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BRIEF OVERVIEW



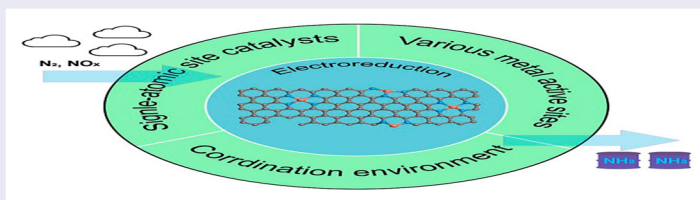
# Single-atomic site catalysts for electrochemical nitrogen fixation

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## ABSTRACT

Renewable-energy-derived electrochemical nitrogen fixation represents a sustainable way to produce green ammonia (NH<sub>3</sub>), but the energy efficiency is limited by its sluggish kinetics and complex reaction pathways. Highly active, selective and robust electrocatalysts are strongly needed to promote the efficiency of nitrogen conversion. Here, we provide an overview of the recent progress in understanding the structure–function correlation of single-atomic site catalysts (SASCs) for electrochemical nitrogen fixation, to provide mechanistic insights and guide the future rational design of SASCs. First, we review the fundamental understanding of both N<sub>2</sub> and oxynitride reduction on SASCs, with different hydrogenation pathways. Afterwards, we present the recent progress in the development of well-defined SASCs with various metal centres and the influence from local chemical environments, such as the coordination number, first-shell and second-sphere coordination. At last, we listed some perspectives on future study in this emerging research field.



## IMPACT STATEMENT

The paper provides mechanistic insights into the single-atomic site catalysts towards electrochemical nitrogen fixation.

## ARTICLE HISTORY

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## KEYWORDS

Single-atomic site catalysts; nitrogen fixation; electrocatalysis; mechanistic understanding

## 1. Introduction

As an irreplaceable component of protein and amino acid, nitrogen plays an integral role for all living organisms and is of great biological significance [1–5]. Given that, the balance of nitrogen shares an equal importance with carbon cycling to human survival and the survival of other animals and plants on Earth. In the natural biological nitrogen cycle, inorganic and organic nitrogen compounds are interconverted ammonification, ammonia assimilation, nitrification, nitrate assimilation, nitrogen fixation, and denitrification [1,2,4–7]. Of the circulation, nitrogen fixation is a key process [8,9]. The vast majority of nitrogen fixation in nature is performed via certain types of bacteria and blue-green algae [10–12]. Abiotic processes, such as lightning and ultraviolet irradiation, also help to fix

smaller amounts of atmospheric N<sub>2</sub> [13]. Dating back to the early 1900s, an industrial Haber–Bosch process was invented to convert N<sub>2</sub> to ammonia (NH<sub>3</sub>) via heterogeneous catalysis under high temperatures (300–500°C) and high pressures (15–30 MPa) [14–21]. This technological breakthrough rendered humans no longer rely on natural nitrogen fertilizer and effectively solved the contradiction between food and population [22–24]. Although this process hugely promoted the development of agriculture and human society, a large amount of fossil fuels was consumed in such a process and resulted in serious negative consequences in environmental issues [25,26]. Therefore, exploring other less-energy-consuming and environment-friendly strategies for nitrogen fixation are particularly significant and urgent [23,27–29].

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Electrochemical nitrogen conversion is considered a green strategy because of its capability to incorporate renewable energy, such as solar and wind, to drive the reaction at the ambient temperature and pressure [21,30–34]. No contamination issue is accompanied by such a process. Even more attractively, the primary reactants in such a process can be oxynitride pollutants instead of  $N_2$ , such as nitric oxide (NO) [35–38], nitrous oxide ( $NO_2$ ), nitrite ( $NO_2^-$ ) [39,40] and nitrate ( $NO_3^-$ ) [41–45], etc. Those nitrogen-containing wastes not only threaten the environment, causing acid rain and the greenhouse effect but also exert deleterious impacts on human health and ecosystems [46–48]. Therefore, electrochemical nitrogen fixation is beneficial to convert oxynitride-based species into high-value-added products from the point of ‘turning waste into wealth’, and thus decreases the amounts of nitrogen pollutants which can cause numerous environmental issues [30,49–52]. Over the past few years, electrochemical nitrogen fixation aroused broad attention worldwide [53]. However, the nitrogen conversion is strongly limited by the low faradic efficiency (FE) and low  $NH_3$  yield as a result of the high-energy barrier for the reactant activation, complex electron-transfer step and competing hydrogen evolution reaction (HER) [54–56]. Current strategies to address these issues have focused on the electrocatalyst design for effective nitrogen activation and concomitant HER suppression [57–60]. Abundant electrocatalysts, such as metals, metal oxides, metal phosphides/chalcogenides and molecular complexes, etc., have been extensively explored in  $N_2$  and oxynitride (such as  $NO_3^-$ ,  $NO_2^-$  and NO) reduction [61–63].

Ever since the concept of ‘single-atomic site catalysts’ (SASCs) was proposed in 2011 [64], single-atom catalysis has been rapidly becoming a research frontier in the field of catalysis [65–69]. This category of catalysts affords an opportunity for obtaining the maximum active site utilization and high durability towards electrocatalysis [70,71]. Simultaneously, compared with inorganic solids, the single-atomic sites and surrounding ligands can be controlled and designed more precisely, thus can serve as a model system to bridge the homogeneous and heterogeneous systems [72,73]. To date, SASCs have been widely applied in almost all types of electrochemical small molecule transformation, such as hydrogen evolution reduction (HER) [74–76], oxygen reduction reaction (ORR) [77–79], oxygen evolution reaction (OER) [80,81], carbon dioxide reduction reaction ( $CO_2$ RR) [82,83] and  $N_2$  and  $NO_3^-$  reduction, etc. Relative to other heterogeneous catalysts, the unique properties of SASCs render them marvellous electrocatalysts for nitrogen fixation, providing an ideal system to understand the structure-performance relationship

due to the uniform chemical environments surrounding active sites [55,84]. Despite that numerous SASCs for nitrogen conversion have been reported, the correlation between the electronic/coordination structure of active sites and catalytic performance remains to be discussed with caution.

In this review, we emphasized the recent progress in the realm of electrochemical nitrogen and oxynitride reduction from the perspective of SASCs. To begin with, we introduced a fundamental understanding towards the hydrogenation pathways from  $N_2$  and  $NO_3^-$ . Then, we reviewed some recent progress on the development of well-defined SASCs with various metal centres, and showed some mechanistic studies on the influence of local chemical environments of active centres, such as the coordination number, first-shell and second-sphere coordination. Finally, the outlooks in this direction were proposed for the future rational design of high-performance SASCs.

## 2. Mechanistic understanding

Nitrogen displays various oxidation states ranging from  $-3$  to  $+5$ .  $NH_3$ , as the most reductive species, generally serves as the ultimate product in electrochemical  $N_2$  reduction reaction (ENRR) and electrochemical  $NO_x$  reduction reaction ( $ENO_x$ RR). Figure 1 depicts the multiple electron transfer steps involved along the nitrogen reduction pathway, wherein variable nitrogen-containing species are possible to be produced [9,62]. Despite  $NH_3$  is the thermodynamically favourable product, the sluggish kinetics strongly limits the yield and FE of  $NH_3$  in ENRR because of the chemically stable  $N \equiv N$  triple bond, complex electron transfer steps and the competitive proton reduction in an aqueous media [50,85]. Compared with  $N_2$ , oxynitride species are much easier to get reduced, leading to a broad range of reduced nitrogen products, such as ammonia ( $NH_3$ ), hydroxylamine ( $NH_2OH$ ), nitrous oxide ( $N_2O$ ) and nitrogen ( $N_2$ ), etc. Consequently, one of the most significant challenges in electrochemical nitrogen fixation is to improve the catalytic efficiency of ENRR and regulate the product distribution in  $ENO_x$ RR [41]. To achieve this, a fundamental mechanistic understanding of the reduction pathways is needed, to guide the rational design of electrocatalysts with impressive activity, selectivity and durability [51,86,87].

### 2.1. Fundamental understanding of ENRR

In a typical ENRR electrolyser,  $N_2$  is fed into the cathode chamber as the reactant and gets reduced to  $NH_3$ . Concurrently, water is oxidized to oxygen at the anode.

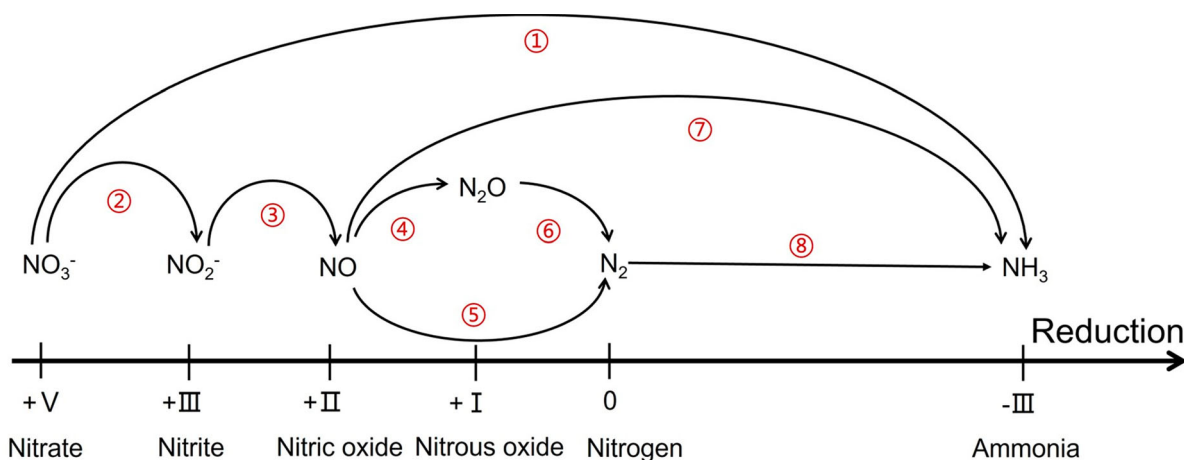


**Figure 1.** Possible reduction pathways in electrochemical nitrogen conversion, leading to a variety of nitrogen-containing species with different nitrogen oxidation states.

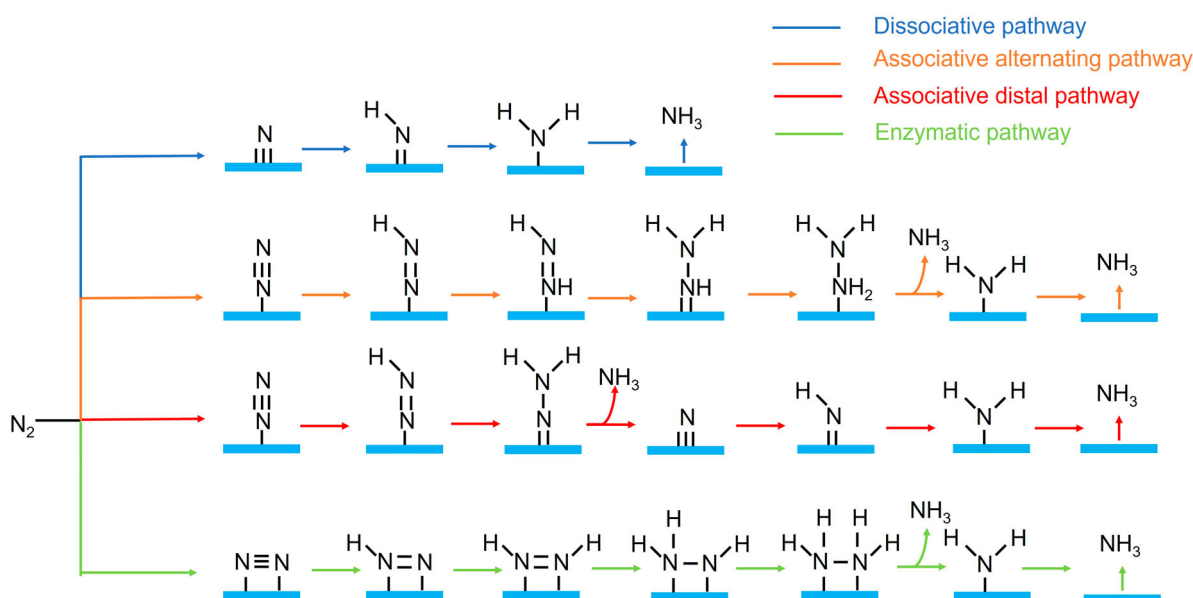


**Figure 2.** Multiple proposed  $\text{N} \equiv \text{N}$  cleavage and hydrogenation pathways in  $\text{N}_2$  reduction.

However, the inertness of the  $\text{N} \equiv \text{N}$  bond strongly limits the cleavage efficiency and product selectivity due to the competitive proton reduction in an aqueous electrolyte [50,56]. To date, the proposed  $\text{NH}_3$  production generally follows a dissociative pathway and an associative pathway in ENRR [88]. As shown in Figure 2, in the dissociative pathway, the strong triple  $\text{N} \equiv \text{N}$  bond is first broken, and the single adsorbed N atom is left on the surface of the catalyst. Subsequently, the hydrogenation on each adsorbed N atom leads to the formation of  $\text{NH}_3$ , which desorbs from the surface afterwards. The industrial Haber–Bosch process for  $\text{NH}_3$  synthesis was proposed to achieve this way [89]. Distinguished from the dissociative pathway, the  $\text{N} \equiv \text{N}$  bond breaking and the formation of  $\text{NH}_3$  take place simultaneously in an associative pathway. Depending on the sequences of

hydrogenation, there are associative alternating pathway, associative distal pathway and enzymatic pathway. In the associative alternating pathway, two nitrogen atoms proceed with hydrogenation alternatively, thus two moles of  $\text{NH}_3$  are released consecutively at the final step. As for the associative distal pathway, hydrogenation occurs on the distal N atom. Only after the first N atom hydrogenates to  $\text{NH}_3$  and gets released from the surface, the other N starts to adsorb proton to produce a second  $\text{NH}_3$  molecule. On the contrary, the hydrogenation sequence of the enzymatic pathway is similar to the alternating pathway, wherein the two N atoms get hydrogenated alternatively. However, the major difference is that both N atoms need to bond with the catalyst surface in a bridge adsorption manner, indicating that the SASCs may not be able to follow this pathway to catalyze nitrogen conversion,

due to the lack of neighbouring metal centres. It is noteworthy that the investigation on  $\text{N}\equiv\text{N}$  cleavage is still far to reach a consensus, and the debate strongly promotes further studies in this field. Recently, a new ENRR mechanism, called Mars–van Krevelen (MvK) mechanism [90], was proposed by Abghoui et al.. They tracked the  $\text{N}_2$  conversion on transition-metal nitride using the density functional theory (DFT) calculations, unveiling a lattice nitrogen-incorporated reduction mechanism, wherein the N on the surface first gets reduced to  $\text{NH}_3$ , creating an N-vacancy that will chemically adsorb other nitrogen molecules, and allowing ENRR to occur continuously. Although some possibilities have been proposed, the complex mechanism is not clear, and more theories and experiments are still in need.

## 2.2. Fundamental understanding of $\text{ENO}_x\text{RR}$

Compared with  $\text{N}_2$  reduction, the reduction of oxynitride is an even more complex process, involving a variety of intermediates and nitrogen-containing products with

a broad range of oxidation states [86,91]. Usually,  $\text{N}_2$  and  $\text{NH}_3$  are two major products in  $\text{ENO}_x\text{RR}$  owing to their thermodynamic stability [41]. Although converting  $\text{NO}_3^-$  into innocuous  $\text{N}_2$  is promising in terms of environmental protection,  $\text{NH}_3$  is a more favourable product due to its potential application in agricultural, pharmaceutical and cosmetics industries as a building-block chemical [92–94]. The related reaction pathways in electrocatalytic  $\text{NO}_3^-$  reduction are shown in Figure 3. The initial step is the adsorption of  $\text{NO}_3^-$ , and the following formation of nitrite ( $\text{NO}_2^-$ ) is generally regarded as the rate-determining step (RDS) along the reduction pathway [61]. Notably,  $\text{NO}$  is a key intermediate and plays an indispensable role in determining further reduced nitrogen products [95]. As for SASCs, two possible  $\text{NO}$ -adsorbing configurations were proposed, which resulted in three possible hydrogenation pathways from  $\ast\text{NO}$  to  $\text{NH}_3$ :  $\ast\text{N}$ -pathway,  $\ast\text{O}$ -pathway and  $\ast\text{NH}_2\text{OH}$ -pathway. Depending on the hydrogenation occurring sites, the adsorbed  $\text{NO}$  may form  $\ast\text{NHO}$  ( $\ast\text{NO}\rightarrow\ast\text{NHO}$ ) or  $\ast\text{NOH}$  ( $\ast\text{NO}\rightarrow\ast\text{NOH}$ ). In the  $\ast\text{N}$ -pathway,  $\ast\text{NOH}$

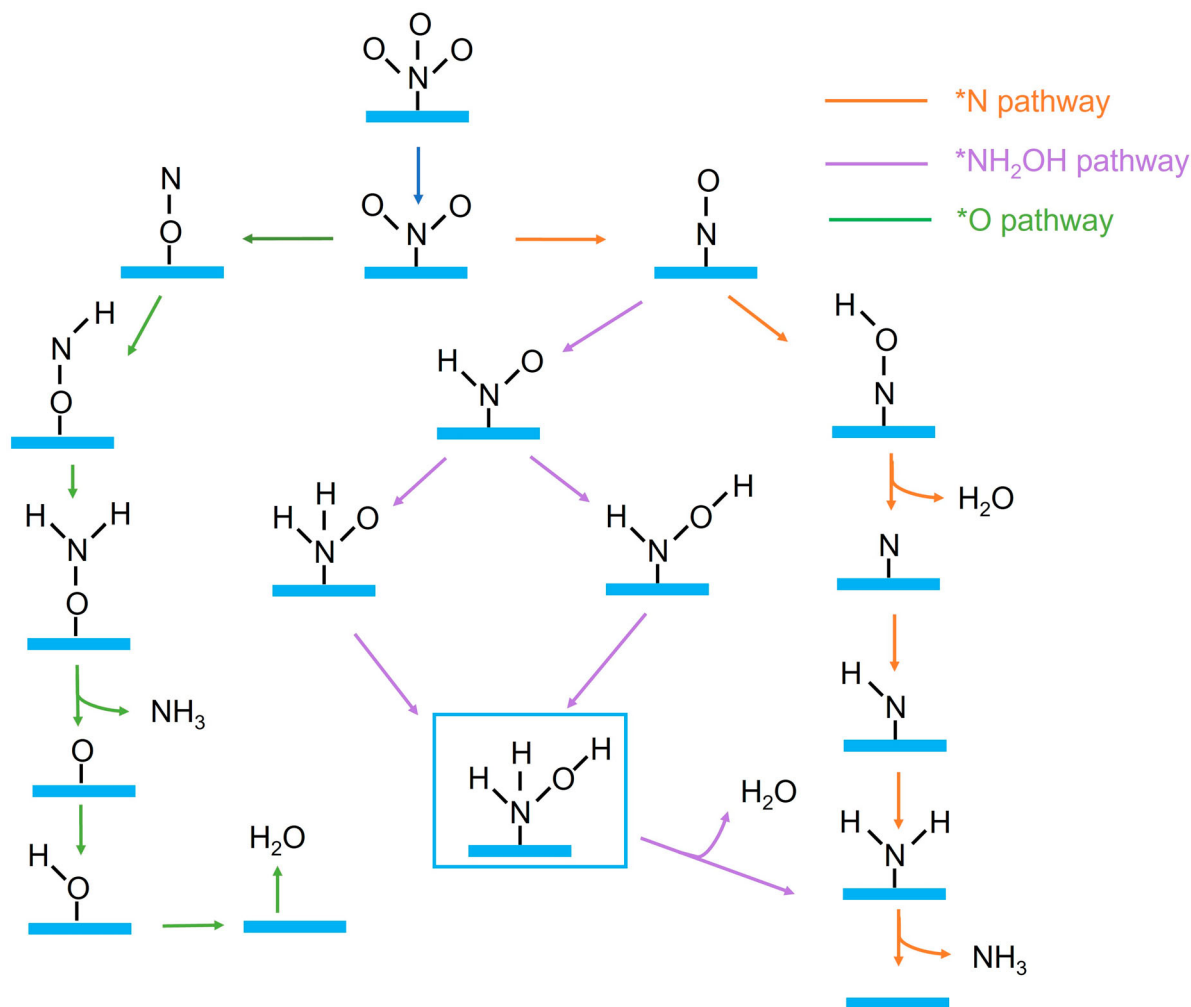


**Figure 3.** Possible reduction pathways of  $\text{NO}_x$  conversion.

is attacked by protons to form  $*N$  and  $H_2O$  and the  $*N$  intermediate continues to adsorb proton and gets reduced in the following steps and ultimately generates  $NH_3$ . Alternatively, in the  $*O$ -pathway, the oxygen atom is adsorbed on the catalyst surface, and the proton consecutively attacks the distal nitrogen atom instead to form  $NH_3$ , leaving oxygen atoms on the surface and finally hydrogenates to a water molecule. However, if the N atom adsorbs on the catalyst surface and gets hydrogenated first, it may lead to another  $*NH_2OH$  pathway, wherein the immediate  $*NH_2OH$  is a critical species to form  $NH_3$ .

### 3. Rational design of SASCs for electrochemical nitrogen fixation

As a category of electrocatalysts featuring maximized metal utilization, lower-coordinated metal centres and tunable structures, SASCs offer remarkable activities and selectivities in nitrogen conversion [69,96]. In SASCs, the electronic structure of metal nuclei strongly influences the formation and adsorption/desorption of key intermediates, and thus plays a deterministic role in the final product distribution [68,73]. In addition, regulating the local chemical environments of metal centres is an efficient way to optimize the electronic structure, and therefore, is important to enhance the productivity

of  $NH_3$  [70]. In this section, we will highlight the structure–function correlation of SASCs in ENRR and  $ENO_xRR$  from two aspects: the various metal centres and the coordination environmental effect.

#### 3.1. Various metal centres for ENRR and $ENO_xRR$

Metal centres of SASCs play an indispensable role to determine the selectivity and yield of  $NH_3$ . To date, a variety of SASCs with monodispersed metal atoms has been studied for nitrogen fixation, including Ru [97–99], Au [100–102], Fe [103–109], Mo [110–113], etc. To obtain a more intuitive understanding of the performance of SASCs with different metal centres, a suit of SASCs reported for nitrogen fixation is listed in Table 1, revealing that various metal sites significantly affect the activity towards  $NH_3$  synthesis.

Experimental studies on SASCs with noble metal centres, such as Ru, Au, Pd [118] and Rh [119], etc., revealed that those sites show excellent electrochemical performance due to their superior electrical conductivities and suitable adsorption capacities towards nitrogen molecules. For instance, a single-atomic Au catalyst anchoring on  $MoSe_2$  nanotube was synthesized by chemical vapour deposition and exhibited a considerable FE of 37.82% towards  $NH_3$  in ENRR with

**Table 1.** Catalytic performances of SASCs for ENRR and  $ENO_xRR$ .

| Reactants | Central metal | Electrolyte                                    | $NH_3$ FE (%) | $NH_3$ yield rate                   | References | Pontential ( $V_{RHE}$ ) |
|-----------|---------------|------------------------------------------------|---------------|-------------------------------------|------------|--------------------------|
| $N_2$     | Au            | 0.1 M HCL                                      | 12.3          | $2.32 \mu g h^{-1} cm^{-2}$         | [101]      | −0.2                     |
| $N_2$     | Au            | 5 mM $H_2SO_4$                                 | 11.1          | $72.5 \mu mol h^{-1} mg_{cat}^{-1}$ | [102]      | −0.1                     |
| $N_2$     | Au            | 0.1 M $Na_2SO_4$                               | 37.82         | $30.83 \mu g h^{-1} mg_{cat}^{-1}$  | [100]      | −0.3                     |
| $N_2$     | Ag            | 0.1 M HCL                                      | 21.9          | $270.9 \mu g h^{-1} mg_{cat}^{-1}$  | [114]      | −0.6                     |
| $N_2$     | Ru            | 0.05 M $H_2SO_4$                               | 29.6          | $120.9 \mu g h^{-1} mg_{cat}^{-1}$  | [99]       | −0.2                     |
| $N_2$     | Ru            | 0.1 M HCL                                      | 21            | $3.655 mg h^{-1} mg_{Ru}^{-1}$      | [98]       | −0.21                    |
| $N_2$     | Ru            | 0.5 M KOH                                      | 8.3           | $23 \mu g h^{-1} mg_{cat}^{-1}$     | [97]       | 0.05                     |
| $N_2$     | Fe            | 0.1 M KOH                                      | 56.55         | $7.48 \mu g h^{-1} mg_{cat}^{-1}$   | [106]      | 0                        |
| $N_2$     | Fe            | 0.05 M HCL                                     | 18.6          | $62.9 \mu g h^{-1} mg_{cat}^{-1}$   | [105]      | −0.4                     |
| $N_2$     | Fe            | 0.5 M $K_2SO_4$                                | 18.8          | $8.63 \mu g h^{-1} mg_{cat}^{-1}$   | [104]      | −0.3                     |
| $N_2$     | Fe            | 0.1 M KOH                                      | 51            | $307.7 \mu g h^{-1} mg_{cat}^{-1}$  | [115]      | −0.15                    |
| $N_2$     | Fe            | 0.1 M HCL                                      | 17.3          | $18.3 \mu g h^{-1} mg_{cat}^{-1}$   | [109]      | −0.2                     |
| $N_2$     | Fe            | 0.1 M KCl                                      | 31.6          | $613 \mu g h^{-1} mg_{cat}^{-1}$    | [103]      | −0.2                     |
| $N_2$     | Co            | 0.05 M $Na_2SO_4$                              | 10.5          | $0.86 \mu mol h^{-1} cm^{-2}$       | [116]      | −0.2                     |
| $N_2$     | Mo            | 0.1 M KOH                                      | 14.6          | $34 \mu g h^{-1} mg_{cat}^{-1}$     | [110]      | −0.3                     |
| $N_2$     | Mo            | 0.1 M KOH                                      | 13.27         | $37.67 \mu g h^{-1} mg_{cat}^{-1}$  | [111]      | −0.4                     |
| $N_2$     | Mo            | 0.1 M $Na_2SO_4$                               | 21            | $145.4 \mu g h^{-1} mg_{cat}^{-1}$  | [112]      | −0.2 (SCE)               |
| $N_2$     | Cu            | 0.1 M KOH                                      | 13.8          | $53.3 \mu g h^{-1} mg_{cat}^{-1}$   | [117]      | −0.35                    |
| $N_2$     | Pd            | 0.05 M $H_2SO_4$                               | 24.8          | $69.2 \mu g h^{-1} mg_{cat}^{-1}$   | [118]      | −0.45                    |
| $N_2$     | Rh            | 9 mM $H_2SO_4$                                 | 73.3          | $271.8 \mu g h^{-1} mg_{cat}^{-1}$  | [119]      | −0.3                     |
| $N_2$     | Nb            | 0.1 M HCL                                      | 10.4          | $209.4 \mu g h^{-1} mg_{cat}^{-1}$  | [120]      | −0.8                     |
| $NO_3^-$  | Fe            | 0.1 M $K_2SO_4$ + 0.5 M $KNO_3$                | 75            | $0.46 mmol h^{-1} cm^{-2}$          | [121]      | −0.66                    |
| $NO_3^-$  | Fe            | 0.1 M NaOH + 0.1 M $Na_2SO_4$ + 0.1 M $NaNO_3$ | 98            | $0.03 mmol h^{-1} cm^{-2}$          | [122]      | −0.3                     |
| $NO_3^-$  | Fe            | 0.1 M KOH + 0.1 M $KNO_3$                      | 99.69         | $2.57 mol h^{-1} g_{cat}^{-1}$      | [123]      | −0.5                     |
| $NO_3^-$  | Cu            | 50 mg $L^{-1}$ $NaNO_3$ -N + 0.5 M $NaSO_4$    | 94            | $9.23 mg h^{-1} mg_{cat}^{-1}$      | [124]      | −1.5 (SCE)               |
| $NO_3^-$  | Cu            | 0.1 M KOH + 0.1 M $KNO_3$                      | 84.7          | $12.5 mol h^{-1} g_{Cu}^{-1}$       | [43]       | −1                       |
| $NO_3^-$  | Rh            | 0.1 M $Na_2SO_4$ + 0.1 M $KNO_3$               | 93            | $1.27 mmol h^{-1} cm^{-2}$          | [125]      | −0.2                     |
| $NO_3^-$  | Au            | 0.1 M KOH + 7.4 mM $KNO_3$                     | 90.5          | $555 \mu g h^{-1} cm^{-2}$          | [126]      | −0.2                     |
| $NO_3^-$  | Ru            | 1 M KOH + 1 M $NaNO_3$                         | 87.3          | $22.2 mol h^{-1} g_{cat}^{-1}$      | [42]       | −0.3                     |
| $NO_3^-$  | Cu            | 1 M KOH + 1 M $KNO_3$                          | 95.5          | $13.8 mol h^{-1} g_{cat}^{-1}$      | [44]       | −1                       |
| $NO_3^-$  | Cu            | 0.5 M $Na_2SO_4$ + 1000 ppm N- $KNO_3$         | 88.46         | $28.73 mg h^{-1} cm^{-2}$           | [45]       | −2                       |
| NO        | Nb            | 0.1 M HCL                                      | 77            | $8398 \mu g h^{-1} mg_{cat}^{-1}$   | [120]      | −0.6                     |

a yield rate of  $30.83 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ , superior to most reported SASCs catalysts (Figure 4a–c) [100]. It was demonstrated that Au lowered the energy barrier for  $\text{N}_2$  adsorption, leading to an easier activation, which was confirmed by *in-situ* Raman spectroscopy and theoretical calculations. Zeng et al. prepared a Ru-SASC by pyrolyzing a zeolitic imidazolate framework for ENRR (Figure 4d) [99]. The isolated Ru sites achieved an impressive  $\text{NH}_3$  yield rate of  $120 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  with an FE of 29.6%, along with a 12-hour electrochemical stability (Figure 4e,f). Furthermore, Tao et al. studied the electro-reduction of nitrogen on Ru-SASC, which demonstrates a remarkable selectivity of 21% [98]. Han

et al. developed a Pd-SASC for nitrogen fixation, achieving a desirable  $\text{NH}_3$  FE of 24.8% [118]. Rh was predicted to be the best candidate for ENRR, locating at near the top of a volcano plot. An Rh-SASC embedded in  $\text{MnO}_2$  was designed, and the selectivity of  $\text{NH}_3$  was greatly improved, achieving a record FE of 73.3% (Figure 4g) [119]. Overall, ENRR on noble-metal SASCs has shown great achievements. To further promote the efficiency of nitrogen conversion, the competitive HER should be rationally suppressed through surface engineering, which could be possibly achieved by increasing the binding energies between nitrogen molecules and metal centres [108].

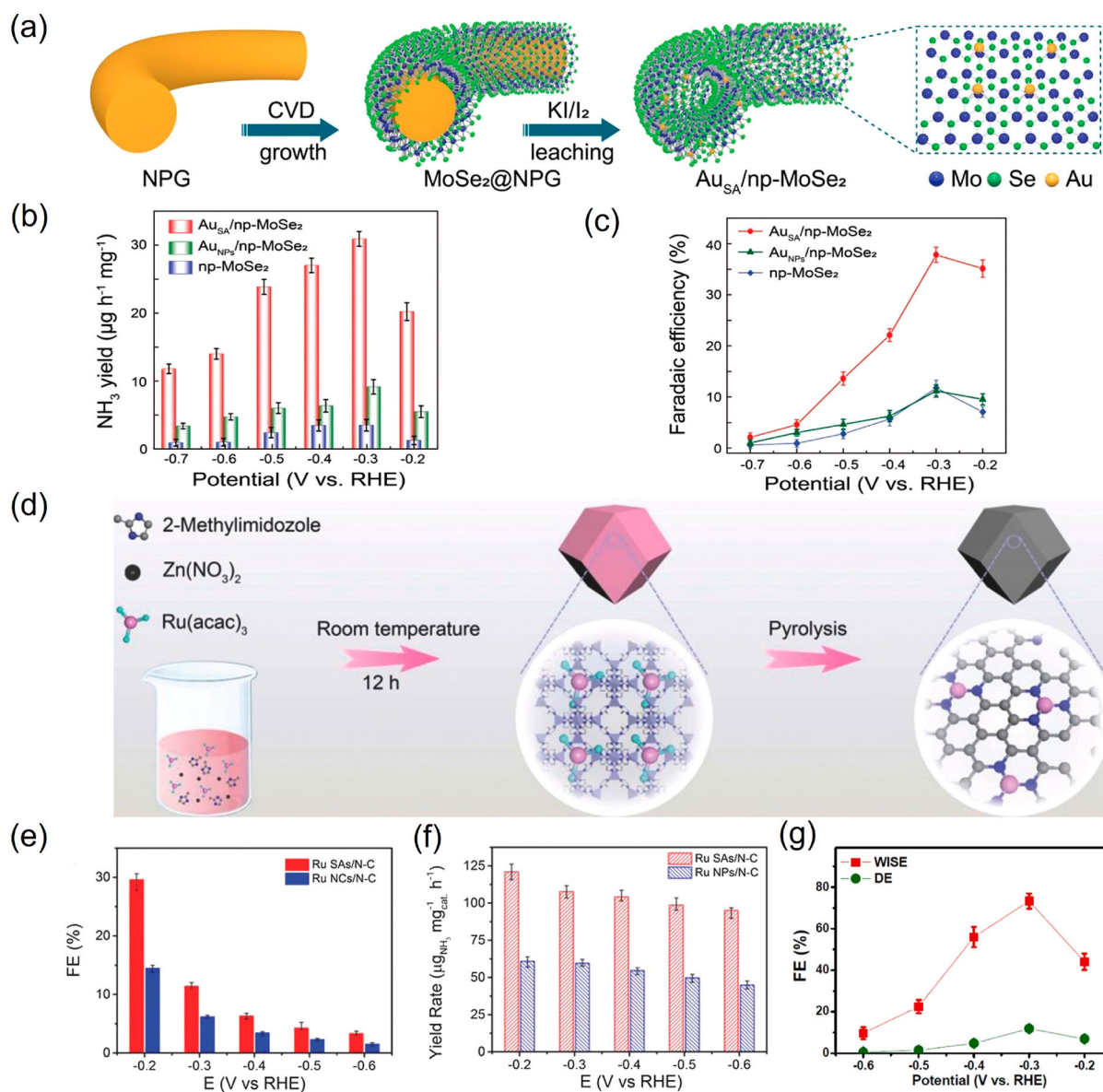


**Figure 4.** (a) Schematic illustration of synthetic procedure for  $\text{Au}_{\text{SA}}/\text{np-MoSe}_2$ . (b)  $\text{NH}_3$  yield rates and (c) FE at different applied potentials. Copyright 2022, John Wiley and Sons [100]. (d) Scheme of the synthetic procedure for Ru SAs/N-C. (e) FE and (f)  $\text{NH}_3$  yield rates at different applied potentials. Copyright 2018, John Wiley and Sons [99]. (g) FEs over Rh/ $\text{MnO}_2$  in a dilute electrolyte and water-in-salt electrolytes. Copyright 2022, Elsevier [119].

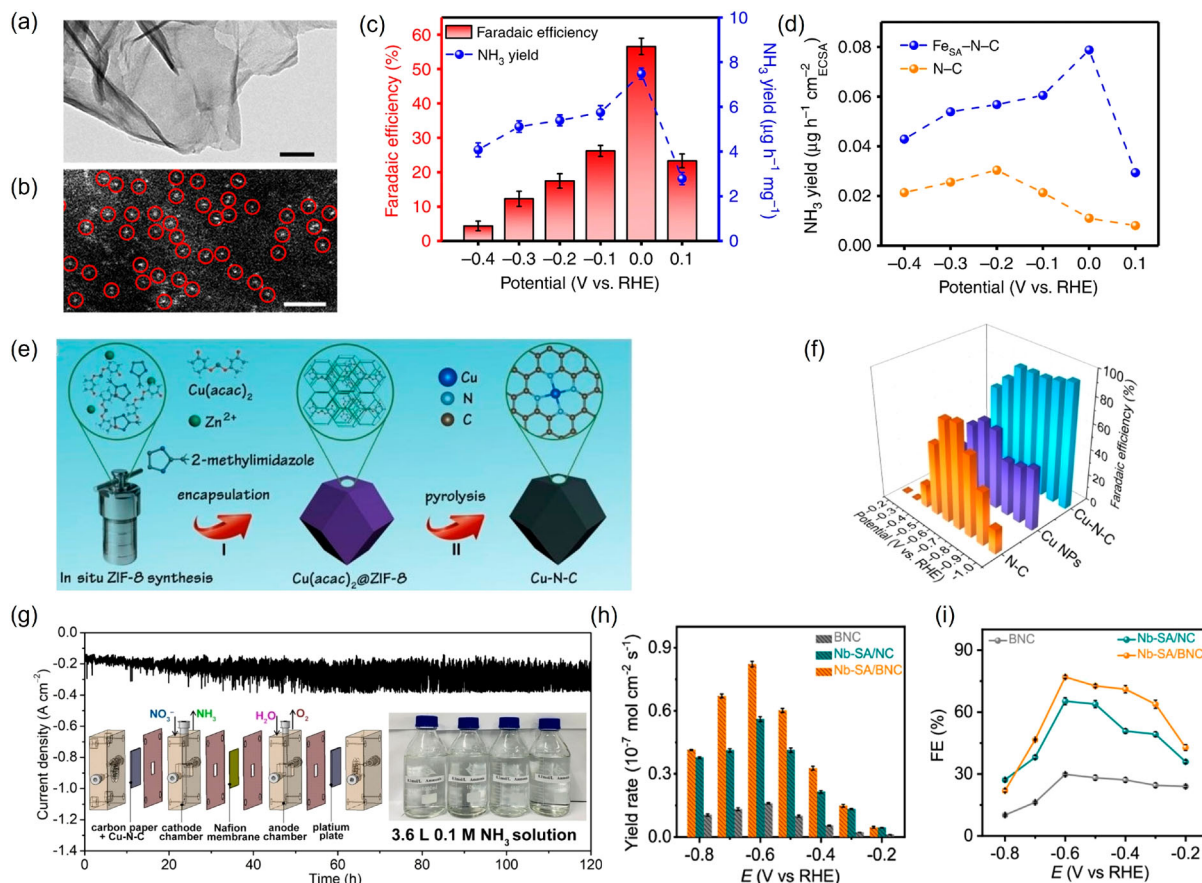


**Figure 5.** (a) Transmission electron microscopy (TEM) image of Fe<sub>SA</sub>-N-C. Scale bar, 50 nm. (b) The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Fe<sub>SA</sub>-N-C. Scale bar, 2 nm. (c) NH<sub>3</sub> yield rates and FE at different applied potentials. (d) Surface-area-normalized NH<sub>3</sub> yield rate at different applied potentials on Fe<sub>SA</sub>-N-C and N-C. Copyright 2019, Spring Nature [106]. (e) Schematic illustration of the synthetic process of Cu-N-C. (f) NH<sub>3</sub> FE at different applied potentials. (g) i-t curve. Copyright 2022, John Wiley and Sons [44]. (h) NH<sub>3</sub> yield rates and (i) FE at various applied potentials. Copyright 2021, Elsevier [129].

SASCs with non-noble metal active sites have also been extensively explored in electrochemical nitrogen fixation. As early as 1996, Burgess and Lowe uncovered the structure and catalytic function of nitrogenase, the active sites of which were confirmed to be Fe and Mo [127,128]. Therefore, Fe- and Mo-based SASCs were regarded as the most ideal catalysts for ENRR. Yan et al. reported Fe-SASC exhibited a remarkable electrochemical NH<sub>3</sub> synthesis with selectivity of over 56.55% (Figure 5a–d) [106]. DFT result showed that the structure of Fe-SASC can capture and enrich N<sub>2</sub> molecules, resulting in an optimal adsorption state due to the lower Gibbs free energy of  $-0.28$  eV. Xin et al. developed an atomically dispersed Mo-SASC anchoring on the porous carbon, achieving an NH<sub>3</sub> FE of 14.6% with a yield rate of  $34 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  [110]. Apart from Fe and Mo, Cu is another promising active centre for electrochemical nitrogen fixation. Zang et al. prepared a Cu-SASC anchored porous nitrogen-doped carbon for ENRR [117], and achieved a remarkable FE of 13.8% in

0.1 M KOH and 11.7% in 0.1 M HCl, demonstrating a desirable pH-universal SASC. Notably Cu is also one of the efficient active sites to perform ENO<sub>3</sub><sup>−</sup>RR, exhibiting over 90% selectivity towards NH<sub>4</sub><sup>+</sup>. Ye et al. synthesized a Cu-SASC using a zeolitic imidazolate framework as a precursor (Figure 5e) [44]. Compared with Cu nanoparticles, these atomically dispersed Cu sites showed a much higher selectivity, activity and stability, e.g. the NH<sub>3</sub> selectivity achieved 95.5% with a partial current density of  $200 \text{ mA cm}^{-2}$  running for 120 h (Figure 5f,g). Relative to ENO<sub>3</sub><sup>−</sup>RR, SASCs for NORR were less reported. Liu et al. developed a family of SASC with various atoms (Al, Mn, Fe and Cu) anchoring on B and N co-doped carbon nanotubes [129]. Among them, the Nb site showed a record high NH<sub>3</sub> yield rate of  $8398 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  with a selectivity of 77% (Figure 5h,i).

In addition, theoretical calculations play an equally important role in designing efficient SASCs for nitrogen fixation, such as density functional theory (DFT), molecular dynamic (MD) simulations and finite element

simulation (FES) [130,131]. Liu et al. theoretically developed a series of transition metal SASCs (MP<sub>3</sub>, M = Fe, Mn, Cr, Mo, V, W and Nb) anchored black phosphorene (BP) surfaces for nitrogen fixation [132]. DFT results demonstrated that WP<sub>3</sub> active site had an outstanding ability to promote nitrogen adsorption and suppressing HER, which was superior to those of other comparable metals. The work not only screened a series of transition metal SASCs for efficient nitrogen fixation but also provided significant guidance for the design of promising BP-based SASCs by DFT. Although the various metal centre SASCs for nitrogen fixation have excellent performance in ENRR, HER at high overpotential is still challenging [133]. Therefore, developing some methods to suppress HER is particularly important, such as the regulation of catalyst surface hydrophobicity [134]. Besides, noble metals' SASCs have been studied as excellent catalysts, but the cost is not negligible. Consequently, non-noble metals or metal-free SASCs for nitrogen fixation are worth considering, such as Bi, Sn, etc., which are potential catalysts for ENRR.

### 3.2. Influence of coordination environments

Similar to natural metalloenzymes in bio-catalysis, the catalytic efficiency of SASCs not only relies on the central metal nuclei but also on the neighbouring coordination environment of the catalytic centre [135]. In some situations, the local coordination of active sites, in particular, the first heteroatom-coordination shell, can directly influence the electronic structure, the oxidation state of the metal centre and/or the adsorption energy of intermediates and thus dominate the catalytic activity, selectivity and stability of SASCs [65,82,136]. Although the second-sphere environment, such as substituents of ligands, has no direct interaction with the metal centre, it can regulate nitrogen reduction to some extent [136,137]. Deciphering how those local environments, e.g. coordination atoms, numbers and chemical environments, etc., affects the nitrogen reduction performance is highly demanded for the rational design of efficient SASCs. Next, we will focus on the influences of the first-shell coordination from different heteroatoms and the second-sphere environment surrounding the active sites.

#### 3.2.1. The type of coordination ligands for SASCs

The interaction between the metal centres and the local environment largely depends on the coordination ligands that directly bond with the catalytic centre [69]. Among all SASCs reported, a metal nucleus with N-coordination is the most common one, given that N can provide higher binding energy to stabilize the metal centre [138]. The

often-used N-coordination supports include g-C<sub>3</sub>N<sub>4</sub>, N-doped carbon materials (e.g. carbon nanotube, graphene, amorphous carbon, etc.), and metal-organic frameworks, etc. Chen et al. theoretically demonstrated that Mo-N sites could efficiently break the N≡N bond and stabilize the reaction intermediates for further hydrogenation [139]. In an experiment, an atomically dispersed Mo-N site achieved a 14.6% FE towards NH<sub>3</sub> in 0.1 M KOH. Ye et al. designed a Mo-SASC anchored on a boron/nitrogen co-doped carbon nanotube scaffold [111]. The coordination configuration of Mo was verified by FT-EXAFS. DFT results showed that N<sub>2</sub> reduction on such Mo-SASC followed a distal pathway, which had a lower reaction energy barrier compared to others (Figure 6a). Oschatz et al. fabricated an Au-N<sub>4</sub> motif anchored on the N-doped porous carbon [101]. X-ray photoelectron spectroscopy (XPS) indicated strong electronic interactions between Au and N. Using the carbon support without N embedding, Au atoms aggregated, verifying that N is indispensable for stabilizing those atomically dispersed Au atoms. The Au-N<sub>4</sub> motif is crucial to activate adsorbed N<sub>2</sub> molecules and provide a remarkable NH<sub>3</sub> yield rate of 2.32 μg h<sup>-1</sup> cm<sup>-1</sup> with an FE of 12.3%. Similarly, Cai et al. synthesized a Co-SASC embedded in N-doped porous carbon support [116]. EXAFS fitting and temperature-programmed desorption of N<sub>2</sub> (N<sub>2</sub>-TPD) confirmed a Co-N<sub>4</sub> configuration that is in favour of adsorbing N<sub>2</sub> molecules and breaking N≡N bond (Figure 6b), which can well explain the excellent performance of 10.5% selectivity towards NH<sub>3</sub> in ENRR.

Beyond the SASCs with M-N coordination motif, other heteroatom-coordinated SASCs have also been explored for ENRR and ENO<sub>x</sub>RR. The nitrogen-free lignocellulose (LC) was applied as SASC support for ENRR by Zhao and co-workers [115]. The oxygen and carbon coordinated single-atomic Fe site displayed a superior NH<sub>3</sub> yield rate of 307.7 μg h<sup>-1</sup> mg<sub>cat.</sub><sup>-1</sup> with a high FE of 51%. Theoretical calculations revealed a back-donation mechanism to activate the N≡N bond via the electron transfer from Fe to the N<sub>2</sub> molecule (Figure 6c). Notably, metal oxide, such as FeO<sub>x</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>, MnO<sub>2</sub>, etc., is a category of scaffold to provide an ideal oxygen coordination environment for other metal dopants [66]. Zhang et al. atomically dispersed Ru atoms on a TiO<sub>2</sub> support (Ru<sub>1</sub>-TiO<sub>x</sub>/Ti), which exhibited a high FE of 87.3% towards NH<sub>3</sub> in ENO<sub>3</sub><sup>-</sup>RR [42]. The charge density difference plot revealed that there was a 0.66 e<sup>-</sup> charge transfer between Ru and the TiO<sub>x</sub>/Ti substrate, showing strong metal-support interactions, which is responsible for the highly efficient NH<sub>3</sub> production (Figure 6d). Beyond nitrogen and oxygen, sulphur can also provide an active coordination environment for nitrogen conversion. MoS<sub>2</sub> has shown a strong superiority in ENRR and

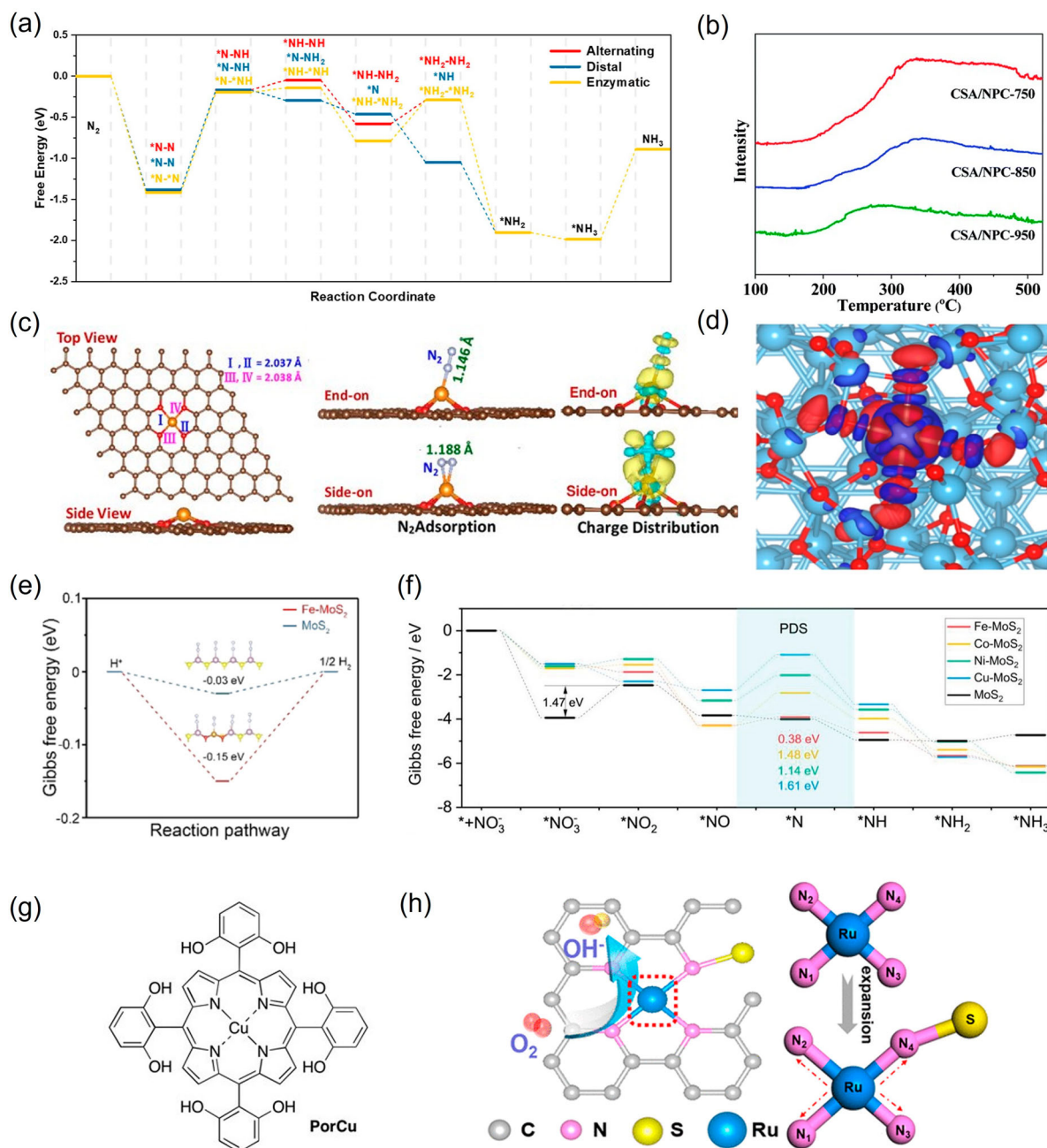


**Figure 6.** (a) Free-energy diagrams for ENRR on Mo/BCN through different reaction pathways. Copyright 2022, American Chemical Society [111]. (b)  $N_2$ -TPD curves of Co single-atom embedded N-doped porous carbon (CSA/NPC). Copyright 2019, Royal Society of Chemistry [116]. (c) Optimized  $Fe-(O-C_2)_4$  configuration,  $N_2$  adsorption at end-on and side-on and corresponding Bader charge distribution of  $*N_2$  (yellow and blue represent charge accumulation and depletion, respectively). Copyright 2020, John Wiley and Sons [115]. (d) Pots of charge density difference. The red and dark blue regions represent electron density depletion and accumulation, respectively. Copyright 2022, John Wiley and Sons [42]. (e) Free-energy diagrams for HER over  $Fe-MoS_2$  and  $MoS_2$ . Copyright 2020, John Wiley and Sons [104]. (f) Free-energy diagrams for  $ENO_3^-$ RR on M- $MoS_2$  nanosheets. Copyright 2021, John Wiley and Sons [123]. (g) Structure for copper-porphyrin molecule with eight substituent groups. Copyright 2016, American Chemical Society [140]. (h) Schematic illustration of the catalyst depicted structure. Copyright 2022, American Chemical Society [141].

$ENO_x$ RR. Zeng et al. designed atomically dispersed Fe site anchoring on  $MoS_2$  nanosheets [104]. They observed that  $Fe-MoS_2$  exhibited a much higher selectivity towards  $NH_3$  in ENRR compared to  $MoS_2$ , revealing that Fe-S coordination efficiently suppressed HER and activated

the cleavage of the  $N_2$  molecule (Figure 6e). In addition, Voiry et al. applied  $Fe-MoS_2$  to achieve an FE of 98% for  $NH_3$  production in  $ENO_3^-$ RR [123], and they attributed the high catalytic performance to d band orbitals of Fe atoms, which resulted in a lower energy barrier for

the conversion of key intermediates from  $\ast\text{NO}$  to  $\ast\text{N}$  (Figure 6f). Various coordination types and environments have been verified to regulate catalytic properties by modulating the surface electronic structure or adsorption abilities for reactants. And most single-atom catalysts for NRR are based on the M-N-C sites. Therefore, heteroatom doping coordination is an efficient strategy to improve catalytic performance. Besides, the stability of SASCs needs further enhancement. Hence, optimization of synthesis conditions and exact control of the coordination environment are necessary.

Apart from the first-sphere coordination, the influence of the second-sphere environment can not be ignored, and sometimes, it plays a critical role for the catalytic activity by regulating the electronic structure during the whole reaction [142]. As for molecular catalysts with a well-defined structure, such as metal-phthalocyanine/porphyrin, the catalytic performance can be controlled by employing different substituents, such as  $-\text{NH}_2$ ,  $-\text{OH}$ , which possessed electron-pulling/pushing ability [143]. This strategy has been well demonstrated in electrochemical  $\text{CO}_2$  reduction, showing an impressive enhancement in catalytic performance, including product selectivities and catalytic durabilities (Figure 6g) [140]. In addition, heteroatomic doping outside the first shell is another strategy to regulate the coordination environment [144–146], which has been

successfully demonstrated in the electrochemical ORR system (Figure 6h) [141].

### 3.2.2. The coordination number

The coordination number of metal centres in SASCs is another non-negligible parameter to determine the  $\text{NH}_3$  selectivity and yield rate [142,147,148]. Heat treatment is an effective way to regulate the metal-N coordination number. Pennycook et al. designed a Cu-N SASC for ENRR and found that central Cu could be coordinated with 2–4 nitrogen atoms in a controlled manner [117]. The electrocatalytic activity of different bonding configurations, including Cu-N<sub>4</sub>, Cu-N<sub>3</sub> and Cu-N<sub>2</sub>, was investigated by DFT, which verified that Cu-N<sub>2</sub> exhibited stronger binding energy towards the  $\text{N}_2$  molecule and thus showed a higher activation capability (Figure 7a,b). Similar studies on  $\text{ENO}_3^-$ -RR showed that Cu-N<sub>2</sub> was beneficial for the adsorption of key intermediates, and was the best candidate to improve the performance. Zhu et al. prepared a Cu-SASC by pyrolysis of a Cu-based metal-organic framework at a different temperature and achieved a high  $\text{NO}_3^-$  conversion of 97.3% and  $\text{NH}_3$  selectivity of 80.5% [149]. To rationalize the high FE, theoretical calculations were performed, which showed that the adsorption energies of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  on Cu SASC with a Cu-N<sub>2</sub> configuration were the lowest (Figure 7c,d).

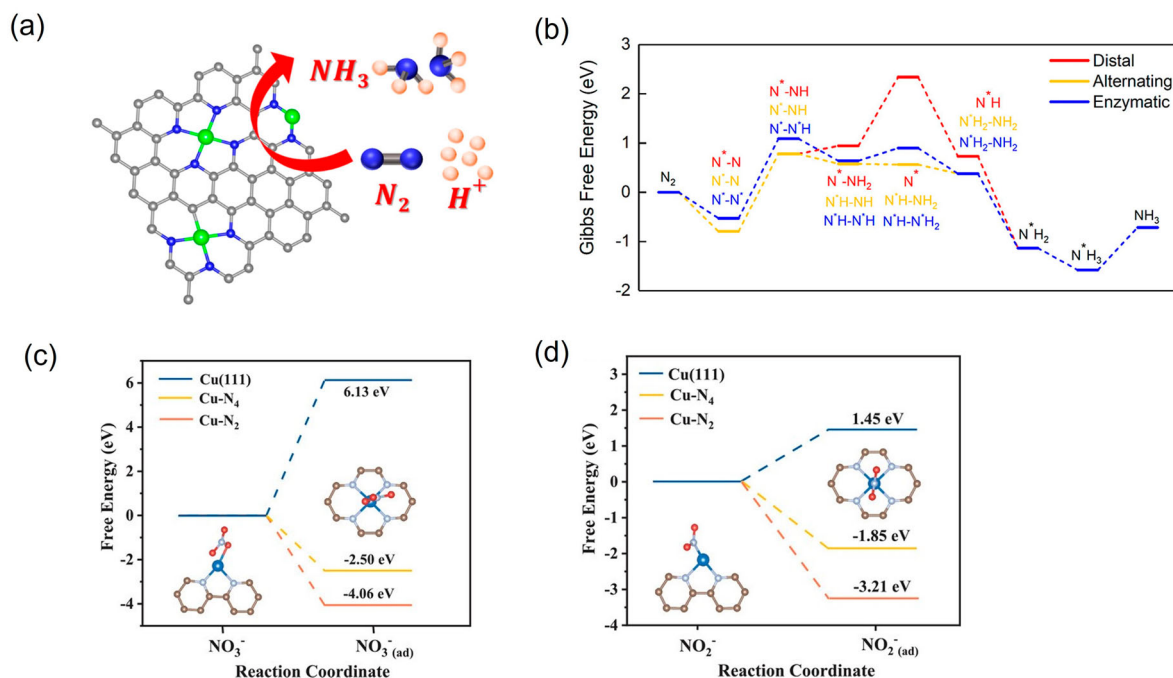


**Figure 7.** (a) Schematic illustration of ENRR for Cu-N<sub>x</sub> structure. (b) Free-energy diagrams for the ENRR on Cu-N<sub>2</sub> through different reaction pathways. Copyright 2019, American Chemical Society [117]. Calculated free energies for (c)  $\text{NO}_3^-$  adsorption and (d)  $\text{NO}_2^-$  adsorption on Cu (111), Cu-N<sub>4</sub>, and Cu-N<sub>2</sub> surfaces, respectively. The brown, grey, blue and red balls represent C, N, Cu and O atoms, respectively. Copyright 2020, John Wiley and Sons [149].

#### 4. Summary and outlook

The unique geometric/electronic properties of SASCs render them compelling in electrochemical nitrogen fixation. Despite that significant progress has been achieved in this emerging research area, further improvements in catalytic activity, selectivity and long-term durability are in urgent need for their practical applications. For this, the intelligent design of SASCs should be considered. Here we introduced a variety of SASCs reported to achieve efficient  $\text{NH}_3$  production in ENRR and  $\text{ENO}_x\text{RR}$ . Overall, the predicted conversion mechanism, regulation of metal centres and the influence of first-shell coordination environment and coordination numbers were presented. Although SASCs are a promising class of catalysts for nitrogen reduction after years of development, significant challenges remain to be addressed. In the following, we listed some aspects of current limitations and prospects for future development.

1. Simulation-guided rational design of SASCs. Over the past few decades, it has reached a consensus that theoretical modelling on the electrochemical interface is quite important to identify the active sites and predict the reaction pathway. However, in previous studies, the diverse properties of active sites and multiple intermediates in the nitrogen cycle resulted in a trial-and-error ideology in catalyst screening, which is quite time-consuming. Advanced numerical calculation techniques with stronger predictive capabilities, such as machine-learning algorithms, bring prospects for high-throughput catalyst screening, which can save huge efforts and promote the rational design of highly efficient SASCs. Luckily for SASCs, one major advantage is that the atomically-dispersed active sites are much more structurally uniform than most heterogeneous bulk catalysts. Given that, the theoretical modelling on SASCs should be easier to perform than the inorganic solids. Beyond the electronic structure, it is also critical to consider the multiscale modelling of reactant feeding (e.g.  $\text{N}_2$ ) and mass transport, particularly for the high surface area SASCs and vapour-fed reactors [70]. Another relevant challenge is that much effort on theoretical prediction so far was focused on analyzing the reaction energetics thermodynamically, e.g. only simulating the Gibbs free energies of the initial and final states. Kinetic modelling is strongly recommended for better understanding the transition states along the pathway and improving the accurate prediction capability.
2. Development of *Operando* techniques. A major disadvantage of the theoretical modelling is that it can work well for well-ordered catalytic systems, but computational screening of less-ordered catalysts remains a grand challenge due to the diversities of active sites, interfacial adsorbates and reaction pathways. In this regard, tracking the evolution of active sites and intermediates involved in an *operando* way is of great importance to rationalize the performance of SASCs. To date, multiple *operando* techniques have been implemented for electrochemical nitrogen fixation, offering new insights. Shen et al. employed *in situ* FTIR/Raman spectra to observe  $\text{N}_2$ -catalyst interaction and related reaction intermediate [119]. The spectrum results exhibited diverse infrared peaks at  $1100\text{--}1500\text{ cm}^{-1}$ , including N-N stretching and  $\text{-NH}_x$  intermediates and a distinct Raman peak at  $\sim 480\text{ cm}^{-1}$  (Rh-N vibrational band), revealing that Rh sites promoted  $\text{N}_2$  activation and hydrogenation to obtain excellent selectivity and activity. Yet, more can be done to expand the capability of currently available techniques. Time-resolved spectroelectrochemistry techniques that can monitor the dynamic surface chemistry have been seldom demonstrated. Further developments of these *operando* techniques will offer crucial insights into nitrogen electrochemical fixation in terms of catalyst compositions, oxidation states and intermediates under operating conditions.
3. Broaden the product scope of SASCs for nitrogen fixation. Although aqueous ENRR and  $\text{ENO}_x\text{RR}$  on SASCs can generate a variety of nitrogen-based products, these products are limited to N-H, N-O and N-N bonds. In contrast to simple nitrogen species such as  $\text{NH}_3$  and  $\text{NH}_2\text{OH}$ , the C-N chemicals are far more desirable in the production of bulk chemicals, synthetic intermediates, fertilizers, agrochemicals and pharmaceuticals. Therefore, it is highly demanded to broaden the product scope by introducing other reactants that can expand the elemental diversity. Electrocatalytic synthesis of C-N bonds has been reported via co-electrocatalysis of  $\text{CO}_2$  and  $\text{N}_2$  (or  $\text{NO}_3^-$  and  $\text{NO}_x$ , etc.) [150–154], offering a promising way to mitigate the accumulation of natural pollutants, such as  $\text{CO}_2$ ,  $\text{NO}_3^-$  and  $\text{NO}_x$ , etc., and at the same time, transform these pollutant molecules to valuable chemicals with renewable energy. During the co-electrocatalysis, the products from nitrogen reduction serve as key intermediates to generate more complex chemicals with C-N bonds (e.g. urea, amides, nitriles, etc.). In future, this strategy is worth more effort to expand the scope of products from nitrogen fixation.

To conclude, as an emerging class of electrocatalysts, SASCs have experienced dramatic growth and demonstrated their enormous advantages in nitrogen fixation over the past years. Although many challenges are to be addressed, we have reasons to expect that more promising developments of highly active, selective and stable SASCs for nitrogen reduction will be created shortly with continued research efforts, thus leaving a nitrogen-neutral world for humanity.

## Disclosure statement

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