully degrade or convert nitrates. Instead, they merely transfer nitrates from dilute solutions to concentrated forms or solid waste with reduced volumes, potentially leading to secondary pollution^[10–11]. This “pollution transfer” model complicates the treatment process and contradicts the principles of sustainable development^[12–13]. Recently, the electrochemical nitrate upgrading process, which refers to the valorization of nitrate pollutants into high value-added ammonia, has been identified as a green technology for sustainable wastewater treatment and ammonia synthesis^[14–15]. Under selective catalytic conditions, electrochemical nitrate reduction to ammonia (NO_3^- RR) effectively eliminates pollutants while simultaneously converting nitrates into valuable chemicals, thereby promoting resource recovery^[16–17]. Currently, industrial ammonia production is predominantly achieved via the Haber-Bosch process, which relies on the reaction of nitrogen (N_2) with hydrogen (H_2) under high-temperature and high-pressure conditions^[18]. This process is energy-intensive, consuming approximately 1%–2% of the global energy supply, and contributes substantially to greenhouse gas emissions. In contrast, NO_3^- RR employs nitrate in aqueous solutions as the nitrogen source and water as the hydrogen source. The $\text{N}=\text{O}$ bond in nitrate possesses a bond dissociation energy of approximately 204 kJ/mol, this value is substantially lower

than the bond energy of the $\text{N}\equiv\text{N}$ triple bond in N_2 molecule, which is 941 kJ/mol^[19]. Therefore, nitrate activation requires substantially less energy, making it theoretically feasible to produce ammonia efficiently under mild conditions^[20–21].

The electrocatalytic reduction of nitrate ions ($\text{NO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$) represents a complicated multi-electron and multi-proton process including different intermediates and potential byproducts^[22–23]. The sluggish kinetics of multi-step NO_3^- RR process result in a high overpotential requirement and a low energy efficiency. Besides, the reduction of NO_3^- into NO_2^- requires less electrons and protons than the formation of NH_3 , making NO_2^- a main byproduct during electrochemical NO_3^- RR process. Moreover, the competition with hydrogen evolution reaction (HER) can further lower the Faradaic efficiency of ammonia synthesis. Previous studies have shown that the efficiency and selectivity of products in NO_3^- RR are significantly affected by the catalyst's composition, structural arrangement, and surface characteristics^[24–25]. Therefore, the systematic design of highly efficient catalysts that optimize electron and proton transfer pathways is a critical strategy to improve NO_3^- RR performance and facilitate its practical application^[26].

In recent years, carbon-based catalysts have gained prominence as a focal point of research in electrocatalysis, owing to their remarkable advantages in catalytic performance, cost-efficiency, and environmental sustainability^[27]. First, carbon-based materials demonstrate enhanced electrical conductivity and chemical durability, which facilitate efficient electron transfer in electrochemical processes while maintaining exceptional long-term durability under harsh operating conditions^[28]. These catalysts have demonstrated excellent performance in key reactions such as the oxygen reduction reaction (ORR), HER, and carbon dioxide reduction reaction (CO_2 RR), particularly when both high stability and rapid reaction rates are essential^[29]. Second, carbon materials possess tunable surface structures and high porosity, which can be strategically modified through surface functionaliza-

tion and heteroatom doping^[30–31]. These modifications facilitate meticulous regulation of the active site distribution and the electronic characteristics of the material, considerably improving both catalytic activity and selectivity. Notably, carbon-based catalysts offer distinct advantages in steering specific reaction pathways^[32]. When compared with conventional metal catalysts, carbon-based materials not only possess abundant resources and lower costs, but also offer a large specific surface area and versatile tunability, which together confer greater flexibility and efficiency in catalytic reactions^[33]. Thus, the application of carbon-based catalysts in NO_3^- RR and the development of advanced carbon-based electrocatalysts with tunable structures and enhanced performance are of significant importance^[34], which not only facilitates efficient nitrate pollution mitigation and ammonia resource recovery but also paves the way for novel green electrochemical conversion technologies^[35].

This review emphasizes the development of advanced carbon-based catalysts for efficient electrochemical nitrate upgrading. The proton–electron coupled transfer mechanism associated with NO_3^- RR process is deeply analyzed with the systematic discussions of various possible reaction pathways and different intermediates. To facilitate real-time monitoring of reaction intermediates and potential phase transformations of the catalyst, a range of advanced in situ characterization techniques are discussed that elucidate the reaction pathways and provide insights into the dynamic evolution of the catalysts. For further improving the NO_3^- RR performance of carbon-based catalysts, a series of material-designing strategies are presented as shown in Fig. 1, highlighting the impact of non-metal heteroatom doping, single-atom catalysts (M–N–C), bimetallic alloy systems and heterostructure construction on catalytic activity. Additionally, we present a scientific projection regarding the future application potential of carbon-based catalysts in NO_3^- RR, providing a theoretical framework and technical guidance to enhance efficient ammonia synthesis and address nitrate pollution mitigation.

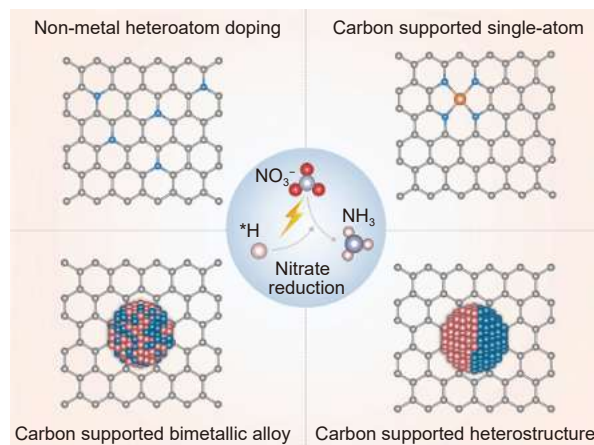


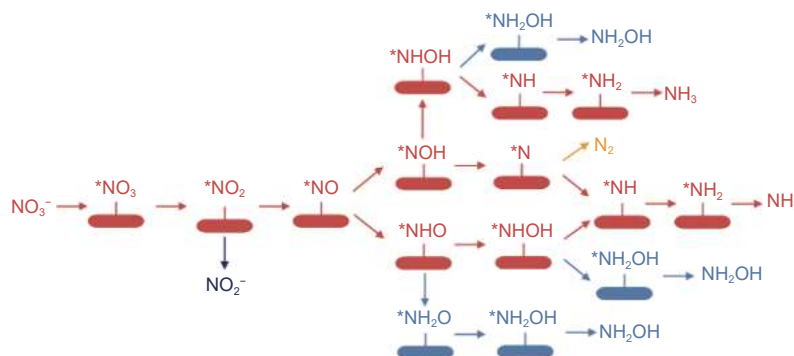
Fig. 1 Design strategies of advanced carbon-based electrocatalysts for NO_3^- RR

2 Electrocatalytic nitrate reduction to ammonia

Before designing and assessing the performance of carbon-based electrocatalysts, it is essential to elucidate the reaction pathway for the electroreduction of nitrate to ammonia to achieve a comprehensive understanding of the intrinsic mechanisms governing the reaction processes^[36]. The electroreduction of nitrate to ammonia is a representative proton–electron coupled transfer (PECT) process, where electrons supply the reducing power, while protons participate in the hydrogenation reaction, facilitating the transformation of nitrate to ammonia^[37]. In this process, elucidating the key intermediates and their associated reaction pathways is critical for the systematic design of catalysts, as it directly determines the choice of active sites, governs catalytic selectivity, and influences overall reaction efficiency^[38].

2.1 Mechanisms of nitrate reduction reaction

As shown in the Fig. 2, the electroreduction of nitrate proceeds through a multi-step sequence of electron transfer and protonation^[39]. Initially, NO_3^- are adsorbed onto the surface of the catalyst, resulting in the formation of the $^*\text{NO}_3$ intermediate, which represents the initial stage of the reaction and serves as a critical determinant of the overall catalytic activity. Then, $^*\text{NO}_3$ undergoes successive electron–proton transfer steps and is reduced to the $^*\text{NO}_2$ intermediate. Subsequently, $^*\text{NO}_2$ can be further reduced to $^*\text{NO}$ or


 Fig. 2 Different reaction pathways and corresponding intermediates of NO_3^- RR

desorbed into NO_2^- . Specifically, $^*\text{NO}$ is considered a crucial intermediate that influences the selectivity of the nitrate reduction reaction. Due to the difference of hydrogenation site, $^*\text{NO}$ could be further reduced into $^*\text{NHO}$ with hydrogen atom bonded to N atom or $^*\text{NOH}$ with hydrogen atom bonded to O atom. The subsequent hydrogenation pathway can determine the final product. If $^*\text{NOH}$ is hydrogenated to $^*\text{N}$ with the release of H_2O , the formed $^*\text{N}$ can be coupled to form N_2 or follow the consecutive hydrogenation steps of “ $^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$ ” to generate NH_3 . If $^*\text{NHO}$ is hydrogenated to $^*\text{NH}_2\text{O}$, the subsequent hydrogenation can result in the formation of NH_2OH . It is noteworthy that both $^*\text{NOH}$ and $^*\text{NHO}$ intermediates can form the $^*\text{NHOH}$, which can produce either NH_2OH or NH_3 , depending on the exact hydrogenation site^[40]. Based on above discussions, beyond the target product of NH_3 , there are different byproducts including NO_2^- , N_2 and NH_2OH in NO_3^- RR. The selective control of these pathways is critical in catalyst design, as it directly influences the Faradaic efficiency (FE) of ammonia production and determines the allocation of the final products^[41].

During the electroreduction of nitrate, the HER inevitably occurs as a competing side reaction^[42]. This behavior primarily arises from the overlapped reaction potential range of NO_3^- RR and HER, which results in the concurrent formation of adsorbed hydrogen ($^*\text{H}$) on the catalyst surface at similar applied potentials^[43]. Although complete suppression of HER could theoretically improve the selectivity of NO_3^- RR, both experimental and computational studies indicate that $^*\text{H}$ is essential for the subsequent hydrogenation steps

leading to NH_3 formation. Thus, for the design of catalysts, it is imperative to carefully consider the equilibrium between the production and utilization of the $^*\text{H}$ species. An insufficient supply of $^*\text{H}$ can limit the rate of NH_3 formation, whereas an excess of $^*\text{H}$ may promote hydrogen recombination to form H_2 , thereby decreasing the Faradaic efficiency of ammonia production. Achieving this equilibrium requires the modulation of both the adsorption energy of the $^*\text{H}$ species on the catalyst surface and the local proton concentration at the reaction interface^[44–45].

The pH value of the electrolyte plays a critical role in determining the reaction pathway, the evolution of intermediates, and the distribution of final products in NO_3^- RR. This influence primarily arises from its effect on proton availability, the adsorption configurations of intermediates, and the surface state of the catalyst. Under acidic conditions, elevated proton concentrations enhance the occurrence of direct PCET processes, which preferentially navigate the N-end reaction pathway. Although the Faradaic efficiency for the desired NH_3 is generally high, the HER presents significant competition, which poses a considerable challenge to maintaining NH_3 selectivity. Under neutral conditions, the availability of protons is restricted, which leads to a reduction in the reaction rate. However, this limitation effectively suppresses HER. Consequently, the $^*\text{NOH}$ pathway becomes increasingly favored, necessitating precise control over product selectivity between NH_3 and NO_2^- . Under alkaline conditions, the proton concentration is significantly diminished, necessitating the use of an indirect reduction mechanism that is facilitated by $^*\text{H}$ gener-

ated from the dissociation of water molecules. Although the adsorption of NO_3^- is enhanced, the hydrogenation step of the oxygen-containing intermediates (such as $^*\text{NO}_3$ to $^*\text{NO}_2$) becomes inhibited, leading to an increased propensity for byproduct formation. Additionally, a metal hydroxide layer may readily form on the catalyst surface, further influencing the reaction pathway. Consequently, the pH value plays a crucial role not only in governing the reaction kinetics and thermodynamic potential barriers but also in directly influencing the stability of intermediates and the overall conversion efficiency.

2.2 In situ characterizations

To further comprehend the mechanism underlying the nitrate reduction reaction, researchers have employed various advanced techniques^[46]. Among these, in situ characterization methods have provided valuable insights into the reaction process, enabling continuous monitoring of intermediate evolution, electron transfer dynamics, and catalyst reconstruction^[47]. To facilitate the systematic comparison of the characteristics and application scopes of different in situ technologies, the detection information, main advantages and limitations are summarized as shown in Table 1. These techniques have offered critical experimental evidence, significantly contributing to the elucidation of the reaction mechanism and the design of more efficient catalysts^[48].

In situ X-ray diffraction (XRD), as an advanced characterization technique, offers distinct advantages in the study of material phase change during NO_3^- RR^[49]. This method enables real-time monitor-

ing of the electrocatalyst's lattice structure evolution under operational conditions, overcoming the limitations of traditional ex situ XRD, which only provides static information before and after the reaction. By capturing dynamic changes during the reaction, in situ XRD facilitates a deeper understanding of the catalyst's performance variations throughout the reaction process. It permits the accurate quantification of peak position shifts, thereby enabling the analysis of lattice strain during the catalytic process. In practical applications, Liu et al.^[50] demonstrated the utility of in situ XRD for monitoring the strains of two-dimensional FeTeSe nanosheet electrocatalysts during the reduction of low-concentration nitrate in an alkaline medium. As illustrated in Fig. 3a, the experimental data reveal that the catalyst induces anisotropic strains during NO_3^- RR, characterized by in-plane tension and out-of-plane compression. Specifically, upon applying a negative bias, the out-of-plane diffraction peak of the (001) plane shifts to the right, indicating a compressive strain of 0.52%, while the in-plane diffraction peak of the (101) plane shifts to the left, corresponding to a tensile strain of 0.27%. This phenomenon illustrates that the reaction-induced anisotropic strain is generated in situ during the catalytic process, offering direct evidence for a more complete understanding of the underlying reaction mechanism. Upon further analysis, in situ XRD revealed that the partial leaching of Se and the preservation of the two-dimensional nanosheet morphology are essential prerequisites for strain formation. In situ XRD also facilitates the monitoring of phase reconfiguration and equilibri-

Table 1 Comparison of different in situ characterization techniques in NO_3^- RR reactions

Technique	Detection information	Main advantages	Limitations
In situ XRD	Bulk crystal structure	Direct monitoring of bulk structural evolution and strain; quantifiable lattice contraction/expansion	Insensitive to surface species; requires high-brightness synchrotron radiation for improved temporal resolution
In situ Raman	Surface species and interfacial water structure	Distinguishes surface species and interfacial water configurations	Fluorescence interference; weak signals; quantitative analysis difficult
In situ ATR-FTIR	Adsorbed intermediates and products	High sensitivity; real-time tracking of multi-intermediate conversion pathways; distinguishes different adsorption configurations	Requires synchrotron radiation; severe water interference (background subtraction needed)
In situ DEMS	Gaseous/volatile intermediates and products	Real-time detection of gaseous and volatile species; low detection limit	Only sensitive to volatile or gaseous species; insensitive to non-volatile intermediates
In situ XPS	Surface elemental chemical states	Directly obtains surface valence changes; can track simultaneous evolution of multiple elements	Probes only top few atomic layers; requires ultra-high vacuum
In situ XAFS	Local atomic structure and oxidation state	Provides local geometric and electronic information of metal centers; distinguishes coordination environment changes	Requires synchrotron radiation; complex data analysis; insensitive to light elements

um by assessing variations in peak intensity. Taking the chromium-doped cobalt-based catalyst reported by our group^[51] as a case study, we observed the phase evolution of the catalyst under different reduction potentials by using in situ XRD. As illustrated in Fig. 3c, a negative shift in the potential leads to a gradual increase in the diffraction peak intensity of $\text{Co}(\text{OH})_2$, accompanied by a corresponding decline in the intensity of the metallic Co peaks. Notably, when the potential reaches -0.4 V vs. RHE, a dynamic equilibrium between the two phases is established. This dynamic equilibrium not only facilitates the efficient adsorption and hydrogenation of NO_3^- at the cobalt sites but also mitigates the risk of irreversible phase transformations that could result in a decline in catalytic activity. This study establishes in situ XRD as an indispensable tool for explaining the authentic active phase

of the catalyst, and for analyzing the mechanisms underlying its reconfiguration. Therefore, the utilization of in situ XRD not only facilitates the monitoring of macroscopic strain evolution but also enables the correlation of applied potentials with active phase change, offering a novel perspective for elucidating the structure–activity relationships of catalysts in NO_3^- RR processes.

In situ Raman spectroscopy enables continuous monitoring of the active species on the surface of electrocatalysts, providing direct evidence for understanding the dynamic processes in catalytic reactions^[52]. In contrast to traditional ex situ characterization techniques, in situ Raman spectroscopy is capable of capturing the dynamic changes of intermediates and surface structures under electrochemical conditions, thereby significantly enhancing the capability

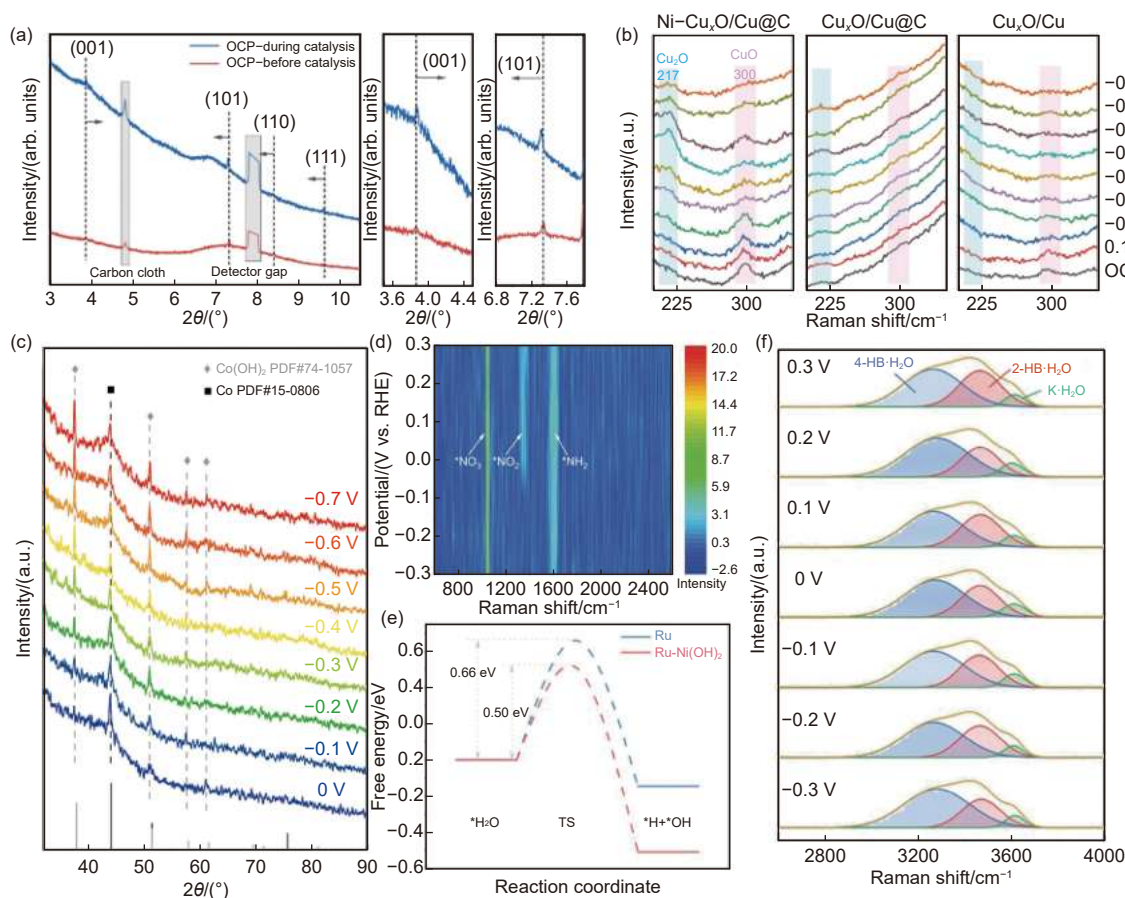


Fig. 3 (a) Operando synchrotron-based XRD patterns of FeTeSe nanosheets before and during catalysis^[50]. Copyright 2025 Springer Nature. (b) In situ Raman spectra of Ni-Cu₂O/Cu@C, Cu₂O/Cu@C and Cu₂O/Cu^[53]. Copyright 2025 Wiley-VCH. (c) In situ electrochemical XRD patterns of the Cr-CoO_x electrocatalyst^[51]. Copyright 2025 Royal Society of Chemistry. (d) In situ Raman contour maps of Ru-Ni(OH)₂ electrocatalyst during NO₃⁻ RR performance measurements from +0.3 to -0.3 V versus RHE. (e) H₂O dissociation kinetic barriers of the Ru and Ru-Ni(OH)₂ electrocatalysts. (f) Potential-dependent in situ Raman spectra of the O-H stretching mode of interfacial water on Ru-Ni(OH)₂ surface^[54]. Copyright 2025 Wiley-VCH

to interpret the catalytic mechanisms. Taking the Ni-doped Cu-based carbon-coated catalyst (Ni-Cu_xO/Cu@C) reported by Wang et al.^[53] as a representative example, in situ Raman spectroscopy was utilized to assess the phase changes of copper oxide species during the electrocatalytic process. As shown in Fig. 3b, at open-circuit potential, the Raman bands observed at 217 and 300 cm⁻¹ can be assigned to the characteristic vibrations of Cu₂O and CuO, respectively. Upon sweeping the potential from 0.1 to -0.7 V, the CuO signal of the Ni-Cu_xO/Cu@C catalyst gradually diminishes, whereas the Cu₂O peak remains largely unchanged. This behavior suggests that the carbon coating effectively suppresses further reduction of Cu⁺, thereby preserving the coexistence of the catalytically active Cu₂O and metallic Cu states. In contrast, the carbon-free Cu₂O/Cu catalyst exhibits complete disappearance of the characteristic Raman signals of CuO and Cu₂O at the same potential, indicating full reduction of the catalyst surface to metallic Cu. This dynamic behavior highlights that the carbon coating not only confers structural stabilization but also preserves the coexistence of Cu⁺ and Cu⁰ species, thereby enhancing the electrochemical efficiency of NO₃⁻RR. Moreover, in situ Raman spectroscopy can also be used to investigate the interfacial water structure. In the investigation conducted by our group^[54] concerning the utilization of a Ru-Ni(OH)₂ electrocatalyst for nitrate reduction, in situ Raman spectroscopy was utilized to monitor the structural dynamics of the interfacial water in real time and to evaluate its influence on the reaction process. As illustrated in Fig. 3d, we initially employed in situ Raman contour maps to measure the reaction intermediates. Subsequently, we acquired the Raman spectra corresponding to the O-H stretching vibration peaks (2900–3700 cm⁻¹) of the interfacial water across various applied potentials (Fig. 3f). The spectra were classified into three distinct types: 4-coordinated hydrogen-bonded water (4-HB·H₂O), 2-coordinated hydrogen-bonded water (2-HB·H₂O), and K⁺ ion hydrated water (K·H₂O). The experiment demonstrated that the incorporation of Ni(OH)₂ species resulted in a decreased concentration

of strongly hydrogen-bonded water (4-HB·H₂O) and an increased concentration of weakly hydrogen-bonded water (2-HB·H₂O) in the Ru-Ni(OH)₂ catalyst compared to pure Ru. This suggests that Ni(OH)₂ promotes the disruption of the hydrogen bond network among water molecules, thereby enhancing the dissociation of H₂O and supplying protons for the hydrogenation conversion of NO₃⁻. Through DFT calculations, it was found that the Ru-Ni(OH)₂ electrocatalyst, as depicted in Fig. 3e, presents a lower activation energy barrier for the dissociation of water. The presence of Ni(OH)₂ enhances the dissociation of H₂O, resulting in the generation of active hydrogen species for accelerating the hydrogenation of NO₃⁻ at the Ru active sites and facilitating its conversion into NH₃. In summary, in situ Raman spectroscopy is a valuable experimental technique for the real-time observation of the active phase and the structural characteristics of interfacial water under catalytic conditions.

The in situ synchrotron radiation Fourier-transform infrared spectroscopy (SR-FTIR) technique enables continuous monitoring of the infrared absorption signatures of reactants, intermediates, and products throughout the catalytic process, allowing precise tracking of reaction process and offering deep mechanistic insights into the nitrate reduction pathway^[55]. Taking the study by Xu et al.^[56] on the Ru nanoparticle and Fe single-atom cascade catalyst (RuNP@FeSA-N-C) as an example, Fig. 4(a-c) illustrates the key intermediates and reaction steps during the nitrate reduction process. The NO₃⁻ consumption peak at 1392 cm⁻¹ indicates the initial NO₃⁻RR, while the appearance of the NO₂⁻ peak at 1270 cm⁻¹ further confirms the sequential reduction pathway of NO₃⁻ → NO₂⁻. Furthermore, the peak observed at 1690 cm⁻¹, ascribed to interfacial water, suggests the generation of active hydrogen during the water dissociation process. Additionally, the N-H bending and stretching vibration peaks at 1630 and 3195 cm⁻¹ provide direct evidence for the formation of ammonia. Notably, compared with the pure Ru nanoparticle catalyst shown in Fig. 4b, the *H-Ru adsorption peak at 1820 cm⁻¹ is absent in the RuNP@FeSA-N-C cata-

lyst. This observation indicates that hydrogen atoms do not accumulate on the Ru sites; instead, they are efficiently transferred to the adjacent Fe sites and promptly participate in the reaction with the nitrogen-containing intermediates. This phenomenon indicates that the rapid effusion of $^*\text{H}$ from the Ru sites prevents excessive hydrogen coverage, thereby effectively mitigating the competition from the HER. The operando SR-FTIR technique clearly reveals the cooperative interaction between the Ru and Fe sites. Specifically, the Fe site is instrumental in the adsorption and activation of NO_3^- , while the Ru site generates active hydrogen. This hydrogen plays a pivotal role in the cascade catalytic process, facilitated by the hydrogen effusion mechanism. As depicted in Fig. 4d, consistent with our group's findings^[54] regarding Ru-Ni(OH)₂ electrocatalysts, in situ attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was also utilized to monitor key intermediates (such as $^*\text{NH}$, $^*\text{NH}_2$, $^*\text{NOH}$) in real time during

the reduction of NO_3^- . Through these applications and mechanistic analyses, the operando SR-FTIR technique not only elucidates the critical steps of the nitrate reduction reaction but also provides valuable mechanistic insights for the systematic design of efficient cascade catalysts, thereby advancing the fundamental understanding of multi-step hydrogenation processes and guiding the optimization of catalyst design.

In-situ differential electrochemical mass spectrometry (DEMS) represents a powerful tool in the investigation of NO_3^- RR. This technique allows the simultaneous continuous detection of intermediates and products, and when integrated with in situ infrared spectroscopy, it facilitates a direct analysis of the underlying reaction pathways. Using the Ru-Co(OH)₂ electrocatalyst reported by our group^[57] as a case study (Fig. 4f), we employed in-situ DEMS to continuously monitor the signals corresponding to different mass-to-charge ratio (m/z) over the course of 5

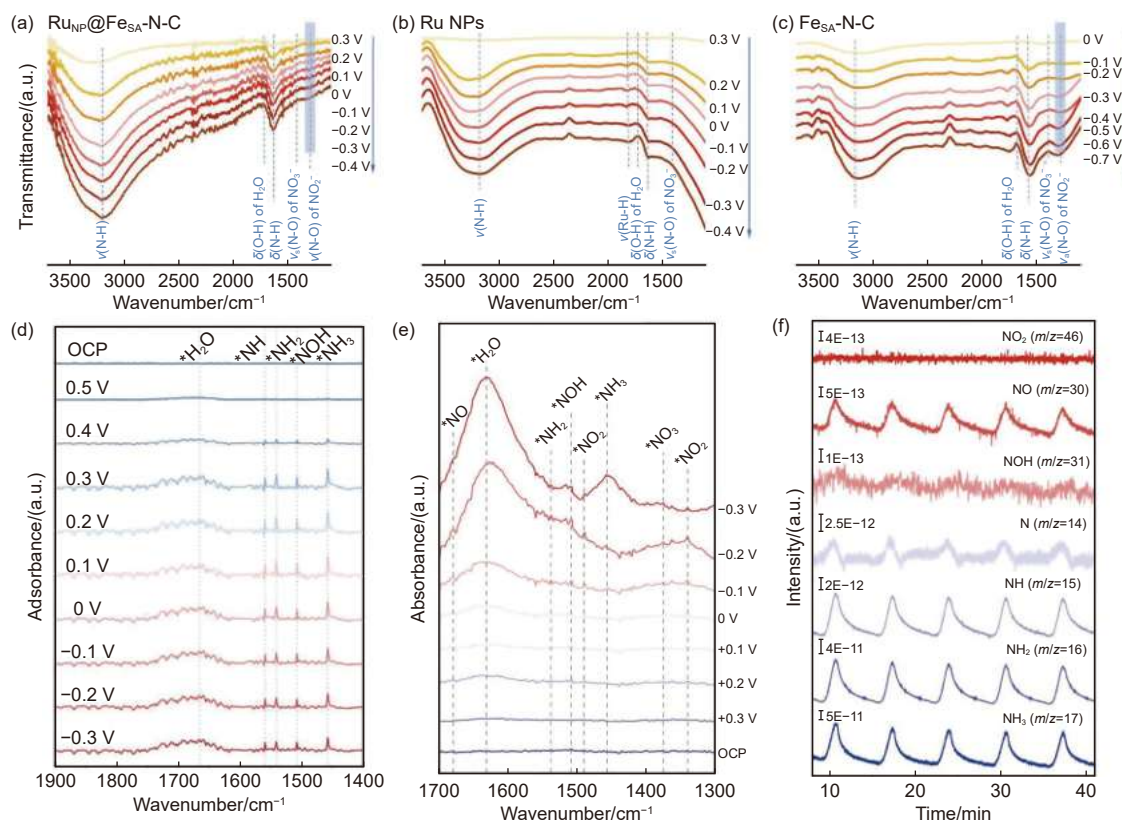


Fig. 4 Operando SR-FTIR spectra over (a) RuNP@FeSA-N-C, (b) Ru NPs, and (c) FeSA-N-C under different applied potentials during NO₃⁻RR in Ar-saturated 1 mol L⁻¹ KOH and 0.1 mol L⁻¹ KNO₃ electrolyte^[56]. Copyright 2025 American Chemical Society. (d) In situ ATR-FTIR spectra of Ru-Ni(OH)₂ electrocatalyst at different applied potentials^[54]. Copyright 2025 Wiley-VCH. (e) In-situ ATR-FTIR spectra of Ru-Co(OH)₂ electrocatalyst. (f) In-situ DEMS measurements of Ru-Co(OH)₂ electrocatalyst during NO₃⁻RR^[57]. Copyright 2026 Springer Nature

cycles. The results indicated that signals corresponding to mass-to-charge values of 30, 14, 15, 16 and 17 were detected, assigning to $^*\text{NO}$, $^*\text{N}$, $^*\text{NH}$, $^*\text{NH}_2$ and $^*\text{NH}_3$ intermediates, respectively. It is worth noting that no signal corresponding to $^*\text{NO}_2$ ($m/z = 46$) was detected during the entire process, suggesting that this intermediate is converted rapidly upon formation and does not accumulate on the surface of the catalyst. Simultaneously, the signal intensity corresponding to $^*\text{NOH}$ ($m/z = 31$) is relatively low, indicating a slow generation rate coupled with a rapid consumption rate. This observation suggests that the formation of $^*\text{NOH}$ represents a rapid step within the overall reaction process. Building upon the real-time mass spectrometry data, in conjunction with in situ ATR-FTIR spectroscopy results (Fig. 4e), we elucidated a comprehensive reduction pathway for NO_3^- RR: $^*\text{NO}_3 \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO} \rightarrow ^*\text{NOH} \rightarrow ^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$. The in situ DEMS technology offers essential online evidence for elucidating the dynamic reaction network occurring on the catalyst surface. It facilitates the verification of key intermediates and aids in identifying the rate-determining steps within the reaction mechanism.

In situ X-ray absorption fine structure (XAFS) spectroscopy offers distinct advantages for investigating catalytic processes in nitrate reduction^[58]. It allows continuous monitoring of the local atomic structure and oxidation state of the catalyst under electrochemical reactions, thereby providing direct insight into its dynamic structural reconfiguration. For instance, Zhang et al.^[59] used in situ electrochemical XAFS to elucidate the structural reconfiguration mechanism of the $\text{Cu}_2\text{O}_{1-\delta}$ catalyst during the nitrate reduction reaction. The XANES spectrum in Fig. 5a reveals that in the presence of NO_3^- , the intensity of the white line increases markedly, indicating an elevation in the average oxidation state of Cu. This change is attributed to electron transfer from Cu_2O to NO_3^- , accompanied by the partial filling of oxygen vacancies. Upon applying a negative bias, the absorption edge shifted negatively by -0.14 eV, and the intensity of the white line decreased, indicating the loss of lat-

tice oxygen and a reduction in the oxidation state of Cu. When the open-circuit potential was restored, the initial electronic structure was reversibly reinstated, demonstrating that $\text{Cu}_2\text{O}_{1-\delta}$ exhibits dynamic reversibility in the presence of NO_3^- . In contrast, in an electrolyte containing only NO_2^- , application of a negative bias induced a pronounced irreversible redshift of the absorption edge (-0.87 eV). As evidenced by the EXAFS data in Fig. 5b, the Cu–Cu coordination signal remained largely unchanged, indicating that NO_2^- was ineffective in restoring the oxygen vacancies. These findings not only elucidate the role of NO_3^- as an electron acceptor in the catalytic process but also reveal the mechanism by which it promotes structural stability of the catalyst through the dynamic regeneration of oxygen vacancies.

In the investigation of NO_3^- RR, in situ X-ray photoelectron spectroscopy (XPS) serves as an effective tool for monitoring the continuous evolution of the chemical states and electronic structures of elements on the catalyst surface. This capability allows for the elucidation of the electron transfer mechanisms and the stability of the active phase throughout the reaction process. Taking the $\text{CoNi-LDH}@ \text{Cu}_2\text{O}$ heterostructure catalyst described by Zheng et al.^[60] as an example, the authors employed in situ XPS to continuously observe the valence state changes of Co, Ni and Cu throughout a 2-hour reaction period at -0.4 V vs RHE. As illustrated in Fig. 5(c-d), during the initial phase of the reaction, the peak positions of Co 2p and Ni 2p exhibited a minor shift towards lower binding energies, indicating a slight decrease in the oxidation states of Co and Ni. Following this initial change, the oxidation state of Co remained stable, whereas the oxidation state of Ni experienced a slight increase. In the LMM Auger spectrum presented in Fig. 5e, the characteristic peak corresponding to Cu(I) was consistently detected throughout the entire reaction process, thereby confirming the stable presence of the Cu_2O phase. However, the peak position gradually shifts toward higher kinetic energy, which corresponds to a decrease in binding energy. Concurrently, as illustrated in Fig. 5f, the Cu 2p peak shifts toward

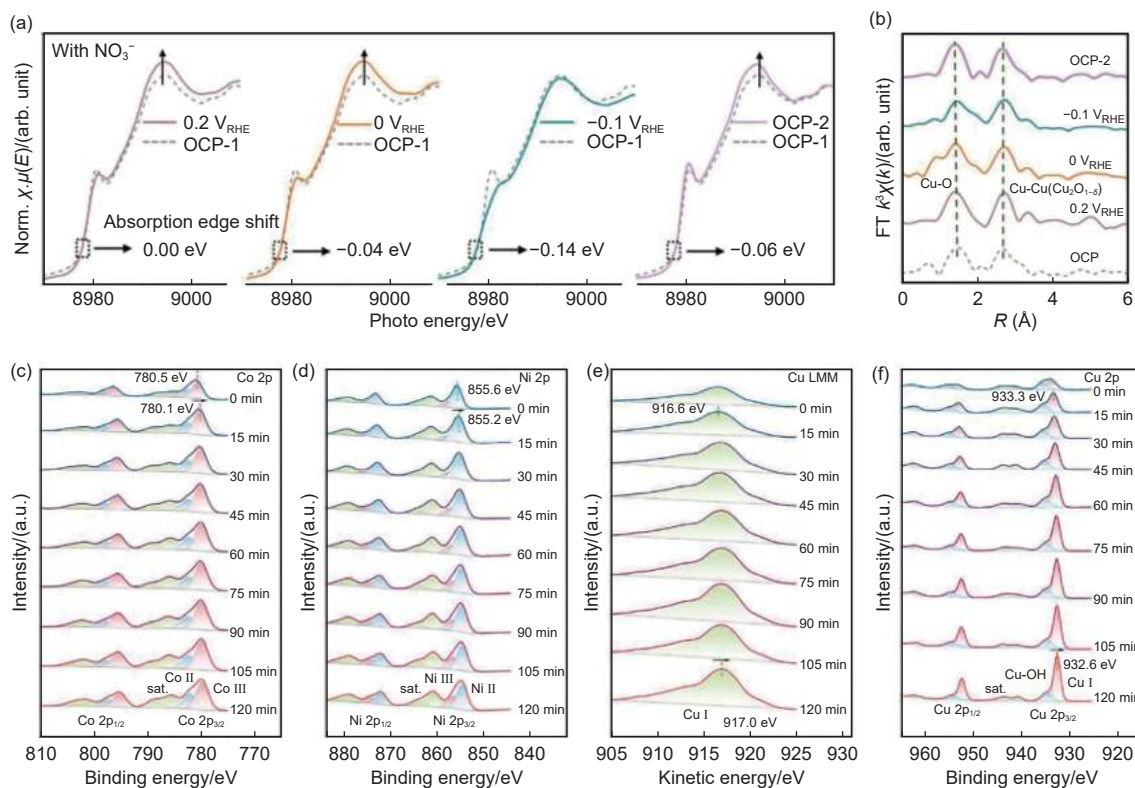


Fig. 5 In situ electrochemical XAFS experiments of $\text{Cu}_2\text{O}_{1-x}$: (a) XANES and (b) FT-EXAFS spectra during the reaction in the NO_3^- electrolyte^[59]. Copyright 2025 Wiley-VCH. In situ XPS characterization of CoNi-LDH@ Cu_2O . (c) Co 2p, (d) Ni 2p, (e) Cu LMM and (f) Cu 2p spectra of CoNi-LDH@ Cu_2O during 2 h NO_3^- RR testing at -0.4 V vs. RHE^[60]. Copyright 2026 Wiley-VCH

lower binding energy, indicating a continuous reduction in the oxidation state of Cu throughout the reaction. This phenomenon can be ascribed to the transfer of electrons from the CoNi-LDH to Cu_2O , which facilitates the reduction of the $^*\text{NO}_3$ species at the electron-deficient Cu sites. In situ XPS offers direct experimental evidence that enhances our understanding of the electronic cooperative effects at the catalyst interface.

Operando characterizations have definitively demonstrated that catalyst reconstruction during the NO_3^- RR is a widespread phenomenon rather than an anomaly, revealing that the true active phases often significantly differ from the initial precursors. Several distinct modes of reconstruction have been identified: (i) modulation of the surface oxidation state, as indicated by the dynamic coexistence of Cu^+ and Cu^0 maintained through carbon coating; (ii) dynamic equilibria induced by phase transformations, exemplified by the interconversion between Co and $\text{Co}(\text{OH})_2$, which optimizes both nitrate adsorption and hydrogenation;

(iii) structural self-repair mediated by oxygen vacancies, where NO_3^- acts as an electron acceptor, enabling the dynamic regeneration of defect sites; and (iv) reconstruction driven by interfacial synergy, illustrated by the in-situ formation of $\text{Co}(\text{OH})_2/\text{Cu}$ heterointerfaces from oxide precursors. Importantly, these operando studies have revealed that the genuine active sites are often not the original metal or oxide phases but rather the dynamically evolved structures that are rich in interfaces or defects, formed under reaction conditions. This insight highlights the importance of linking catalytic performance to operando-determined active phases rather than to ex-situ precursor structures, thereby facilitating a paradigm shift in the rational design of next-generation carbon-based electrocatalysts for NO_3^- RR.

3 Design strategies of carbon-based electrocatalysts

Carbon-based materials demonstrate exceptional stability and catalytic potential in NO_3^- RR, attributed

to their enhanced electrical conductivity, high specific surface area, and structurally tunable properties^[61]. Based on the microscopic structural characteristics of carbon materials, carbon-based catalysts can be categorized into 4 distinct structural types: zero-dimensional (carbon quantum dots, carbon nanospheres), one-dimensional (carbon nanotubes, carbon nanofibers), two-dimensional (graphene, carbon nanosheets), and three-dimensional (ordered mesoporous carbon, hierarchical porous carbon, carbon aerogel). The availability of carbon supports across various dimensions significantly contribute to the optimization of catalytic performance by enabling precise control over key structural features, including surface area, conductive network, and mass transfer channels. The enhancement of its catalytic performance primarily depends on 3 critical factors: precise modulation of the electronic structure, rational engineering of active sites, and the optimization of interfacial synergistic interactions. The primary optimization strategies for carbon-based NO_3^- RR catalysts can be summarized as follows. One approach involves tailoring the local electronic architecture of the carbon support through the doping of non-metallic heteroatoms (such as nitrogen, sulfur, phosphorus, etc.) to enhance the adsorption of nitrate molecules and the activation of intermediates. Second, the highly dispersed anchoring of single-atom metal catalysts onto carbon-based materials enables maximized atomic utilization efficiency while optimizing reaction selectivity. Thirdly, metal and metal nanoparticle materials are integrated with carbon-based substrates to create a bimetallic alloy system. This strategy exploits the synergistic interactions among the metals to enhance both the efficiency of electron transfer and the kinetics of the electrochemical reaction. Fourth, a heterogeneous interfacial structure is engineered to create highly active sites at the interface, thereby enhancing the optimization of proton and electron transfer processes. This arrangement significantly reduces the energy barriers linked to key reaction intermediates, facilitating improved catalytic performance. These material design strategies provide both theoretical insights and empir-

ical foundations for developing efficient, highly selective, and long-term stable carbon-based catalysts for NO_3^- RR.

3.1 Non-metal heteroatom doping

Non-metal heteroatom doping is extensively employed in the electrocatalysis of carbon-based materials, particularly in NO_3^- RR, in which it enhances both catalytic activity and selectivity^[62]. The incorporation of non-metallic elements such as N, S or P can markedly modulate the electronic structure and local charge distribution of carbon-based materials, thereby facilitating the adsorption and activation of nitrate ions, which ultimately leads to an enhancement in electrocatalytic performance. Among these, N doping, being the most widely utilized and extensively studied approach, has become a critical strategy for tuning the catalytic properties of carbon materials, owing to its atomic radius similarity to carbon and its ability to introduce lone pairs of electrons. Nitrogen doping not only optimizes the charge distribution within carbon materials but also increases the adsorption of nitrate ions and their reduction intermediates by introducing additional active sites, thereby enhancing activity. For example, Zhao et al.^[63] employed a two-step synthesis approach to fabricate N-doped graphene catalysts with controlled N species distributions and systematically examined the influence of different nitrogen configurations on the electrocatalytic activity for NO_3^- RR under acidic conditions. Fig. 6(a-b) present the high-resolution N 1s spectra, which provide insights into the nitrogen species composition of the 2 distinct catalysts, NGR1 and NGR2. As shown in Fig. 6c, electrochemical measurements reveal that the N-doped graphene catalyst enriched in pyridinic N (NGR2) exhibits a more positive onset potential (0.932 V vs. SCE) than the pyrrolic N-dominated counterpart (NGR1). In addition, NGR2 demonstrates superior electrocatalytic performance compared with both the pyrrolic N-rich catalyst and pristine graphene. These findings indicate that pyridinic N is crucial for the electrocatalytic reduction of nitrate, effectively increasing the reaction onset potential and facilitating the desorption of intermediate species.

Density functional theory (DFT) calculations further elucidated the specific mechanistic role of pyridinic nitrogen. The results indicate that pyridinic nitrogen facilitates the desorption of the key intermediate $^*\text{NO}$, accelerates the regeneration of the active site, and significantly enhances reaction rate.

During the electrochemical NO_3^- RR on nitrogen-doped carbon materials, the roles of various nitrogen species in alkaline environment can be different from that in acidic media. For example, Li et al.^[64] tuned the composition and spatial distribution of nitrogen species—including pyridinic, pyrrolic, graphitic, and pyridinic N-oxide functionalities—in carbon aerogels by varying the calcination temperature, and systematically elucidated the distinct impacts of these nitrogen configurations on catalytic NO_3^- RR performance in alkaline electrolyte. As illustrated in Fig. 6d, an increase in calcination temperature was associated with a gradual decrease in the contents of pyridinic-N and pyrrolic-N within the material. Conversely, there was a marked increase in the ratio of graphitic-N to pyridinic-N-oxide. In the sample N-C-1000 synthesized at 1000 °C, the concentration of graphitic-N (N3) reached its maximum. Furthermore, as shown in

Fig. 6e, the optimal catalytic performance is achieved at -0.7 V vs. RHE with a Faradaic efficiency for ammonia production of 95% and a production rate of $1.33 \text{ mg h}^{-1} \text{ cm}^{-2}$, highlighting its superior activity and selectivity. This result suggests that the targeted modulation of specific nitrogen species can substantially improve the performance of NO_3^- reduction, with graphitic nitrogen particularly demonstrating a pronounced advantage in alkaline environments. From a mechanistic standpoint, theoretical calculations offer robust support for the experimental observations. The DFT results (Fig. 6f) reveal that graphitic nitrogen sites exhibit a stronger adsorption affinity for NO_3^- , while the proton adsorption energy is optimized, facilitating the efficient execution of the critical hydrogenation steps in the reaction. Furthermore, in the rate-limiting step of the $^*\text{NO}$ to $^*\text{HNO}$ conversion, graphitic nitrogen demonstrates the lowest energy barrier. Additionally, the desorption of the final product, $^*\text{NH}_3$, at this site is an exothermic process, which facilitates the release of the product and promotes the continuous progression of the catalytic cycle. In contrast, other nitrogen species did not exhibit comparable advantages in the adsorption and transformation

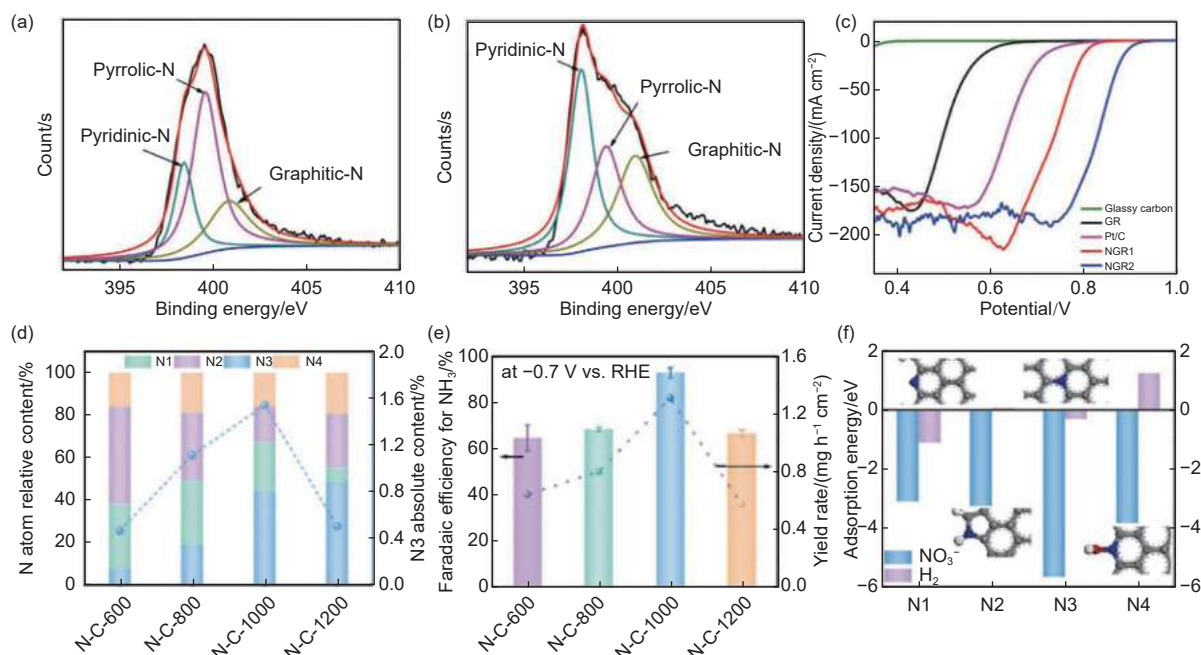


Fig. 6 High-resolution N 1s spectra of NGR1 (a) and NGR2 (b), respectively. (c) Linear sweep voltammograms of glassy carbon, GR, Pt/C, NGR1 and NGR2 in $5 \text{ mol L}^{-1} \text{ HNO}_3$ solution with a scan rate of 10 mV s^{-1} ^[63]. Copyright 2021 MDPI. (d) N atoms relative content (N1: pyridinic-N moiety, N2: pyrrolic-N moiety, N3: graphitic-N moiety, and N4: pyridinic-N-oxide moiety) and absolute content of N3 for N-C-600, N-C-800, N-C-1000 and N-C-1200 (e) Comparison of Faradaic efficiency and yield rate of N-C-T at -0.7 V vs. RHE. (f) Adsorption energy of NO_3^- and hydrogen^[64]. Copyright 2023 Elsevier

of key intermediates. This discovery not only provides important insights for the rational design of nitrogen-doped carbon materials but also underscores the necessity of incorporating in situ or operational characterization techniques in future research endeavors. Such approaches will be important for further uncovering the dynamic evolution and synergistic mechanisms of different nitrogen species in the actual reaction environment, thus advancing the targeted development of efficient electrocatalysts.

In conclusion, the active sites of nitrogen species exhibit considerable differences across various acidic and alkaline systems, indicating that their dominant role is largely determined by the reaction conditions, such as the pH value of the electrolyte, as well as the structural characteristics of the catalyst. This process is not only intricately linked to the initial activation step in NO_3^- RR but also closely associated with the subsequent hydrogenation steps. Specifically, nitrogen species play a critical role in nitrate reduction by enhancing the electrocatalytic reduction process through the direct modulation of the adsorption characteristics of intermediate species. Furthermore, while a substantial body of research has been devoted to nitrogen-doped non-metallic catalysts, studies on doping with other non-metallic heteroatoms remain limited and warrant further investigation. This highlights the necessity for a more thorough investigation into the variety of non-metallic doped materials and their impact on the catalytic performance of NO_3^- RR.

3.2 Carbon supported single-atom catalysts

Single-atom catalysts (SACs) have drawn considerable interest in a range of catalytic reactions due to their exceptional catalytic performance^[65–66]. These catalysts are distinguished by the homogeneous distribution of metal atoms on carbon-based support materials, leading to the formation of a distinctive metal-nitrogen-carbon (M-N-C) structure. The metal atoms are stabilized on the carbon-based support through coordination with nitrogen atoms^[67]. This configuration not only facilitates the uniform dispersion of the metal atoms but also prevents metal agglomeration, thereby enhancing atom utilization and improving

catalytic efficiency. The carbon-based materials in this system primarily function to provide excellent electrical conductivity and an optimized pore structure, which promote electron transfer as well as the adsorption of reactants, thereby enhancing the overall catalytic performance. The metal active sites of M-N-C catalysts are typically comprised of transition metals (such as Ni, Co, Fe, etc.) coordinated with N atoms within the carbon support, forming an M-N_x coordination structure. The most prevalent active configuration is M-N_4 , where the metal atoms are integrated into the carbon framework and establish a stable coordination structure through interactions between the N and metal atoms. This configuration not only promotes the uniform dispersion of metal atoms but also efficiently modulates electronic structure, thereby optimizing catalytic activity. Moreover, the synergistic interactions between the N-doped carbon support and the metal active sites significantly enhance the overall stability and catalytic efficiency of the system, allowing the catalyst to exhibit exceptional activity and prolonged durability across a range of electrocatalytic applications.

As shown in the Fig. 7a, Yin et al.^[68] conducted an extensive examination of the performance of single transition metal atom catalysts (M-N_4 , where M = Ga, Mn, Ru, Ni, Mo, Pd, Pt, Cu) supported on nitrogen-doped carbon for NO_3^- RR. They explored the activity trends and established design principles for various metal monometallic catalysts. Through XAFS analysis and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization, it was confirmed that each metal center is atomically dispersed and forms an M-N_4 coordination structure. As depicted in Fig. 7b, the electrochemical testing results demonstrate a significant variation in the catalytic activities of different single-metal-atom catalysts, with the Cu/NC catalyst particularly exhibiting exceptional catalytic performance. At an applied potential of -0.7 V vs. RHE, the Faradaic efficiency for ammonia formation reached 100%, accompanied by a nitrate conversion efficiency as high as 99.5%. As illustrated

in Fig. 7c, the ammonia production rate reaches $32\ 300\ \mu\text{g h}^{-1}\text{mg}^{-1}$ at -2.0 V vs. RHE, which is markedly higher than that of other single-atom metal catalysts as well as the Cu nanoparticle reference sample. DFT calculations demonstrated that the improved catalytic activity of the Cu monomer originates from its unique $3d_{10}$ electronic configuration. This configuration enables strong orbital coupling with the oxygen atom in NO_3^- , facilitating efficient electron transfer (0.36 e) to NO_3^- , thereby significantly enhancing the adsorption and activation efficiencies of NO_3^- . However, the limitations of Cu single-atom catalysts in the conversion of NO_2^- intermediates have also been identified. Specifically, their weak adsorption affinity for NO_2^- highlights the constraints of a single active site in facilitating multi-step reactions. Consequently, the development of a tandem catalytic system has emerged as a potent approach to improve the efficacy of single-atom catalysts^[69–70].

Building on this concept, Liu et al.^[71] proposed coupling Cu single-atom with Co_3O_4 nanoparticles to establish a tandem catalytic mechanism, enabling functional specialization and spatially coordinated reaction pathways. Within this catalytic system, the NO_2^- intermediate produced via Cu single-atom is rapidly intercepted and converted by Co_3O_4 , suppressing both its accumulation and desorption. This synergistic interaction substantially improves the overall reaction rate and ammonia selectivity. As illustrated in Fig. 7d and 7e, the tandem system achieved a remarkable Faradaic efficiency of 97.7% and an ammonia production rate of $114.0\text{ mg h}^{-1}\text{cm}^{-2}$, substantially outperforming that of the Cu single-atom catalyst. In situ Raman spectroscopy verified that the Cu sites were responsible for generating NO_2^- , whereas the Co_3O_4 sites facilitated its consumption. Complementarily, in situ FTIR spectroscopy elucidated the full reaction pathway of the nitrogen-containing intermedi-

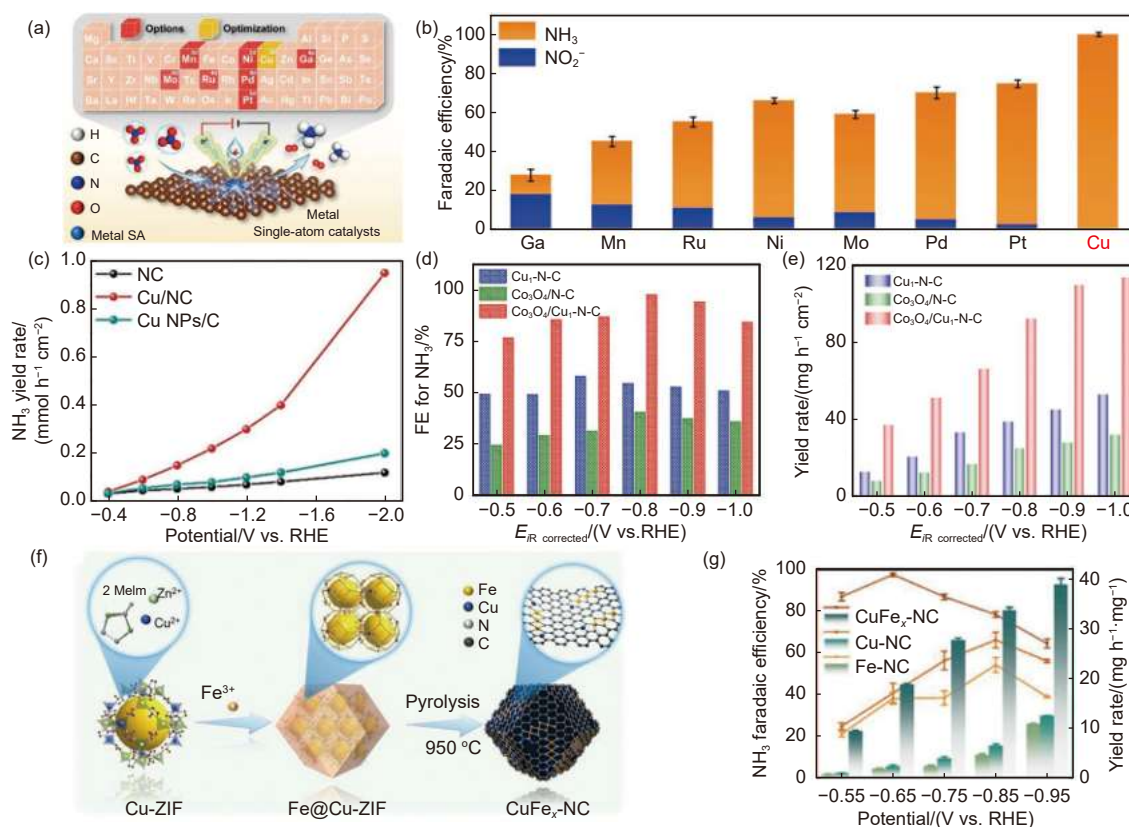


Fig. 7 (a) Schematic diagram of the reaction mechanism of NO_3^- RR on single-atom metal catalysts. (b) Faradaic efficiencies of NH_3 (orange) and NO_2^- (blue) of metal SACs under a potential of -0.7 V vs. RHE. (c) NH_3 yield rates of NC, Cu/NC and Cu NPs/C^[68]. Copyright 2023 American Chemical Society. (d) FE for NH_3 and (e) yield rate for NH_3 of $\text{Cu}_1\text{-N-C}$, $\text{Co}_3\text{O}_4\text{/N-C}$, and $\text{Co}_3\text{O}_4\text{/Cu}_1\text{-N-C}$ at different applied potentials with $1\text{ mol L}^{-1}\text{ NO}_3^-$ ^[71]. Copyright 2024 Springer Nature. (f) Schematic diagram for the synthesis of $\text{CuFe}_x\text{-NC}$ catalyst. (g) Diagram of Faraday efficiency and yield rate of $\text{CuFe}_x\text{-NC}$, Cu-NC and Fe-NC ^[72].

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ates. This study demonstrates that tandem catalysis not only effectively addresses the limitations of single-metal catalysts in multi-step reactions but also offers a novel approach for enhancing overall catalytic performance.

Furthermore, inspired by the bimetallic active centers of natural nitrate reductase, Liu et al.^[72] constructed a novel nitrogen-doped carbon catalyst (CuFe-NC) featuring a single Cu atom (Cu-N₃) in close proximity to an Fe₃ cluster (Fe₃-N₈) as depicted in Fig. 7f. This catalyst establishes a spatial charge polarization gradient through the alteration of electronic structures of the Cu and Fe sites. The electron-deficient Cu sites facilitate NO₃⁻ adsorption, whereas the electron-rich Fe₃ clusters enhance NO₂⁻ adsorption and supply *H for water activation. This synergistic electronic effect effectively suppresses both NO₂⁻ accumulation and the competitive HER. As illustrated in Fig. 7g, under neutral conditions, the CuFe-NC catalyst achieved an ammonia Faradaic efficiency of 97.1% and an ammonia yield rate of 18.83 mg h⁻¹ mg⁻¹, indicating its exceptional catalytic efficiency.

Although single-atom catalysts have exhibited remarkable efficacy in NO₃⁻RR, challenges remain regarding the dispersion and stability of the metal species. Monometallic catalysts are prone to agglomeration or migration on carbon supports, resulting in the depletion of active sites and a subsequent decrease in catalytic efficiency. Therefore, effectively controlling the stable dispersion of monometallic catalysts during the preparation process and preventing metal agglomeration are critical issues that require urgent attention.

3.3 Carbon supported bimetallic alloy catalysts

The composite strategy of integrating metallic catalysts into carbon-based materials has emerged as a pivotal method for improving catalytic effectiveness in the electrochemical reduction of nitrate to ammonia^[73]. By immobilizing nanoscale active components onto carbon-based materials such as carbon papers, graphene, and carbon nanotubes—characterized by high specific surface areas, excellent electrical conductivity, and tunable structures, both the electronic

conductivity of the catalyst and the accessibility of active sites can be significantly enhanced^[74]. Carbon supported bimetallic alloy catalytic system, in particular, achieve advancements in activity, selectivity, and stability through synergistic interactions between distinct metal sites^[75].

Among different carbon nanomaterials, graphene as the catalyst support can offer distinct advantages in the design of bimetallic catalysts. As depicted in Fig. 8a, the graphene-encapsulated CuFe alloy catalyst (CuFe-G) developed by Chen et al.^[76] enables efficient NO₃⁻RR under neutral conditions through dynamic surface redox regulation. As illustrated in Fig. 8b, the spontaneous interaction between the CuFe alloy and the NO₃⁻ solution generates a dynamic CuFe active layer that chemically reduces NO₃⁻ to NO₂⁻. Upon application of a cathodic potential, this active layer is regenerated to its metallic state, thereby accelerating the hydrogenation process. This “chemical-electrochemical relay” mechanism optimizes the adsorption geometry of *NO and reduces the activation energy barrier. The encapsulation with graphene not only stabilizes the dynamic active species but also enhances conductivity and structural stability. This catalyst exhibited a Faradaic efficiency of 99.63% and an ammonia production rate of 8.03 mg h⁻¹ mg⁻¹ at -1.0 V vs. RHE, while maintaining excellent long-term stability under neutral conditions.

The previous discussion on the graphene-encapsulated CuFe alloy catalyst emphasizes the importance of the carbon carrier in stabilizing active species and influencing the reaction pathway. Furthermore, carbon defect engineering introduces an additional level of complexity, as the carbon carrier not only serves as a physical encapsulation layer but also contains intrinsic defect sites that significantly impact catalytic performance at the atomic level. Unlike the macroscopic stability provided by graphene encapsulation, defect engineering offers a more refined approach for anchoring metal clusters and modulating the electronic structure. This is achieved through the intentional creation of vacancies, topological distortions, or edge sites within the carbon framework, en-

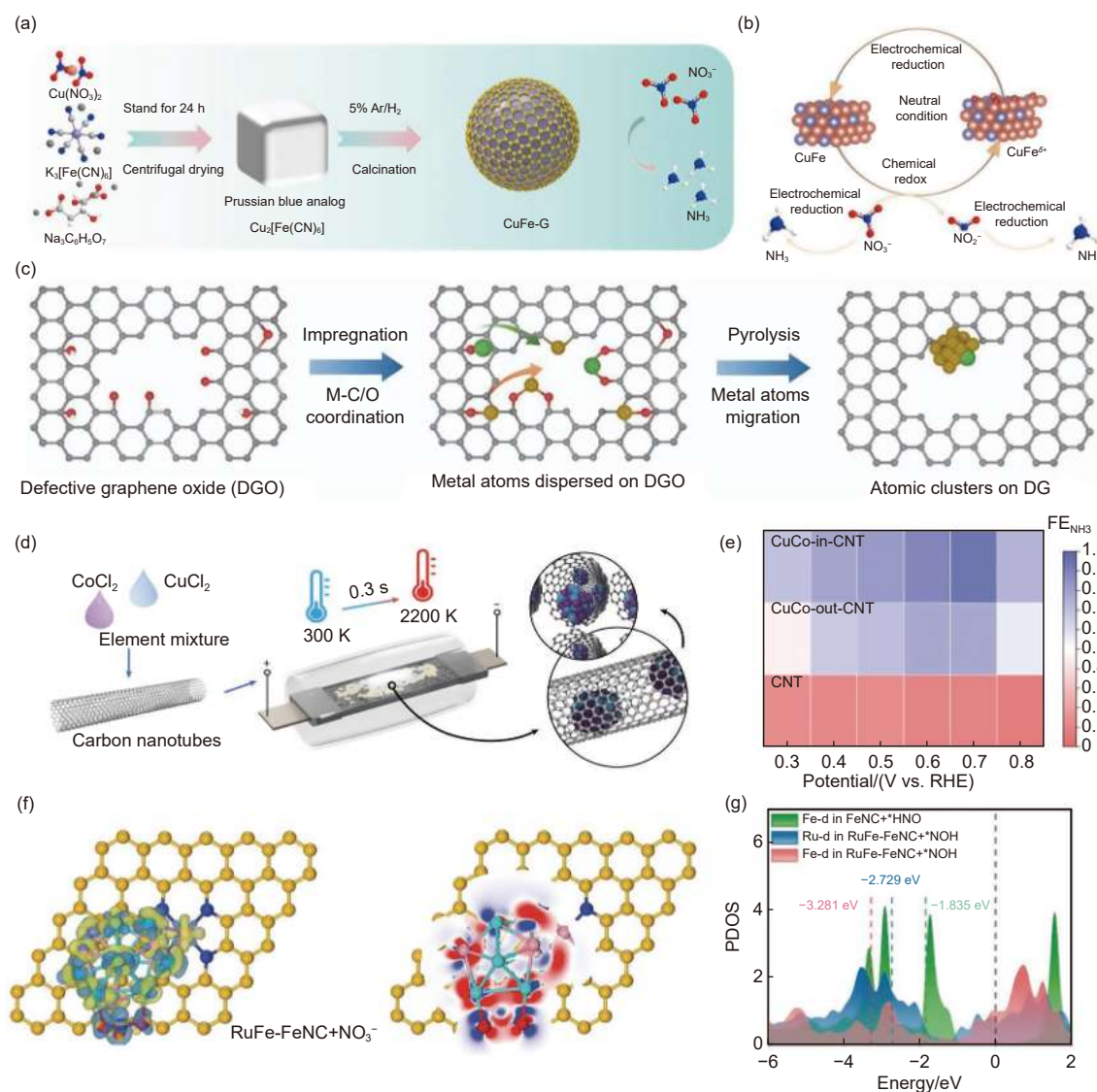


Fig. 8 (a) Schematic illustration for the synthesis of CuFe-G. (b) The reaction mechanism diagram of the CuFe-G catalyst in NO_3^- RR [76]. Copyright 2026 Wiley-VCH. (c) Schematic diagram of the synthesis processes of SnCu-DG catalyst [77]. Copyright 2025 Wiley-VCH. (d) A schematic diagram depicting the fabrication route of CuCo-in-CNT. (e) The FE of CNT, CuCo-out-CNT and CuCo-in-CNT at various working potentials [78]. Copyright 2026 Springer Nature. (f) The 2D and 3D electron density differences of NO_3^- on RuFe-FeNC. The accumulation and depletion of the electron density are marked in blue and yellow, respectively. (g) PDOS of Fe-d and Ru-d for FeNC after absorbing $^*\text{HNO}$ and RuFe-FeNC after absorbing $^*\text{NOH}$. The black and different color dash lines are the position of E_f and d-band center, respectively [79]. Copyright 2023 Wiley-VCH

abling enhanced catalytic performance. For instance, a recent study by Wu et al. [77] demonstrates that SnCu atomic clusters can be effectively anchored at the edge of defective graphene. As shown in the Fig. 8c, in this configuration, the carbon defect sites serve dual purposes: they act as confinement reactors that inhibit metal agglomeration and promote asymmetric charge polarization at the Sn—Cu—C interface through robust metal-adsorbate interactions. This disruption of the linear scaling relationship among the adsorption energies of intermediates in multi-step reactions not

only enhances catalytic activity but also accelerates the dissociation of water molecules, thereby ensuring a sufficient supply of active hydrogen. This defect-mediated electronic regulation complements the dynamic surface redox modulation afforded by graphene encapsulation. Specifically, the former adjusts the intrinsic electronic properties of the active sites at the atomic level, while the latter dynamically enhances the surface chemical environment during reaction conditions.

In addition to graphene, carbon nanotubes, ow-

ing to their hollow confined structure, high electrical conductivity, and facile surface functionalization, also serve as an effective support and a versatile platform for the modulation of active sites in bimetallic alloy catalytic systems. As illustrated in Fig. 8d, Meng et al.^[78] employed the flash Joule heating method to synthesize CuCo alloy nanoparticles confined within the inner cavities of carbon nanotubes. This configuration induces a strong electronic interaction between the electron-rich alloy and the electron-deficient carbon framework, thereby redirecting the reaction pathway from the conventional hydrogen-species-mediated mechanism toward a PCET pathway. As shown in the Fig. 8e, under neutral conditions, this confined system attained a Faradaic efficiency of 93.8% and an NH_3 production rate of $2.23 \text{ mg h}^{-1} \text{ cm}^{-2}$. After 20 cycles, the performance exhibited negligible degradation, thereby highlighting the potential of the carbon nanotube-confined environment in modulating reaction pathways and significantly enhancing catalytic stability.

Beyond pure carbon support, functional single-atom catalyst can also serve as the support for alloy, which can show unique synergistic effect for enhancing electrochemical NO_3^- RR performance. For example, on a single-atom carbon-supported catalyst platform, Zhao et al.^[79] realized the precise regulation of the multi-step intermediates of NO_3^- RR by constructing RuFe bimetallic alloy nanoparticles anchored on Fe—N—C support (RuFe-FeNC). As illustrated in Fig. 8f, g, alloying leads to the merging of the d-bands of Ru and Fe at the Fermi level, thereby altering the electronic structure. This modification simultaneously enhances NO_3^- adsorption, stabilizes intermediates, and facilitates NH_3 desorption. Additionally, it effectively leverages the electron transfer-enhancing effect of the Fe—N—C support on the hydrogenation reaction. This catalyst demonstrated a Faradaic efficiency of 92.2% and an ammonia production rate of $118.8 \text{ mg h}^{-1} \text{ mg}^{-1}$ at -1.4 V vs. RHE, emphasizing the capacity to address the performance limitations of single-atom catalysts through the incorporation of bimetallic alloy nanoparticles.

In summary, the carbon supported bimetallic alloy system offers distinct advantages by simultaneously improving the activity, selectivity, and stability of NO_3^- RR through electronic structure modulation, dynamic surface regulation, and spatial confinement effects. The interaction between various metal components and the supporting material not only enhances the adsorption and desorption characteristics of reaction intermediates but also offers essential mechanistic understanding that informs the rational design of efficient and long-lasting catalysts for the electroreduction of nitrate to ammonia.

3.4 Carbon supported heterostructure

Heterostructure refers to the distinct physical and chemical characteristics that emerge at the interface between two different materials, arising from their mutual interactions^[80]. In the NO_3^- RR, the construction of a hetero-interface between metal/oxide or metal oxide/non-metal on a carbon-based support can generate highly active interface sites, thereby optimizing the proton and electron transfer processes. Specifically, these interfaces not only modulate the adsorption dynamics of reactants and promote charge transfer, but also effectively lower the energy barrier of critical reaction steps, thereby improving catalytic activity, selectivity and stability.

Notably, during the electrochemical NO_3^- RR process, the pristine catalyst can be reconstructed into the fresh heterostructure. As shown in the Fig. 9a, Mei et al.^[81] employed an in-situ electrochemical reconstruction approach to convert the carbon paper supported Cu-Co oxide precursor into an $\text{Co(OH)}_2/\text{Cu}$ heterostructure catalyst with high density of oxygen vacancies (O_v). During the high-current reduction process, Cu^{2+} is reduced to metallic Cu, while the Co component undergoes transformation into Co(OH)_2 nanosheets enriched with oxygen vacancies, resulting in the formation of a well-defined metal/hydroxide oxide interface. DFT calculations suggest that this interface can enhance the kinetics of water decomposition, increase the rate of $^*\text{H}$ generation, optimize the adsorption of $^*\text{NOOH}$, and lower the energy barrier for the conversion of $^*\text{NO}_2$ to $^*\text{NOOH}$ (Fig. 9b). The

Cu component further catalyzes the reduction of NO_3^- to NO_2^- , thereby enabling the catalyst to demonstrate outstanding cascade catalytic performance at industrial current densities. As shown in the Fig. 9c, the ammonia production rate achieves $167.8 \text{ mg h}^{-1} \text{ cm}^{-2}$, with a Faraday efficiency of 97.7% at -0.4 V vs. RHE, and the catalyst maintains stable operation for 25 h. The integration of metallic and metal hydroxide components enables the formation of heterostructures with distinct electronic and lattice structures, thereby promoting reactant adsorption and facilitating the overall reaction kinetics.

In addition to the heterostructures at nanoscale levels, it can also be integrated to form heteroclusters at the sub-nanometer scale. In this heterocluster configuration, the electronic structure undergoes significant reorganization, and the dual active sites operate

synergistically at near-atomic distances, facilitating the concurrent optimization of reactant adsorption and proton transfer. For instance, Hu et al.^[82] used carbon nanomaterials with rich microporous structure and nitrogen dopants as the carrier, and employed a double confinement strategy to synthesize sub-nanometer-sized Ni-P heteroclusters (Ni-P HCs), where Ni and P atoms form an active $\text{Ni}^{\delta+}\text{-P}^{\delta-}$ pair through strong atomic coupling (Fig. 9d). The sub-nanometer dimensions facilitate electron transfer from Ni to P. The $\text{Ni}^{\delta+}$ sites serve to activate NO_3^- , whereas the $\text{P}^{\delta-}$ sites modulate the interfacial water hydrogen-bond network via electrostatic enrichment of K^+ ions, thereby accelerating proton transfer and suppressing competitive hydrogen evolution. This cooperative mechanism involving dual active sites substantially reduces the energy barrier associated with the rate-limiting step

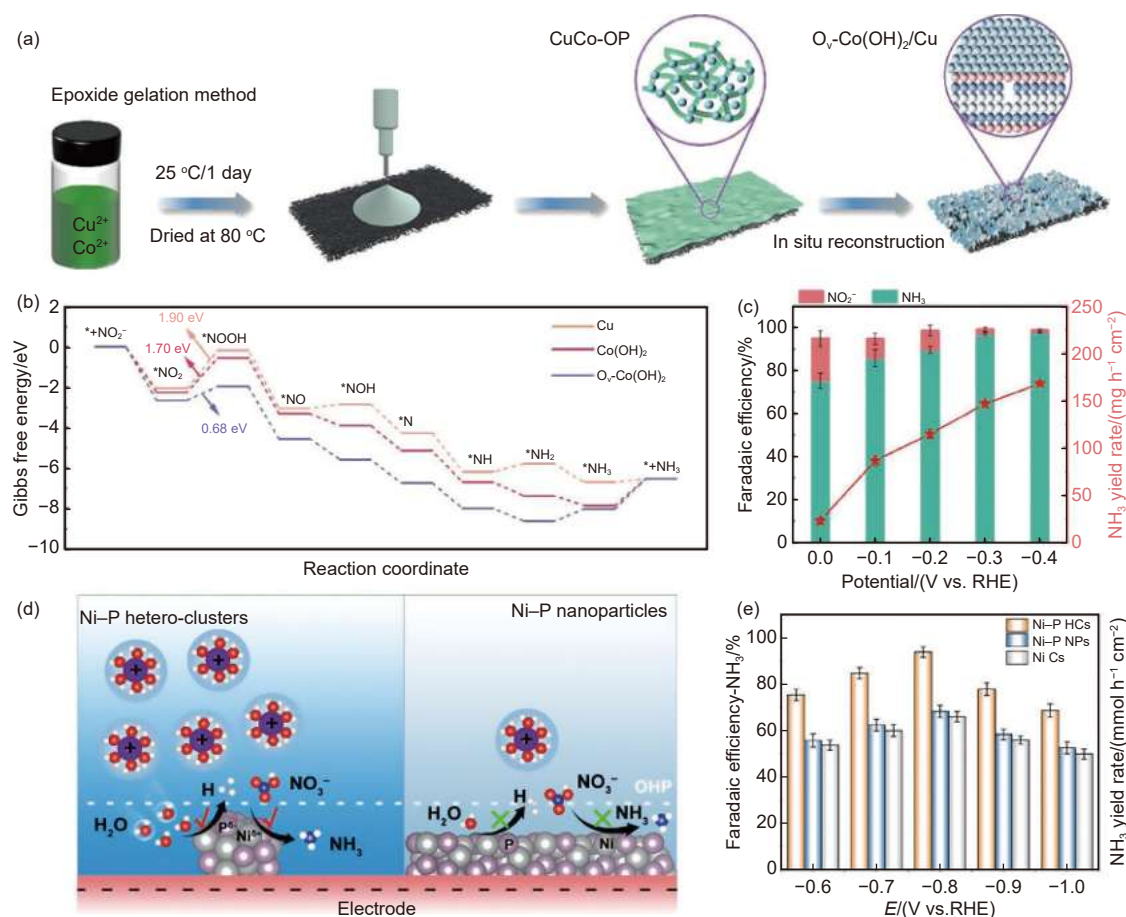


Fig. 9 (a) Schematic diagram of the synthesis process of CuCo-OP and $\text{O}_v\text{-Co(OH)}_2/\text{Cu}$ electrocatalysts. (b) Free energy diagram of NO_2^- RR. (c) FE_{NH_3} and NH_3 yield rate of Cu, $\text{O}_v\text{-Co(OH)}_2$, $\text{Co(OH)}_2/\text{Cu}$, and $\text{O}_v\text{-Co(OH)}_2/\text{Cu}$ at -0.3 V versus RHE^[81]. Copyright 2025 Wiley-VCH. (d) Schematic diagram of the reaction mechanism of NO_3^- RR on Ni-P HCs catalysts. (e) FE of NO_3^- to NH_3 over Ni-P HCs, Ni-P NPs, and Ni Cs at different potentials^[82].

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(*NO $\rightarrow$ *NOH), enabling Ni-P HCs to achieve a Faraday efficiency of 93.7% and an ammonia production rate of 0.61 mmol h⁻¹ cm⁻² under neutral conditions (Fig. 9e), far surpassing the performance of conventional Ni-P nanoparticles or pure Ni clusters. This highlights a novel catalytic approach for NO₃⁻RR utilizing strongly electron-coupled heterogeneous clusters at sub-nanometer-scale.

The aforementioned studies suggest that the construction of carbon-supported heterostructure can markedly enhance NO₃⁻RR performance through modulation of the electronic structure and the cooperative interaction of dual active sites. In the future, as interfacial design principles evolve and novel composite materials are developed, the creation of carbon-supported heterostructures featuring distinctive interfaces is expected to emerge as a pivotal strategy for improving the efficacy of catalysts for NO₃⁻RR. Nevertheless, challenges such as interfacial stability and metal particle aggregation remain, necessitating further optimization through precise material design and advanced fabrication techniques. The rational construction of heterogeneous interfaces in carbon-supported metal/metal oxide composite catalysts thus offers a promising avenue for the next-generation optimization of NO₃⁻RR systems.

4 Summary and outlook

Electrochemical reduction of nitrate to ammonia is an innovative technology that holds considerable promise for both environmental remediation and sustainable synthesis. Unlike the traditional, energy-demanding, and emission-intensive Haber-Bosch process, nitrate reduction by electrochemical method means employs water as a proton donor and functions under mild conditions (ambient temperature and pressure). This approach facilitates the transformation of surplus nitrate contaminants in water into valuable ammonia, while also presenting the potential to establish carbon-neutral energy cycles. Nevertheless, this process encompasses a complex mechanism that entails the simultaneous transfer of eight electrons and nine protons, accompanied by different byproducts

(such as NO₂⁻, N₂ and NH₂OH), as well as the competing HER. These challenges impose stringent demands on the catalyst's selectivity, activity, and stability. Carbon-based materials have emerged as a key area of investigation in NO₃⁻RR catalysis due to their superior electrical conductivity, adjustable surface chemistry, substantial specific surface area, and diverse structural attributes. This review provides an overview of the most recent developments in carbon-based electrocatalysts tailored for NO₃⁻RR, addressing aspects such as reaction mechanisms, in situ characterization, and design strategies. It highlights the pivotal role of carbon materials in modulating electronic structures, stabilizing active sites, and optimizing both electron transfer and proton supply pathways.

Although carbon-based electrocatalysts have achieved considerable advancements in NO₃⁻RR (Table 2), several challenges remain before their practical implementation. Firstly, as illustrated in Fig. 10a, the majority of current carbon-based catalysts exhibit a relatively high overpotential for the nitrate reduction reaction, which does not fulfill the necessary criteria for industrial application. The underlying cause of the high overpotential is attributed to the difficulty of simultaneously achieving effective NO₃⁻ adsorption and facilitated water dissociation for *H supply. This limitation leads to sluggish reaction kinetics, impeding the overall efficacy of the catalytic process. Therefore, the co-doping of the carbon substrate with other aromatic atoms, such as B and P could modify its electronic structure. This can be coupled with the design of carbon carriers featuring multidimensional architectures to improve the adsorption of nitrate ions and water dissociation. This constitutes a promising research avenue that warrants further investigation. As illustrated in Fig. 10b, the majority of existing carbon-based catalysts can only sustain long-term stability at low current densities. Substantial enhancement of their long-term stability under industrially relevant high current densities is highly desirable. This is due to the fact that at high current density, mass transfer restrictions and significant local pH variations further exacerbate the deactivation of active sites, in addition

Table 2 Comparison of the electrocatalytic NO_3^- RR performance of carbon-based electrocatalysts

Catalyst	Potential (vs. RHE)	FE/(%)	NH_3 yield rate ($\text{mg h}^{-1} \text{cm}^{-2}$)	Stability ($\text{h} @ \text{mA cm}^{-2}$)	Electrolyte	Loading ($\text{mg} \cdot \text{cm}^{-2}$)	Ref.
NC-1000	-0.7 V	95.0	1.3	5@20	0.1 M KOH+0.1 M KNO_3	0.6	[63]
Cu/NC	-0.7 V	~ 100	16.2	20@50	0.5 M Na_2SO_4 +200ppm NaNO_3	0.5	[68]
$\text{Co}_3\text{O}_4/\text{Cu}_1\text{-N-C}$	-0.8 V	97.7	114.0	20@1800	1 M KOH+1 M KNO_3	1	[71]
CuFe-NC	-0.7 V	97.1	94.0	50@150	0.5 M Na_2SO_4 +0.1 M NaNO_3	5	[72]
RuFe-FeNC	-1.4 V	92.2	11.8	6@100	0.5 M K_2SO_4 +0.1 M KNO_3	0.1	[79]
CuFe-G	-1.0 V	99.6	4.0	70@40	0.5 M K_2SO_4 +0.1 M KNO_3	0.5	[76]
CuCo-in-CNT	-0.7 V	93.8	2.2	20@20	0.1 M Na_2SO_4 +0.1 M NaNO_3	1	[78]
$\text{O}_v\text{-Co(OH)}_2/\text{Cu}$	-0.3 V	97.7	167.8	25@2000	1 M KOH+0.5 M KNO_3	2	[81]
Ni-P HCs	-0.8 V	93.7	10.4	25@100	0.5 M Na_2SO_4 +0.1 M KNO_3	2	[82]
$\text{FeN}_4/\text{Fe}_x@\text{CNR}$	-0.3 V	98.6	5.5	20@80	1 M KOH+0.1 M KNO_3	1	[33]
W-CCNs	-0.3 V	91.3	0.5	20@50	1 M KOH+0.1 M KNO_3	0.1	[34]
Ni-Cu ₂ O/Cu@C	-0.4 V	98.0	56.1	160@1000	1 M NaOH+0.1 M NaNO_3	—	[53]
$\text{Co}_6\text{Ni}_4@\text{CP}$	-0.5 V	99.2	93.5	120@140	1 M KOH+0.3 M KNO_3	5	[75]
J-Cu@Co/NC	-0.3 V	98.3	12.8	12@40	0.1 M KOH+0.01 M KNO_3	0.1	[73]
np-CuCo	-0.2 V	85.3	4.58	5@100	1 M KOH+200ppm KNO_3	0.39	[74]

Note: All ammonia detection methods employed in the cited studies are based on the indophenol blue colorimetric method and ^1H NMR method.

M: mol L^{-1} . ppm: 10^{-6} .

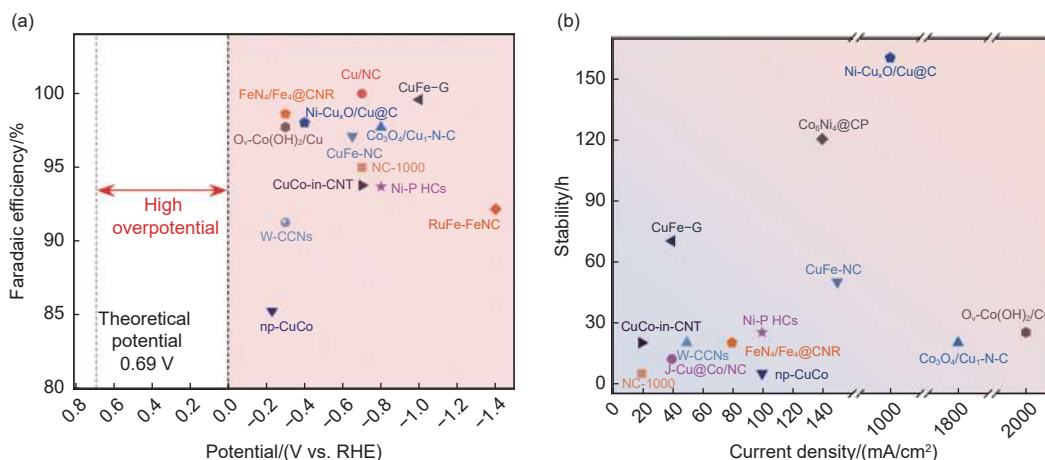


Fig. 10 (a) Comparison of the optimal Faradaic efficiency of carbon-based NO_3^- RR electrocatalysts at different potentials. (b) Comparison of the stability of NO_3^- RR for carbon-based electrocatalysts at different current densities

to intensifying the competition with hydrogen evolution reactions. Building on this, strategies including the construction of stable metal-carbon interfaces, the development of more advanced bimetallic or even multi-metallic high-entropy systems, and the exploration of novel heterogeneous structures deserve further investigation.

Secondly, the four design strategies for carbon-based catalysts outlined in this article specifically target the mechanistic requirements of NO_3^- RR from different aspects. Non-metallic heteroatoms improve the interaction with NO_3^- and nitrogen-containing intermediates by modulating the local charge distribution of the carbon support. Single-atom catalysts facilitate

the efficient activation of NO_3^- and the conversion of NO due to their atomically dispersed metal active sites. However, their limited adsorption capacity for NO_2^- often results in the accumulation of NO_2^- byproducts in electrolyte. Furthermore, the selectivity for various products among different metal catalysts exhibits considerable variation. Metals such as Cu, Fe, Co, and Ni typically favor the reduction of nitrate ions to the desired NH_3 . However, copper-based catalysts are often susceptible to producing nitrite as an undesirable by-product. In contrast, precious metals like palladium and platinum tend to preferentially reduce nitrate ions to N_2 , a product that is advantageous for nitrogen removal in wastewater treatment applica-

tions. To address this challenge, the integration of a dual-metal alloy or heterogeneous structure is essential for constructing a tandem catalytic system. The dual-metal alloy leverages the electronic cooperative effects of adjacent metal sites to modulate the adsorption configuration of $^*\text{NO}$ and lower the energy barrier associated with the transformation from $^*\text{NO}$ to $^*\text{NOH}$. In contrast, the heterogeneous structure enhances the dissociation of water molecules, thereby supplying $^*\text{H}$ and accelerating crucial protonation steps, such as the conversion of $^*\text{NO}_2$ to $^*\text{NOOH}$. All of these strategies converge on a central objective: to facilitate the “precise relay” of intermediates within the complex reaction network. This approach aims to prevent the accumulation of undesirable by-products and suppress HER, thereby ensuring high ammonia selectivity of $\text{NO}_3^- \text{RR}$.

Finally, beyond laboratory-scale evaluations, the practical implementation of carbon-based $\text{NO}_3^- \text{RR}$ catalysts encounter several critical challenges. Low-concentration nitrate sources, typically below 100 ppm (ppm: 10^{-6}), found in real wastewater face significant mass transfer limitations and competing side reactions, necessitating the development of electrode architectures with enhanced NO_3^- enrichment capabilities. Furthermore, the presence of coexisting ions such as Cl^- , SO_4^{2-} can poison active sites, alter local pH levels, or consume reactive hydrogen species, thereby impairing catalytic performance and stability. Operating at high current densities exacerbates local pH gradients and intensifies competition with the HER, requiring catalysts that demonstrate rapid reaction kinetics and robust structural integrity. Additionally, transitioning from H-type cells to flow-cell configurations introduces new complexities, including electrolyte management, gas product separation, and the long-term durability of membranes. Addressing these challenges through the design of hierarchical porous structures, anti-poisoning active sites, and industrially compatible membrane-electrode assemblies will be essential for bridging the gap between fundamental research and practical nitrate upgrading technologies.

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