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ammonia



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## Recent advances in electrocatalytic NO<sub>x</sub> reduction into ammonia

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Ammonia (NH<sub>3</sub>) is an essential ingredient for the production of numerous chemicals which have a wider usage as fertilizers, explosives, and plastics. Currently, NH<sub>3</sub> is mainly produced from the conventional Haber–Bosch process, which is energy-consuming and involves the risk of emitting greenhouse gases into the atmosphere. In contrast, electrochemical ammonia synthesis (EAS) from the nitrogen reduction reaction is evolving as a viable solution for sustainable NH<sub>3</sub> production under ambient conditions. However, the high N≡N dissociation energy and the competitive hydrogen evolution reaction result in an unsatisfactory ammonia yield rate and Faradaic efficiency. In this regard, EAS from reactive nitrogen (NO<sub>x</sub>) species, especially through the nitric oxide reduction reaction (NORR), could be a sustainable way as it produces valuable NH<sub>3</sub> and simultaneously mitigates the gaseous NO<sub>x</sub> pollutant. Various NORR electrocatalysts have been designed and investigated. The electrocatalytic activity hugely depends on the composition, Gibbs free energy for 'NO' or intermediate adsorption on the catalyst surface, and the rate of proton/electron transfer at the solid–liquid–gas interface. Besides, different electrolyte additives have been employed to improve the solubility of NO in aqueous electrolytes. Thus, this review presents an overview of the NORR mechanism, recent advancements in electrocatalysts, and factors influencing the NH<sub>3</sub> yield and selectivity. After that, the forthcoming challenges associated with practical realisation of EAS via NORR are discussed.

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### Broader context

Recently, electrochemical ammonia synthesis (EAS) has drawn significant attention for replacing the energy consuming and environmentally polluting Haber–Bosch process. In this context, the electrochemical nitrogen reduction reaction (NRR) is considered to be a viable solution for sustainable NH<sub>3</sub> production under ambient conditions. However, the high N≡N dissociation energy and the competitive hydrogen evolution reaction cause challenges to attain satisfactory ammonia production with good selectivity. Meanwhile, the nitric oxide (NO<sub>x</sub>) pollutant could be an alternative N-source for EAS as it possesses low N=O bond dissociation energy and a distinctive reduction potential (0.71 V vs. RHE). To catalyze the electrochemical nitric oxide reduction reaction (NORR), the development of suitable catalysts with good catalytic activity and product (NH<sub>3</sub>) selectivity is highly desirable. Hence, the scientific community has attempted to design and develop various electrocatalysts and evaluate their performance towards the NORR. The electrocatalytic activity of the materials is found to be dependent on the composition, Gibbs free energy for 'NO' or intermediate adsorption on the catalyst surface, and the rate of proton/electron transfer at the solid–liquid–gas interface. Besides, the addition of 'NO' complexing agents into an aqueous electrolyte is found to increase the solubility of 'NO', thereby enhancing the ammonia production rate. Although the developed catalysts show considerable NH<sub>3</sub> yield rates, there is still a necessity to develop efficient and earth-abundant catalysts for practical NH<sub>3</sub> production. Hence, we present this Review article to give an overview of the NORR mechanism, recent advancements in the electrocatalysts, and factors influencing the NH<sub>3</sub> yield and selectivity. Furthermore, the key issues related to the efficient electroreduction of NO to NH<sub>3</sub> are described.

## Introduction

The thirst for energy keeps expanding with the growing technological society of humankind in this modern era.<sup>1</sup> The rise in

the human population, urbanization, and industrial activities increases the energy demand worldwide.<sup>2–6</sup> This huge energy demand results in the over-exploitation of fossil fuels and causes a surge in carbon and greenhouse gas (GHG) emissions. These emissions trap the thermal radiation in the earth's atmosphere, raise the global temperature, and cause climate change.<sup>7</sup> Thus, the energy crisis leads to domino effects related to global warming and accelerated climate change.<sup>8</sup>

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With reference to the U.S. Energy Information Administration (EIA) data in 2021, the transportation sector utilizes around 28% of the total energy consumption of the U.S., which is mainly derived from fossil fuels.<sup>9</sup> In the transportation sector, maritime transport controls 90% of global goods trading, accounting for 3.1% of global CO<sub>2</sub> emissions.<sup>10,11</sup> To mitigate environmental pollution, the Intergovernmental Panel on Climate Change (IPCC) formed a crucial strategy of decarbonizing the transport sector to reach the goals of the Paris climate change agreement to limit global temperature raise within 1.5 °C of pre-industrial levels.<sup>12,13</sup> Therefore, the International Maritime Organization (IMO) set several checkpoints to complete the decarbonization of maritime transportation. The IMO GHG strategy sets out to reduce CO<sub>2</sub> emission per transport work by up to 40% by 2030 and 70% by 2050 as of 2008 emission levels.<sup>14,15</sup> Utilizing zero-

carbon fuels in marine transport is the key strategy of IMO to meet the aims of the GHG strategy. Ammonia has attracted everyone's attention as a potential zero-carbon fuel for maritime transport and has been applied in direct ammonia fuel cells and solid oxide fuel cells (SOFCs).<sup>16,17</sup> Compared with liquid hydrogen (8.5 MJ L<sup>-1</sup>), ammonia possesses a high energy density of 12.7 MJ L<sup>-1</sup>.<sup>18</sup> Moreover, storing ammonia at -33 °C with less energy consumption for storage is more convenient, whereas hydrogen needs a cryogenic condition of -235 °C.<sup>19,20</sup> With these considerations, many researchers foresee ammonia as a potential decarbonization fuel for heavy transportation like maritime transport.<sup>21-24</sup>

Besides, ammonia (NH<sub>3</sub>) is a crucial substance for various industries to produce fertilizers, medicines, refrigerants, explosives, and pesticides. Thus, NH<sub>3</sub> is extensively produced from a



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well-established very old Haber–Bosch Process (HBP).<sup>25</sup> However, the ammonia produced by the conventional HBP is not a green commodity. The required hydrogen feedstock for the HBP is exclusively extracted from fossil fuels by steam methane reforming or coal gasification processes. Thus, the HBP consumes 2% of global fossil fuel usage. As the HBP depends on the fossil fuel for the H<sub>2</sub> source, it is not a sustainable and greener process. The ammonia production by the energy consuming HBP currently accounts for 2% of global energy consumption and 1.4% of global CO<sub>2</sub> emission (carbon emission during gas extraction is excluded).<sup>21,26</sup> Therefore, the decarbonization of ammonia production will decarbonize the energy, transportation, and chemical sectors so that the effects of GHG emissions and climate change can be controlled. MacFarlane *et al.* pointed out that the ammonia industry's decarbonization will occur in three phases, with different technologies.<sup>21</sup> As shown in Fig. 1, today the “grey ammonia” is exclusively produced from fossil fuels with the enormous release of CO<sub>2</sub> into the environment. Therefore, the first generation will utilize carbon capture and storage technology to capture all the CO<sub>2</sub> emissions from HBP (and SMR) to produce “purple ammonia”. The second generation will produce “blue

ammonia” or “renewable ammonia”. At this stage, the HBP will be electrified with renewable energy and the hydrogen feedstock will be switched from fossil resources to green hydrogen produced by water electrolysis. Eventually, in the third generation, the HBP will no longer be needed as the renewable energy-assisted electrochemical reduction of the N-source and the H-source from water will be commercialized to produce “sustainable ammonia” or “green-ammonia”.

The energy-intensive HBP is carried out under harsh conditions such as high temperature (300–500 °C) and high pressure (150–200 atm). Moreover, each pass in the HBP results in only 15% conversion efficiency and it needs multiple passes to achieve a high conversion efficiency of 97%.<sup>27</sup> Therefore, it is a substantial challenge to develop alternative routes to produce NH<sub>3</sub> in a sustainable way. Recently, electrochemical NH<sub>3</sub> synthesis (EAS) through the nitrogen reduction reaction (NRR) has greatly attracted attention for the production of NH<sub>3</sub> under ambient conditions.<sup>28,29</sup> The electroreduction of N<sub>2</sub> to NH<sub>3</sub> only requires protons (H<sup>+</sup>) from water and the electricity drawn from renewable energy resources, and could be conducted under ambient conditions with no carbon emission.<sup>30–34</sup> However, the electrochemical ammonia yield from the NRR is unsatisfactory

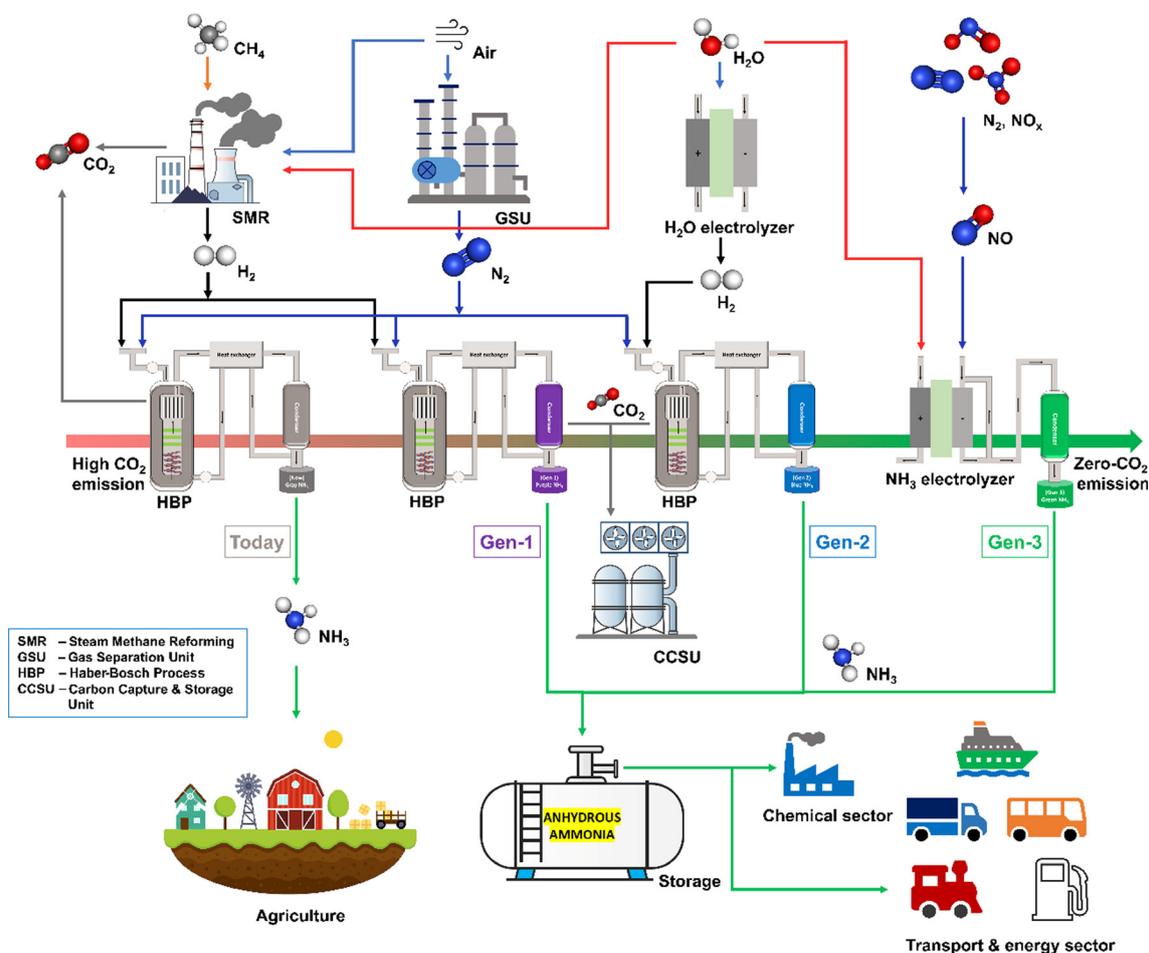
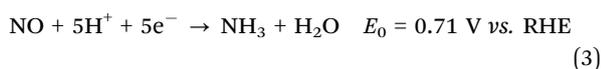
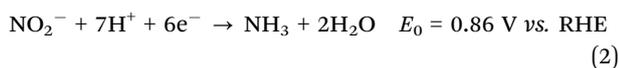
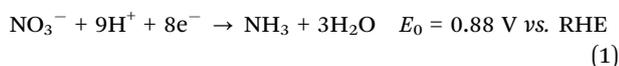


Fig. 1 Ammonia economy roadmap showing current and projected contributions of the current and Gen 1 (purple), Gen 2 (light blue), and Gen 3 (green) ammonia production technologies.



because of high  $\text{N}\equiv\text{N}$  bond dissociation energy, low polarizability, and limited solubility of electrolytes. In addition, the competitive hydrogen evolution reaction (HER) in the NRR potential range (0.148 V vs. RHE) is another bottleneck to attaining high  $\text{NH}_3$  Faradaic efficiency.<sup>30,35</sup> In contrast to  $\text{N}_2$ , nitric oxide (NO) is partly active due to its lower bond energy ( $\text{N}=\text{O}$  607  $\text{kJ mol}^{-1}$ ,  $\text{N}\equiv\text{N}$  941  $\text{kJ mol}^{-1}$  at 25 °C).<sup>36</sup> The electronic structure of NO containing unpaired electrons and the lower energy of its  $2\pi^*$  orbital make it noticeably polar and reactive to undergo electrochemical reactions.<sup>37</sup> NO possesses a positive electron affinity (0.024 eV) and a lower ionization potential (9.2 eV) compared to molecular  $\text{N}_2$  (−1.9 eV and 15.8 eV, respectively), allowing it to be more readily active toward redox reactions.<sup>38,39</sup> Moreover, the standard reduction potential for NO to  $\text{NH}_3$  is about 0.71 V vs. RHE, which is advantageous to attain a high  $\text{NH}_3$  yield along with high Faradaic efficiency.<sup>40,41</sup>

Besides, groundwater pollutants (such as  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ) have also been used as reactive nitrogen species for EAS. Meanwhile, this process could be a promising alternative to biological denitrification and physical separation processes for removing nitrate ions from wastewater.<sup>42</sup> Despite the electroreduction of nitrogen species that could lead to the formation of various products such as  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{NH}_2\text{OH}$ , the thermodynamic potentials for  $\text{NH}_3$  production are as follows:<sup>41,43</sup>



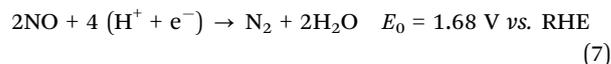
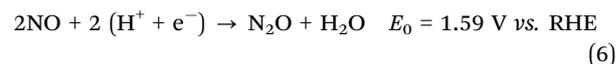
The EAS by the electroreduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  is a more energy consuming and complex process compared with the NRR and NO reduction reaction (NORR) owing to the involvement of more number of electrons in the former (*i.e.*,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  electroreduction requires 8 and 6 electrons, whereas the NORR requires only 5 electrons).<sup>44–49</sup> In addition,  $\text{NO}_3^-/\text{NO}_2^-$  to  $\text{NH}_3$  production proceeds through the formation of ‘NO’ as a key intermediate.<sup>50,51</sup> Besides,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  electroreductions are liquid phase reactions, so it would require additional expenses and systems to separate the electrochemically synthesized  $\text{NH}_3$  from the electrolyte. In contrast, EAS through the NORR is advantageous for practical implementation as the NORR can be conducted in the gas phase using a membrane electrode assembly, and the present gas separation and liquefying units in HBP plants can be reused.

On the other hand, mitigating hazardous  $\text{NO}_x$  species from the atmosphere is a substantial challenge as it reacts with atmospheric oxygen and moisture to produce nitrous or nitric acid, which causes acid rain, smog, *etc.*<sup>52</sup> The current technology used to convert hazardous  $\text{NO}_x$  into harmless  $\text{N}_2$  is selective catalytic reduction (SCR), which uses valuable  $\text{NH}_3$  and  $\text{H}_2$  as reductants.<sup>53,54</sup> The SCR also requires high temperature and pressure application to reduce  $\text{NO}_x$  to  $\text{N}_2$ , which has no chemical use.

Thus, the development of efficient technologies to remove  $\text{NO}_x$  from the atmosphere is a substantial challenge. In this regard, the NORR into  $\text{NH}_3$ ,  $\text{N}_2$ , *etc.*, through renewable energy resources such as solar and wind, could be a viable and practical solution. Thus, electrochemical NORR to  $\text{NH}_3$  production is a kind of “kill two birds with one stone” strategy as it mitigates the  $\text{NO}_x$  pollutant and produces a value-added product. Additionally, as a potential alternative to the traditional HBP, NORR electrolysis will decarbonize the above-mentioned energy, transport, and chemical industries to save the global ecology. However, the practical implementation of this technology is hugely dependent on the development of efficient electrocatalysts that can catalyze the NORR at low overpotentials along with good product selectivity. Hence, this review provides an overview of the NORR mechanism, recent advancements in electrocatalyst development, and factors influencing the  $\text{NH}_3$  yield and selectivity. In addition, the associated challenges that still need to be addressed for the practical realization of EAS as an alternative to the HBP will be discussed.

## Mechanism of $\text{NO}_x$ reduction

The electrocatalytic NORR process can produce various products such as hydroxylamine ( $\text{NH}_2\text{OH}$ ), ammonia ( $\text{NH}_3$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), and nitrogen ( $\text{N}_2$ ) owing to the multi-electron coupled proton reactions. The thermodynamic potentials for the corresponding products are as follows:



In addition, hydrogen ( $\text{H}_2$ ) can be formed at more cathodic potentials (below 0 V vs. RHE). The product selectivity of the NORR is hugely dependent on the catalyst surface, applied potential, ‘NO’ coverage, *etc.* For instance, the NORR over nanostructured Pd/C has only produced  $\text{H}_2$ , while the PdCu/C catalyst has generated  $\text{N}_2$  as a main product (~68%) by forming  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  as side products.<sup>55</sup> Meanwhile, Cu exhibits higher selectivity towards  $\text{NH}_3$ .<sup>34</sup> Thus, the chemical composition and the electronic structure of the catalyst are the key to obtaining desirable products. Electrode potential also plays a significant role in product selectivity. Both theoretical and experimental studies on transition metal electrodes manifest that at more positive potentials (>0.3 V)  $\text{N}_2\text{O}$  forms as a main product, whereas  $\text{NH}_3$  can be generated along with  $\text{H}_2$  at more negative potentials.<sup>56</sup>  $\text{N}_2$  and  $\text{NH}_2\text{OH}$  products can be observed at the intermediate potential window. Besides, low ‘NO’ coverage over the catalyst surface preferentially produces single-N products ( $\text{NH}_3$ ,  $\text{NH}_2\text{OH}$ ), while high coverage leads to ‘NO’ dimerization resulting in the N–N coupled product ( $\text{N}_2$ ,  $\text{N}_2\text{O}$ ) formation.<sup>57</sup>

During the NORR, initially ‘NO’ adsorption on the catalyst surface occurs with different configurations such as N-end, O-



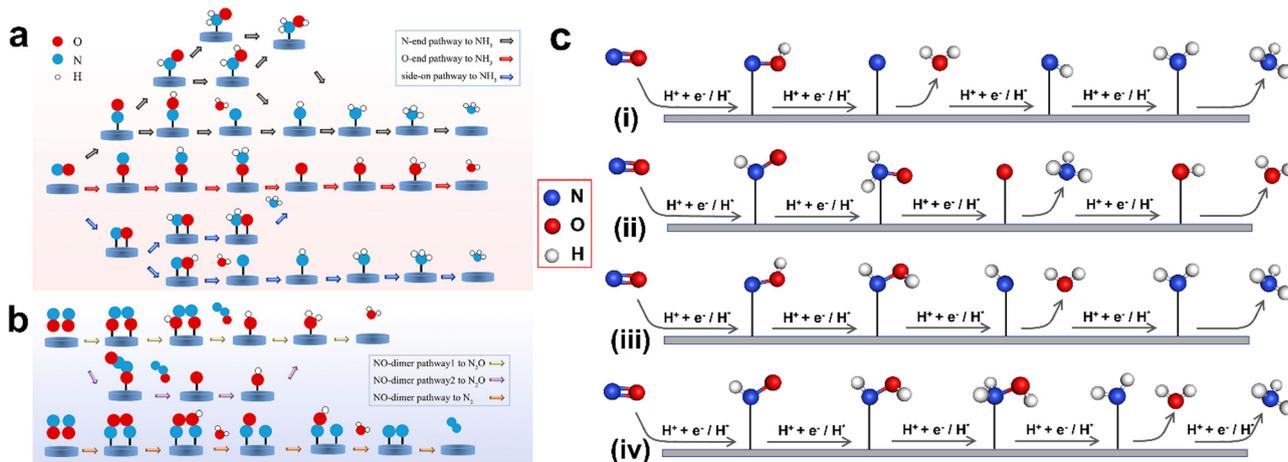
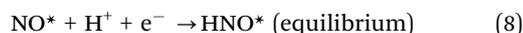


Fig. 2 (a) Schematic pathways of the NORR process toward NH<sub>3</sub> synthesis. (b) Schematic pathways of the NORR process toward N<sub>2</sub>O/N<sub>2</sub> synthesis. Reproduced with permission from ref. 67, copyright 2022, ACS. (c) Scheme of distal-O (i), distal-N (ii), alternating-O (iii), and alternating-N pathways (iv), which are all assigned to the associative mechanism. The H<sup>+</sup> + e<sup>-</sup> and H\* represent protons and adsorbed H\*, corresponding to the Heyrovsky and Tafel-type hydrogenation, respectively.

end, and side-on. The subsequent electron transfer leads to the formation of various reaction intermediates and products (Fig. 2). The 'NO' adsorption to NH<sub>3</sub> occurs *via* either a dissociative or associative pathway. In the dissociative pathway, the first step is splitting the N–O bond on the active site. Then, each adsorbed atom (N\* or O\*) will be hydrogenated separately to yield NH<sub>3</sub> and H<sub>2</sub>O. In the case of the associative pathway, both 'N' and 'O' atoms in the NO molecule will be protonated consequently to produce a 'H<sub>x</sub>NOH<sub>y</sub>' intermediate, which will eventually reduce to NH<sub>3</sub>. In both routes, the hydrogenation process proceeds *via* either the Tafel or Heyrovsky-type mechanism. In the former case, prior to the 'NO' hydrogenation, the solvated protons will be adsorbed onto the catalyst's surface to form H\*, whereas the hydrogenation of 'NO' molecules or the intermediates occurs directly on the catalyst surface in the latter case. Based on the type of hydrogenation, the dissociative and associative pathways are further divided into four categories, termed as dissociative-Tafel (D-T), associative-Tafel (A-T), dissociative-Heyrovsky (D-H), and associative-Heyrovsky (H-A) mechanisms.<sup>34</sup> Furthermore, the associative mechanisms are classified into distal-O, distal-N, alternating-O, and alternating-N pathways. In the distal pathway, one of the two atoms (N or O) in NO will be completely hydrogenated to produce NH<sub>3</sub> or H<sub>2</sub>O. Thereafter, O\* or N\* will undergo the hydrogenation process. In contrast, both N and O atoms undergo alternative hydrogenation steps in the alternating pathway.

Due to the involvement of multi-electron transfers, there are numerous varieties of mechanisms, intermediates, and rate-determining steps proposed for the NORR in the literature. The mechanistic studies are initially performed on the Pt surface in an aqueous electrolyte using various techniques such as voltammetry, *in situ* infrared spectroscopy, and online mass spectroscopy.<sup>37,58,59</sup> Earlier, Colucci *et al.* suggested that continuous NO reduction occurs through the rate-determining step (RDS) of NO\* + H<sup>+</sup> + e<sup>-</sup> → NOH\*.<sup>60</sup> After that, Gootzen *et al.* demonstrated the involvement of the NO dissociation step

(NO\* → N\* + O\*) in the mechanism.<sup>61</sup> Meanwhile, the adsorbate reduction (NO adsorbed onto the Pt electrode) and continuous reduction (NO saturated electrolyte) products of the NORR are found to be different. Later, Vooy's *et al.* clarified the mechanistic pathways in both scenarios with the help of kinetic parameters and product selectivity by utilizing the potential, pH, NO surface coverage, and the effect of supporting electrolytes as variables.<sup>58</sup> During the adsorbate NO reduction in an acidic medium, NH<sub>3</sub> is predominantly formed, whereas the continuous NO reduction yields N<sub>2</sub>O and NH<sub>3</sub> products at above and below 0.4 V, respectively. The similar Tafel slope observed for the first two reduction peaks in adsorbate NO reduction indicates that the first proton-coupled electron transfer is in electrochemical equilibrium, and NH<sub>3</sub> will be generated through the N–O bond breaking after the RDS, as given below.



At below 0.4 V, the continuous NO reduction also produces the NH<sub>3</sub> in a similar mechanistic pathway. Above 0.4 V, N<sub>2</sub>O is produced through the dimerization of NO\* with the 'NO' present in the solution. In another report, Rosca *et al.* proposed that the NORR mechanism on Pt (100) follows the NO → HNO\* → NH\* + O\* → NH<sub>3</sub> + H<sub>2</sub>O pathway, in which HNO\* → NH\* + O\* is the RDS.<sup>59</sup> Thereafter, several DFT studies were also carried out to attempt to understand the exact mechanism over the Pt surface.<sup>62–64</sup> However, the conclusive mechanism could not be derived as the kinetic barriers were not considered in these studies.<sup>65</sup>

Besides Pt, the NORR mechanism was studied on various transition metals such as Pd, Rh, Ru, Ir, and Au.<sup>66</sup> Except Au, all the metals showed high selectivity towards N<sub>2</sub>O and NH<sub>3</sub> at more positive and negative potentials, respectively, like Pt. The similar onset potentials of all metals indicate that the N<sub>2</sub>O



formation occurs through a common mechanism, while the various Tafel slopes manifest the different RDSs over metal surfaces. This could be most likely due to the shift in the occurrence of the first electron-transfer step during the catalytic process. Among all the metals, Pd is found to be the most active catalyst for selective  $N_2$  formation *via* the  $N_2O$  intermediate. However, the NO to  $NH_3$  mechanism over these metals is still unclear.

Recently, several DFT studies attempted to correlate the NORR activity of various metals by using the adsorption energies of  $*NO$  and  $*N$  intermediates as descriptors.<sup>43,67,68</sup> Furthermore, to understand the selectivity of  $NH_3$  formation over  $H_2$ , the adsorption energy of  $*H$  is also considered. As shown in Fig. 3a, metals present on the left of the vertical line (Pt and Pd) show higher binding ability towards both  $*NO$  and  $*H$ , leading to dominant  $H_2$  production below 0  $V_{RHE}$ . The  $NH_3$  formation over the metals located above the horizontal line (Ag and Au) is limited due to the weak binding of  $*NO$ . Meanwhile, Cu shows selective binding towards  $*NO$  over  $*H$ , thereby indicating ideal catalytic behavior towards  $NH_3$  formation.<sup>43</sup> Furthermore, the limiting potential *vs.* adsorption energy of  $*N$  plot shows that Cu is located on the weak binding side. Cu is predicted to follow the distal-O pathway to produce  $NH_3$ , and the rate-limiting step is  $*NO \rightarrow *NHO$  (Fig. 3b). The limiting potential of 'Cu' can be reduced by adjusting the metal surface with a slightly negative adsorption energy (not higher than  $-1.5$  eV) of  $*N$ . Besides, the DFT studies performed on different metal compounds predicted that the  $NH_3$  formation occurs through various mechanistic pathways, intermediates, and RDSs.<sup>54,69</sup> In transition metal compounds, the significant overlap between the metal d-orbitals and the  $\pi$  orbitals of NO is the primary criterion for the adsorption and activation of NO molecules through the "acceptance-donation" mechanism, *i.e.*, simultaneous depletion and accumulation of electron density in NO orbitals.<sup>54</sup> The above studies indicate that the NORR activity and product selectivity are determined by various parameters such as

the catalyst surface, operating potential, NO coverage, and hence, the favorable pathways and RDSs over the catalytic materials could differ.

## Electrocatalysts for the $NO_x$ reduction reaction (NORR)

Different classes of materials have been developed to investigate their electrocatalytic performance towards the NORR. Based on the chemical composition, the electrode materials can be classified into three categories: precious transition metal-based, non-precious transition metal-based, and p-block element-based electrocatalysts. Meanwhile, several attempts were made to identify the reaction intermediates and unveil the possible reaction mechanism of the NORR over the catalyst surfaces, which will guide the design and production of efficient electrocatalysts with good product selectivity. This section will briefly describe the materials and their catalytic activity in terms of overpotential, selectivity,  $NH_3$  yield rates, and Faradaic efficiency (FE). In addition, the efforts toward identifying reaction intermediates to understand the  $NO_x$  mechanism through computational and experimental studies will be discussed.

### 1. Precious transition metal-based electrocatalysts

Precious metals such as Pt, Pd, and Ru are renowned for numerous electrocatalytic applications owing to their high electronic conductivity and the ability to bind the various reaction intermediates on their polycrystalline surfaces.<sup>70</sup> Despite these metals being found to be active catalysts towards the NORR, the product selectivity is hugely varied as the catalytic surfaces possess different inherent Gibbs free energies for adsorption of  $NO^*$  and  $H^*$  intermediates. In the 20th century, the research was extensively focused on the mechanistic investigation of NORR activity over platinum surfaces. In contrast, the recent focus has shifted towards developing efficient electrocatalysts with abundant active sites, optimal Gibbs free energies for adsorption of intermediates

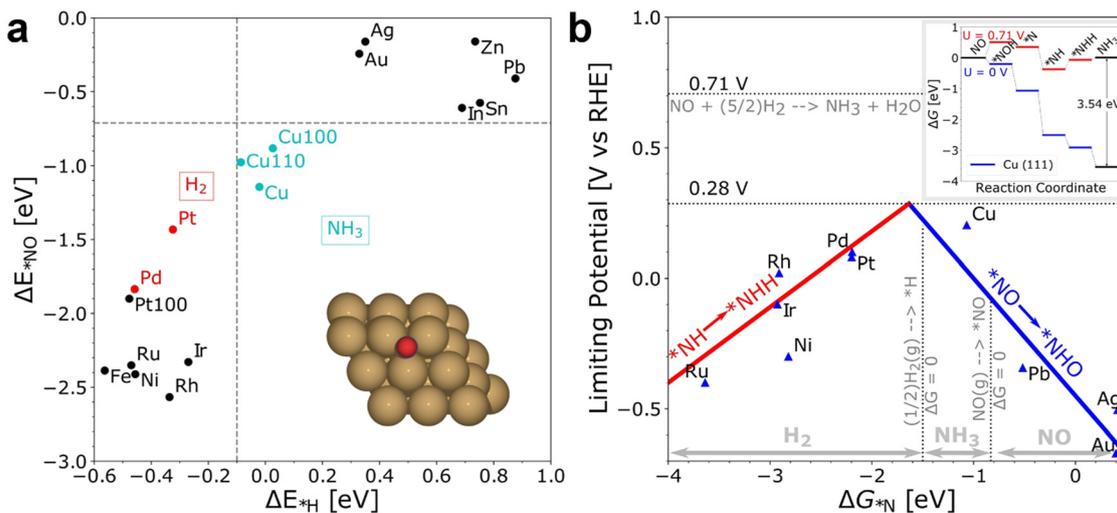


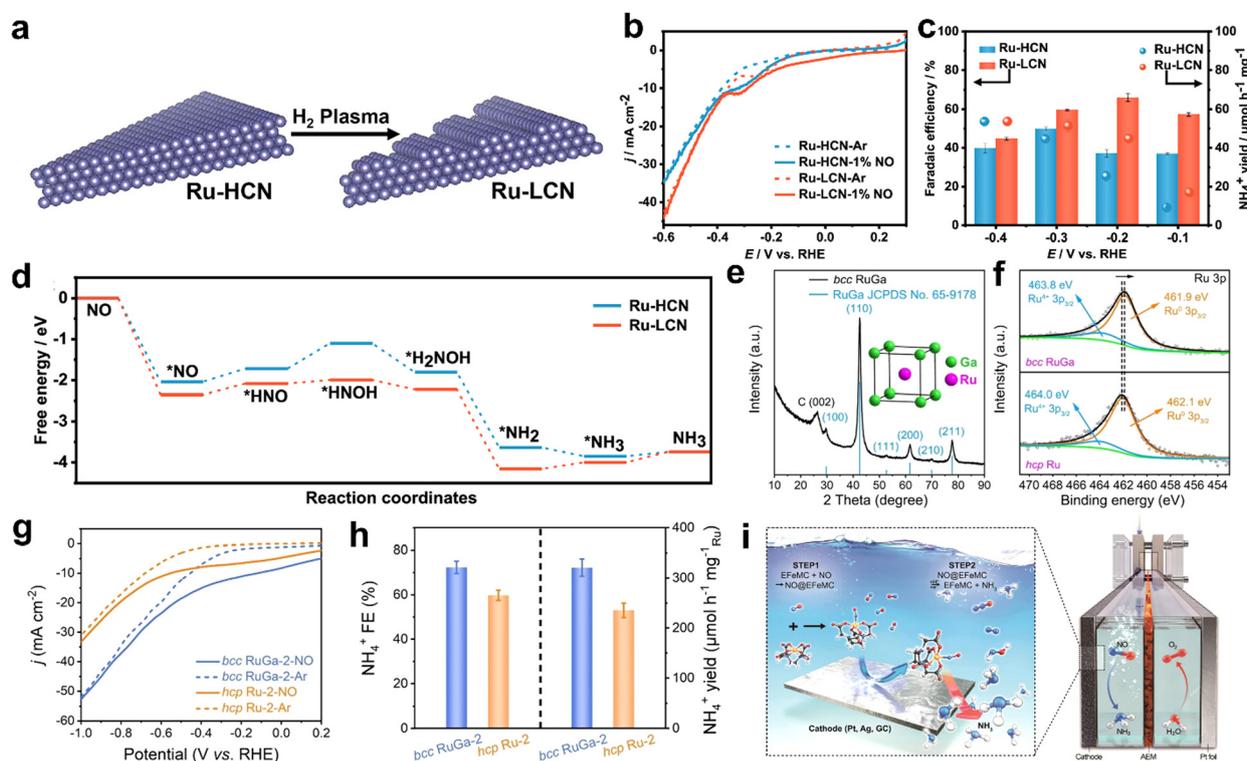
Fig. 3 (a) The adsorption energies of the intermediates  $\Delta E_{*NO}$  are plotted against  $\Delta E_{*H}$  on various metal surfaces. (b) The limiting potential volcano plot for NO reduction to  $NH_3$  on various metal surfaces. Reproduced with permission from ref. 43 copyright 2021, Wiley-VCH.



to attain high ammonia ( $\text{NH}_4^+$ ) yield rates, and high FEs at lower overpotentials.

For instance, Yu and co-workers have prepared Ru nanosheets with low coordination numbers (Ru-LCN) through the plasma treatment of Ru nanosheets with a high coordination number (Ru-HCN) (Fig. 4a).<sup>71</sup> As shown in Fig. 4b, Ru-LCN possesses enhanced NORR activity as compared to Ru-HCN in 1% NO (99% argon)-saturated 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte. At an optimal potential of  $-0.2$  V vs. RHE, Ru-LCN achieved a high  $\text{NH}_4^+$  yield rate ( $45.03 \mu\text{mol h}^{-1} \text{mg}^{-1}$ ) and FE (65.96%) in a H-type electrolytic cell (Fig. 4c). Moreover, the FE remains unaltered when the feeding gas is replaced with 99.9% NO instead of 1% NO, which is beneficial to produce  $\text{NH}_3$  with a wide range of pollutant concentrations. In addition, they demonstrated an improved  $\text{NH}_4^+$  yield rate of up to  $84.20 \mu\text{mol h}^{-1} \text{mg}^{-1}$  at  $-0.2$  V vs. RHE by constructing a flow electrolyzer (cathode: Ru-LCN, feed gas: 1% NO). The combined *in situ* measurements and DFT results indicated that the  $\text{NH}_3$  molecule formation over the Ru surface has occurred through the alternating-N mechanistic pathway. As shown in Fig. 4d, the low coordination number of Ru not only helps in the  $\text{NO}^*$  adsorption onto the Ru surface but also facilitates the subsequent hydrogenation step (PDS) *i.e.*,  $\text{NO}^*$  to

$\text{HNO}^*$ , thereby enhancing the NORR performance. However, the yield rate of Ru-LCN is not sufficiently high to meet the practical ammonia production rate. Recently, Lu *et al.* observed enhancement in the NORR activity of Ru active sites through the electronic structure optimization by forming an RuGa intermetallic compound (RuGa IMC).<sup>72</sup> Furthermore, RuGa nanoparticles were anchored onto the three-dimensional interconnected n-doped reduced graphene oxide nanosheets to improve the reaction kinetics *via* thermal annealing. Interestingly, the incorporation of Ga into Ru has altered the crystal structure from fcc-Ru to bcc-RuGa in which the isolated Ru atoms are occupied at the center of cubes (Ga atoms occupied at the vertex) (Fig. 4e). Meanwhile, an electron-rich Ru atom has been created through the electron transfer from Ga to Ru in RuGa IMC (Fig. 4f). As shown in Fig. 4g and h, bcc-RuGa exhibits an extraordinary NORR performance ( $\text{NH}_4^+$  yield rate:  $320.6 \mu\text{mol h}^{-1} \text{mg}^{-1}$  Ru and FE: 72.3%), which is superior to that of fcc-Ru (yield rate:  $235.4 \mu\text{mol h}^{-1} \text{mg}^{-1}$  Ru, and FE: 59.8%) in 20% NO-saturated 0.1 M  $\text{K}_2\text{SO}_4$  at  $-0.2$  V vs. RHE. In another report, Shi *et al.* also showed higher intrinsic NORR activity of the  $\text{Ru}_{0.05}\text{Cu}_{0.95}$  alloy prepared through the coprecipitation of  $\text{Ru}_x\text{Cu}_{1-x}(\text{OH})_2$ , followed by an electrochemical reduction step.<sup>73</sup> Online differential electrochemical mass



**Fig. 4** (a) Diagram for the preparation of Ru-LCN *via* plasma treatment on Ru-HCN, (b) LSV curves of Ru-HCN and Ru-LCN at a scan rate of  $10 \text{ mV s}^{-1}$  in Ar- and 1% NO-saturated 0.5 M  $\text{Na}_2\text{SO}_4$  solution, (c) Faradaic efficiency and yield rate of  $\text{NH}_4^+$  with 1% NO over Ru-HCN and Ru-LCN at each given potential, and (d) reaction Gibbs free energy diagrams of the NORR over Ru-HCN and Ru-LCN on FCC (111) surfaces at 0 V vs. RHE. Reproduced with permission from ref. 71 copyright 2022, ACS. (e) XRD pattern of bcc RuGa IMCs on N-rGO nanosheets, the inset is the crystal structure (unit-cell) model of bcc RuGa IMCs, (f) high-resolution Ru 3p XPS spectra of bcc RuGa IMCs and hcp Ru NPs, (g) LSV curves of bcc RuGa-2 IMCs and hcp Ru-2 NPs in Ar-saturated (dashed lines) or NO-saturated (solid lines) 0.1 M  $\text{K}_2\text{SO}_4$  electrolyte, and (h)  $\text{NH}_4^+$  Faradaic efficiencies and  $\text{NH}_4^+$  yield rates over bcc RuGa-2 IMCs and hcp Ru-2 NPs at 0.2 V in NO-saturated 0.1 M  $\text{K}_2\text{SO}_4$  electrolyte. Reproduced with permission from ref. 72 copyright 2023, Wiley-VCH. (i) Schematic diagram showing NO capture by EFeMC present in the electrolyte and its electrochemical reduction to ammonia. Reproduced with permission from ref. 74 copyright 2020, ACS.



spectrometry (DEMS) confirms that ammonia ( $\text{NH}_3$ ) is formed over the alloy through the alternating-N mechanistic pathway. Besides, Kim *et al.* have achieved the selective  $\text{NH}_4^+$  formation using a nanostructured silver (Ag) electrode with nearly 100% FE in a large potential window (0.04 to  $-0.34$  V vs. RHE) by using an EDTA- $\text{Fe}^{2+}$  metal complex (EFeMC) electrolyte that is saturated with 'NO'.<sup>74</sup> They claimed that initially the 'NO' molecule gets trapped in the metal complex and subsequent proton-coupled electron transfer from the silver electrode to the metal complex occurs through the outer sphere electron transfer to produce  $\text{NH}_3$  along with the regeneration of EFeMC (Fig. 4i). During electroreduction, Ag stabilizes the reaction intermediates such as  $[\text{*}(\text{II})\text{-HNO}]$ ,  $[\text{*}(\text{II})\text{-NHOH}]$ , and  $[\text{*}(\text{II})\text{-NH}_2\text{OH}]$ , where  $[\text{*}(\text{II})] = \text{EFeMC}$  through donor-acceptor interaction by binding with the oxygen atoms of intermediates, which are trapped in the metal complex. In addition, the performance and durability of the Ag electrode are tested in a flow cell with the EFeMC electrolyte. In the flow cell, the  $\text{NH}_4^+$  production rate has reached as high as  $3.6 \text{ mol m}^{-2} \text{ h}^{-1}$ , along with 100% FE at  $-0.165$  V vs. RHE and the same performance has been maintained for 100 h. Since they have used an additional metal complex in the electrolyte, it is especially important to estimate the economy of the system as compared to the commercial ammonia production cost. The economic analysis suggests that the  $\text{NH}_3$  production cost through the NORR in the EFeMC-designed electrolyte is 2.5 times higher than the commercial price of ammonia but can be market competitive with an electricity price of  $\$0.03 \text{ kW h}^{-1}$  and with a current density of  $>125 \text{ mA cm}^{-2}$ . Thus, designing efficient electrocatalysts and integrating the electrolyzer with renewable energy sources could be a viable solution for implementing the EFeMC-electrolyte based NORR electrolyzer. In another report, Choi *et al.* have shown a notable NORR performance from commercial 20 wt% Au supported on Vulcan carbon to produce  $\text{NH}_4^+$  at a relatively lower overpotential ( $-0.3$  V), whereas the electrode is inert towards the NRR.<sup>75</sup> Xiong *et al.* reported improved NORR activity from electrochemically synthesized Au/rGO electrodes. Ferrous citrate ( $\text{Fe}^{\text{II}}\text{Cit}$ ) solution was chosen as an electrolyte for the 'NO' complexation.<sup>76</sup> The  $\text{NH}_3$  yield of Au/rGO increased linearly with the concentration of  $\text{Fe}^{\text{II}}\text{Cit}$  in the electrolyte, while maintaining the same FE. This indicates that the coordinated NO within the metal complex can only participate in electroreduction, which could solve the limited solubility problem of 'NO' in the aqueous electrolyte. Meanwhile, they observed that the FE of  $\text{NH}_3$  can be

maximized up to 98% with the adjustment of electrolyte pH to 1, as the key protonation step of  $\text{*NOH}$  is more facile in an acidic medium. Furthermore, they hypothesized that selective  $\text{NH}_3$  formation over the Au surface is due to the stabilization of  $\text{*N}$  and  $\text{*NH}$  intermediates. At  $-0.47$  V vs. RHE, an excellent  $\text{NH}_4^+$  yield rate of  $438.8 \mu\text{mol cm}^{-2} \text{ h}^{-1}$  and FE of 93.2% were achieved from 7.6 wt% atomically dispersed iridium (Ir) confined in amorphous  $\text{MoO}_3$  ( $\text{Ir}/\text{MoO}_3$ ).<sup>77</sup> In this material, the Ir- $\text{O}_5$  moiety is found to be the active site for preferential binding of 'NO' over 'H' and possesses a very low energy barrier (0.01 eV) for the rate determining  $\text{*NHO} \rightarrow \text{*NHOH}$  step, thereby delivering the high  $\text{NH}_3$  yield rates and FE. Table 1 summarizes the NORR activity of different precious transition metal-based electrocatalysts.

## 2. Non-precious transition metal-based electrocatalysts

(i) **Zero valent transition metals.** Despite the high NORR performance of precious metals, their utilization for large-scale  $\text{NH}_3$  production is hindered by the low abundance and high electrode cost. This demands the exploration of other alternatives for realizing the practical implementation of the NORR to  $\text{NH}_3$  technology. In this context, Long *et al.* have performed computational screening over different transition metal catalysts towards NORR by choosing the  $\text{N}^*$  adsorption free energy [ $G_{\text{ad}}(\text{N})$ ] as an activity descriptor.<sup>34</sup> Among the chosen transition metals, copper (Cu) is found to be the ideal candidate for selective  $\text{NH}_3$  production through the NORR (Fig. 5a). In addition, the  $\text{NH}_3$  formation over the Cu (111) surface is predicted to occur *via* an associative Heyrovsky distal-O mechanism (AHDO), in which the protonation of  $\text{NOH}^*$  (0.54 eV) is the rate-limiting step. As shown in Fig. 5b, the high energy barriers for N-N, N-NO, and H-H couplings, as compared to  $\text{N}^*$  continual protonation steps over Cu (111), have successfully eliminated the formation of  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2$  side products, thereby leading to high activity and selectivity towards  $\text{NH}_3$  production. They have validated the above predictions by performing electrocatalytic NORR experiments on copper substrates. A porous Cu foam has shown excellent NORR activity to produce  $\text{NH}_3$  as a dominant product in a wide potential range from  $-1.2$  to  $0.3$  V vs. RHE in  $0.25 \text{ M Li}_2\text{SO}_4$  (Fig. 5c). A maximum  $\text{NH}_3$  formation rate of about  $517 \mu\text{mol cm}^{-2} \text{ h}^{-1}$  along with high FE (93.5%) was achieved at  $-0.9$  V vs. RHE and the activity was maintained for 100 hours. In contrast, hardly

**Table 1** Summary of the NORR activity shown by different precious transition metal-based electrocatalysts

Catalyst	Synthetic route	Electrolyte	$\text{NH}_3$ yield rate	FE (%)	Potential (vs. RHE) (V)	Ref.
Ru-LCN	Plasma treatment	0.5 M $\text{Na}_2\text{SO}_4$ (1% NO)	$45.03 \mu\text{mol h}^{-1} \text{ mg}^{-1}$	65.96	-0.2	71
RuGa IMCs	Thermal annealing method	0.1 M $\text{K}_2\text{SO}_4$ (20% NO)	$320.6 \mu\text{mol h}^{-1} \text{ mg}^{-1}_{\text{Ru}}$	72.3	-0.2	72
$\text{Ru}_{0.05}\text{Cu}_{0.95}$	Coprecipitation-electrochemical reduction	0.5 M $\text{Na}_2\text{SO}_4$ (20% NO)	$17.68 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	64.9	-0.5	73
Nanostructured Ag electrode	Chlorination/dechlorination method	PBS-EDTA- $\text{Fe}^{2+}$ metal complex (99.9% NO)	$2.29 \text{ mol h}^{-1} \text{ m}^{-2}$	~100	-0.34	74
20 wt% Au/C	Commercial	0.5 M $\text{K}_2\text{SO}_4$ (1 mM NO)	$8.1 \pm 0.9 \times 10^2 \text{ pmol s}^{-1} \text{ cm}^{-2}$	N. A.	-0.30	75
Au/rGO	Two-step electrochemical reduction	Citrate- $\text{Fe}^{2+}$ complex (2% NO)	$14.6 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	65.2	-0.1	76
$\text{Ir}/\text{MoO}_3$	Supercritical $\text{CO}_2$ approach	NO-saturated 0.5M $\text{Na}_2\text{SO}_4$ (99.9% NO)	$439 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	93.2	-0.47	77



any  $\text{NH}_3$  is formed when the Cu foam electrode is subjected to the NRR, thereby indicating the competitiveness of the NORR over the NRR on the Cu surface. Later, Chen *et al.* used the chemical reduction method for uniform decoration of ultra-small 'Cu' nanoparticles onto the porous  $\text{TiO}_2$ , which was synthesized by the sol-gel method.<sup>78</sup> The electrode exhibited a high  $\text{NH}_3$  yield of  $3520.80 \mu\text{g h}^{-1} \text{mg}^{-1}$  and FE of 86.49% at  $-0.3 \text{ V vs. RHE}$  in 'NO'-saturated  $0.1 \text{ M K}_2\text{SO}_4$ . The improved surface area and porous channels of  $\text{TiO}_2/\text{Cu}$  have improved the 'NO' molecule adsorption, leading to high  $\text{NH}_3$  production. Nevertheless, the poor solubility of  $\text{NO}_x$  in electrolytes is another roadblock to further development. This necessitates evaluating the NORR activity of electrocatalysts in a flow cell configuration by supporting them onto gas diffusion electrodes (GDEs) to alleviate the mass transport limitation. Ko *et al.* have demonstrated the gaseous  $\text{NO}_x$  ( $\text{NO}$  and  $\text{N}_2\text{O}$ ) reduction at high reaction rates ( $400 \text{ mA cm}^{-2}$ ) over various transition metals deposited on GDEs in a gas-fed three-compartment flow cell.<sup>57</sup> In contrast to the previous reports, all the transition metals showed good electrocatalytic performance towards the NORR, while the product selectively is hugely varied (Fig. 5d). The higher activity shown by all metals could be due to the NO-

saturated environment in the flow cell (100% NO). Among all the metals, Cu showed excellent selectivity ( $> 80\%$ ) towards  $\text{NH}_3$  from the NORR, whereas other metals, such as Fe, and Pd, have produced  $\text{N}_2\text{O}$  as a major product in an alkaline medium (Fig. 5e). Besides, Cu also showed good  $\text{N}_2\text{ORR}$  activity and it has selectively produced  $\text{N}_2$  as a reduction product. In addition, they have studied the effect of NO partial pressure in a flow cell on product selectivity. It was found that irrespective of the electrocatalyst, N-N coupled products ( $\text{N}_2$  and  $\text{N}_2\text{O}$ ) and single-N products ( $\text{NH}_3$  and  $\text{NH}_2\text{OH}$ ) will be formed at low and high 'NO' coverages, respectively, thereby indicating the importance of the NO concentration over the catalyst surface towards product selectivity (Fig. 5f and g). In addition, they showed the pH dependency of the NORR towards  $\text{NH}_3$  FE over Cu. It could deliver nearly 100% FE at  $\text{pH} = 0.5$ , as the first proton transfer step of NO ( $^*\text{NO} + \text{H}^+ \leftrightarrow ^*\text{NOH}$ ) is the rate determining step (RDS) of  $\text{NH}_3$ . Besides,  $\text{NH}_3$  production from low concentrated 'NO' is of practical significance, especially while using flue gas as a NO source in the flow cell. Cheon *et al.* also reported excellent NORR activity from zero valent iron (Fe)-incorporated carbon black, which is supported on GDE at low NO concentrations (1–10%).<sup>79</sup> As shown in Fig. 5h, Fe/C-

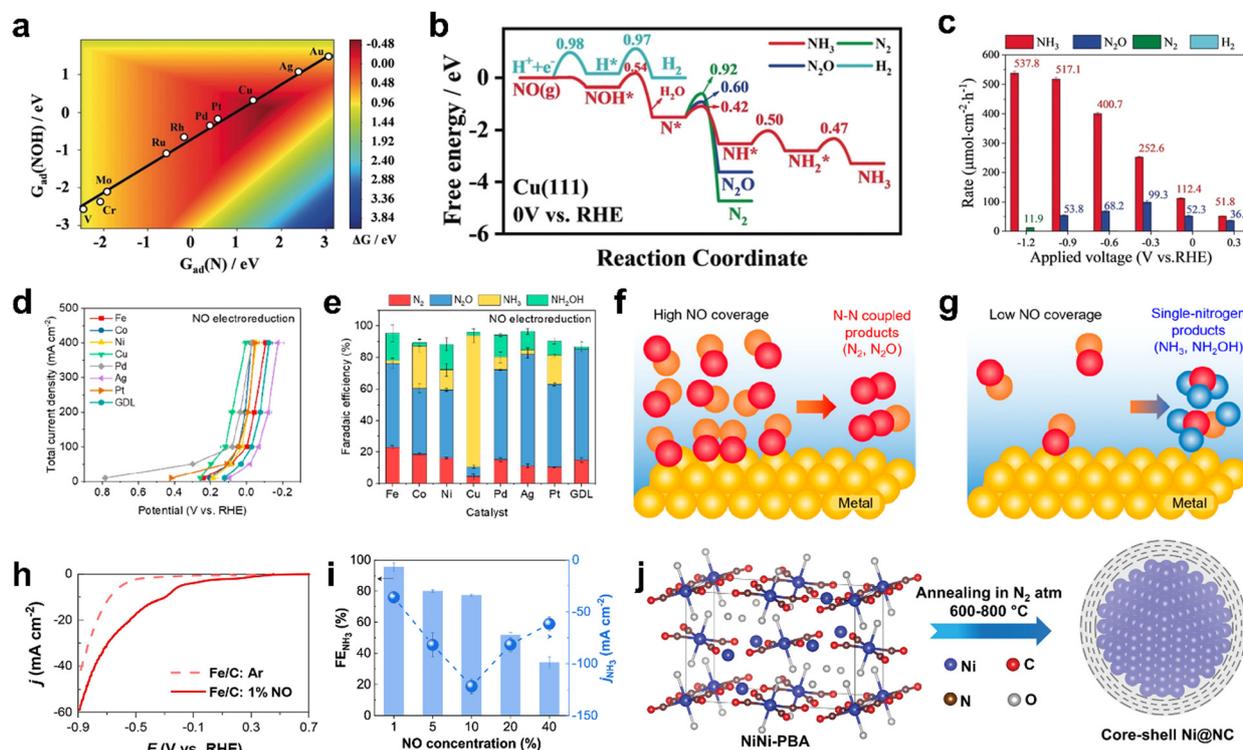


Fig. 5 (a) A two-dimensional activity map of different metals for ammonia production. All the reaction free energies are shown at 0 V vs. RHE, (b) free-energy diagrams for the HER, NORR to  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  over Cu (111) under 0 V vs. RHE, the kinetic barriers are shown in eV, and (c) reaction rates of the NORR on Cu foam at various potentials. Reproduced with permission from ref. 34 copyright 2020, Wiley-VCH. (d) Total current density vs. potential plots of various metal catalysts towards NO electroreduction performance, and (f and g) schematics showing the effect of NO coverage on product selectivity in high and low NO coverages. Reproduced with permission from ref. 57 copyright 2022, ACS. (h) Linear sweep voltammetry scan of the Fe/C-incorporated GDE cell for 1% NO reduction using 0.5 M PBS electrolyte (pH 7), (i) the effect of NO concentration on  $\text{NH}_3$  faradaic efficiency and  $\text{NH}_3$  partial current density in a NO electrolyzer operated at  $-0.6 \text{ V vs. RHE}$  and 0.5 M PBS (pH 7). Reproduced with permission from ref. 79 copyright 2022, ACS. (j) Schematic synthesis route of Ni@NC from NiNi-PBA. Reproduced with permission from ref. 40 copyright 2022, Wiley-VCH.



supported GDE has achieved a maximum  $\text{FE}_{\text{NH}_3}$  of 91% at  $-0.4$  V vs. RHE and  $j_{\text{NH}_3}$  of  $19 \text{ mA cm}^{-2}$  at  $-0.6$  V vs. RHE, respectively, with 1% NO as a feed gas in a GDE cell. In addition, a maximum  $j_{\text{NH}_3}$  of  $122 \text{ mA cm}^{-2}$  was achieved at 10% NO (FE: 77%). A further increase in the NO concentration led to a decrease in  $j_{\text{NH}_3}$  and FE, owing to the formation of N-N coupled products ( $\text{N}_2$  and  $\text{N}_2\text{O}$ ) at high 'NO' coverage over the electrode surface (Fig. 5i). The computational calculations revealed that the ammonia formation over the Fe (110) surface occurred through the breaking of the N-O bond in the  $\text{H}_2\text{NO}$  intermediate. Although the  $\text{NH}_3$  yield rate of Fe/C-supported GDE is significantly improved in 0.5 M  $\text{H}_2\text{SO}_4$  compared to PBS buffer, the dissolution of Fe in an acidic medium causes a decline in activity during long term NO electrolysis. The above studies show that the  $\text{NH}_3$  production rate is significantly higher in the acidic medium than in neutral and alkaline electrolytes, owing to the facile protonation steps in the acidic medium. However, transition metals tend to dissolve in acidic environments, which causes catalyst degradation. Hence, it is necessary to protect the catalytic metal centers for durable ammonia production. To resolve this issue, our group attempted to protect catalytic Ni centers with a thin graphitic carbon coating by making a core-shell Ni@NC architecture *via* one-step pyrolysis of the  $\text{Ni}[\text{Ni}(\text{CN})_4]$  PBA precursor at different temperatures from 600 to 800 °C (Fig. 5j).<sup>40</sup> Among them, Ni@NC synthesized at 800 °C produced the highest  $\text{NH}_3$  yield rate of  $34.6 \mu\text{mol cm}^{-2} \text{ h}^{-1}$  with a high FE (72.3%) at a low overpotential of 550 mV (0.16 V vs. RHE) and maintained the catalytic activity for 24 h in 0.1 M HCl. In contrast, bare Ni nanoparticles displayed a moderate  $\text{NH}_3$  yield rate ( $8.9 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ ) and they were etched away from the electrode surface during the NORR measurements. The improved activity of Ni@NC is attributed to the facile ionic/gaseous transport through the porous multilayer NC shell to the catalytically active Ni core. In addition, the anti-corrosive property of the multilayer NC shell retards the dissolution of the Ni core in an acidic medium, thereby ensuring the stability of Ni@NC. Furthermore, a solar powered NORR/OER electrolyzer (constructed by employing Ni@NC and  $\text{RuO}_2$  as the cathode and anode, respectively) has achieved a  $\text{NH}_3$  FE of > 50%, with a solar-to-fuel (STF) efficiency of  $\approx 1.7\%$ . Another work observed a stable NORR performance from N-doped carbon-wrapped nickel nanoparticles supported onto the carbon fiber (NiNC@CF).<sup>80</sup> Initially, nanoflake-like Ni-MOF was directly grown onto the CF *via* a solvothermal method. The subsequent thermal pyrolysis led to the decomposition of organic matter, producing a zero-valent Ni nanoparticle-dispersed porous N-doped carbon microstructure on CF. The resulting electrode achieved a maximum FE of 87% with an  $\text{NH}_3$  yield rate of  $94 \text{ mmol cm}^{-2} \text{ h}^{-1}$  at  $-0.5$  V vs. RHE and showed good durability in the PBS electrolyte (pH 7). Meanwhile, the corresponding prototype two-electrode electrolyzer (NORR/OER) has delivered a  $\text{NH}_3$  yield rate of  $27 \text{ mmol cm}^{-2} \text{ h}^{-1}$  with the highest FE (80%), at a cell potential of 2.75 V. Wang and coworkers have attained a high  $\text{NH}_3$  yield of  $439.5 \mu\text{mol cm}^{-2} \text{ h}^{-1}$  ( $1465.0 \mu\text{mol h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ ) and an FE of 72.58% at  $-0.6$  V vs. RHE from the hexagonal-close-packed cobalt nanosheets

(hcp-Co) prepared through a facile hydrothermal method.<sup>81</sup> In contrast, the face-centered cubic phase of the Co nanosheets (fcc-Co) showed inferior activity ( $\text{NH}_3$  yield:  $142.10 \mu\text{mol cm}^{-2} \text{ h}^{-1}$  and FE: 57.12%), thereby indicating that the crystal structure/phase of the material has a significant role in the NORR. The DFT studies unveil that hcp-Co activates the adsorbed 'NO' molecule through the donation of  $0.6 e^-$  through d- $\pi^*$  orbitals and facilitates the rate determining first protonation step ( $\text{NO}^* \rightarrow \text{NOH}^*$ ) with a low energy barrier of 0.32 eV. Despite both hcp-Co and fcc-Co possessing a similar energy barrier for the RDS, the proton diffusion/shuttling is highly favourable over hcp-Co ( $-0.80$  eV) as compared to fcc-Co ( $-0.67$  eV). Hence, the improved activity of hcp-Co could be attributed to the expedited protonation kinetics during the NORR. Table 2 summarizes the NORR activity of different zero valent non-precious transition metal-based electrocatalysts.

**(ii) Multi-valent transition metal compounds.** The NORR activity and the  $\text{NH}_3$  selectivity hugely depend on the electronic structure, morphology, and vacancies of electrocatalysts. In this regard, various metal compounds, such as oxides, sulfides, and phosphides, have been explored and it is found that all the materials can perform NORR activity with high  $\text{NH}_3$  selectivity. As the biological reduction of NO into  $\text{N}_2\text{O}$  is catalyzed by an iron-centered heme group of 'NO reductase' Fe-based electrocatalysts are expected to show good 'NO' binding and perform the subsequent reduction.<sup>83-85</sup> Sun *et al.* have directly grown a uniform  $\text{Fe}_2\text{O}_3$  nanorod array onto a 3-dimensional carbon paper ( $\text{Fe}_2\text{O}_3/\text{CP}$ ) and evaluated its NORR activity with diluted NO (10%).<sup>86</sup> In addition, to improve the 'NO' solubility, they introduced Fe(II)EDTA complex into the 0.1 M  $\text{Na}_2\text{SO}_4$  electrolyte.  $\text{Fe}_2\text{O}_3/\text{CP}$  has shown a good  $\text{NH}_3$  yield of  $41.6 \mu\text{mol h}^{-1} \text{ cm}^{-2}$  (FE: 86.73%) at  $-0.4$  V vs. RHE and maintained the activity for 12 h. Meanwhile, they found that  $\text{NO}_3^-$  contamination (resulting from the reaction between NO and  $\text{O}_2$  followed by the dissolution in water) in the electrolyte causes interference of cathodic currents, thereby hindering the NORR activity judgment of electrodes. Hence, it is necessary to perform NORR in gas-tight (without the aeration of NO) cells to obtain reliable results. Besides, they demonstrated the  $\text{NH}_3$  production ( $145.28 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ ) at a high-power density ( $1.18 \text{ mW cm}^{-2}$ ) from the Zn-NO battery, which is assembled using  $\text{Fe}_2\text{O}_3/\text{CP}$  and a zinc plate as the cathode and anode, respectively. DFT studies predict that 'NO' strongly binds onto the  $\text{Fe}_2\text{O}_3$  (104) surface through an "acceptance-donation" mechanism and subsequently gets activated through the  $2p^*$  back-donation effect to give rise to  $\text{NH}_3$  molecule formation. The same group has shown boosted NORR activity using an oxygen vacancy ( $\text{V}_\text{O}$ )-rich  $\text{MnO}_2$  nanowire array ( $\text{MnO}_{2-x}$  NA) supported on a Ti mesh in 0.2 M  $\text{Na}_2\text{SO}_4$ .<sup>87</sup> The  $\text{V}_\text{O}$  in  $\text{MnO}_{2-x}$  NA is created by annealing the as prepared  $\text{MnO}_2$  NA in an Ar atmosphere at 350 °C.  $\text{MnO}_{2-x}$  NA has achieved a high  $\text{NH}_3$  yield ( $27.51 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ ) and FE (82.8%) as compared to pristine  $\text{MnO}_2$  NA ( $8.83 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ , 44.8%) at  $-0.7$  V vs. RHE, thereby highlighting the advantage of  $\text{V}_\text{O}$  in  $\text{MnO}_{2-x}$  for enhanced NORR activity. DFT calculations reveal that the hydrogenation step of  $\text{MnO}_2$  (211) is associated with a high energy barrier due to the strong binding ( $-1.4$  eV) of 'NO'. In contrast,  $\text{V}_\text{O}$  in the  $\text{MnO}_{2-x}$  (211) surface allows the moderate binding



Table 2 Summary of the NORR activities shown by different zero valent non-precious transition metal-based electrocatalysts

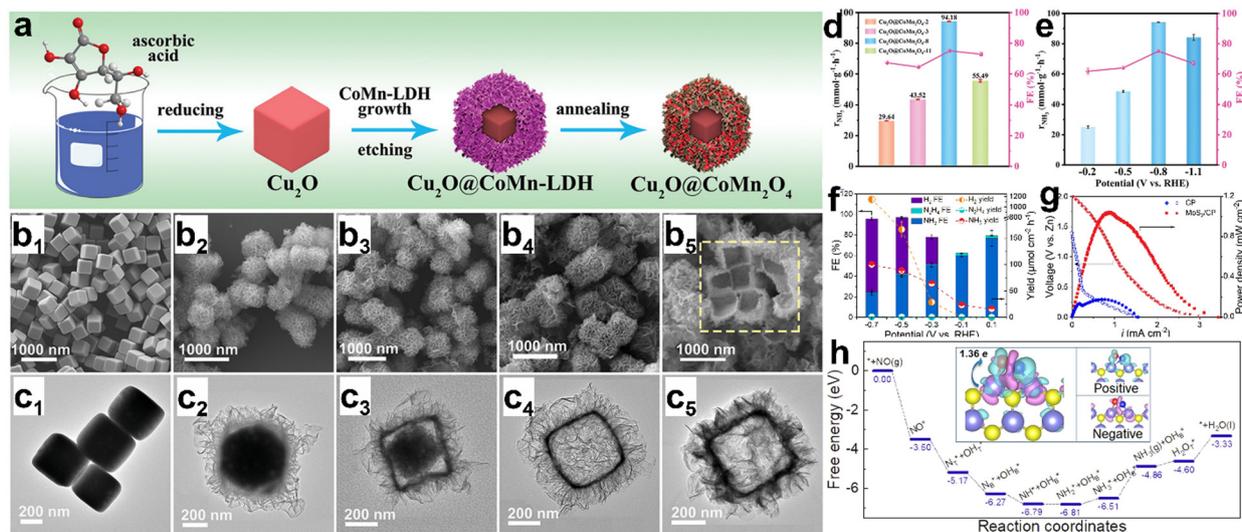
Catalyst	Synthetic route	Electrolyte	NH <sub>3</sub> yield rate	FE (%)	Potential (vs. RHE) (V)	Ref.
Cu foam	Commercial	0.25 M Li <sub>2</sub> SO <sub>4</sub> (30 ml min <sup>-1</sup> )	517.1 μmol cm <sup>-2</sup> h <sup>-1</sup>	93.5	-0.9	34
TiO <sub>2</sub> /Cu	Sol-gel followed by chemical reduction	0.1 M K <sub>2</sub> SO <sub>4</sub> (10% NO)	3520.80 μg h <sup>-1</sup> mg <sup>-1</sup>	86.49	-0.3	78
Cu Ti fibers	Air spraying	0.05 M Na <sub>2</sub> SO <sub>4</sub> (10% NO)	400 μmol cm <sup>-2</sup> h <sup>-1</sup>	90	-0.6	82
Copper nanoparticles (GDE)	Commercial	0.1 M NaOH + 0.9 M NaClO <sub>4</sub> (100% NO)	1246 μmol cm <sup>-2</sup> h <sup>-1</sup>	78	0	57
Fe/C-incorporated GDE	Physical mixture of Fe and C	0.5 M PBS solution (10% NO)	908 μmol cm <sup>-2</sup> h <sup>-1</sup>	77	-0.6	79
Ni@NC	Pyrolysis of NiNi-PBA	0.1 M HCl (99.9% NO)	34.6 μmol cm <sup>-2</sup> h <sup>-1</sup>	72.3	0.16	40
NiNC@CF	Solvothermal + annealing	0.5 M PBS solution (pH 7) (99.9% NO)	94 mmol cm <sup>-2</sup> h <sup>-1</sup>	87	-0.5	80
hcp-cobalt nanosheets	Hydrothermal method	0.1 M Na <sub>2</sub> SO <sub>4</sub>	439.5 μmol cm <sup>-2</sup> h <sup>-1</sup>	72.58	-0.6	81

(-0.5 eV) of 'NO' molecules, which makes the subsequent hydrogenation step more facile. Similarly, an oxygen vacancy-rich TiO<sub>2</sub> nanoarray supported on a Ti plate (TiO<sub>2-x</sub>/TP) has shown superior NORR activity compared to TiO<sub>2</sub>/TP as the 'NO' adsorption is more facile in the former.<sup>88</sup> Encouragingly, an open nano array structure of TiO<sub>2-x</sub>/TP enables the exposure of abundant active sites for generating greater NH<sub>3</sub> yields. Wu *et al.* have achieved an exceptionally high NH<sub>3</sub> yield rate of 20 mg h<sup>-1</sup> cm<sup>2</sup> with nearly unit FE from CoNi<sub>(5:5)</sub>O<sub>x</sub>@Cu at -0.68 V vs. RHE.<sup>89</sup> Moreover, the material maintained its NORR activity for 36 h. The *in situ* Raman spectroscopic and DFT studies concurrently manifest that 'NO' most likely adsorbs onto the Co site of CoNi<sub>(5:5)</sub>O<sub>x</sub>@Cu more spontaneously as compared to individual Co<sub>3</sub>O<sub>4</sub>@Cu and NiO@Cu. Subsequently, NH<sub>3</sub> is selectively produced through the O-end distal pathway, as the energy barriers are significantly high for the formation of other products (N<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, *etc.*). Besides, the confinement of reaction intermediates in nanoreactors is proven to be a prudent approach for efficient NORR. Bai *et al.* have developed a synthetic strategy to prepare hollow Cu<sub>2</sub>O@CoMn<sub>2</sub>O<sub>4</sub> nanoreactors from a Cu<sub>2</sub>O nanocube template through the simultaneous etching of Cu<sub>2</sub>O and growth of CoMn-LDH followed by annealing in Ar (Fig. 6a).<sup>90</sup> Meanwhile, they found that the NO adsorption ability linearly increases with nanoreactor internal space, which can be controlled by the etching time (Fig. 6b and c). The void-confinement effect of the Cu<sub>2</sub>O@CoMn<sub>2</sub>O<sub>4</sub> nanoreactors is beneficial to maintain high reactant concentration and intermediate confinement inside the nanoreactor space and improve the electron transfer efficiency. The optimized material Cu<sub>2</sub>O@CoMn<sub>2</sub>O<sub>4</sub>-8 (etched for 8 min) has shown remarkable NORR activity with a high NH<sub>3</sub> production rate of 94.18 mmol g<sup>-1</sup> h<sup>-1</sup> and an FE of 75.05% at -0.8 V vs. RHE (Fig. 6d and e). Zhang *et al.* found that 2H-MoS<sub>2</sub> flakes grown on graphite felt (MoS<sub>2</sub>/GF) can efficiently convert NO into NH<sub>3</sub> in an acidic electrolyte.<sup>54</sup> As shown in Fig. 6f and g, the electrode has shown a maximum NH<sub>3</sub> yield rate of 99.6 μmol h<sup>-1</sup> cm<sup>-2</sup> (FE<sub>NH<sub>3</sub></sub> < 30%) at -0.7 V vs. RHE from the electrocatalytic NORR and the corresponding Zn-NO battery has achieved a power density of 1.04 mW cm<sup>-2</sup> (an NH<sub>3</sub> yield of 411.8 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup>). DFT studies unveiled that 'NO' adsorption on MoS<sub>2</sub> (101) occurs through an 'acceptance-donation mechanism' and the subsequent activation is enabled by the electron transfer from MoS<sub>2</sub> to the anti-bonding orbital of 'NO' (Fig. 6h). However, the competitiveness of the HER over the NORR on the MoS<sub>2</sub> surface at high cathodic potentials resulted in low FE<sub>NH<sub>3</sub></sub>. To suppress the

HER on MoS<sub>2</sub>, Liu's group performed NORR in an ionic liquid (IL)-based electrolyte, which can significantly limit the proton concentration over the electrode surface.<sup>91</sup> They regulated the electronic structure of MoS<sub>2</sub> *via* phosphorous (P) doping to enhance the NH<sub>3</sub> yield. As expected, FE<sub>NH<sub>3</sub></sub> on P-MoS<sub>2</sub> nanospheres in 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)-trifluoro phosphate increased up to 70% and achieved an NH<sub>3</sub> yield rate of 237.7 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> at -0.6 V vs. RHE, which is superior to that of pristine MoS<sub>2</sub>. Additionally, the computational studies showed that the associated energy barriers from NO adsorption to NH<sub>3</sub> formation on the MoS<sub>2</sub> surface are significantly lowered after P-doping, which could be the reason for such an enhanced NH<sub>3</sub> yield from P-MoS<sub>2</sub>. Besides doping, creating sulfur vacancies in metal sulfides is also proven to be an effective way to enhance the electrocatalytic NORR performance. The sulfur vacancy-rich CoS<sub>1-x</sub> nanosheets prepared through the plasma treatment have shown an NH<sub>3</sub> yield rate of 44.67 μmol cm<sup>-2</sup> h<sup>-1</sup> (FE: 54%) at -0.4 V vs. RHE in 0.2 M Na<sub>2</sub>SO<sub>4</sub>.<sup>92</sup> The 'S' vacancy-free CoS counterpart could only display an NH<sub>3</sub> yield rate of 27.02 μmol cm<sup>-2</sup> h<sup>-1</sup> (FE: 37%), as it possesses low active site density (reflected from double layer capacitance (C<sub>dl</sub>) measurements) as compared to CoS<sub>1-x</sub>. In addition, the 'NO' activation barrier is found to be relatively lower on CoS<sub>1-x</sub> (100) facets, which may be attributed to the localization of electrons around the sulfur vacancies.

Transition metal phosphides have also shown promising catalytic activity by catalyzing the NORR at relatively low onset potentials (about -0.01 V vs. RHE). However, the excellent NH<sub>3</sub> selectivity is limited to low overpotentials as the competitive HER prevails at larger cathodic potentials on metal phosphides. For instance, Mou *et al.* synthesized a Ni<sub>2</sub>P nanosheet array supported on carbon paper (Ni<sub>2</sub>P/CP) through the vapor phase phosphorization of the as prepared Ni(OH)<sub>2</sub>/CP precursor (Fig. 7a and b).<sup>93</sup> As shown in Fig. 7c and d, Ni<sub>2</sub>P/CC has achieved a maximum NH<sub>3</sub> yield of 33.47 μmol h<sup>-1</sup> cm<sup>-2</sup>, high FE up to 77% at -0.2 V vs. RHE in 0.1 M HCl saturated with 10% NO, and maintained good long-term stability for up to 12 h. The assembled Zn-NO battery using Ni<sub>2</sub>P/CP as the cathode delivered a discharge power density of 1.53 mW cm<sup>-2</sup> by producing an ammonia yield of 62.05 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup>. Theoretical calculations indicate that two-way charge transfer occurs between Ni<sub>2</sub>P (111) and NO, which can simultaneously accumulate and deplete the electron density in the antibonding and bonding orbitals of NO, respectively. Consequently, the N-O bond will





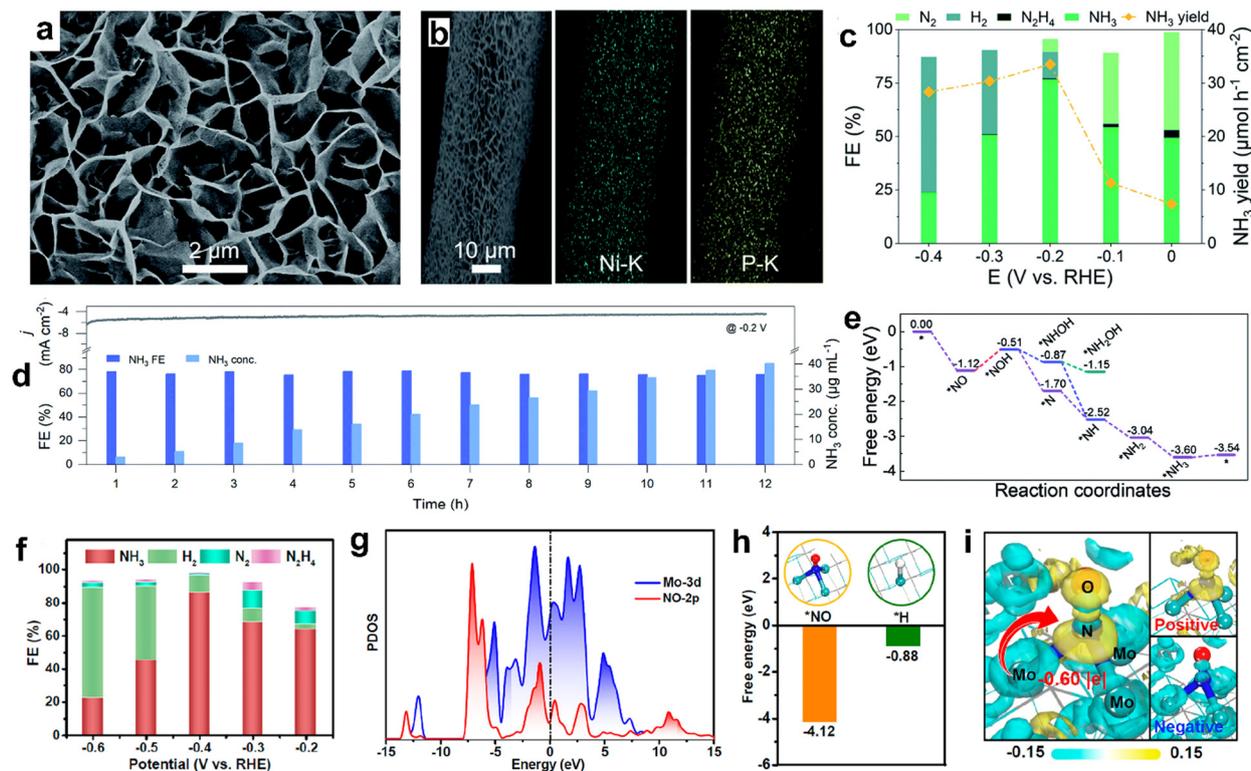
**Fig. 6** (a) Schematic illustration of the preparation of a hollow  $\text{Cu}_2\text{O}@CoMn_2O_{4-x}$  nanoreactor. SEM images of (b<sub>1</sub>)  $\text{Cu}_2\text{O}$ , (b<sub>2</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-2}$ , (b<sub>3</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-3}$ , (b<sub>4</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-8}$  and (b<sub>5</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-11}$ . TEM images of (c<sub>1</sub>)  $\text{Cu}_2\text{O}$ , (c<sub>2</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-2}$ , (c<sub>3</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-3}$ , (c<sub>4</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-8}$  and (c<sub>5</sub>)  $\text{Cu}_2\text{O}@CoMn_2O_{4-11}$ . (d)  $\text{NH}_3$  production rate and selectivity of  $\text{Cu}_2\text{O}@CoMn_2O_{4-x}$ , and (e)  $\text{NH}_3$  production rate and selectivity of  $\text{Cu}_2\text{O}@CoMn_2O_{4-8}$ . Reproduced with permission from ref. 90 copyright 2022, Wiley-VCH. (f) Product distribution for  $\text{MoS}_2/\text{GF}$  at each given potential in a NO-saturated 0.1 M HCl electrolyte containing 0.5 mM  $\text{Fe}^{\text{II}}/\text{SB}$ , (g) polarization and power density plots of CP and  $\text{MoS}_2/\text{CP}$ , and (h) free energy landscape for NORR on  $\text{MoS}_2$  (101). The charge density differences for the adsorbed NO are displayed as insets and cyan (positive) and red (negative) regions represent electron accumulation and loss, respectively. Reproduced with permission from ref. 54 copyright 2021, Wiley-VCH.

elongate and gets weakened on the  $\text{Ni}_2\text{P}$  (111) surface to facilitate the successive hydrogenation steps and produces  $\text{NH}_3$  through the distal pathway (Fig. 7e). Similarly, CoP nanowire and FeP nanorod arrays are also revealed to be excellent candidates for catalyzing the NORR at low overpotentials, and both have achieved high  $\text{FE}_{\text{NH}_3}$  (88%) at  $-0.2$  V vs. RHE in  $\text{Na}_2\text{SO}_4$  and PBS electrolytes, respectively.<sup>94,95</sup> Transition metal carbides are another class of materials predicted to show a strong affinity towards NO adsorption owing to the good orbital overlap between d and p-orbitals of the metal and NO, respectively. This could facilitate the back-donation of electrons from metal centers to NO, activating the NO molecule to produce ammonia. Chu's group developed molybdenum carbide ( $\text{Mo}_2\text{C}$ ) nanosheets by using methane gas as a carbon source through the carbonization of  $\text{MoO}_3$  nanosheets at  $700$  °C.<sup>96</sup> As shown in Fig. 7f,  $\text{Mo}_2\text{C}$  nanosheets produced the main product  $\text{NH}_3$  with a yield rate of  $122.7 \mu\text{mol h}^{-1} \text{cm}^{-2}$  ( $\text{FE}_{\text{NH}_3}$ : 86.3%) at  $-0.4$  V vs. RHE in  $\text{Na}_2\text{SO}_4$  and the same efficiency is retained for continuous 20 h electrolysis. As shown in Fig. 7g–i, DFT studies verify the preferred adsorption of 'NO' over the 'H' atom on the  $\text{Mo}_2\text{C}$  surface and the subsequent electron transfer from the 'Mo' center to adsorbed NO. Hence, the  $\text{Mo}_2\text{C}$  surface has helped to enhance the NORR and delivers high  $\text{NH}_3$  selectivity by impeding HER kinetics. In another report, Liu and coworkers demonstrated stable NORR performance with high  $\text{NH}_3$  selectivity from MoC nanocrystals confined in N-doped carbon nanosheets ( $\text{MoC}/\text{NCS}$ ).<sup>97</sup> Carbon support is found to be beneficial for abundant active site exposure and accelerated electron transport. In addition, the corresponding Zn–NO battery exhibited a peak power density of  $1.8 \text{ mW cm}^{-2}$  and a large  $\text{NH}_3$  yield rate of  $782 \pm 10 \mu\text{g h}^{-1} \text{cm}^{-2}$ . Furthermore, the potential determining step on the MoC (111) surface is predicted to be the hydrogenation of

\*NH, which is associated with a small energy barrier of 0.35 eV, leading to high  $\text{NH}_3$  selectivity over the other side products ( $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{N}_2\text{O}$ ). Table 3 summarizes the NORR activity of different multi-valent non-precious transition metal compounds.

**(iii) Transition metal-based single atom catalysts (SACs).** Recently, SACs have evolved as promising materials for various electrocatalytic applications such as the HER and ORR/OER owing to their maximized atom-utilization efficiency.<sup>102,103</sup> Meanwhile, their NORR activity and product selectivity are hugely dependent on the coordination environment around the metal center.<sup>104,105</sup> For instance, Peng *et al.* have shown good NORR activity from single-atom Nb sites supported on B, N co-doped carbon nanotubes (Nb-SA/BNC) prepared through the pyrolysis of melamine foam that was soaked in a precursor solution consisting of Nb(v) oxalate hydrate, polyethylene glycol, urea, and boric acid (Fig. 8a).<sup>106</sup> The atomic dispersion of Nb atom sites over the amorphous carbon nanotubes is identified using a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 8b and c). As shown in Fig. 8d, each Nb atom in Nb-SA/BNC is found to be coordinated with two B atoms and two N atoms to create the Nb-B<sub>2</sub>N<sub>2</sub> unit. The 'NO' adsorption is predicted to occur on the Nb site through the d-π\* orbital overlap and subsequently gets activated through the electron donation from the Nb atom. An appreciable NORR activity along with high  $\text{NH}_3$  selectivity was noted from atomically dispersed cobalt (Co) single atoms onto the  $\text{MoS}_2$  basal planes ( $\text{Co}/\text{MoS}_2$ ).<sup>107</sup> It exhibited a maximum  $\text{NH}_3$  yield and  $\text{FE}_{\text{NH}_3}$  of  $217.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$  and 87.7%, respectively, at  $-0.5$  V vs. RHE and showed excellent durability for 15 h. X-Ray absorption fine structure (EXAFS) analysis confirms the atomic level dispersion of Co atoms and is coordinated with three surface S atoms of  $\text{MoS}_2$  to





**Fig. 7** (a) SEM image of Ni<sub>2</sub>P/CP, (b) EDX elemental map of Ni<sub>2</sub>P/CP, (c) FEs of the major reduction products and NH<sub>3</sub> yields for Ni<sub>2</sub>P/CP, (d) long-term stability tests for continuous generation of NH<sub>3</sub> on Ni<sub>2</sub>P/CP, and (e) free energy diagrams for the NORR on the Ni<sub>2</sub>P (111) surface along the distal and alternating pathways. Reproduced with permission from ref. 69 copyright 2021, RSC. (f) FEs of Mo<sub>2</sub>C at various potentials, (g) projected density of states (PDOS) profiles of adsorbed NO and its bonded Mo atoms, (h) comparison of \*NO and \*H adsorption on Mo<sub>2</sub>C, and (i) electron density distributions of NO adsorption on Mo<sub>2</sub>C (001). Reproduced with permission from ref. 96 copyright 2023, ACS.

form a Co–S<sub>3</sub> moiety, which is predicted to be the active site for NO reduction. In addition, they emphasized that during the NORR, the N=O bond activates through the electron donation from the Co–S<sub>3</sub> moiety, and the consecutive hydrogenation steps occur through the NHO pathway (\*NO → \*NHO → \*NHOH → \*NH<sub>2</sub>OH → \*NH<sub>2</sub> → \*NH<sub>3</sub>). Similarly, Cu–S<sub>3</sub> moieties of the single-atomic copper supported on MoS<sub>2</sub> (Cu/MoS<sub>2</sub>) also served as efficient catalytic centers for the NORR.<sup>105</sup> Meanwhile, the same group has used a combined strategy of atomic doping and vacancy engineering to improve the NORR activity of SACs.<sup>108</sup> They have prepared atomically Fe-doped and S-vacancy-rich MoS<sub>2</sub> (Fe/MoS<sub>2-x</sub>) nanoflowers using a facile one-step hydrothermal method and achieved a high NH<sub>3</sub> yield rate of 288.2 μmol h<sup>-1</sup> cm<sup>-2</sup> (FE: 82.5%) at -0.6 V vs. RHE. EXAFS spectra of Fe K-edge and Mo K-edge confirm the existence of atomically distributed Fe dopants coordinated with lattice S atoms and the abundant sulfur vacancies (V<sub>S</sub>) in Fe/MoS<sub>2-x</sub> (Fig. 8e–h). In addition, the DFT calculations reveal that the cooperative effect of Fe-doping and V<sub>S</sub> has facilitated the NO adsorption and activation on Fe–Mo dual sites (Fig. 8i). Furthermore, the high ‘H’ adsorption barrier on Fe–Mo dual sites of Fe/MoS<sub>2-x</sub> has prohibited HER thereby resulting in high NH<sub>3</sub> selectivity (Fig. 8j). Table 4 summarizes the NORR activity of different Transition metal based single-atom catalysts.

### 3. p-Block element based electrocatalysts

The previous section showed that d-block element-based electrocatalysts show promising NO molecule adsorption and

activation owing to their unoccupied d-orbitals. However, the unoccupied d-orbitals are also favorable for ‘H’ atom binding, facilitating the competing HER and hindering the NH<sub>3</sub> selectivity in a wide potential window.<sup>111,112</sup> In contrast, excellent NH<sub>3</sub> selectivity is expected from p-block element-based electrocatalysts as they exclusively bind to ‘NO’ rather than ‘H’. Lin *et al.* achieved an excellent FE<sub>NH<sub>3</sub></sub> of about 90% and a high NH<sub>3</sub> yield rate of 1194 μg h<sup>-1</sup> mg<sup>-1</sup><sub>cat</sub> at -0.5 V vs. RHE from Bi nano dendrites (Fig. 9a).<sup>111</sup> Moreover, a good FE<sub>NH<sub>3</sub></sub> is maintained in a wide potential window of -0.3 V to -0.6 V. At the same time, the H<sub>2</sub> gas is only detectable at high cathodic potentials (Fig. 9b). In addition, the DFT calculations predict that ‘NO’ binds strongly over the Bi (012) surface as compared to the hydrogen atom, and subsequently gets activated through a two-way charge transfer mode thereby resulting in high NH<sub>3</sub> FE. Similarly, an outstanding FE<sub>NH<sub>3</sub></sub> of 93% is observed at -0.4 V vs. RHE of Bi nanoparticles decorated onto the carbon nanosheet. The corresponding Zn–NO battery has produced a maximum NH<sub>3</sub> yield of 355.6 μg h<sup>-1</sup> cm<sup>-2</sup> at a discharge current density of 4 mA cm<sup>-2</sup>. Sulfur vacancy (V<sub>S</sub>)-rich SnS<sub>2-x</sub> also showed an exceptional FE<sub>NH<sub>3</sub></sub> of 90.3% (NH<sub>3</sub> yield rate: 78.6 μmol h<sup>-1</sup> cm<sup>-2</sup>) at a large cathodic potential of -0.7 V vs. RHE, as the HER is significantly suppressed over the SnS<sub>2-x</sub> surface.<sup>112</sup> Compared to SnS<sub>2-x</sub>, the SnS<sub>2</sub> counterpart showed an inferior NH<sub>3</sub> yield rate and FE<sub>NH<sub>3</sub></sub>, thereby highlighting the advantage of the defect engineering strategy towards enhanced NORR. Theoretical computations unraveled that a V<sub>S</sub>-



Table 3 Summary of the NORR activity shown by different multi-valent non-precious transition metal compounds

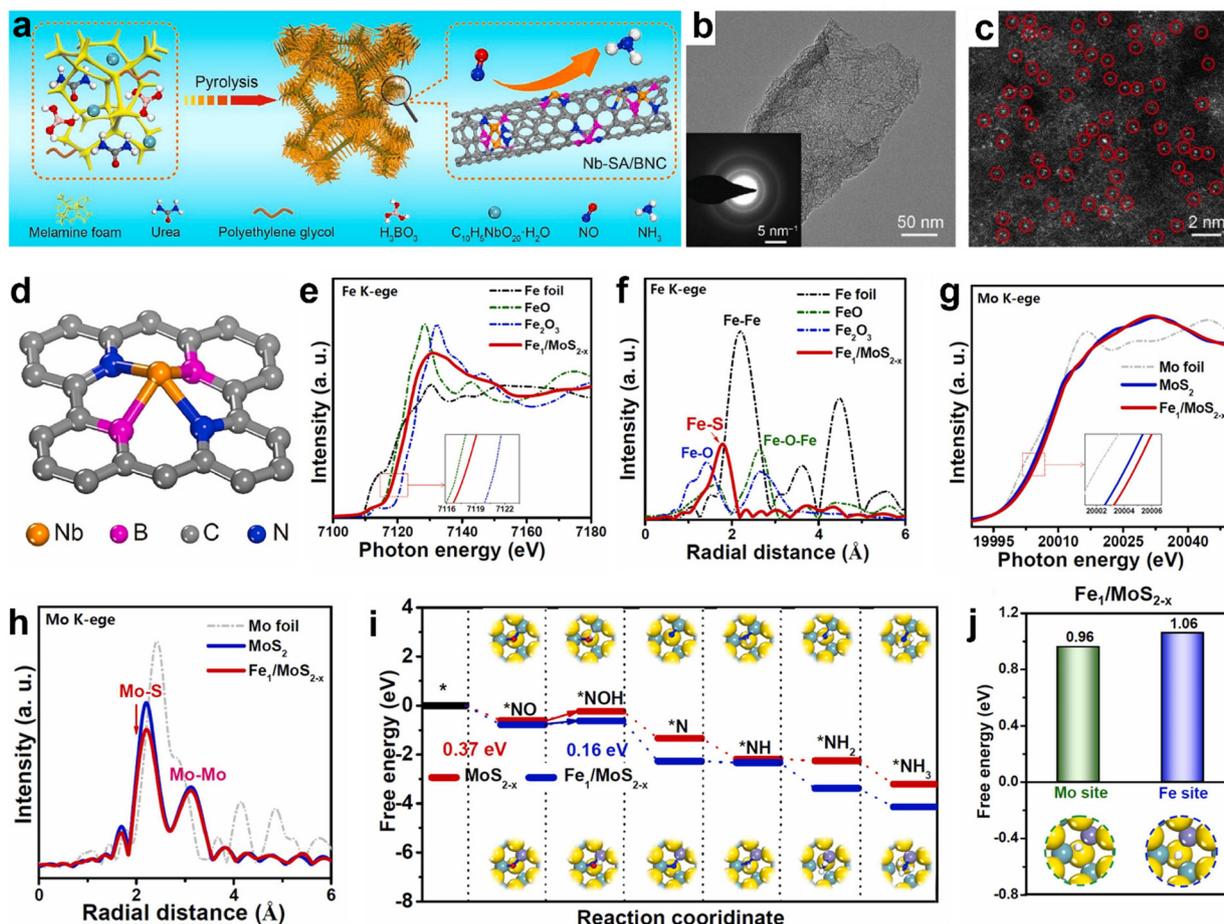
Catalyst	Synthetic route	Electrolyte	NH <sub>3</sub> yield rate	FE (%)	Potential (vs. RHE) (V)	Ref.
Fe <sub>2</sub> O <sub>3</sub> nanorods	Hydrothermal + annealing in Ar	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.5 mM Fe(II)EDTA (10% NO)	41.6 μmol h <sup>-1</sup> cm <sup>-2</sup>	86.73	-0.4	86
MnO <sub>2-x</sub> nanowires	Solvothermal + annealing in Ar	0.2 M Na <sub>2</sub> SO <sub>4</sub> (10% NO)	27.51 × 10 <sup>-10</sup> mol s <sup>-1</sup> cm <sup>-2</sup>	82.8	-0.7	87
TiO <sub>2-x</sub> nanoarray	Hydrothermal + H <sup>+</sup> exchange + annealing	0.2 M PBS (10% NO)	1233.2 μg h <sup>-1</sup> cm <sup>-2</sup>	~65	-0.7	88
CoNi <sub>(5:5)</sub> O <sub>x</sub> @Cu	Electrodeposition	1 M KOH	20 mg h <sup>-1</sup> cm <sup>-2</sup>	~100	-0.68	89
NiO nanosheets	Hydrothermal + calcination in air	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.5 mM Fe(II)EDTA (10% NO)	2130 μg h <sup>-1</sup> cm <sup>-2</sup>	90	-0.6	98
NiFe LDH nanosheets	Hydrothermal method	0.25 M Li <sub>2</sub> SO <sub>4</sub> + 0.5 mM Fe(II)EDTA (99.99% NO)	112 μmol h <sup>-1</sup> cm <sup>-2</sup>	82	-0.7	99
Cu <sub>2</sub> O@CoMn <sub>2</sub> O <sub>4</sub> hollow nanoreactors	CoMn-LDH growth on Cu <sub>2</sub> O nano-cube + annealing in Ar	0.1 M Na <sub>2</sub> SO <sub>4</sub> (99% NO)	94.18 mmol g <sup>-1</sup> h <sup>-1</sup>	75	-0.8	90
MoS <sub>2</sub> /GF	Hydrothermal method	0.1 M HCl + 0.5 mM iron(II) sodium benzoate (10% NO)	99.6 μmol cm <sup>2</sup> h <sup>-1</sup>	<30	-0.7	54
P-doped MoS <sub>2</sub> nanospheres	Hydrothermal + heat treatment with NaH <sub>2</sub> PO <sub>2</sub>	0.1 M 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate (99.99% NO)	237.7 μg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	69	-0.6	91
CoS <sub>1-x</sub> nanosheet	Hydrothermal + plasma treatment	0.2 M Na <sub>2</sub> SO <sub>4</sub> (10% NO)	44.67 μmol cm <sup>-2</sup> h <sup>-1</sup>	53.62	-0.4	92
Ni <sub>2</sub> P nanosheets	Hydrothermal + vapor phase phosphorization	0.1 M HCl (10% NO)	33.47 μmol h <sup>-1</sup> cm <sup>-2</sup>	76.9	-0.2	93
CoP nanowires	Hydrothermal + vapor phase phosphorization	0.2 M Na <sub>2</sub> SO <sub>4</sub> (10% NO)	47.22 μmol h <sup>-1</sup> cm <sup>-2</sup>	88.3	-0.2	94
FeP nanorods	Hydrothermal + vapor phase phosphorization	0.2 M PBS solution (10% NO)	85.62 μmol h <sup>-1</sup> cm <sup>-2</sup>	88.49	-0.2	95
Mo <sub>2</sub> C nanosheets	Liquid exfoliation of MoO <sub>3</sub> + vapor phase carbonization	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	122.7 μmol h <sup>-1</sup> cm <sup>-2</sup>	86.3	-0.4	96
MoC/NCS	Pyrolysis of a molybdenum complex and melamine	0.1 M HCl + 0.5 mM iron(II) sodium benzoate (99.99% NO)	1350 μg h <sup>-1</sup> cm <sup>-2</sup>	89	-0.8	97
Amorphous NiB <sub>2</sub>	Reflux approach	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	167.1 μmol h <sup>-1</sup> cm <sup>-2</sup>	90	-0.4	100
Nanoporous VN film	Vapor phase nitridation of V <sub>2</sub> O <sub>5</sub>	0.1 M HCl + 0.5 mM iron(II) sodium benzoate (99.99% NO)	1.05 × 10 <sup>-7</sup> mol cm <sup>-2</sup> s <sup>-1</sup>	85	-0.6	101

induced unsaturated Sn site in SnS<sub>2-x</sub> donates about -0.6 electrons to the adsorbed 'NO' to cause the N=O bond elongation and activation, while the electron donation is restricted over the Sn site of pristine SnS<sub>2</sub>. Additionally, the free energies for all protonation steps on SnS<sub>2-x</sub> are lower than those of SnS<sub>2</sub> and the RDS in the former is \*NH<sub>2</sub> → \*NH<sub>3</sub> with an uphill of 0.4 eV. Liang *et al.* have observed the efficient 'NO' activation on amorphous B<sub>2.6</sub>C, which is enabled by the effective electron injection into NO (π2p\*) from the B-C bond.<sup>113</sup> Given that, the amorphous B<sub>2.6</sub>C is sputtered onto a Ti plate-supported TiO<sub>2</sub> nanobelt array (a-B<sub>2.6</sub>C@TiO<sub>2</sub>/Ti) and found that the electrode can deliver a high NH<sub>3</sub> yield rate of 3678.6 μg h<sup>-1</sup> cm<sup>2</sup> and a FE<sub>NH<sub>3</sub></sub> of 87.6% at -0.9 V vs. RHE, which are far higher than those of B<sub>2.6</sub>C/Ti and TiO<sub>2</sub>/Ti (Fig. 9c and d). Meanwhile, the electrode maintained the same activity for up to 12 hours for bulk electrolysis. In addition, a maximum NH<sub>3</sub> yield of 1125.2 μg h<sup>-1</sup> cm<sup>-2</sup> was obtained for the corresponding Zn-NO battery at a discharge current of 10 mA cm<sup>-2</sup>. Metal-free boron phosphide (BP) also delivered a high FE of 83.3% with an NH<sub>3</sub> yield rate of 96.6 μmol h<sup>-1</sup> cm<sup>2</sup> at -0.7 V vs. RHE.<sup>114</sup> The DFT calculations indicate that both B and P atoms of BP can synergistically activate 'NO' through a strong p-p orbital overlap. In addition, the first hydrogenation step (\*NO → \*NHO) is found to be the RDS with a low energy barrier of 0.68 eV over BP(111). A promising NORR activity is noted from antimony single atoms confined in amorphous MoO<sub>3</sub> (Sb/a-MoO<sub>3</sub>) nanosheets (Fig. 9e).<sup>115</sup> In Sb/a-MoO<sub>3</sub>, Sb exists in a +3valence state and is surrounded by five O atoms to form Sb<sub>1</sub>-O<sub>5</sub> units, as is confirmed by the Sb K-edge XANES and EXAFS studies. As shown

in Fig. 9f, Sb/a-MoO<sub>3</sub> has exhibited an excellent FE<sub>NH<sub>3</sub></sub>, of about 92%, and a high NH<sub>3</sub> yield rate of 273.5 μmol h<sup>-1</sup> cm<sup>-2</sup> at -0.6 V vs. RHE in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. The combined *in situ* electrochemical studies and theoretical calculations demonstrated that Sb/a-MoO<sub>3</sub> prefers to follow an alternating-N pathway (Fig. 9g-i). Nevertheless, the 'Sb' site possesses optimal binding free energy for \*NO and unfavorable binding free energies for both \*H<sub>2</sub>O and \*H, thereby impeding the competing HER (Fig. 9j).

Meanwhile, atomically isolated, and unsaturated Sb sites located on Sb<sub>2</sub>S<sub>3</sub> also showed a significant NH<sub>3</sub> yield rate and excellent FE<sub>NH<sub>3</sub></sub> ~94% owing to the powerful 'NO' activation through the electron donation-back donation phenomenon and the selective 'NO' adsorption over H<sub>2</sub>O/H.<sup>116</sup> Besides, metal-free carbon-based materials are also found to be promising candidates toward efficient electroreduction of NO into NH<sub>3</sub> in a neutral medium. For instance, a honeycomb like carbon nanofiber coated onto a carbon paper has achieved a high FE<sub>NH<sub>3</sub></sub> and NH<sub>3</sub> yield of 88.33%, 22.35 μmol h<sup>-1</sup> cm<sup>-2</sup>, respectively, at -0.6 V vs. RHE and showed good durability for up to 10 h.<sup>117</sup> During the NORR, the interconnected nanocavities in the carbon fiber can effectively entrap the NO gas, after that, the electrochemically active -OH functional groups on the fiber can facilitate the NO reduction with a low energy input. Similarly, metal-free g-C<sub>3</sub>N<sub>4</sub> nanosheets deposited onto carbon paper (CNNS/CP) also showed remarkable NORR performance.<sup>118</sup> In addition, the regulation of the interface microenvironment around the CNNS/CP electrode through hydrophobic treatment is found to be beneficial for the improved gas-liquid-solid triphasic interface. Therefore, the NO





**Fig. 8** (a) Schematic diagram of the synthetic procedure of Nb-SA/BNC, (b) TEM image and SAED pattern of Nb-SA/BNC (inset of Fig. 5b), (c) HAADF-STEM image of Nb-SA/BNC, in which some of the SA Nb sites are highlighted by red circles, and (d) atomic model of Nb-SA/BNC. Reproduced with permission from ref. 106 copyright 2020, Elsevier. Fe K-edge (e) XANES, and (f) EXAFS spectra of Fe/MoS<sub>2-x</sub> and reference samples of Fe foil, FeO, and Fe<sub>2</sub>O<sub>3</sub>. Mo K-edge, (g) XANES and (h) EXAFS spectra of Mo foil, MoS<sub>2</sub>, and Fe/MoS<sub>2-x</sub>. (i) Free energy diagrams for the NORR on MoS<sub>2-x</sub> and Fe/MoS<sub>2-x</sub>, and (j) free energies of \*H adsorption on MoS<sub>2</sub> and Fe/MoS<sub>2-x</sub>. Reproduced with permission from ref. 108 copyright 2023, Elsevier.

**Table 4** Summary of the NORR activity shown by different transition metal-based single-atom catalysts

Catalyst	Synthetic route	Electrolyte	NH <sub>3</sub> yield rate	FE (%)	Potential (vs. RHE) (V)	Ref.
Nb/BNC	Carbonization in Ar	0.1 M HCl (100% NO)	$8.2 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$	77	-0.6	106
Ce/NHCS	Impregnation + carbonization	0.05 M HCl + 0.5 mM iron(II) sodium benzoate (99.99% NO)	$1023 \mu\text{g h}^{-1} \text{ mg}^{-1} \text{ cat}$	91	-0.7	109
W/MoO <sub>3-x</sub>	Supercritical CO <sub>2</sub> approach	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	$\sim 250 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	91.2	-0.4	110
Co/MoS <sub>2</sub>	Hydrothermal + impregnation method	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	$217.6 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	87.7	-0.5	107
Cu/MoS <sub>2</sub>	Hydrothermal + impregnation method	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	$337.5 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	90.6	-0.6	105
Fe/MoS <sub>2-x</sub>	Hydrothermal method	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	$288.2 \mu\text{mol h}^{-1} \text{ cm}^{-2}$	82.5	-0.6	108

mass transfer and availability over the electrode surface significantly increased, leading to 2 times enhancement in the NH<sub>3</sub> production. Table 5 summarizes the NORR activity of different p-block element-based electrocatalysts.

## Perspectives and challenges

The research progress indicates that the electrocatalytic NORR has great potential to replace the conventional Haber-Bosch

process for NH<sub>3</sub> production. However, the practical implementation of the NORR for NH<sub>3</sub> production is hindered by several challenges. First, most reported catalysts show high cathodic potentials (overpotentials) and exhibit unsatisfactory NH<sub>3</sub> yield rates and FE<sub>NH<sub>3</sub></sub> values. Thus, developing efficient electrocatalysts with high NH<sub>3</sub> product selectivity is of paramount interest for reducing the cell potential in a commercial electrolyzer. In this context, strategies to modulate the electronic structure of the electrocatalysts through alloying, doping, and defect engineering



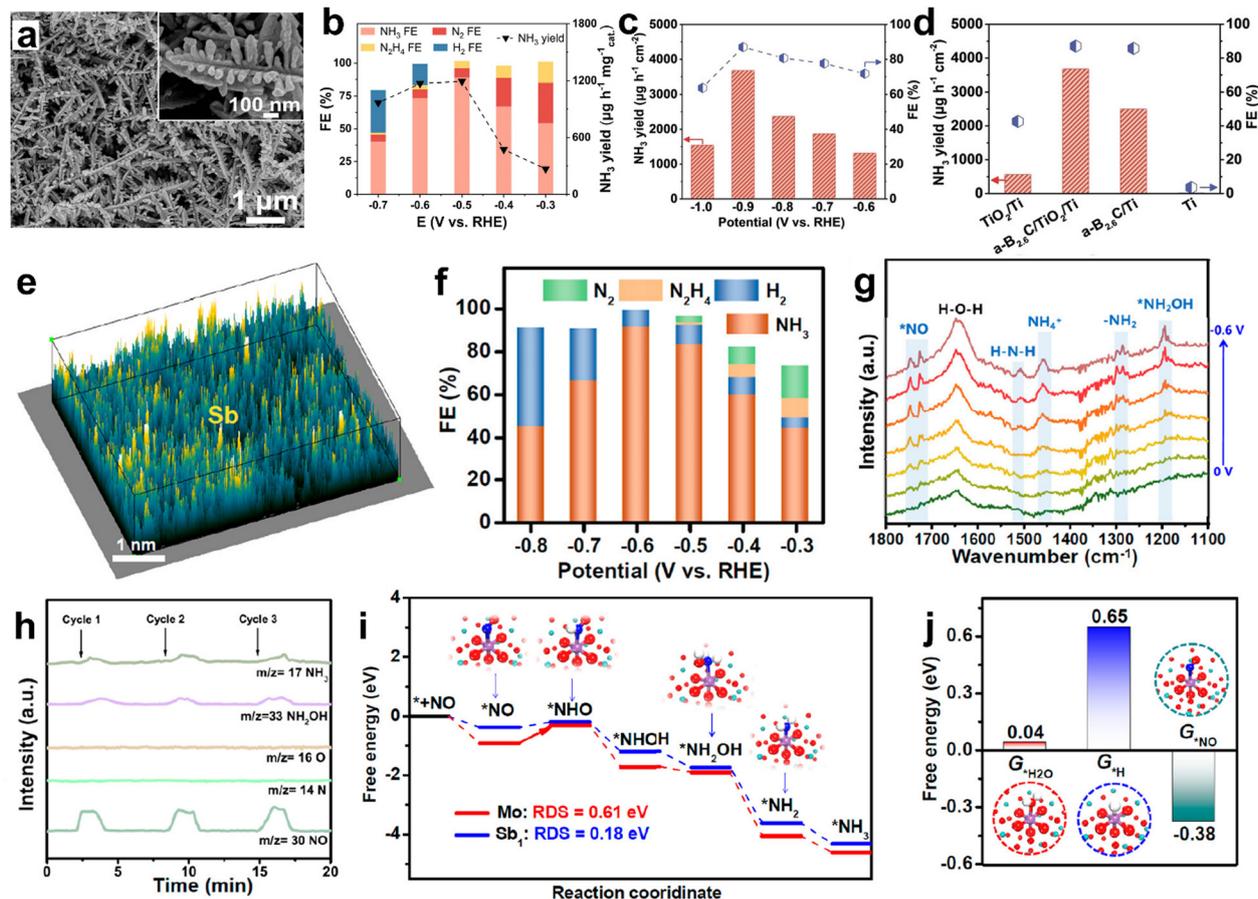


Fig. 9 (a) SEM image (inset: high-magnification image) of Bi NDs, (b) FEs of the major reductive products and  $\text{NH}_3$  yields for Bi NDs/CP at each given potential. Reproduced with permission from ref. 111 copyright 2022, Elsevier. (c) FEs and  $\text{NH}_3$  yields of  $\text{a-B}_{2.6}\text{C@TiO}_2/\text{Ti}$  at different potentials, (d) performance comparison. Reproduced with permission from ref. 113 copyright 2022, Wiley-VCH. (e) 3D atom image of p-block Sb single atoms confined in amorphous  $\text{MoO}_3$  ( $\text{Sb/a-MoO}_3$ ), (f) FEs of different products at various potentials, (g) potential-dependent *in situ* FTIR spectrum of  $\text{Sb/a-MoO}_3$  from 0 to  $-0.6$  V, (h) online DEMS spectrum of  $\text{Sb/a-MoO}_3$  during the NORR electrolysis at  $-0.6$  V, (i) free energy diagrams of alternating-N pathways on  $\text{a-MoO}_3$  and  $\text{Sb/a-MoO}_3$ , and (j) binding free energies of  $^*\text{H}_2\text{O}$ ,  $^*\text{H}$ , and  $^*\text{NO}$  on  $\text{Sb/a-MoO}_3$ . Reproduced with permission from ref. 115 copyright 2023, ACS.

could be considered. The operando and computational studies also guide the designing of the catalysts with ideal crystal facets and compositions for selective 'NO' adsorption over 'H' and the subsequent NORR intermediate stabilization. In addition, the materials can be grown with unique morphologies, high surface area, and ideal porosity to improve the charge transport and active site density.

Second, most of the NORR studies have used expensive 100% NO gas as a source for  $\text{NH}_3$  production as the solubility of 'NO' is poor in aqueous electrolytes (H-type cells). Although the utilization of 'NO' complexation agents in the electrolyte seems a promising strategy for attaining high  $\text{NH}_3$  yield rates from dilute NO (10%), the additional cost of the reagent, recyclability, and the  $\text{NH}_3$  separation from the electrolyte could be worrisome. In contrast, few studies have demonstrated that  $\text{NH}_3$  can be produced from dilute NO (1–10% NO) through the gas phase electrolysis using gas diffusion electrodes (GDEs) coated with electrocatalysts in a flow cell configuration. Thus, to understand the feasibility of  $\text{NH}_3$  synthesis from diluted 'NO' or exhaust gas, the NORR performance of the materials must be

evaluated in the gas phase (GDE and flow cells) along with 'NO-saturated electrolytes' (in H-type cells) by using the diluted 'NO' reactant (1–10%). The catalysts should possess ideal Gibbs free energy and significant orbital overlap for 'NO' adsorption and the subsequent hydrogenation steps. Also, the gas phase electrolysis of diluted 'NO' could eliminate the formation of N–N coupled side products ( $\text{N}_2$  and  $\text{N}_2\text{O}$ ).

Third, the NORR measurements must be performed in gas-tight cells to obtain reliable results as there is a high probability of interference of cathodic currents from  $\text{NO}_3^-$  contamination. Furthermore, to identify the exact nitrogen source for  $\text{NH}_3$  formation,  $^{15}\text{NO}$  isotopic labelling experiments should be carried out. Despite most of the reports relying only on the colorimetric method for  $\text{NH}_3$  quantification, the concurrent NMR measurements should be considered for further verification. DFT studies are used extensively to identify the active sites, Gibbs free energies for 'NO' and intermediate adsorption, RDS, and probable mechanistic pathways over different catalytic surfaces. However, the most favorable pathway of the NORR to  $\text{NH}_3$  is still elusive as the results are hugely varied over the different crystalline planes



Table 5 Summary of the NORR activity shown by different p-block element-based electrocatalysts

Catalyst	Synthetic route	Electrolyte	NH <sub>3</sub> yield rate	FE (%)	Potential (vs. RHE) (V)	Ref.
Bi nanodendrites	Electrodeposition	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.5 mM Fe(II)EDTA (10% NO)	1194 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat</sub>	89.2	-0.5	111
Bi@C	Annealing of bismuth citrate	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.5 mM Fe(II)EDTA (10% NO)	1164.8 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat</sub>	93	-0.5	119
SnS <sub>2-x</sub>	Hydrothermal + plasma treatment	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	78.6 μmol h <sup>-1</sup> cm <sup>-2</sup>	90.3	-0.7	112
B <sub>2.6</sub> C@TiO <sub>2</sub>	Magnetron sputtering of B <sub>2.6</sub> C onto TiO <sub>2</sub>	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.5 mM Fe(II)EDTA (10% NO)	3678.6 μg h <sup>-1</sup> cm <sup>-2</sup>	87.6	-0.9	113
BP	Vacuum-sealing approach	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	96.6 μmol h <sup>-1</sup> cm <sup>-2</sup>	83.3	-0.7	114
Sb/a-MoO <sub>3</sub>	Supercritical CO <sub>2</sub> approach	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	273.5 μmol h <sup>-1</sup> cm <sup>-2</sup>	91.7	-0.6	115
In/a-MoO <sub>3</sub>	Supercritical CO <sub>2</sub> approach	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	242.6 μmol h <sup>-1</sup> cm <sup>-2</sup>	92.8	-0.6	120
Sb/Sb <sub>2</sub> S <sub>3</sub>	Solvothermal method	0.5 M Na <sub>2</sub> SO <sub>4</sub> (99.99% NO)	168.6 μmol h <sup>-1</sup> cm <sup>-2</sup>	93.7	-0.7	116
Honeycomb carbon nanofiber	Electrospinning followed by carbonization	0.2 M Na <sub>2</sub> SO <sub>4</sub> (10% NO)	22.35 μmol h <sup>-1</sup> cm <sup>-2</sup>	88.3	-0.6	117
g-C <sub>3</sub> N <sub>4</sub> nanosheets	Calcination of melamine + ultrasonication	0.1 M PBS solution (20% NO)	30.7 μmol h <sup>-1</sup> cm <sup>-2</sup>	45.6	-0.8	118

and compounds. This makes it difficult to predict the ideal catalytic surfaces for efficient NORR to NH<sub>3</sub>. Along with the computational studies, the real-time FTIR and DEMS studies could be beneficial to identify the reaction intermediates and to understand the favorable mechanism.

Fourth, the NORR performance of many reported electrocatalysts was evaluated in neutral and alkaline media. However, to obtain NH<sub>3</sub> from commercial PEM electrolyzers, efficient and durable catalysts that could function in an acidic medium are highly desirable. In addition, the durability tests on the developed catalysts must be performed at high NH<sub>3</sub> yield rates to unveil their suitability for bulk NH<sub>3</sub> production. Apart from the H-type cell, the demonstration of NH<sub>3</sub> production from a prototype membrane electrode assembly (MEA) electrolyzer will pave the way for practical NH<sub>3</sub> synthesis. Besides, replacing of conventional anodic oxygen evolution reaction in the MEA electrolyzer with NO<sub>x</sub>/SO<sub>x</sub> oxidation reactions simultaneously produces the value-added NH<sub>3</sub> and nitric acid/sulfuric acid chemicals in the cathodic and anodic compartments, respectively.

In the future, screening of electrocatalysts to selectively produce urea from the co-reduction of NO and CO<sub>2</sub> will be of great significance. The sustainable urea generation using the MEA electrolyzer through the injection of the industrial exhaust (flue gas) could be a futuristic goal. With sincere efforts in electrocatalyst development and rigorous evaluation methods, we anticipate that the production of value-added products from pollutants could be realized soon.

## Conflicts of interest

There are no conflicts to declare.

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