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# Ammonia synthesis from nitrate reduction by the modulation of a built-in electric field and external stimuli

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Ammonia (NH<sub>3</sub>) is a vital chemical feedstock and a carbon-free energy source. The reduction of nitrate (NO<sub>3</sub><sup>−</sup>) from environmental pollutants is a sustainable method for NH<sub>3</sub> production compared with the industrially intensive Haber–Bosch method, which can mitigate energy and environmental concerns. However, due to the involvement of multi-electron transfer-proton coupling processes, the NO<sub>3</sub><sup>−</sup> reduction reaction (NO<sub>3</sub>RR) exhibits sluggish kinetics and significant side reactions. This review provides a comprehensive summary of recent research progress in facilitating NO<sub>3</sub>RRs using a built-in electric field and external stimuli. The paper commences by introducing the mechanisms and challenges of the NO<sub>3</sub>RR, subsequently focusing on strategies for built-in electric field/external stimuli-assisted catalytic reactions. The internal electric field can be triggered by constructing a Mott–Schottky heterojunction and a semiconductor–semiconductor heterojunction, adjusting the coordination environment of active sites, and regulating the electrical double layer, while the external stimuli include optical, stress, and thermal stimuli. This review focuses on the activation and adsorption processes of reactants and intermediates by a built-in electric field/external stimuli, and their influence on the thermodynamics and kinetics of reactions. Finally, we summarize the strategies for built-in electric field/external stimuli-assisted NO<sub>3</sub>RRs, highlight the challenges of achieving high activity and selectivity in NH<sub>3</sub> production, and provide clear guidance for future research.

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## Broader context

Ammonia (NH<sub>3</sub>) plays an essential role in agriculture, industry, and pharmaceuticals, with its global demand greatly increasing. However, traditional NH<sub>3</sub> production relies on the energy-intensive Haber–Bosch process, which involves nitrogen and hydrogen as raw materials under high-temperature, high-pressure conditions, resulting in significant CO<sub>2</sub> emissions. The aqueous-based reduction of NO<sub>3</sub><sup>−</sup> utilizes water and the pollutant NO<sub>3</sub><sup>−</sup> as raw materials, converting them into NH<sub>3</sub> through various forms of energy input such as electrocatalysis and photocatalysis. This process concurrently addresses both energy crises and environmental pollution issues. However, the NO<sub>3</sub><sup>−</sup> reduction reaction (NO<sub>3</sub>RR) to generate NH<sub>3</sub> involves a nine-proton and eight-electron transfer process, leading to sluggish kinetics and severely competitive hydrogen evolution. Therefore, multiple strategies have been proposed to enhance the performance of NO<sub>3</sub><sup>−</sup> reduction. Among them, introducing a built-in electric field/external stimuli to modulate the activation and adsorption behavior of reactants and intermediates, thereby promoting reaction kinetics and thermodynamics, becomes a promising strategy. Based on this, this review provides a comprehensive summary of the latest research progress in built-in electric field/external stimuli-assisted NO<sub>3</sub>RRs, including material analysis, mechanistic elucidation, problem summarization, and future prospects. This review aims to facilitate NO<sub>3</sub>RR performance and provide guidance for NO<sub>3</sub>RR processes in future industrial implementations.

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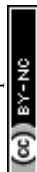
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## 1. Introduction

Ammonia (NH<sub>3</sub>) is indispensable in fertilizer manufacturing and the pharmaceutical industry, and it is a promising energy carrier because of its high hydrogen content.<sup>1–4</sup> However, the production of NH<sub>3</sub> currently relies heavily on the industrially intensive Haber–Bosch process, which requires high pressure and high temperatures, leading to significant greenhouse gas emissions.<sup>5–7</sup> Therefore, aqueous-based NH<sub>3</sub> synthesis, utilizing water molecules as proton sources and nitrogen gas (N<sub>2</sub>)/



nitrate ions ( $\text{NO}_3^-$ ) as nitrogen sources, has garnered widespread attention.<sup>8–10</sup> In comparison to the high dissociation energy of the  $\text{N}\equiv\text{N}$  bond in nitrogen molecules ( $941 \text{ kJ mol}^{-1}$ ), the dissociation energy of the  $\text{N}=\text{O}$  bond is only  $204 \text{ kJ mol}^{-1}$ ,<sup>11</sup> which suggests that the  $\text{NO}_3^-$  reduction reaction ( $\text{NO}_3\text{RR}$ ) has more potential in  $\text{NH}_3$  synthesis. Furthermore,  $\text{NO}_3^-$  exhibits higher solubility in aqueous solutions than  $\text{N}_2$ , providing the foundation for scalable and efficient production of  $\text{NH}_3$ .<sup>12,13</sup> Simultaneously, the extensive application of nitrate fertilizers to boost crop growth, along with animal manure, particularly from intensive livestock farming, excessive irrigation on agricultural lands, decomposition of crop residues in soil, and activities like mining, explosives manufacturing, and fertilizer industries, lead to the accumulation of nitrates in water bodies, posing a significant threat to human health.<sup>14–18</sup> In this context, the  $\text{NO}_3\text{RR}$  not only produces high-value, zero-carbon hydrogen-rich fuel but also effectively removes  $\text{NO}_3^-$  pollutants from water bodies, which mitigates energy crises and environmental pollution, offering broad and crucial prospects for application.

However, the  $\text{NO}_3\text{RR}$  is a complex reaction involving proton-coupled electron transfer (PCET).<sup>19,20</sup> A series of essential steps are interconnected in a sequential manner:<sup>21</sup> (a) the  $\text{NO}_3^-$  migrates to the catalyst surface. (b) The electrons successively transfer to the active sites to participate in the catalytic process. (c) Active sites facilitate the adsorption and activation of  $\text{NO}_3^-$ , the intermediate conversion, and  $\text{NH}_3$  desorption. The primary challenge in achieving high-performance catalysis lies in the sluggish reaction kinetics induced by restricted mass transfer, complex multi-electron and proton transfer processes, and inappropriate adsorption/desorption of  $\text{NO}_3^-$  and intermediates, leading to poor activity for  $\text{NH}_3$  production and severe competing hydrogen evolution reactions.<sup>22–24</sup> Based on this, various strategies have been proposed, including controlling the nanostructure of the catalyst,<sup>25,26</sup> tandem catalysis,<sup>27,28</sup> introducing defects,<sup>29,30</sup> designing single/dual atoms,<sup>31,32</sup> and forming alloys.<sup>33,34</sup> Besides, constructing a built-in electric field is vital in optimizing the adsorption and desorption processes of reactants and intermediates.<sup>21,35</sup> A composite catalyst leads to the spontaneous electron transfer resulting from the various work functions of different components, thereby establishing a built-in electric field.<sup>36</sup> This strategy regulates the electronic distribution on the catalyst surface, thereby enhancing its intrinsic activity. Additionally, adjusting the coordination environment of active sites and modulating the catalyst-electrolyte electrical double layer can effectively introduce an electric field.<sup>37,38</sup> Besides constructing a built-in electric field, introducing external stimuli can effectively regulate the thermodynamic and kinetic performance of the  $\text{NO}_3\text{RR}$ . For instance, renewable solar energy can stimulate catalysts possessing localized surface plasmon resonance (LSPR) effects to generate high-energy hot electrons and an intense electric field, thereby promoting the  $\text{NO}_3\text{RR}$ .<sup>39</sup> The introduction of a built-in electric field and external stimuli has been proven to facilitate the  $\text{NO}_3\text{RR}$  to produce  $\text{NH}_3$ . However, a comprehensive summary and in-depth understanding of strategies involving built-in electric field/external stimuli for the  $\text{NO}_3\text{RR}$  are deficient.

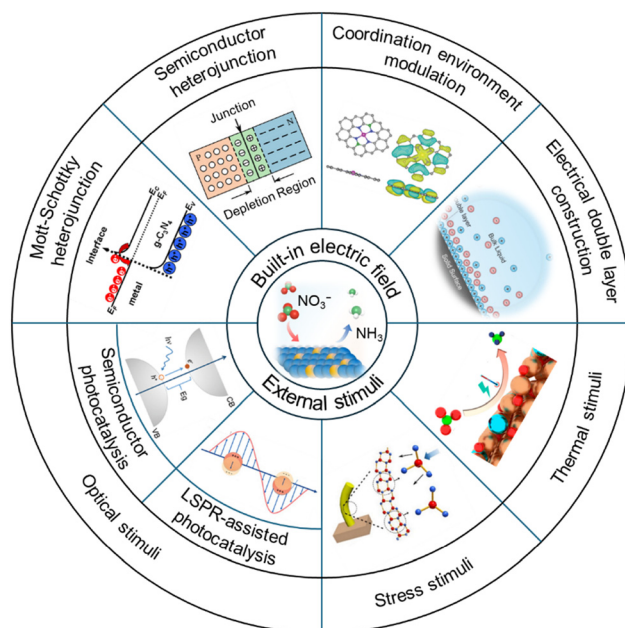


Fig. 1 Schematic of a built-in electric field/external stimuli-assisted  $\text{NO}_3\text{RR}$ .

In this review, we thoroughly summarized various strategies involving a built-in electric field/external stimuli in enhancing the  $\text{NO}_3\text{RR}$  and analyzed their mechanisms (Fig. 1). The aim is to provide insights into such modulation strategies for  $\text{NO}_3^-$  reduction to produce  $\text{NH}_3$ . This paper begins by introducing the fundamental principles and challenges of the  $\text{NO}_3\text{RR}$ , then reviews strategies for introducing a built-in electric field through constructing Schottky heterojunctions, semiconductor-semiconductor heterojunctions, adjusting active site coordination environments, and modulating electrical double layers in promoting the  $\text{NO}_3\text{RR}$ . Additionally, we summarize the effects of various external stimuli, including light, stress, and thermal, on  $\text{NH}_3$  production. Finally, we emphasize the challenges and perspectives of modulation strategies from the built-in electric field or external stimuli to enhance the  $\text{NO}_3\text{RR}$ .

## 2. Fundamentals of $\text{NH}_3$ synthesis

### 2.1. Mechanism of the $\text{NO}_3\text{RR}$

Diverse reaction intermediates and products can be obtained in the  $\text{NO}_3\text{RR}$  involving various pathways because of the wide range of nitrogen's oxidation states ( $-3$  to  $+5$ ).<sup>40</sup> The  $\text{NO}_3^-$  concentration and pH value of the electrolyte closely influence the mechanism in the  $\text{NO}_3\text{RR}$ .<sup>41</sup> The  $\text{NO}_3\text{RR}$  can be broadly categorized into indirect and direct reduction processes. The indirect reduction process involves intermolecular self-catalysis to generate active species, typically occurring in high  $\text{NO}_3^-$  concentrations ( $>1 \text{ mol L}^{-1}$ ) in acidic electrolytes. Current research mainly centers on the direct reduction process, which includes electron-mediated and hydrogen atom-mediated reductions (Fig. 2).<sup>42</sup>



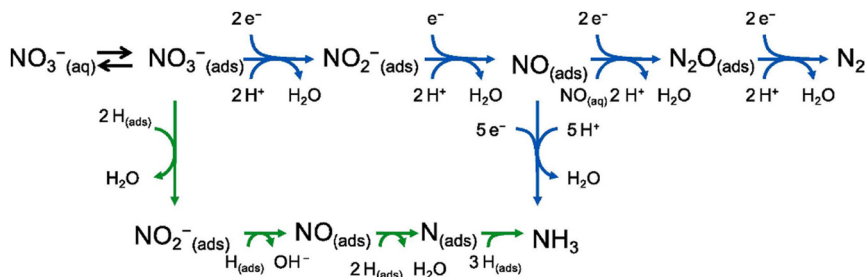
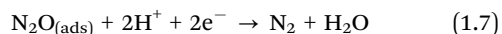
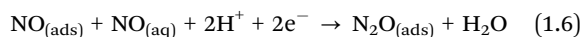
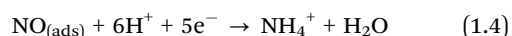
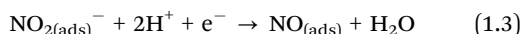
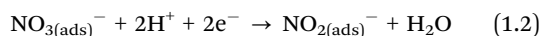
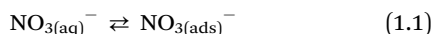
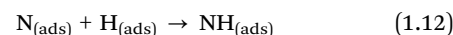
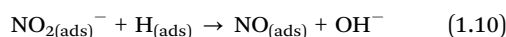


Fig. 2 The electron-mediated (blue arrow) and hydrogen atom-mediated (green arrow) pathways of the  $\text{NO}_3\text{RR}$ . Reproduced with permission.<sup>42</sup> Copyright 2021, Elsevier B.V.

In electron transfer-mediated  $\text{NO}_3\text{RR}$ s, various products can be generated through the reaction, including  $\text{NO}_2$ ,  $\text{NO}_2^-$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{NH}_2\text{OH}$ , and  $\text{NH}_3$ . Notably,  $\text{N}_2$  and  $\text{NH}_3$  are primary products owing to their high thermodynamic stability.<sup>43</sup> In this process,  $\text{NO}_3^-$  is firstly adsorbed onto the active sites of the catalyst (eqn (1.1)).<sup>44</sup> The subsequent reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  is usually considered the rate-determining step (RDS) in the  $\text{NO}_3\text{RR}$  (eqn (1.2)).<sup>45</sup> Thus, the  $\text{NO}_3\text{RR}$  performance is affected by the concentration of  $\text{NO}_3^-$ . In the electrolyte with low  $\text{NO}_3^-$  concentrations, the reaction process is influenced by co-adsorbed ions, whereas in cases of high  $\text{NO}_3^-$  concentrations, the active site density of the catalyst becomes the pivotal factor.<sup>41</sup> The intermediate  $\text{NO}_2^-$  demonstrates obvious reactivity on the catalyst, leading to adsorbed  $\text{NO}$  (eqn (1.3)), significantly determining product distribution.<sup>46</sup>  $\text{NO}_{(\text{ads})}$  can either undergo reduction to  $\text{NH}_4^+$  (eqn (1.4)), serving as the final product or desorb from the active sites to produce  $\text{NO}$  in the electrolyte (eqn (1.5)).<sup>47</sup> The  $\text{NO}$  dimers with weak adsorption are formed in the presence of  $\text{NO}_{(\text{aq})}$  in the electrolyte, serving as precursors for  $\text{N}_2\text{O}$  (eqn (1.6)), which is subsequently reduced to  $\text{N}_2$  (eqn (1.7)).<sup>48–51</sup>



Meanwhile,  $\text{NO}_3\text{RR}$ s can also occur following the hydrogen atom ( $\text{H}_{(\text{ads})}$ )-mediated reduction process. The Volmer step of water dissociation provides  $\text{H}_{(\text{ads})}$  as shown in eqn (1.8).<sup>52,53</sup> Atomic hydrogen ( $\text{H}$ ) is a potent reducing agent ( $E^\circ(\text{H}^+/\text{H}) = -2.31 \text{ V vs. SHE}$ ),<sup>54</sup> which can reduce  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}$  adsorbed on the active sites (eqn (1.9)–(1.11)).<sup>55</sup> Kinetically, the formation of N–H bonds occurs more readily than the formation of N–N bonds, resulting in  $\text{NH}_3$  being the primary product of this pathway (eqn (1.12)–(1.14)).<sup>56,57</sup>



The  $\text{H}_{(\text{ads})}$ -mediated  $\text{NO}_3\text{RR}$  generally occurs at low overpotentials, which is essential for inhibiting side reactions. This pathway is particularly advantageous in noble metal catalysts, owing to their strong affinity for hydrogen.<sup>58</sup> Conversely, the electron transfer pathway is more probable on catalysts that exhibit a high adsorption capacity for  $\text{NO}_3^-$ .

## 2.2. Challenges and dilemmas in the $\text{NO}_3\text{RR}$

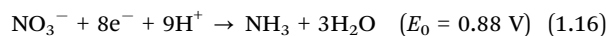
The  $\text{NO}_3\text{RR}$  occurs at the solid–liquid interface, presenting a lower reaction barrier than the solid–gas–liquid interface associated with the  $\text{NRR}$ . However, thermodynamically, the overpotential for  $\text{NH}_3$  production is similar to that of several byproducts, such as  $\text{N}_2\text{O}$  (1.12 V vs. RHE),  $\text{NO}$  (0.96 V vs. RHE), and  $\text{NH}_2\text{OH}$  (0.73 V vs. RHE).<sup>59</sup> Additionally, to achieve higher  $\text{NH}_3$  yield rates, it may be necessary to apply more negative electrode potentials, but this can simultaneously promote the competitive HER and reduce the faradaic efficiency of  $\text{NH}_3$  production, leading to unsatisfactory energy efficiency in the  $\text{NO}_3\text{RR}$ .<sup>2,31,53,60,61</sup> Furthermore, from a kinetic perspective, the  $\text{NO}_3\text{RR}$  pathway for  $\text{NH}_3$  generation is complex, involving an eight-electron and nine-proton transfer process, resulting in sluggish kinetics.<sup>62</sup> Consequently, developing catalysts for the  $\text{NO}_3\text{RR}$  that achieve high  $\text{NH}_3$  yield rates and selectivity remains a significant challenge.

Meanwhile, the necessary overpotential for the  $\text{NO}_3\text{RR}$  and the source of protons depend on the pH of the electrolyte. Under acidic conditions, protons come from  $\text{H}^+$ , leading to the following reaction equation:

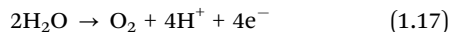
Overall reaction:



Cathode:

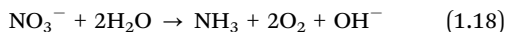


Anode:

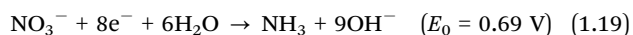


Under neutral and alkaline conditions,  $\text{H}_2\text{O}$  acts as the source of protons, resulting in the following reaction equation:

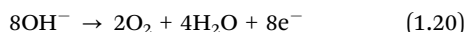
Overall reaction:



Cathode:



Anode:



The information above indicates that the reduction potential ( $E_0$ ) for the  $\text{NO}_3\text{RR}$  is lower under acidic conditions (0.88 V) compared to alkaline electrolytes (0.69 V), resulting in more favorable thermodynamics.<sup>63,64</sup> Nevertheless, under acidic conditions, the intense competition for hydrogen adsorption on the active sites impedes the  $\text{NO}_3\text{RR}$  process. While  $\text{NH}_3$  synthesis costs in alkaline environments are already below the commercial price,<sup>2</sup> the slow mass transfer requires higher voltages to achieve substantial yields, leading to increased energy consumption. This challenge is particularly pronounced in neutral media.

The activity and selectivity of the  $\text{NO}_3\text{RR}$  are influenced by different factors, including the  $\text{NO}_3^-$  concentration, catalyst type, and diffusion dynamics. For a specific catalyst, enhancing the mass transfer can significantly improve the  $\text{NO}_3\text{RR}$ . Increasing the concentration of  $\text{NO}_3^-$  enhances the accessibility of active sites to  $\text{NO}_3^-$ , thereby accelerating the reduction reaction. However, as the reaction progresses, the concentration of  $\text{NO}_3^-$  in the electrolyte diminishes, resulting in a gradual decrease in the  $\text{NH}_3$  yield rate. It is also crucial to understand whether the decrease in  $\text{NH}_3$  yield rate is related to catalyst deactivation or is simply due to a reduction in reactant concentration. Nevertheless, addressing mass transfer limitations in the  $\text{NO}_3\text{RR}$  requires different strategies to those in  $\text{CO}/\text{CO}_2$  reduction reactions.<sup>65,66</sup> To alleviate the limitations of mass diffusion issues in the  $\text{CO}/\text{CO}_2$  reduction reaction, gas diffusion electrodes can be utilized in flow-cell reactors to directly provide gaseous reactants to the electrolyte/electrode interface, which is not applicable to the  $\text{NO}_3\text{RR}$  because  $\text{NO}_3^-$  is dissolved in the electrolyte.<sup>67</sup> Consequently, developing methods to enhance the mass transport of  $\text{NO}_3^-$  under different conditions remains a significant challenge for future research.

Based on the mechanism and the challenges in the  $\text{NO}_3\text{RR}$ , proposing a well-designed strategy to regulate the adsorption and activation of  $\text{NO}_3^-$  at active sites, control the transfer behavior of electrons and active hydrogen to suppress side reactions and facilitate the hydrogenation process, and manage mass diffusion to ensure a sufficient supply of reactants is essential for achieving high activity and selectivity for  $\text{NH}_3$  production *via*  $\text{NO}_3\text{RR}$ s. The strategy not only enhances the efficiency of the reaction but also provides a pathway for the industrial application of the  $\text{NO}_3\text{RR}$ .

### 3. $\text{NH}_3$ synthesis enhanced by built-in electric fields

Enhancing  $\text{NH}_3$  synthesis through manipulating built-in electric fields represents a promising avenue in catalysis.<sup>68–72</sup> These fields can profoundly impact the energies of key reaction steps, ultimately influencing the catalytic process. Researchers can fine-tune the adsorption energies of reactants and intermediates by designing these fields within catalysts, thereby steering the reaction towards more favorable pathways. This approach can boost the catalytic activity and facilitate the selectivity of the  $\text{NH}_3$  synthesis reaction, offering a pathway towards more sustainable and efficient  $\text{NO}_3\text{RR}$ s.

#### 3.1. Mott–Schottky heterojunction

Utilizing the difference in work functions between metals and semiconductors to construct a Mott–Schottky heterojunction is an effective strategy for introducing a built-in electric field.<sup>73</sup> When a metal and a semiconductor come into contact to form a rectifying junction, the energy bands of the semiconductor bend to match the work function ( $\Phi$ ) of the metal, triggering electrons to transfer from the component of lower work function to that with a higher work function, ultimately resulting in the alignment of the Fermi levels of both components.<sup>74</sup> In detail, as shown in Fig. 3a, when the metal's work function is greater than that of the semiconductor, electrons irreversibly transfer towards the metal upon contact, leading to electron accumulation on the metal side and depletion on the semiconductor side at the interface, resulting in an upward bending of the semiconductor's conduction and valence bands at the interface, forming an intrinsic electric field.<sup>75</sup> Conversely, when the metal's work function is lower than that of the semiconductor (Fig. 3b), electrons migrate irreversibly toward the semiconductor until the Fermi levels of both materials align. This process leads to electron accumulation on the semiconductor side and depletion on the metal side at the interface, resulting in a downward bending of the semiconductor's conduction and valence bands at the interface, thereby establishing a built-in electric field.<sup>73</sup> Based on the mechanism mentioned above, the charge distribution state and the built-in electric field on the metal–semiconductor contact interface can be controlled by constructing different Mott–Schottky heterojunctions, potentially regulating the transfer of electrons in catalytic reaction processes and significantly altering the adsorption and desorption of specific reactants. Therefore, the development of Mott–Schottky heterojunction catalysts presents a strategy conducive to enhancing performance in the synthesis of  $\text{NH}_3$ .

To introduce the electric field induced by the Schottky barrier for promoting  $\text{NH}_3$  production, Li and colleagues<sup>76</sup> fabricated electron-deficient Ni nanoparticles within nitrogen-rich carbon matrices ( $\text{Ni}_x/\text{NC-sd}$ ). Computational simulations showed that the localized electric field at the charged electrodes can significantly enhance the density of  $\text{NO}_x^-$  ions (Fig. 3c), thereby accelerating the reduction process. This strategy facilitates the capture activation of  $\text{NO}_x^-$  and leads to high catalytic efficiencies for  $\text{NH}_3$  synthesis across a wide range of  $\text{NO}_x^-$  concentrations, maintaining a faradaic efficiency exceeding 95% in  $\text{NH}_3$  production and



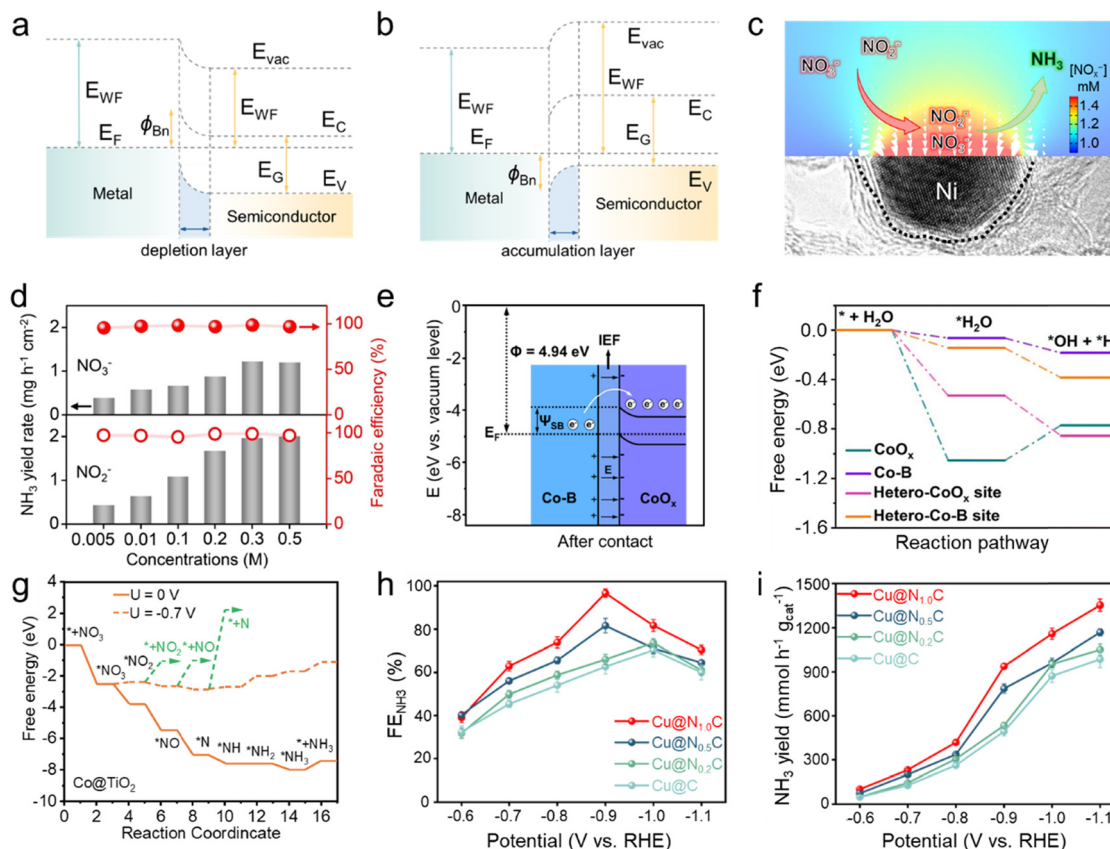


**Fig. 3** (a) and (b) Energy band diagrams.  $E_{vac}$ , vacuum level;  $E_G$ , energy gap;  $E_{WF}$ , work function;  $E_C$ , conduction band edge;  $E_V$ , valence band edge;  $E_F$ , Fermi energy;  $\phi_{Bn}$ , Schottky barrier. (c) The distribution of NO<sub>x</sub><sup>-</sup> anions on the surface of Ni<sub>x</sub>/NC-sd. The size and orientation of each arrow indicate the density and location of NO<sub>x</sub><sup>-</sup> anions. The lower part of the image shows a high-resolution transmission electron microscopy image of Ni<sub>x</sub>/NC-sd. (d) NH<sub>3</sub> yield rate and faradaic efficiency of Ni<sub>35</sub>/NC-sd in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with various NO<sub>x</sub><sup>-</sup> concentrations at -0.5 V vs. RHE. Reproduced with permission.<sup>76</sup> Copyright 2021, Wiley-VCH. (e) Energy band diagrams of Co-B, and CoO<sub>x</sub> after contact.  $E_F$ , Fermi energy; IEF, built-in electric field;  $\psi_{SB}$ , Schottky barrier. (f) Free energy diagrams of H<sub>2</sub>O dissociation on different sites. Reproduced with permission.<sup>36</sup> Copyright 2024, Royal Society of Chemistry. (g) Free energy diagram of Co@TiO<sub>2</sub> adsorbing different intermediates in the NO<sub>3</sub>RR. Reproduced with permission.<sup>77</sup> Copyright 2023, Wiley-VCH. (h) Faradaic efficiency and (i) yield rate of NH<sub>3</sub> for Cu@N<sub>x</sub>C obtained in 0.5 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M NaNO<sub>3</sub>. Reproduced with permission.<sup>78</sup> Copyright 2024, Royal Society of Chemistry.

achieving a NH<sub>3</sub> yield rate of 5.1 mg h<sup>-1</sup> cm<sup>-2</sup> from NO<sub>3</sub><sup>-</sup> reduction and 25.1 mg h<sup>-1</sup> cm<sup>-2</sup> from NO<sub>2</sub><sup>-</sup> reduction at -0.5 V vs. RHE (Fig. 3d). The remarkable NH<sub>3</sub> production performance can be reproduced over 5 consecutive cycling tests, indicating its robust stability. The work by Wang *et al.*<sup>36</sup> further evidenced the effectiveness of Mott-Schottky heterojunctions in enhancing NH<sub>3</sub> production performance. Based on the work functions and band energies of metallic Co-B and p-type semiconductive CoO<sub>x</sub>, the formation of the Schottky contact in Co-B@CoO<sub>x</sub> results in charge redistribution and the establishment of a built-in electric field (Fig. 3e). This phenomenon regulates the adsorption behavior of reactants and intermediates during the NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub> process. Additionally, as protons derived from H<sub>2</sub>O serve as essential reactants in the NH<sub>3</sub> production process, their research also demonstrates the influence of Schottky junction-induced electron redistribution on the behavior of H<sub>2</sub>O molecules. As illustrated in Fig. 3f, Co-B@CoO<sub>x</sub> exhibits enhanced capabilities in H<sub>2</sub>O molecule adsorption and dissociation compared to counterparts, thereby facilitating

proton provision for participation in the hydrogenation process. Zheng and colleagues<sup>77</sup> fabricated a Mott-Schottky heterojunction by loading Co nanoparticles onto TiO<sub>2</sub> nanobelt arrays and demonstrated the promoting effect of the built-in electric field on the NO<sub>3</sub>RR by DFT calculations. The Schottky contact can mediate the electronic structure of Co@TiO<sub>2</sub>, increasing the electron density on the surface of Co, which facilitates the adsorption of NO<sub>3</sub><sup>-</sup>, thereby enhancing the reduction process. The free energy diagram of Co@TiO<sub>2</sub> adsorbing various species at different potentials in Fig. 3g exhibited the rate-determining step, \*NH to \*NH<sub>2</sub>, was only 0.69 eV. Meanwhile, the calculated free energy, which discourages the generation of NO<sub>2</sub>, NO, and N<sub>2</sub>, validates that the Schottky junction enhances the selectivity of the NH<sub>3</sub> production catalytic process. In addition to directly utilizing the built-in electric field of Schottky junctions to regulate the adsorption of reactants and intermediates, Yu and his colleagues<sup>78</sup> also employed Schottky junctions to promote the NO<sub>3</sub>RR by adjusting the state of active sites. They uniformly dispersed Cu nanoparticles on N-doped carbon substrates, where

the N doping adjusted the carbon bandgap and regulated Mott-Schottky heterostructures. Due to the Schottky contact, electrons transferred irreversibly from Cu to the substrate, forming a built-in electric field and converting Cu sites into electron-deficient states, increasing the  $\text{Cu}^+$  concentration. This adjustment facilitated the activation and adsorption of  $\text{NO}_3^-$ , resulting in a faradaic efficiency for  $\text{NH}_3$  production of 96.2% at  $-0.9$  V vs. RHE (Fig. 3h), along with an  $\text{NH}_3$  yield rate of  $1353.1 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  at  $-1.1$  V vs. RHE (Fig. 3i).

### 3.2. Semiconductor-semiconductor heterojunction

A semiconductor heterojunction is a structure composed of different types of semiconductor materials, mainly categorized as p-n and non-p-n junctions. Taking the p-n junction as an example (Fig. 4a), when p-type and n-type semiconductors come into contact, a built-in electric field is formed at the interface due to the diffusion of electrons and holes. This electric field effectively separates electrons and holes and inhibits their recombination, prolonging the lifetime of charges. Additionally, this unique structure allows for spatial

separation of oxidation-reduction sites. To utilize the distinctive properties of semiconductor heterojunctions for  $\text{NO}_3\text{RR}$ , Lu and colleagues<sup>35</sup> developed a novel electrocatalyst by layering CuCl (111) and rutile  $\text{TiO}_2$  (110) with distinct work functions. The electron transfer from  $\text{TiO}_2$  to CuCl leads to a built-in electric field (BEF), and is hence named CuCl\_BEf. They utilized molecular dynamics simulation in the electrolyte containing  $100 \text{ mg L}^{-1} \text{ NO}_3^-$  and concluded that after 10 ns, the peak concentration of  $\text{NO}_3^-$  positioned on the CuCl\_BEf side reached  $12.3$  ions per  $\text{nm}^3$ , surpassing the concentration observed on the pure CuCl surface ( $6.3$  ions per  $\text{nm}^3$ , as shown in Fig. 4b). Consequently,  $\text{NO}_3^-$  with ultra-low concentrations ( $100 \text{ mg L}^{-1}$ ) was converted to  $\text{NH}_3$  at a remarkable production rate of  $1.82 \text{ mg h}^{-1} \text{ cm}^{-2}$  (Fig. 4c). In contrast, CuCl + MXene without a built-in electric field exhibited a lower rate. The CuCl\_BEf catalyst displayed negligible fluctuations in selectivity during consecutive recycling tests, indicating its superior stability (Fig. 4d). The theoretical calculation shows that the electric field facilitated the accumulation of  $\text{NO}_3^-$  ions on the catalyst surface, enhancing the reaction rate and lowering the energy

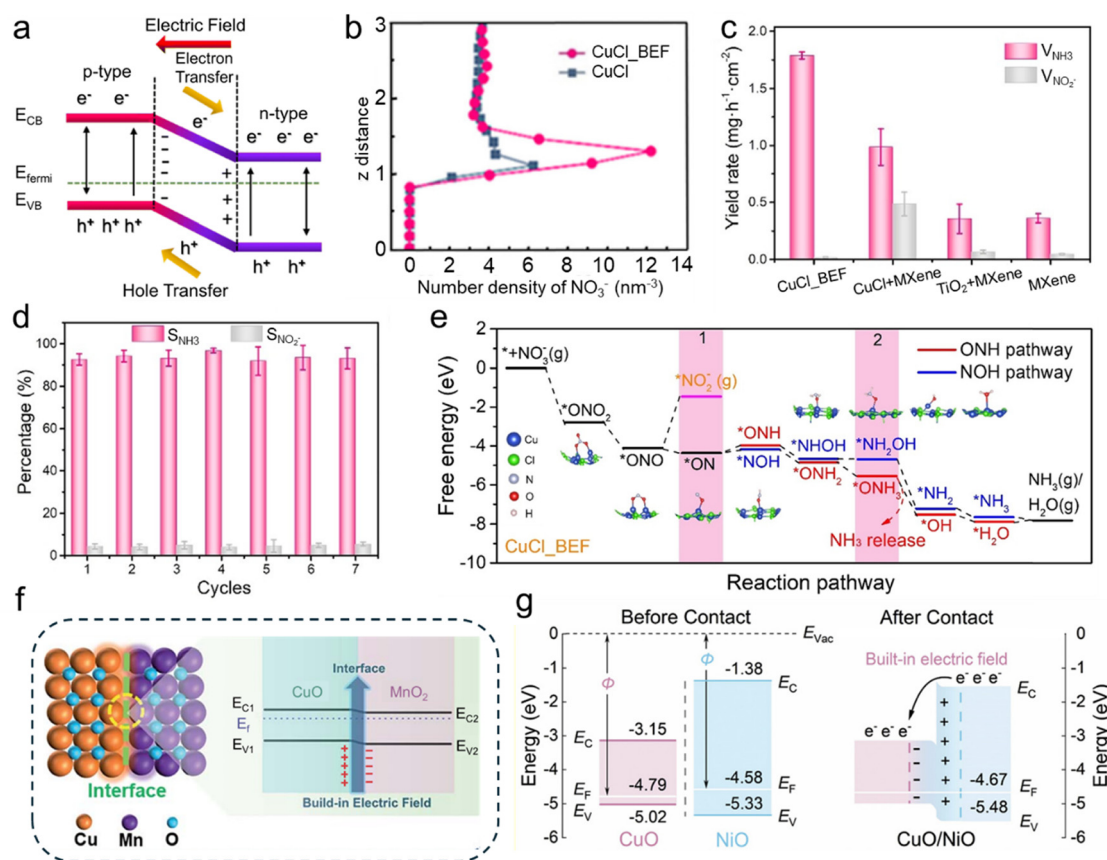


**Fig. 4** (a) Schematic demonstrating the band structure and built-in electric field formation mechanisms in the p-n heterojunction. Reproduced with permission.<sup>79</sup> Copyright 2024, Royal Society of Chemistry. (b) Spatial distribution of  $\text{NO}_3^-$  on the catalyst surface obtained from molecular dynamics simulation. CuCl\_BEf represents a heterojunction composed of CuCl and  $\text{TiO}_2$  with an induced built-in electric field. (c) Average  $\text{NH}_3$  yield rate over 6 h for various electrocatalysts. (d) Consecutive recycling tests at  $-1.0$  V vs. RHE for CuCl\_BEf. (e) Free energy diagram of reaction pathways for reducing  $\text{NO}_3^-$  to  $\text{NH}_3$  on the CuCl\_BEf. Reproduced with permission. Copyright 2021, Wiley-VCH. (f) Schematic presenting the band structures and built-in electric field formation of CuO/MnO<sub>2</sub>. Reproduced with permission.<sup>80</sup> Copyright 2022, Royal Society of Chemistry. (g) Band structures of CuO and NiO pre-contact (left) and post-contact (right). Reproduced with permission.<sup>69</sup> Copyright 2024, Elsevier B.V.

barrier of the RDS for the key reaction intermediate  $^*\text{NO}$  (Fig. 4e). The presence of the electric field in this semiconductor heterojunction can enhance ion adsorption, thereby boosting catalytic efficiency. This strategy suggests new avenues for designing innovative catalysts tailored for reactions involving ions as reactants.

Meanwhile, Wang and colleagues<sup>80</sup> developed a novel hierarchical structure of  $\text{CuO}@\text{MnO}_2$  1D core–2D shell nanoarrays supported on a Cu foam substrate ( $\text{CuO}@\text{MnO}_2/\text{CF}$ ). Integrating  $\text{MnO}_2$  nanosheets onto the CuO nanowire arrays offers a high density of active sites and enhances mass transfer. Notably, the  $\text{CuO}/\text{MnO}_2$  heterojunction establishes an built-in electric field at the interface, promoting the accumulation of  $\text{NO}_3^-$  and expediting  $\text{NO}_3^-$  reduction kinetics through optimized adsorption processes (Fig. 4f). As a result, the  $\text{CuO}@\text{MnO}_2/\text{CF}$  composite demonstrates an exceptional  $\text{NH}_3$  faradaic efficiency of 94.92%, remarkable  $\text{NH}_3$  selectivity of 96.67%, and superior  $\text{NO}_3^-$  conversion of 99.38% in the  $\text{NO}_3\text{RR}$ . In another study, benefiting from the superior  $\text{H}_2\text{O}$ -to- $\text{H}^*$  conversion capabilities of nickel-based semiconductors,<sup>81,82</sup> Zou and co-workers<sup>69</sup> created a heterojunction by combining CuO and NiO due to their matched work functions. Through analyses using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS), a semiconductor–semiconductor heterojunction between CuO and NiO was validated, which can trigger a built-in electric field. The catalytic performance of  $\text{CuO}/\text{NiO}$  in the  $\text{NO}_3\text{RR}$  under low  $\text{NO}_3^-$  concentrations including  $\text{NO}_3^-$  conversion rates, product selectivity ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ , and  $\text{N}_2$ ), and faradaic efficiency, was assessed by comparing with the performance of pure CuO and NiO. The influence of applied potentials, pH of the electrolyte, and  $\text{NO}_3^-$  concentrations on the catalytic performance of  $\text{CuO}/\text{NiO}$  in the  $\text{NO}_3\text{RR}$  was also investigated. Density functional theory (DFT) calculations revealed that the  $\text{CuO}/\text{NiO}$  system, with its built-in electric field, is conducive to enhancing reactant mass transfer and  $\text{H}^*$  provision. Based on the experimental and theoretical results, they summarized the origination of the promotion of  $\text{CuO}/\text{NiO}$  in the  $\text{NO}_3\text{RR}$ . As illustrated in Fig. 4g, upon the contact between CuO and NiO, the spontaneous electron flow leads to band bending, creating a built-in electric field that accelerates charge transfer and the rate of the  $\text{NO}_3\text{RR}$ .

### 3.3. Coordination-environment modulation

In addition to heterojunction interfaces, introducing an electric field by adjusting the coordination environment of catalysts can also enhance catalytic processes. The coordination structure near active sites can effectively influence electron distribution and induce built-in electric fields, thereby modulating the adsorption behavior of reactants and intermediates. Moreover, it has been demonstrated that modulating the built-in electric field between dual-layer single-atom catalysts can also effectively adjust polarization, suppressing competitive reactions in the  $\text{NO}_3\text{RR}$ .<sup>37</sup>

Frauenheim and colleagues<sup>37</sup> proposed a universal strategy of heterogeneous bilayer single-atom catalysts with tunable surface chemistry to enhance the  $\text{NO}_3\text{RR}$ . The asymmetric atomic design of these catalysts leads to a dipole moment that can strengthen built-in electric fields, regulating the activation of reactants and the adsorption of intermediates, thus

modulating reaction pathways and enhancing  $\text{NH}_3$  selectivity and activity. They investigated a series of bilayer N-doped graphene (GN) supported single-atom catalysts. High-throughput calculations revealed that  $\text{TiV-N}_4$ ,  $\text{NbV-N}_4$ , and  $\text{GaV-N}_4\text{-GN}$  can all suppress competitive HERs with favorable limiting potentials of  $-0.32$ ,  $-0.20$ , and  $-0.25$  V, respectively. In the free energy diagrams of  $\text{V}_2\text{-N}_4\text{-GN}$  (Fig. 5a), apart from the  $^*\text{NO}_3^- \rightarrow ^*\text{NO}_3\text{H}$  and  $^*\text{NO} \rightarrow ^*\text{NOH}$  steps showing an upward  $\Delta G$ , the remaining hydrogenation processes exhibit a downward  $\Delta G$ .  $\text{NH}_3$  desorbs from the adsorption site after overcoming a small final free energy barrier of 0.1 eV, indicating fast  $\text{NH}_3$  desorption from the catalyst surface. Therefore, the rate-determining step in this system is the  $^*\text{NO} \rightarrow ^*\text{NOH}$  transformation. The authors also summarized the limiting potential and RDS of the  $\text{NO}_3\text{RR}$  on  $\text{MV-N}_4\text{-GN}$  (Fig. 5b), indicating a strong dependence of the RDS and limiting potential on polarization. Compared to the upward  $\Delta G$  for  $^*\text{NO}_3^- \rightarrow ^*\text{NO}_3\text{H}$  in  $\text{V}_2\text{-N}_4\text{-GN}$ , the corresponding step in  $\text{NbV-N}_4\text{-GN}$  shows a downward  $\Delta G$  (Fig. 5c). Furthermore, in the subsequent hydrogenation steps, polarization did not alter the most stable NO adsorption mode and the most favorable adsorption pathway for the  $\text{NO}_3\text{RR}$ . Instead, the RDS shifted to the desorption of  $\text{NH}_3$  from the surface.

Polarization can adjust the strength of interactions between intermediates and catalysts, thereby influencing the selectivity of reactions. Consequently, the limiting potential of byproducts was calculated to investigate the ease of byproduct formation on  $\text{NbV-N}_4\text{-GN}$ . For most  $\text{MV-N}_4\text{-GN}$  catalysts (excluding  $\text{ZrV}$ ,  $\text{MgV}$ , and  $\text{CaV}$ , as shown in Fig. 5d), the  $\Delta G_{\text{H}}$  values are significantly higher than those of the  $\text{NO}_3\text{RR}$ , indicating that  $\text{MV-N}_4\text{-GN}$  retains its inhibitory effect on the HER. Therefore, the unique atomic structure and electronic properties of heterogeneous BSACs contribute to the polarization dependence and controllable selectivity of the  $\text{NO}_3\text{RR}$ . Furthermore, the volcano-shaped relationship between the limiting potentials ( $U_{\text{L}}$ ) and adsorption free energy of  $\text{NO}_3^-$  ( $\Delta G_{^*\text{NO}_3^-}$ ) indicates that heterogeneous BSACs exhibit a higher activity compared to their counterparts (Fig. 5e). The plane-average potential of  $\text{NbV-N}_4\text{-GN}$  in Fig. 5f further confirms the existence of an electric field and that can be modulated through substituting other atoms. As shown in Fig. 5g and h, after Nb substitution, the color deepens around the V atom, indicating an enhanced electric field around V, further validating the feasibility of regulating the coordination environment to enhance the electric field. Therefore, the built-in electric field in BSACs can promote the accumulation of  $\text{NO}_3^-$  and mass transfer on the surface of the catalyst for an improved  $\text{NO}_3\text{RR}$  (Fig. 5i). Meanwhile, Zhao and co-workers<sup>83</sup> doped boron into carbon substrate to adjust the coordination structure of Ni SACs and construct B–N bonds to trigger the electric field that could facilitate the adsorption of  $\text{NO}_3^-$ . Compared to the catalyst without an electric field, that is, without doping boron, the faradaic efficiency of  $\text{NiSA}@\text{BNG}$  increased to  $\approx 95\%$  from 51% and the yield rate is 2 times higher. As shown in the density of states for  $\text{NiSA}@\text{BNG}$ , the B atoms significantly increase the density of states and redistribute the density of state (DOS; as shown in Fig. 5j and k), indicating the promoted



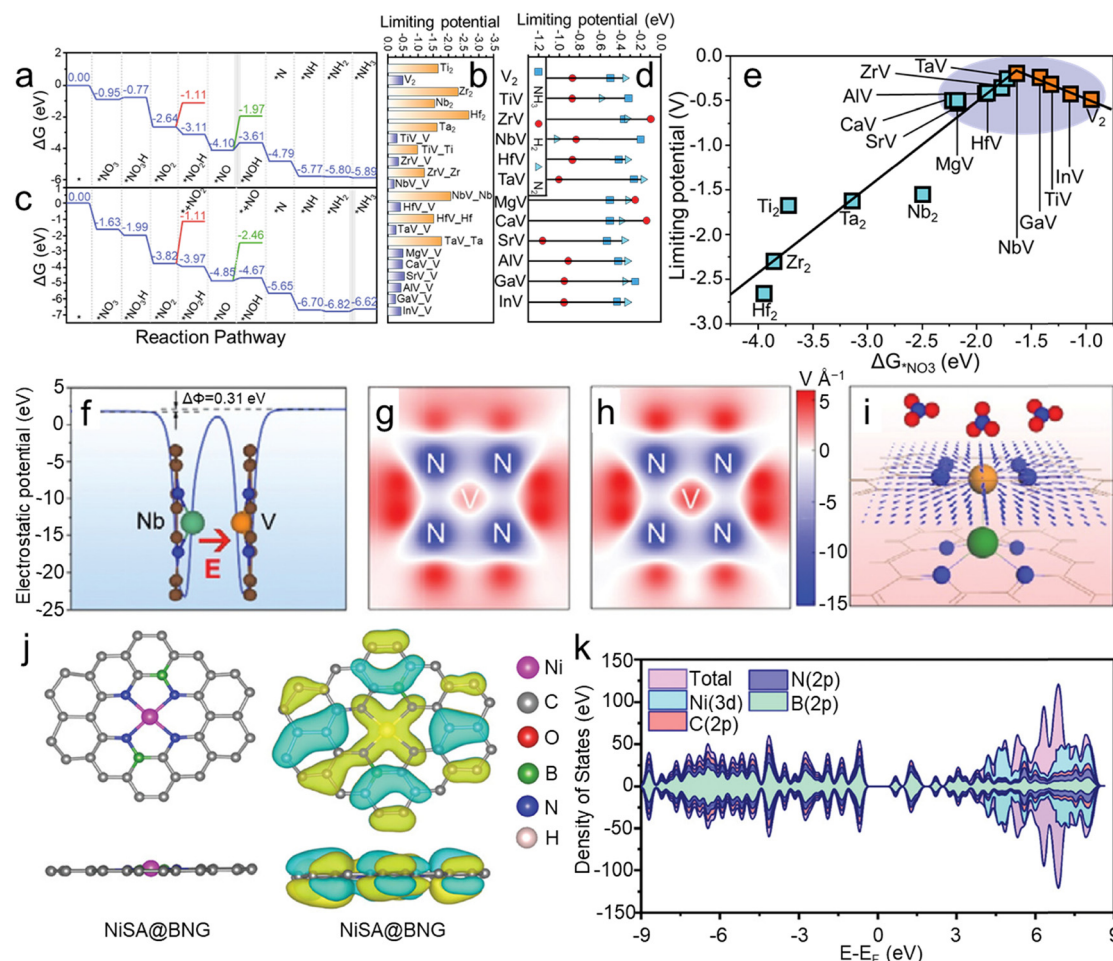


**Fig. 5** Free energy diagram for the reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  on (a)  $\text{V}_2\text{-N}_4\text{-GN}$  and (c)  $\text{NbV-N}_4\text{-GN}$ . (b) Limiting potentials on  $\text{M}_2\text{-N}_4\text{-GN}$  and  $\text{MV-N}_4\text{-GN}$  for the  $\text{NO}_3\text{RR}$ . (d) Limiting potentials for generating various products during the  $\text{NO}_3\text{RR}$  process. (e) Volcano-shaped relationship between  $U_L$  and  $\Delta G^*_{\text{NO}_3}$ . (f) Plane-averaged potential of  $\text{NbV-N}_4\text{-GN}$ . The simulated electric field on (g)  $\text{V}_2\text{-N}_4\text{-GN}$  and (h)  $\text{NbV-N}_4\text{-GN}$ , in which the unit is  $\text{V \AA}^{-1}$ . (i) Schematic depicting the electric field from  $\text{NbV-N}_4\text{-GN}$ , with each arrow's size and direction indicating the field's strength and orientation. Reproduced with permission.<sup>37</sup> Copyright 2022, Wiley-VCH. (j) Optimized structures and charge distribution of  $\text{NiSA@BNG}$ . (k) The DOS for the  $\text{NiSA@BNG}$  catalyst. Reproduced with permission.<sup>83</sup> Copyright 2024, Wiley-VCH.

conductivity of  $\text{NiSA@BNG}$ . Meanwhile,  $\text{NiSA@BNG}$  demonstrates superior stability, as evidenced by no significant decrease in faradaic efficiency and yield rate over 5 consecutive recycling tests. In conclusion, the introduced electric field declines the reaction energy barrier, promotes the adsorption of  $\text{NO}_3^-$  and enhances the stabilization of the catalyst.

### 3.4. Electrical double layer construction

Due to the electrode–electrolyte interface being the site of catalytic processes, research on the electrical double layer formed when the electrode contacts the electrolyte is crucial. As shown in Fig. 6a, the electrical double layer comprises the inner Helmholtz layer, outer Helmholtz layer, and diffusion layer.<sup>84</sup> The type and concentration of solvated ions in the electrical double layer play a critical role in catalytic reactions, where cations in the electrolyte can stabilize negatively charged reaction intermediates through local electric field effects. In this context, Yu and colleagues<sup>38</sup> studied the  $\text{NO}_3\text{RR}$  performance by using bulk Cu as the cathode and adjusting the types and concentrations of alkali metal ions in the electrolyte.

As shown in Fig. 6b, various alkali metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) were selected for COMSOL multi-physics simulations, and the resulting electric double layer (EDL) all exhibited negative potentials, which indicates the effectiveness of utilizing alkali metal cations in the electrolyte to modulate the electrolyte microenvironment within the EDL. This phenomenon can promote the dissociation of water molecules on the electrode surface and facilitate the rapid movement of generated  $\text{OH}^-$  away from the electrode surface towards regions of positive electrostatic potential (ESP). During this process,  $\text{OH}^-$  near alkali metal cations removed an  $\text{H}^+$  from adjacent water molecules, thus facilitating proton transfer. The authors further compared the  $\text{NO}_3\text{RR}$  current obtained in electrolytes containing various alkali metal cations (Fig. 6c), with the current ordering as  $\text{K}^+ > \text{Na}^+ > \text{Li}^+ \approx \text{Cs}^+$ , consistent with the results shown in Fig. 6b. This alignment demonstrates that modulating the EDL effectively promotes the  $\text{NO}_3\text{RR}$  for  $\text{NH}_3$  production. Adding  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  alkali metal cations had little effect on the potential-determining step, but introducing  $\text{Cs}^+$  increased the reaction barrier of the potential-determining step, thereby inhibiting the  $\text{NO}_3\text{RR}$  (Fig. 6d).



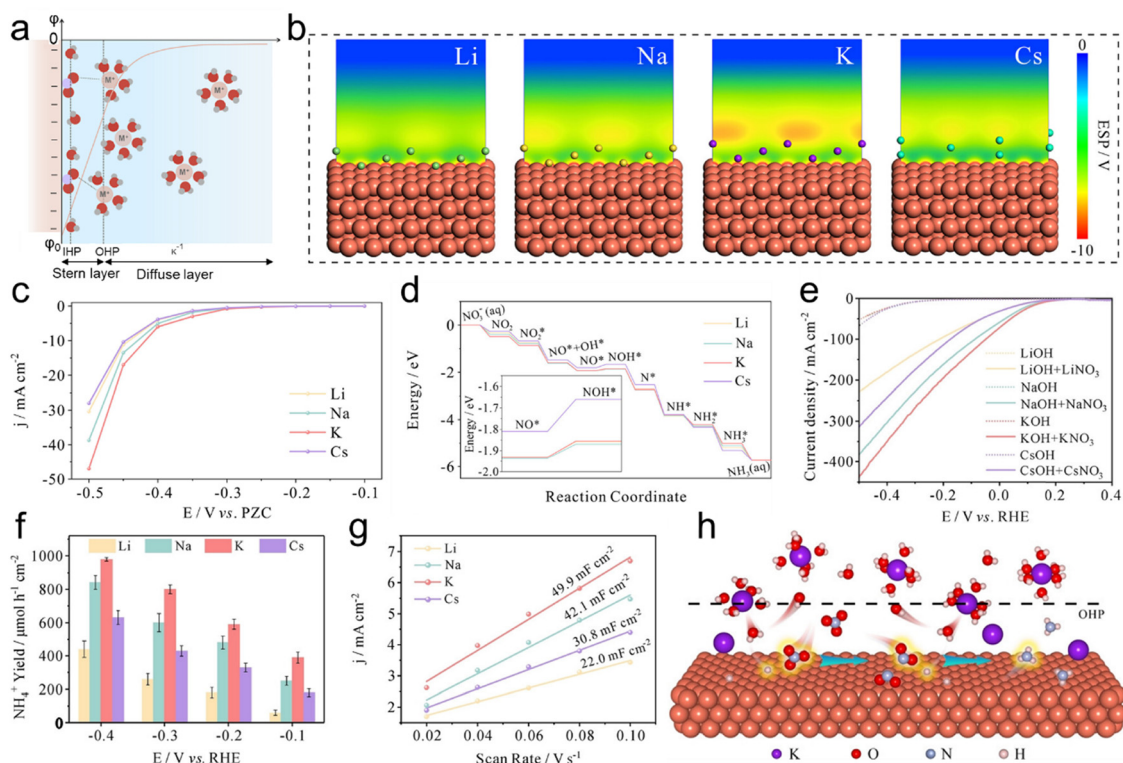


**Fig. 6** (a) Schematic of the EDL. Reproduced with permission.<sup>84</sup> Copyright 2022, Elsevier B.V. (b) ESP distribution obtained from models with various alkali metal ions. (c) Simulated partial current densities of the  $\text{NO}_3\text{RR}$  using electrolytes with various alkali metal cations. PZC represents the potential of zero charge. (d) Free energy diagram for reducing  $\text{NO}_3^-$  to  $\text{NH}_3$  with different alkali metal cations. (e) Linear sweep voltammetry (LSV) curves of  $\text{Cu}/\text{Cu}_2\text{O}$  in the electrolyte containing 1 M MOH and 1 M MOH + 0.05 M  $\text{MnO}_3$ . (f)  $\text{NH}_4^+$  yield rate at different potentials in the electrolyte containing 1 M MOH and 0.05 M  $\text{MnO}_3$  at 0.4 V vs. RHE. (g) Double-layer capacitance ( $C_{\text{dl}}$ ) values in 1 M MOH with 0.05 M  $\text{MnO}_3$ . (h) Schematic diagram of the EDL-assisted  $\text{NO}_3\text{RR}$  process. Reproduced with permission.<sup>38</sup> Copyright 2024, Wiley-VCH.

The evaluation through electrochemical testing of the  $\text{NO}_3\text{RR}$  using  $\text{Cu}/\text{Cu}_2\text{O}$  with different alkali metal cations added to the electrolyte also assessed the promoting effect of local electric field effects on the reaction. In the presence of  $\text{NO}_3^-$ , the addition of various cations showed significant  $\text{NO}_3^-$  catalytic activity (Fig. 6e and f). The charge accumulation at the catalytic interface shows the most significant decrease in  $C_{\text{dl}}$  after adding  $\text{K}^+$  (Fig. 6g). The conversion of  $\text{NO}_3^-$ , faradaic efficiency, selectivity for  $\text{NH}_4^+$ , and yield rate achieved 99%, 98%, 99.5%, and  $980 \mu\text{mol h}^{-1} \text{cm}^{-2}$  in 1 M KOH, indicating the effectiveness of local electric field effects in promoting the reduction of  $\text{NO}_3^-$ . Combining the theoretical and experimental findings, a more comprehensive insight into the alkali metal cation-mediated strategy in the  $\text{NO}_3\text{RR}$  process was proposed (Fig. 6h). Alkali metal cations near the OHP regulate proton migration and impact the interactions between protons and intermediates. Among these cations,  $\text{K}^+$  emerges as the most advantageous electrolyte component. It facilitates proton adsorption on the catalyst surface, promoting the hydrogenation process and enhancing the  $\text{NO}_3\text{RR}$ .

## 4. $\text{NH}_3$ synthesis enhanced by external stimuli

The reasonable design of external stimuli-assisted catalysis, that is, efficiently harnessing energy abundant on earth,

including solar energy, thermal energy, and mechanical energy, has significant potential for producing renewable fuels and removing environmental pollutants. Recent studies have indicated that certain external stimuli, such as light and stress, can trigger the built-in electric field within the catalyst, effectively achieving charge separation and impacting catalytic activity, reaction kinetics, and selectivity in reducing  $\text{NO}_3^-$  to  $\text{NH}_3$ . Additionally, external stimuli can influence the catalytic reaction process through other pathways such as overcoming thermodynamic barriers in the  $\text{NO}_3\text{RR}$ . However, there is a lack of comprehensive summaries and an in-depth understanding of the research progress on the  $\text{NO}_3\text{RR}$  under different external stimuli.

### 4.1. Optical stimuli

Photocatalysis is a process that utilizes light energy to drive chemical reactions and is widely applied in pollutant removal and energy conversion.<sup>85–87</sup> It is primarily categorized into semiconductor photocatalysis and localized surface plasmon resonance (LSPR)-assisted photocatalysis. Semiconductor photocatalysis utilizes electron–hole pairs generated in semiconductor materials under light stimulation to catalyze reactions.<sup>88,89</sup> On the other hand, LSPR-assisted catalysis relies on the localized electric field enhancement effect and high-energy hot electrons and holes produced by metal nanoparticles under specific



wavelength light, enhancing the efficiency of photocatalytic reactions.<sup>90,91</sup>

**4.1.1 Semiconductor photocatalysis.** Photocatalysis is an environmentally friendly technology using solar energy to facilitate chemical reactions. The photocatalyst, generally a semiconductor photocatalyst, plays a key role in photocatalysis.<sup>92</sup> The band theory serves as the theoretical basis for elucidating semiconductor photocatalysts. A solid is regarded as an infinite collection of atoms, each possessing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).<sup>93</sup> Atomic clusters can be described as combinations of atomic orbitals, resulting in closely spaced filled orbitals with higher energy and a set of closely spaced empty orbitals. As the size of the atomic clusters increases to an infinite collection, discrete energy levels decrease further, eventually forming energy bands. The band formed by the HOMO orbitals is called the valence band (VB), while the band formed by the LUMO orbitals is called the conduction band (CB). As shown in Fig. 7a,<sup>94</sup> the energy disparity between the VB and the CB is termed the band gap energy ( $E_g$ ). When a photon carrying energy equal to or greater than  $E_g$  excites a semiconductor, it can elevate an electron from

the VB to the CB.<sup>95</sup> The initial electron-hole pair formed is referred to as an exciton, held together by the electrostatic attraction between the opposite charges. After thermal relaxation, these charge carriers may recombine or migrate to the semiconductor's surface through non-radiative or radiative pathways. The positively charged holes with oxidation potential and the negatively charged electrons with reduction potential can participate in the redox of the reactant adsorbed on the active sites, constituting the semiconductor photocatalytic process. The band gap and the positions (potentials) of the VB and CB in a semiconductor play a crucial role in the light absorption capacity and the thermodynamics of the photocatalytic processes. Consequently, in the design of photocatalysts, it is essential to design both the VB and CB positions (representing oxidation-reduction potential) and the band gap (reflecting light absorption ability) of the semiconductor to satisfy the necessary conditions for the redox reactions.

Dong and co-workers<sup>97</sup> synthesized subnanometric alkaline-earth oxide clusters ( $\text{MO}_{\text{NCs}}$ ,  $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$  or  $\text{Ba}$ ) through the operando construction for  $\text{NH}_3$  photosynthesis from  $\text{NO}_3^-$ . The electron paramagnetic resonance (EPR) measurements in Fig. 7b

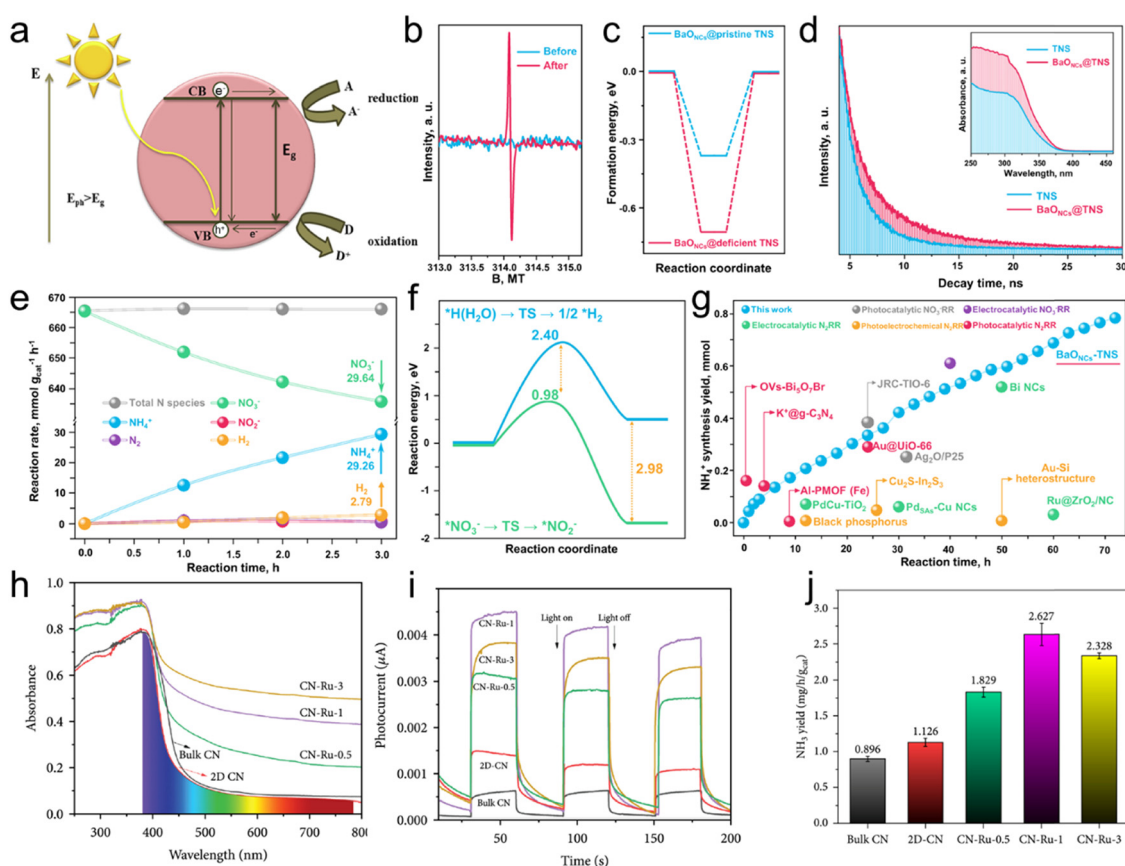
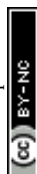


**Fig. 7** (a) Schematic of semiconductor photocatalysis. Reproduced with permission.<sup>96</sup> Copyright 2020, Elsevier Ltd. (b) EPR results of TNS before and after introducing oxygen vacancies. (c) The formation energy of  $\text{BaO}_{\text{NCs}}$  loading on pristine and defected TNS. (d) Time-resolved fluorescence emission decay spectra. The inset is UV-vis DRS. (e) Reaction rate of various products in the  $\text{NO}_3\text{RR}$ . (f) Activation energy for  $\text{NO}_3^-$  reduction and  $\text{H}_2\text{O}$  dissociation. (g) Stability test of  $\text{BaO}_{\text{NCs}}\text{-TNS}$  and the performance comparison with other works. Reproduced with permission.<sup>97</sup> Copyright 2022, Springer Nature. (h) UV-Vis DRS and (i) photocurrent response of various samples. (j) Comparison of  $\text{NH}_3$  yield rate by different catalysts. Reproduced with permission.<sup>98</sup> Copyright 2021, AAAS.



confirm the introduction of oxygen vacancies on TiO<sub>2</sub> nano-sheets (TNS). DFT calculations (Fig. 7c) demonstrated the feasibility of uniformly depositing MO<sub>NCS</sub> on photoinduced vacancies on TNS. Time-resolved fluorescence emission decay spectra in Fig. 7d revealed a significant enhancement in the charge separation capability of the composite structure. They employed ethylene glycol (EG) as the hole sacrificial agent. The oxidation of EG and the reduction of nitrate ions (NO<sub>3</sub><sup>−</sup>) occur simultaneously, where the oxidation of EG consumes the holes that, in turn, can accelerate the NO<sub>3</sub>RR, promoting NH<sub>3</sub> synthesis. As an essential parameter for evaluating performance in the NO<sub>3</sub>RR, the selectivity of NH<sub>3</sub> production on BaO<sub>NCS</sub>-TNS was investigated. As shown in Fig. 7e, 29.26 mmol g<sub>cat</sub><sup>−1</sup> NH<sub>4</sub><sup>+</sup> was obtained after 3 h of photocatalysis. The total N species in the electrolyte during the catalyst remained stable, confirming the five-electron transfer process for N<sub>2</sub> generation was suppressed. The resulting selectivity for NH<sub>3</sub> production reached 97.67%. The activation energies for synthesizing NH<sub>4</sub><sup>+</sup> from NO<sub>3</sub><sup>−</sup> and water splitting for H<sub>2</sub> production were determined through calculations (Fig. 7f). A significant reduction of 1.42 eV in activation energy was observed for the NO<sub>3</sub><sup>−</sup> reduction reaction compared to water splitting, indicating the potential for effectively suppressing electron consumption in side reactions. A long-term stability test of BaO<sub>NCS</sub>-TNS was carried out as shown in Fig. 7g, in which 0.78 mmol NH<sub>4</sub><sup>+</sup> was obtained after 72 h of photocatalysis, demonstrating leading-edge performance in the NO<sub>3</sub>RR for NH<sub>3</sub> generation. Meanwhile, Ni and colleagues<sup>98</sup> loaded Ru on g-C<sub>3</sub>N<sub>4</sub> in a photocatalyst for the NO<sub>3</sub>RR. As shown in the UV-vis diffuse reflection spectra (DRS) of various samples (Fig. 7h), a significant redshift and improved light absorption in the visible light region were observed after Ru decorating on 2D-C<sub>3</sub>N<sub>4</sub>. The introduction of Ru facilitates the separation of photogenerated electrons and holes, leading to an increased photo response (Fig. 7i). Benefiting from this strategy, the optimal catalyst displays a superior NH<sub>3</sub> yield rate of 2.627 mg h<sup>−1</sup> g<sub>cat</sub><sup>−1</sup>, 2.93 times higher than bulk g-C<sub>3</sub>N<sub>4</sub> (Fig. 7j).

**4.1.2 LSPR-assisted catalysis.** When incident light strikes the surface of non-continuous metal nanostructures, such as metal nanoparticles, the electrons capable of oscillating freely within these structures efficiently absorb photons of similar frequencies in the incident light.<sup>99–101</sup> This absorption process takes place within the metal nanostructures, giving rise to the formation of surface plasmon resonance waves at the metal-dielectric interface. However, owing to the discontinuity of the nanostructures, the surface plasmon resonance waves are constrained to the immediate vicinity of the metal nanostructure's surface and cannot propagate indefinitely along the metal-dielectric interface. This phenomenon is known as localized surface plasmon resonance (LSPR).<sup>102–104</sup> Illustrated in the schematic of LSPR in Fig. 8a, in the case of spherical metal nanoparticles, when the electron cloud oscillates freely within the nanoparticles and absorbs the energy from incident photons, the high-energy electron cloud experiences a displacement from the nanoparticle's center.<sup>105</sup> Simultaneously, the Coulomb force between the metal atoms and the electrons induces a corresponding restoring force on the displaced

electron cloud, leading to vigorous oscillations of the electron cloud near the metal atoms.<sup>106</sup> This excited oscillation of free electrons within the metal nanoparticles, triggered by incident light, can instigate the generation of LSPR within the metal nanoparticles through localized electric fields.

The effect generated on the surface of metal nanostructures can decay through relaxation processes, generating numerous hot electron-hole pairs.<sup>109</sup> Efficiently separating these hot electron-hole pairs shows promise for advancing catalytic processes like oxygen reduction, water splitting, methanol oxidation, and NH<sub>3</sub> synthesis.<sup>110–113</sup> Consequently, the effective separation and direct utilization of hot electron-hole pairs produced by the photoinduced metal LSPR effect, along with leveraging the improved catalytic activity and stability conferred by this effect, have captured considerable interest among researchers in the area of innovative sustainable and environmentally friendly energy research.

In LSPR-assisted NH<sub>3</sub> electrosynthesis, Jain and colleagues<sup>39</sup> synthesized Au nanoparticles with LSPR effects, serving as both photon-capturing materials and active sites for the NO<sub>3</sub>RR. Their electrosynthesis and overall electrochemical activities were enhanced by a factor of 15 compared to traditional electrocatalysis (Fig. 8b–d), while the faradaic efficiency for NH<sub>4</sub><sup>+</sup> production increased from 71% to 76% (Fig. 8e). Additionally, they proposed that the enhancement of kinetics due to the LSPR effect is most pronounced near the onset potential under applied bias. At  $\Delta E = -10$  mV, the LSPR effect boosted the NH<sub>4</sub><sup>+</sup> yield rate by 15 times, a level of activity that required an additional 140 mV of potential in the dark for the catalyst to achieve this (Fig. 8f). In conclusion, under light irradiation, the LSPR of Au nanoparticles is stimulated, generating electron-hole pairs through interband and intraband damping (Fig. 8g). High-energy electrons in the sp states drive the reduction of NO<sub>3</sub><sup>−</sup> to NH<sub>4</sub><sup>+</sup>, producing OH<sup>−</sup>, while the holes are consumed by electrons in the circuit. This leads to an alkaline oxygen evolution reaction at the counter electrode, with the OH<sup>−</sup> being oxidized.

Zhao and colleagues<sup>108</sup> utilized the internal electromagnetic field generated by Au NRs to synthesize Au NR@Cu<sub>2</sub>O–AuPd NPs. The internal electromagnetic field (Fig. 8h) results from the distinct optical response properties of the bimetallic components and enhanced ability to adsorb NO<sub>3</sub><sup>−</sup> and reaction intermediates, boosting the activity and selectivity in the NO<sub>3</sub>RR. This led to an NH<sub>3</sub> yield rate of 4587.00  $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  and a faradaic efficiency of 93.09% under neutral conditions (Fig. 8i and j).

## 4.2. Stress stimuli

Piezoelectricity is a fundamental material property that generates electric potential in response to stress stimuli. Typically, semiconductors exhibiting piezoelectric characteristics are polar materials possessing crystal structures that lack a center of symmetry. When subjected to stress, separating positive and negative charge centers within the lattice creates a piezoelectric potential on the material's surface. The most well-known piezoelectric materials, such as perovskite-structured Pb(Zr,Ti)O<sub>3</sub> (PZT), zinc oxide (ZnO), gallium nitride (GaN), and zinc sulfide (ZnS), are extensively utilized in diverse fields like mechanical



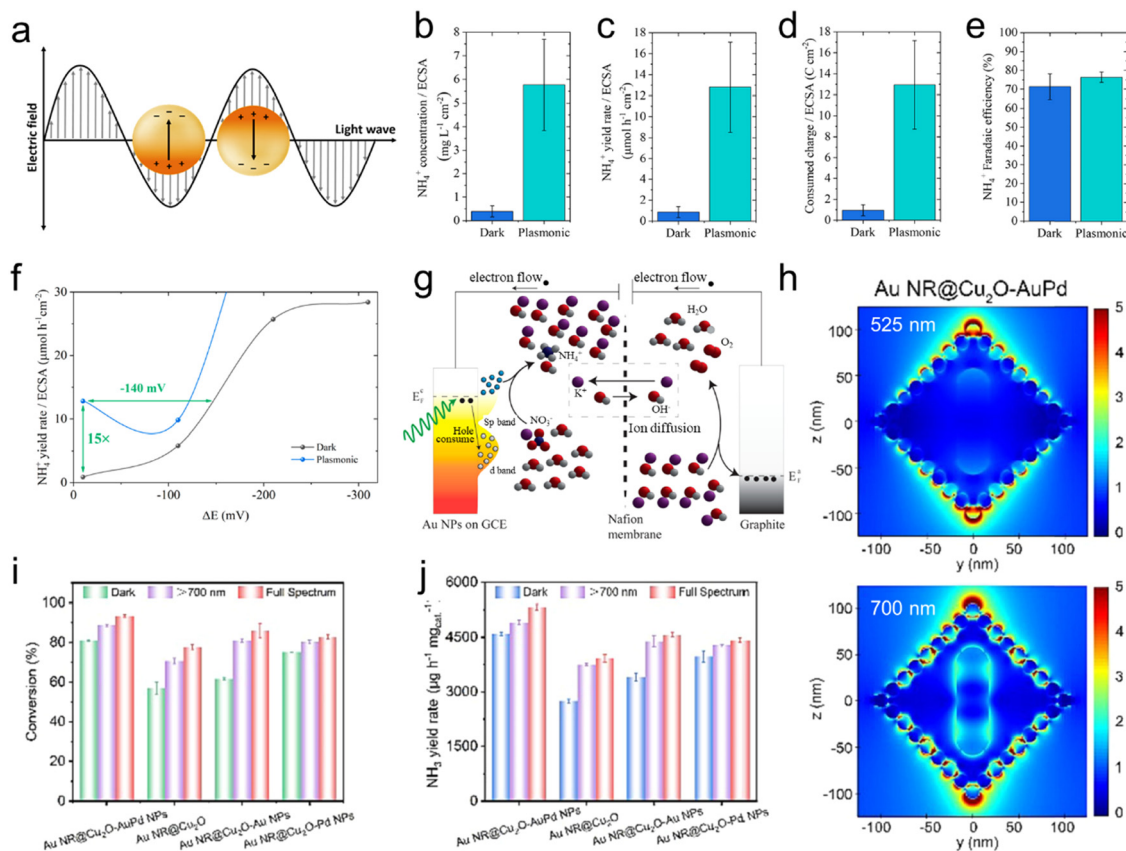


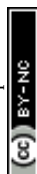
**Fig. 8** (a) Schematic of LSPR. Reproduced with permission.<sup>107</sup> Copyright 2021, Springer Nature. (b)  $\text{NH}_4^+$  concentration, (c)  $\text{NH}_4^+$  yield rate, (d) consumed charge, and (e)  $\text{NH}_4^+$  faradaic efficiency obtained in the dark and under 532 nm light irradiation. (f)  $\text{NH}_4^+$  yield rate at various  $\Delta E$  under different conditions. (g) Scheme of LSPR-assisted  $\text{NH}_4^+$  electrosynthesis. The working electrode in (b)–(g) is Au nanoparticles on a glassy carbon electrode. Reproduced with permission.<sup>39</sup> Copyright 2022, American Chemical Society. (h) The finite-difference time-domain (FDTD) simulated electric-field distribution on Au NR@ $\text{Cu}_2\text{O}$ –AuPd NPs. (i)  $\text{NO}_3^-$  conversion rate and (j)  $\text{NH}_3$  yield rate of different catalysts. Reproduced with permission.<sup>108</sup> Copyright 2024, Elsevier B.V.

energy harvesting, active sensing, and self-powered systems. This generated potential can facilitate the transfer of electrons and holes towards the material's surface, leading to the development of catalytic research based on the mechanical-to-chemical energy conversion using piezoelectric materials.<sup>114</sup>

The concept of piezoelectric catalysis is depicted in Fig. 9a. When subjected to external forces, piezoelectric materials generate an internal electric field because of spontaneous polarization. This electric field facilitates the separation of carriers towards the material's surface, thereby facilitating redox on the active sites. By adjusting external stress, such as controlling the frequency and power of the stress, both the orientation and strength of polarization can be manipulated. This dynamic regulation of surface properties has potential for the catalytic process. Research efforts have explored leveraging piezoelectric polarization to drive a series of catalytic processes, including water splitting, pollutant degradation,  $\text{CO}_2$  adsorption/reduction, and the selective transformation of organic compounds.<sup>115–118</sup> In our previous work, we utilized the piezoelectric effect of the electron-rich  $\text{BaTiO}_3$  (BTO-OV<sub>1</sub>) to promote the catalytic performance of metal nanoparticles in the  $\text{NO}_3\text{RR}$ .<sup>119</sup> After introducing stress stimuli, the contact state between metal nanoparticles and the BTO-OV<sub>1</sub> substrate was

modulated. The  $I$ – $V$  curves in Fig. 9b go from curves to straight lines as the pressure increases, which confirms the contact state was from Schottky contact to ohmic contact. The DFT calculations further demonstrated that the stress stimuli adjusts the local electron distribution and promotes the interaction between metal nanoparticles and BTO-OV<sub>1</sub> (Fig. 9c). Based on the experimental and computational results, we proposed the mechanism of this strategy (Fig. 9d). After introducing stress stimuli, the contact state between metal nanoparticles and BTO-OV<sub>1</sub> was modulated due to the piezoelectric effect. Because of the difference in the work function, a large number of the electrons in BTO-OV<sub>1</sub> were transferred smoothly to the metal nanoparticles, which led to the generation of active hydrogen that participated in the hydrogenation process in the  $\text{NO}_3\text{RR}$ . The charge transfer also triggers the charge redistribution, suppressing the Volmer–Heyrovsky step of the competing HER. The optimized catalyst displays a superior faradaic efficiency of 95.3% and a yield rate of  $6.87 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$  for  $\text{NH}_3$  generation.

The piezoelectric polarization electric field triggered by stress stimuli also has the potential to assist photocatalysis. Chen and colleagues<sup>120</sup> synthesized a naphthalene-linked perylene diimide polymer (N-PDA) with rigidity and polarity for



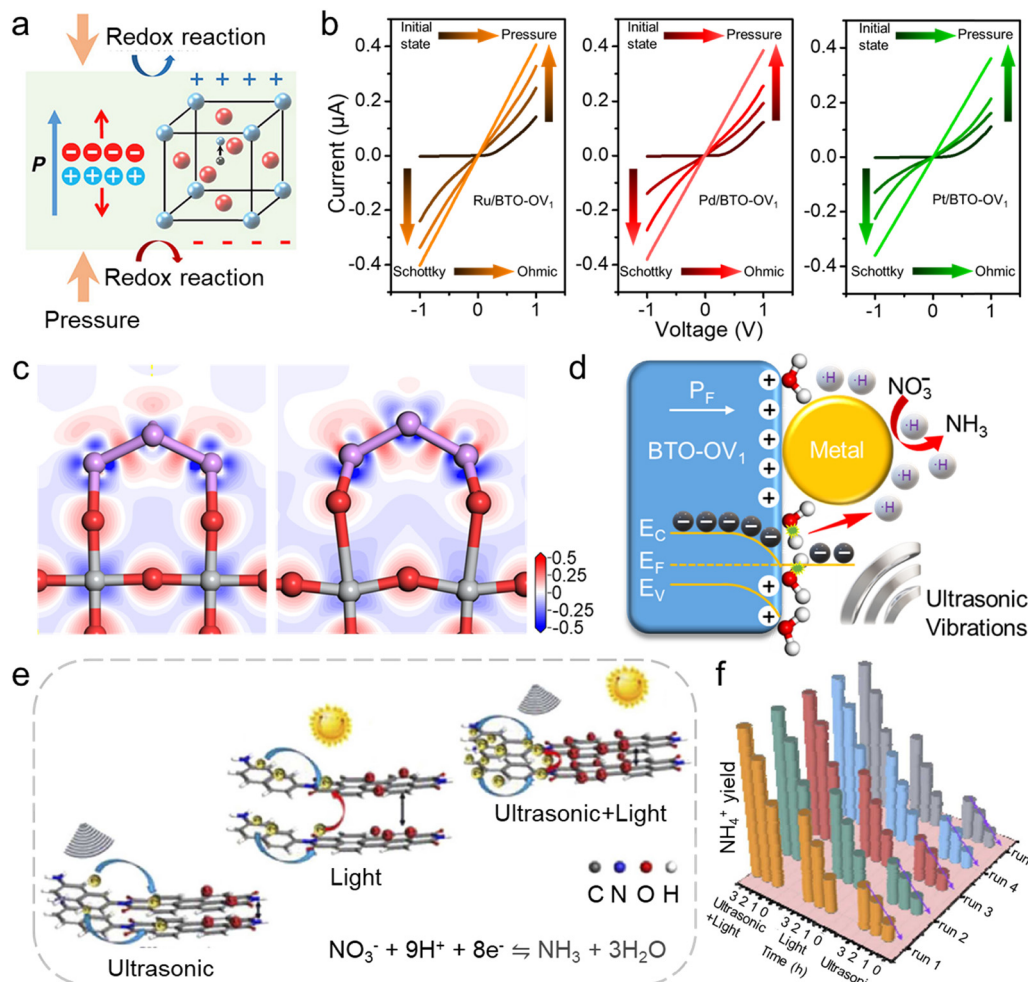


**Fig. 9** (a) Schematic of the piezoelectric catalysis. Reproduced with permission.<sup>115</sup> Copyright 2020, American Chemical Society. (b) *I*–*V* curves measured at different pressure using M/BTO-OV<sub>1</sub> (M = Ru, Pd, and Pt). (c) Electron density difference mappings obtained from Ru/BTO-OV<sub>1</sub> without (left) and with pressure (right). (d) Schematic diagram of piezoelectric-assisted electrochemical NO<sub>3</sub>RR. In (c) and (d), the red, gray, purple, and white balls represent O, Ti, Ru, and H atoms, respectively. Reproduced with permission.<sup>119</sup> Copyright 2023, Elsevier Ltd. (e) Schematic of charge transfer of N-PDA under various conditions. (f) NH<sub>4</sub><sup>+</sup> yield rate measured under different conditions. Reproduced with permission.<sup>120</sup> Copyright 2024, Elsevier B.V.

producing NH<sub>3</sub> from NO<sub>3</sub><sup>−</sup>. The stress stimuli triggers the piezoelectric polarization electric field of the catalyst, further facilitating the separation of photogenerated charge carriers and suppressing their recombination (Fig. 9e). The NH<sub>3</sub> production rate through piezo-photocatalysis exceeded the sum of the yield rates obtained by piezoelectric catalysis and photocatalysis, further confirming the promotion of the stress stimuli in the NO<sub>3</sub>RR (Fig. 9f).

#### 4.3. Thermal stimuli

Thermal catalysis primarily involves heating to provide the energy needed for catalytic reaction systems to overcome thermodynamic barriers, thus driving the conversion of reactants into products.<sup>121–124</sup> In catalysis, electrons are typically driven and facilitated to transfer through electrical work under an applied voltage. Nevertheless, in steps except for electron transfer, the electric potential may not effectively influence the thermodynamics of the reaction. Introducing thermal

stimuli offers a promising strategy for adjusting reaction thermodynamics, and the overpotential arising from kinetic barriers exceeding thermodynamic barriers can also be regulated through the thermal stimuli.<sup>125</sup> In the NO<sub>3</sub>RR involving multi-PCET, electron transfer can be modulated through electrochemical methods. However, the proton transfer steps in the hydrogenation process cannot be controlled by the electric potential. Therefore, the introduction of thermal stimuli presents a promising approach for synergistically regulating both electron and proton transfer processes.

Yu and colleagues<sup>125</sup> dispersed Ni on a Cu substrate to prevent the accumulation of localized active hydrogen, synthesizing Ni-decorated Cu single-atom alloy oxide nanowire (Ni<sub>1</sub>Cu SAAO NW) to suppress the competing HER in NH<sub>3</sub> production from NO<sub>3</sub><sup>−</sup>. While inhibiting side reactions by enhancing the active hydrogen coverage, merely applying voltage alone cannot promote proton transfer in the hydrogenation process effectively. Therefore, they introduced thermal stimuli to facilitate



the conversion of  $\text{NO}_3^-$  (Fig. 10a), enhance water molecule dissociation, and reduce the energy barrier in the reaction. Compared with  $\text{Cu}_2\text{O}$  NWs under room temperature,  $\text{Ni}_1\text{Cu}$  SAAO NWs exhibited significantly enhanced activity and selectivity in alkaline electrolytes at 60–80 °C (Fig. 10b and c). As shown in Fig. 10d, even at 0.1 V vs. RHE, the faradaic efficiency of  $\text{NH}_3$  production and temperature showed a positive correlation, increasing from 34.6% at 25 °C to 79.8% at 80 °C, with an  $\text{NH}_3$  yield rate of  $9.7 \text{ mg h}^{-1} \text{ cm}^{-2}$ . In contrast, with increasing temperature,  $\text{Cu}_2\text{O}$  NWs showed only limited improvement in faradaic efficiency. Furthermore, Fig. 10e illustrates the performance of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  conversion at different temperatures. With increasing temperature,  $\text{Ni}_1\text{Cu}$  SAAO NWs demonstrated a gradual decrease in  $\text{NO}_2^-$  faradaic efficiency and yield rate, indicating that introducing thermal stimuli promoted the conversion of  $\text{NO}_3^-$  to  $\text{NH}_3$ . Conversely,  $\text{Cu}_2\text{O}$  exhibited a noticeable increase in  $\text{NO}_2^-$  yield with increasing temperature, maintaining a relatively high level of  $\text{NO}_2^-$  faradaic efficiency.

This suggests that introducing thermal stimuli also promoted the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  on  $\text{Cu}_2\text{O}$  NWs, but the relatively weak hydrogen affinity of  $\text{Cu}_2\text{O}$  NWs limited further performance enhancement.

Singh and colleagues<sup>126</sup> compared the thermal catalytic and electrocatalytic mechanisms of Pt/C, PtRu/C, and  $\text{Pt}_{75}\text{Ru}_{25}/\text{C}$  under different electrochemical reaction parameters, demonstrating the promoting effect of thermal stimuli in  $\text{NH}_3$  production from  $\text{NO}_3\text{RR}$ s. They proposed that increasing the hydrogen (electro)chemical potential could enhance the conversion rate of  $\text{NO}_3^-$  (Fig. 10f). Furthermore, changes in pH significantly influenced the reaction performance of thermal catalysis and electrocatalysis in synthesizing  $\text{NH}_3$  (Fig. 10g). The  $\text{NH}_3$  yield rate of PtRu/C *via* thermal catalysis and electrocatalysis was also compared with industrial Haber–Bosch processes regarding rate and cost. As shown in Fig. 10h, the results indicated that the  $\text{NH}_3$  yield rate of PtRu/C under pH = 1 was comparable to the Haber–Bosch process, with lower standard costs per ton of  $\text{NH}_4\text{NO}_3$  consumed.

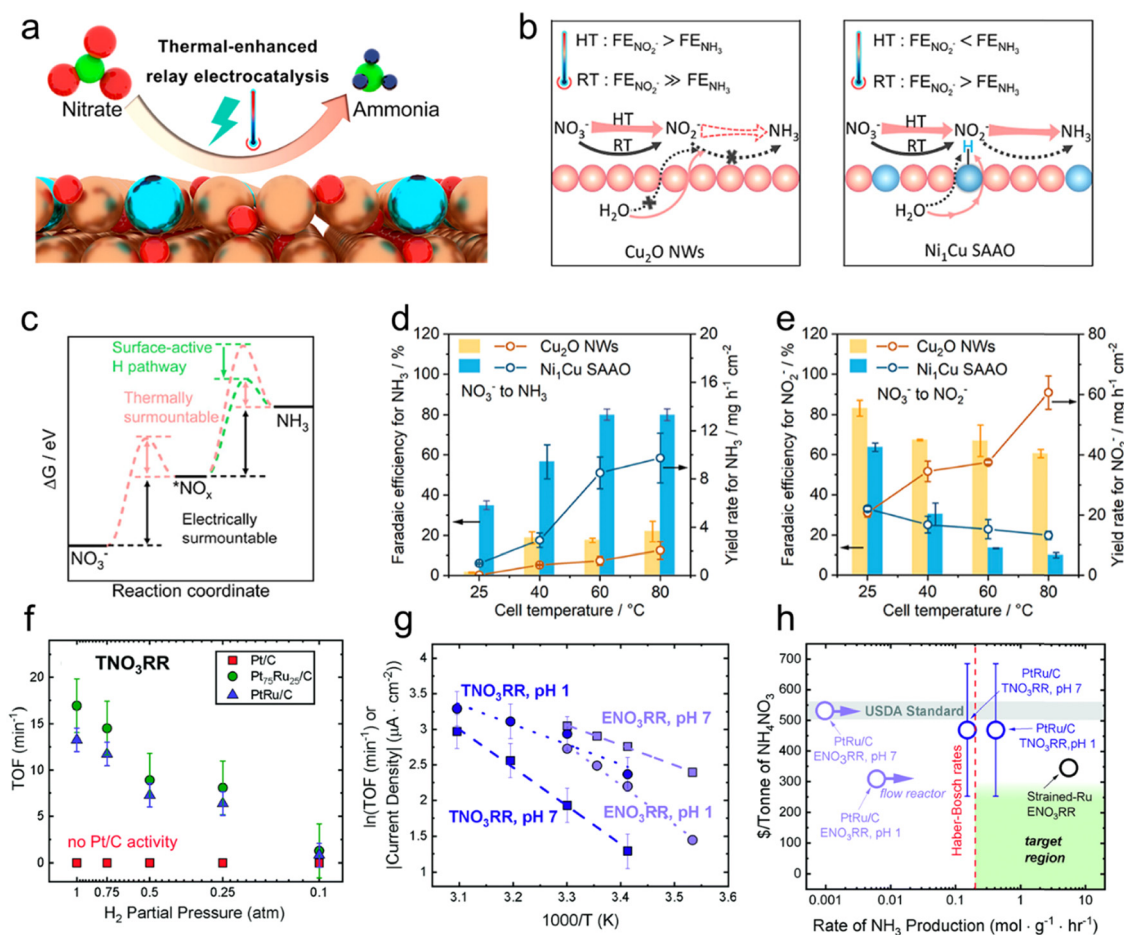


**Fig. 10** (a) Thermal-assisted electrocatalysis  $\text{NO}_3\text{RR}$ s on  $\text{Ni}_1\text{Cu}$  SAAO NWs. (b) Mechanism diagram of the  $\text{NO}_3\text{RR}$  at different temperatures using  $\text{Ni}_1\text{Cu}$  SAAO and  $\text{Cu}_2\text{O}$  NWs. HT, RT, and FE are high temperature, room temperature, and faradaic efficiency, respectively. (c) The energy barrier overcome by thermally boosted electrocatalysis and surface-active hydrogen during  $\text{NO}_3^-$  reduction on  $\text{Ni}_1\text{Cu}$  SAAO. Faradaic efficiency and yield rate for (d)  $\text{NH}_3$  and (e)  $\text{NO}_2^-$  production at different temperatures using  $\text{Ni}_1\text{Cu}$  SAAO and  $\text{Cu}_2\text{O}$  NWs at 0.1 V vs. RHE. Reproduced with permission.<sup>125</sup> Copyright 2024, American Chemical Society. (f) The activity of various catalysts in thermocatalytic  $\text{NO}_3\text{RR}$  at different  $\text{H}_2$  partial pressures in pH 7 solution with 0.1 M  $\text{NaNO}_3$ . (g) Arrhenius plots of PtRu/C for thermocatalytic and electrocatalytic  $\text{NO}_3\text{RR}$ s. (h) The cost per tonne of  $\text{NH}_4\text{NO}_3$  in thermocatalytic and electrocatalytic  $\text{NO}_3\text{RR}$ s vs.  $\text{NH}_3$  yield rate. Reproduced with permission.<sup>126</sup> Copyright 2021, Royal Society of Chemistry.



## 5. Conclusion and outlook

In this review, we comprehensively summarized strategies involving a built-in electric field and external stimuli to enhance the performance of the NO<sub>3</sub>RR for NH<sub>3</sub> production. The approach of introducing built-in electric fields includes the construction of Mott–Schottky heterojunctions, semiconductor–semiconductor heterojunctions, modulation of coordination structures for active sites, and the construction of double layers. Additionally, the external stimuli modulation strategies such as introducing optical, stress, and thermal stimuli for enhancing NH<sub>3</sub> production *via* NO<sub>3</sub>RR were also summarized. Thoughtful design of built-in electric fields and external stimuli can effectively boost both the activity and selectivity of NH<sub>3</sub> production, with the potential to address energy crises and environmental pollution simultaneously. However, due to limited characterization techniques and design strategies, such modulation in the NO<sub>3</sub>RR still faces significant challenges.

(1) Designing advanced characterization techniques to elucidate the specific roles of built-in electric field and external stimuli is crucial. For instance, introducing optical stimuli triggers the LSPR effect, generating high-energy hot electrons and holes and strong electric fields. However, distinguishing and quantifying the contributions of high-energy hot electrons and electric fields to catalytic reactions is challenging. Similarly, in semiconductor photocatalysis, light illumination induces the generation of carriers, accompanied by localized temperature changes on the electrode surface. Understanding the varying degrees of contribution from different enhancement mechanisms to catalysis facilitates the design of more efficient strategies to enhance catalytic efficiency.

(2) Developing *in situ* testing techniques is crucial for reactions involving built-in electric fields and external stimuli. Catalytic processes primarily occur on the catalyst surface, where such modulation can influence the adsorption and activation of reactants and intermediates, as well as control product distribution. *In situ* testing with built-in electric field/external stimuli participation can deepen the understanding of how they regulate catalytic processes. Catalytic reactions can be monitored in real-time, allowing observation of intermediate species behavior and changes in reaction kinetics. In short, developing *in situ* testing techniques will be pivotal in propelling the NO<sub>3</sub>RR, offering real-time insights into reaction mechanisms, catalyst performance, and reaction dynamics. This progress will aid in designing enhanced and environmentally friendly NH<sub>3</sub> synthesis procedures.

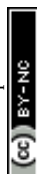
(3) Optimize the methods of introducing external stimuli. For instance, stress stimuli are introduced primarily through ultrasonic waves. Nonetheless, it is vital to adjust catalyst structures and investigate approaches that make materials more responsive to external influences, allowing the piezoelectric effect to be activated by natural stimulation like water flow or wind pressure. Utilizing these natural disturbances augments the applicability of piezoelectric catalysis for enhancing NH<sub>3</sub> production efficiency. Moreover, as a distinctive piezoelectric material, ferroelectric materials possess inherent polarization, creating an internal electric field that originates from the collective polarization effect formed by

the spontaneous alignment of electric dipoles. Pre-treating ferroelectric materials and introducing electric fields to facilitate the NO<sub>3</sub>RR for NH<sub>3</sub> synthesis could also be an effective approach.

(4) Designing cost-effective catalysts in NH<sub>3</sub> production. For instance, using noble metals as the electrode material increases the cost of the NO<sub>3</sub>RR in LSPR-assisted NH<sub>3</sub> production. Therefore, developing non-noble metal alternatives and designing effective strategies to amplify their LSPR effects and utilize high-energy hot electrons and strong electric fields to enhance NH<sub>3</sub> synthesis is crucial for reducing the cost associated with this approach. One promising avenue is the exploration of plasmonic nanostructures composed of non-noble metals, such as Cu and Al. These materials also possess unique plasmonic properties that can be harnessed to enhance the NO<sub>3</sub>RR. By precisely tailoring the size, shape, and composition of these nanostructures, it is possible to tune their LSPR to the desired wavelength range for efficient NH<sub>3</sub> synthesis. Additionally, synergistic coupling of LSPR with other catalytic mechanisms can further enhance the efficiency of NH<sub>3</sub> synthesis. Integrating non-noble metal plasmonic nanostructures with suitable cocatalysts or semiconductors makes it feasible to harness the high-energy hot electrons generated during LSPR excitation and leverage the strong electric fields for selective and efficient NH<sub>3</sub> production. Developing cost-effective strategies for LSPR-assisted NH<sub>3</sub> synthesis using non-noble metals is essential for realizing sustainable and economically viable NH<sub>3</sub> production processes. Continued research in this direction has great promise for reducing the overall cost and improving the scalability of LSPR-based NH<sub>3</sub> synthesis technologies.

(5) In the research on regulating the NO<sub>3</sub>RR to produce NH<sub>3</sub> through built-in electric field/external stimuli, exploring the coupling of multiple field/stimuli to enhance NH<sub>3</sub> production performance has significant importance and promising prospects. A variety of built-in electric fields, produced by Mott–Schottky heterojunctions, semiconductor–semiconductor heterojunctions, coordinated active site environments, and electrical double-layer modulation, along with external stimuli, including optical, stress, and thermal stimuli, can synergistically enhance one another when introduced simultaneously. This synergy influences the reaction kinetics and site activity, ultimately enhancing the efficiency of NH<sub>3</sub> production. Indeed, in the reaction of water splitting, studies have utilized the electric field generated by stress stimuli to further enhance the effective separation of photogenerated carriers, synergistically promoting reaction kinetics with the photogenerated electric field. In conclusion, by developing the combined effects of various field/stimuli, precise control over the catalytic process can be achieved, leading to improved performance in NH<sub>3</sub> production.

(6) Developing theoretical computations is pivotal for designing rational strategies to modulate catalytic reactions using built-in electric field/external stimuli. Current theoretical models still exhibit significant discrepancies between simulating fields and actual systems, posing substantial challenges in designing built-in electric field/external stimuli-assisted reaction strategies. Therefore, optimizing theoretical methods to more precisely predict the atomic configurations and band



structures of catalysts may obtain catalysts with higher performance. Meanwhile, tailored theoretical models can be explored for different fields to accurately assess the impact of built-in electric field/external stimuli on enhancing the performance of the NO<sub>3</sub>RR for NH<sub>3</sub> synthesis from a theoretical perspective, elucidating their mechanisms. Machine learning can be employed to establish correlations between various built-in electric field/external stimuli and catalytic activity and selectivity, facilitating the identification of more suitable strategies.

(7) Developing stable catalysts. Stability is a crucial metric for evaluating catalyst performance. By designing catalysts with structural stability and employing methods to regulate the catalyst microenvironment for extending the catalyst's lifespan, there is potential to better adapt to external stimuli and to carry out NO<sub>3</sub>RRs for NH<sub>3</sub> production under varying pH environments. Furthermore, common stability tests often consist of only a few dozen or even just a few cycles, which may not adequately reflect the catalyst's stability. Extending stability tests for longer durations until performance degradation occurs can help explore the catalyst's limit of stability, enabling rational design of the catalyst. Moreover, enhancing the stability of catalysts through strategic approaches can significantly increase their potential for industrial applications.

(8) A well-designed reactor effectively achieves high performance in reducing NO<sub>3</sub><sup>−</sup> to produce NH<sub>3</sub>. One potential direction for future research is introducing a flow cell system into the NO<sub>3</sub>RR. The flow cells allow for continuous and controlled flow of reactants, enhancing mass transfer and improving reaction kinetics. This may lead to higher conversion rates and improved selectivity of electrochemical systems. Additionally, using flow cells enables better control of reaction conditions such as temperature, pressure, and flow rate, which is conducive to introducing external stimuli. Moreover, integrating flow cells can facilitate online monitoring and characterization techniques. This real-time monitoring capability can provide deeper insights into reaction kinetics, offering valuable insights for process optimization and catalyst design. Furthermore, flow cell systems can be easily scaled up for industrial applications, making it a promising approach for large-scale electrochemical NH<sub>3</sub> synthesis. In conclusion, the application of flow cells in the NO<sub>3</sub>RR has the potential for improving reaction kinetics, better control of reaction conditions, enhanced online monitoring capabilities, and scalability for industrial implementation. Further research and development in this area will contribute to the advancement of efficient and practical NH<sub>3</sub> production technologies.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

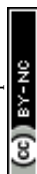
There are no conflicts of interest to declare.

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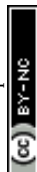
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