Rational Design of Atomic Site Catalysts for Electrocatalytic Nitrogen Reduction Reaction: One Step Closer to Optimum Activity and Selectivity

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Abstract
The electrocatalytic nitrogen reduction reaction (NRR) has been one of the most intriguing catalytic reactions in recent years, providing an energy-saving and environmentally friendly alternative to the conventional Haber–Bosch process for ammonia production. However, the activity and selectivity issues originating from the activation barrier of the NRR intermediates and the competing hydrogen evolution reaction result in the unsatisfactory NH3 yield rate and Faradaic efficiency of current NRR catalysts. Atomic site catalysts (ASCs), an emerging group of heterogeneous catalysts with a high atomic utilization rate, selectivity, and stability, may provide a solution. This article undertakes an exploration and systematic review of a highly significant research area: the principles of designing ASCs for the NRR. Both the theoretical and experimental progress and state-of-the-art techniques in the rational design of ASCs for the NRR are summarized, and the topic is extended to double-atom catalysts and boron-based metal-free ASCs. This review provides guidelines for the rational design of ASCs for the optimum activity and selectivity for the electrocatalytic NRR.

Keywords Nitrogen reduction reaction · Atomic site catalysts · Design principles · Activity · Selectivity

1 Introduction
Ammonia (NH3) is an important chemical in both industry and agriculture because it can serve as a precursor to various foods, fertilizers, pharmaceuticals, and detergents [1, 2]. In addition, ammonia is also a clean, carbon-free energy carrier since its combustion only produces water and dinitrogen (N2), both of which are environmentally friendly [3]. Therefore, converting dinitrogen—the most abundant gas in Earth’s atmosphere (over 78%)—into ammonia, one of the nitrogen fixation processes, is a topic with vital significance in Earth’s nitrogen cycle [2]. According to Mineral Commodity Summaries from the US Geological Survey, approximately 170 million tons of ammonia in total were produced globally in 2018 [4]. A major challenge in nitrogen fixation is breaking the chemically inert N≡N triple bond, which has a high bond energy (940.95 kJ mol−1) [5, 6]. Traditionally, ammonia production is conducted through the Haber–Bosch (H–B) process, which demands high temperature (~ 800 K) and high pressure [200–300 atm (1 atm = 101 325 Pa)] to proceed. The H–B process accounts for approximately 1.4% of the global energy consumption, among which ~ 75% is used in steam reforming instead of ammonia synthesis (Fig. 1) [7–10]. Moreover, the H–B process may worsen environmental issues, such as the emission of greenhouse gases, as it accounts for approximately 1% of global emissions [11, 12].

The electrocatalytic or photo(electro)catalytic nitrogen reduction reaction (NRR) is viewed as an energy-saving alternative to the H–B process for ammonia production because it can proceed under ambient conditions [11, 13–17]. Other advantages of the NRR include the elimination of carbon fuel consumption and carbon dioxide emissions, high energy efficiency, and smaller plant infrastructure.
The key task for the NRR is the rational design of electrocatalysts or photocatalysts with outstanding activity and selectivity \([11, 16, 18–21]\). Transition metals (TMs) \([14, 22]\) and their nitrides \([23–25]\), carbides \([26]\), and phosphides \([27]\) have been theoretically predicted to be outstanding catalysts for the NRR, and many of them have been confirmed experimentally \([28–33]\). However, their NRR performance still has much room for improvement: (1) the activities of the reported catalysts are limited by the activation barrier of the hydrogenation process in the NRR; and (2) the selectivity is often hindered by the competition between \(\text{N}_2\) and H adsorption, and the hydrogen evolution reaction (HER) largely competes with the NRR \([34]\).

The concept of atomic site catalysts (ASCs) was first proposed in 2011 when Pt\(_1/\text{FeO}\) ASCs were applied for CO oxidation \([35]\). TM ASCs, compared with their bulk or nanoparticle counterparts, exhibit high atomic utilization efficiency (AUE), activity, and selectivity stemming from their atomically dispersed nature \([36–41]\). Therefore, ASCs have attracted the attention of researchers for their applications in water splitting \([42–44]\), the oxygen reduction reaction (ORR) \([45, 46]\), and the CO\(_2\) reduction reaction (CO\(_2\)RR) \([47]\). The application of ASCs in the NRR is a relatively new and emerging topic due to the complex mechanisms and the challenges of the experimental setup \([48, 49]\). The rational design of ASCs with optimum activity and selectivity for NRR through the combination of theoretical predictions and experimental characterizations is thus imperative to unravel the mechanisms and minimize the economic and time cost of trial-and-error experiments alone (Fig. 2).

Although several review articles about NRR ASCs that compare the catalytic performance of element-specific ASCs have been published \([50–52]\), a systematic review of fundamental design principles of NRR ASCs from both theoretical and experimental perspectives is currently lacking. We try to fill this gap in the current review, which is organized as follows. In part 2, we first briefly introduce the NRR mechanisms and the design principles, including computational schemes, descriptors of NRR performance, and the theoretical progress in the rational design of NRR ASCs. Next, we summarize the current experimental research into ASCs for the NRR, with cases ranging from noble metal, nonprecious metal, to rare-earth metal ASCs, followed by the detailed introduction of two specific topics related to experimental and theoretical investigations: double-atom catalysts and boron-based metal-free ASCs. Finally, a summary and perspective about ASCs for the NRR is provided.

\section*{2 Mechanisms and Theoretical Design Principles of ASCs for the NRR}

In this section, the NRR mechanisms and computational schemes, including high-throughput density functional theory (DFT) calculations and machine learning, are first introduced, followed by the summation of activity and selectivity descriptors proposed in the recent literature, which play an essential role in the rational design of ASCs. Finally, several advanced issues, challenges, and perspectives for the theoretical design of NRR ASCs are listed.
2.1 NRR Mechanisms

The prevailing opinions suggest that NRR is a six proton-coupled electron transfer (PCET) process, and possible mechanisms include dissociative and associative pathways [7, 13, 53, 54]. For ASCs, the direct dissociation of the N≡N triple bond in the first step is unfavorable because it has a large energy barrier, so usually only the associative NRR pathway is considered [53]. Associative mechanisms include distal, alternating, enzymatic, and consecutive pathways, depending on whether the end-on or side-on N₂ adsorption pattern is more energetically favorable (Fig. 3). In end-on N₂ adsorption, the N atom further from the active center is first hydrogenated to form the first NH₃ molecule in the distal pathway, while the two N atoms are hydrogenated simultaneously in the alternating pathway. Similarly, in side-on N₂ adsorption, one of the N atoms is first hydrogenated to form the first NH₃ molecule in the consecutive pathway, and two N atoms are simultaneously hydrogenated in the enzymatic pathway. In the determination of the potential-limiting step (PLS) and the maximum Gibbs free energy change (ΔG), it is noteworthy that unlike in the NRR and thermal nitrogen fixation under basic conditions, the last step of NH₃ desorption in the NRR under acidic/slightly basic conditions is usually not considered in the calculations since protonation from *NH₃ to NH₄⁺ is usually facile [55, 56].

2.2 Computational Schemes for the NRR

Because of the difficulty in the experimental determination of the catalytic active sites and underlying mechanisms for ASCs, theoretical calculations, especially DFT calculations, play an essential role in the study of ASCs [57]. The prevailing computational schemes for the NRR are based on Nørskov’s computational hydrogen electrode (CHE) model, in which the Gibbs free energy of the proton–electron pair is calculated by $G(H^+ + e^-) = 0.5G(H_2) - eU$, where $U$ is the applied potential [58, 59]. The applied potential required to diminish the energy barrier of all steps in the NRR is defined as the limiting potential ($U_L$), and overpotential $\eta$ is calculated by $\eta = U_{\text{equil}} - U_L$, where $U_{\text{equil}} \approx -0.16$ V is the equilibrium potential for the NRR [53]. The $U_L$ values (at the DFT-generalized gradient approximation (GGA) level), energetically favorable pathway, and PLS with the maximum ΔG of recently reported NRR ASCs are summarized in Table 1 based on categories of the substrates (note that * denotes an atomic active site in this review unless otherwise specified).

2.2.1 High-Throughput DFT Calculations

Due to the various TM elements, coordination environments, and substrates, a comprehensive search for NRR ASCs can lead to a large number of combinations, appealing for high-throughput DFT calculations. A typical example is TM atoms supported on N-doped graphene (Table 1), where

Fig. 3 Associative NRR pathways for TM-based ASCs with (a) end-on and (b) side-on N₂ adsorption configurations.
Table 1  Summary of the limiting potentials, favorable pathways, and potential-limiting steps (PLSs) for DFT-predicted TM-based NRR ASCs

| Systems | Best sample | Limiting potential $U_l/N$ | Favorable pathway | PLS | Year of publication |
|---------|-------------|-----------------------------|-------------------|-----|-------------------|
| ASCs on graphene- and N-doped-graphene-based materials | | | | | |
| TM @ N$_4$/N$_5$/C$_3$/C$_3$ | Ti @ N$_4$ | −0.69 | Distal | *NH$_2$→*NH$_3$ | 2018 [60] |
| Cu, Pd, Pt, Mo @ N$_1$/C$_2$ (N–doped carbon) | Mo @ N$_1$/C$_2$ | −0.40 | Enzymatic | *N–*N→*N–*NH | 2018 [61] |
| TM @ N$_4$–doped graphene | W @ C$_3$ (three C atom coordination) | −0.25 | Enzymatic | *NH$_2$→*NH$_2$→*NH$_2$–*NH | 2018 [62] |
| | Mo @ N$_3$–G | −0.50 | Distal-to-alternating mixed | *N$_2$→*N$_2$H | 2019 [63] |
| TM @ N$_4$–graphene | Mo @ N$_4$–graphene | −0.67 | Distal | *NH$_2$→*NH$_3$ | 2019 [64] |
| Fe @ N$_x$–graphene (single vacancy, $x$ = 0–3) | Fe @ N$_3$–graphene | −0.66 | Distal | *N$_2$→*NH$_3$ | 2019 [65] |
| Fe @ N$_x$–graphene (double vacancy, $x$ = 0–4) | Fe @ N$_2$–opp-graphene | −0.63 | Distal | *N$_2$→*N$_2$H | 2019 [66] |
| TM @ pyrrolic–N$_3$–graphene | W @ pyrrolic–N$_3$–graphene | −0.33 | Distal | *N$_2$→*N$_2$H | 2021 [67] |
| Ru @ C$_2$N, T–C$_3$N$_4$, γ–graphene | Ru @ T–C$_3$N$_4$ | −0.94 | Distal | *NH$_2$→*NH$_3$ | 2018 [68] |
| Mo @ X–decorated graphene (X = B, N, P, Se, Cl) | Mo @ Se–decorated graphene | −0.41 | Enzymatic | *NH$_2$–*NH$_2$→*NH$_2$ | 2019 [69] |
| Ru–N$_2$/four-coordinate Ru ASCs | Ru–N$_2$C$_2$–I | −0.43 (grand-canonical DFT) | Distal | *N$_2$→*N$_2$H | 2020 [70] |
| TM @ B–doped graphene | CrB$_x$C$_y$ | −0.29 | Distal | *N$_2$→*N$_2$H | 2020 [71] |
| B–doped Fe–N–C | Fe–B$_2$N$_2$ | −0.65 | Distal | *N$_2$→*N$_2$H | 2021 [72] |
| TM @ B$_x$C$_y$N$_z$ | FeB$_z$ | −0.55 | Distal | *N$_2$→*N$_2$H | 2020 [73] |
| W @ N–doped graphyne | – | −0.29 | Distal | *N$_2$→*N$_2$H | 2019 [74] |
| TM @ graphdiyne (GDY) | Mo @ GDY | −0.33 | Distal | *N$_2$→*N$_2$H | 2020[75] |
| | V @ GDY | −0.67 | Distal | *N$_2$→*N$_2$H | 2020 [76] |
| TM @ g–CN | W @ g–CN | −0.34 | Distal | *N$_2$→*N$_2$H | 2020 [77] |
| | W @ g–CN | −0.29 | Distal | *N$_2$→*N$_2$H | 2020 [78] |
| TM @ C$_2$N | Mo @ C$_2$N | −0.17 | Distal | *NH$_2$→*NH$_3$ | 2018 [79] |
| Au/Fe @ C$_2$N | Fe @ C$_2$N | −0.70 | Distal/Alternating | *N$_2$→*N$_2$H | 2020 [80] |
| TM @ g–C$_2$N$_4$ | Ti @ g–C$_2$N$_4$ | −0.51 | Enzymatic/Consecutive mixed | *NH$_2$→*NH$_3$ | 2018 [81] |
| | W @ g–C$_2$N$_4$ | −0.35 | Enzymatic | *NH$_2$→*NH$_3$ | 2018 [82] |
| | Ru @ g–C$_2$N$_4$ | −0.33 | Distal | *N$_2$→*N$_2$H | 2019 [83] |
| | Pt @ g–C$_2$N$_4$ | −0.24 | Alternating | *N$_2$H→*NH–NH | 2019 [84] |
| TM @ gt–C$_2$N$_4$ | V @ gt–C$_2$N$_4$ | −0.79 | Enzymatic | *NH$_2$→*NH$_3$–*NH$_3$ | 2019 [85] |
| TM @ C$_9$N$_4$ | W @ C$_9$N$_4$ | −0.24 | Distal | *N$_2$→*N$_2$H | 2021 [86] |
| TM-porphyrin (Pp) | Mo-Pp | −0.58 | Distal | *N$_2$→*N$_2$H | 2020 [87] |
| ASCs on hexagonal boron nitrides (BN) | | | | | |
| TM @ BN | Mo @ BN | −0.35 | Enzymatic | *NH$_2$→*NH$_3$ | 2017 [53] |
| | V @ BN | −0.41 | Enzymatic | *NH$_3$→*NH$_3$–*NH$_3$ | 2020 [88] |
| ASCs on boron monolayer | | | | | |
| TM @ β$_1$–boron monolayer | V @ β$_1$–boron monolayer | −0.28 | Distal-alternating mixed | *N$_2$→*N$_2$H | 2019 [89] |
many types of coordination are thermodynamically possible and can be controlled experimentally (C₃, C₂N₁, C₁N₂, N₃, C₄, C₃N₂, C₂N₂, C₁N₃, and N₄, Fig. 4a) [60–65]. Du, Wang, and coworkers proposed a two-step high-throughput screening strategy for designing NRR ASCs with a significantly lower computational cost [62]. With the nine above-mentioned types of coordination, 30 TM element selections, and two adsorption patterns (end-on and side-on), 540 ASCs constituted the database for screening. In the first step, the authors used the N₂ adsorption energy (Δ\text{E}_\text{N}_2) and free
energy change required to break the $\text{N}=\text{N}$ triple bond (the first hydrogenation step, $\Delta G_{\text{N}_2-\text{N}_2H}$) as descriptors to rule out ASCs with low activity. In the second step, the descriptors were the free energy for $\text{NH}_3$ desorption and the hydrogenation from $-\text{NH}_2$ to $-\text{NH}_3$ ($\Delta G_{\text{NH}_2-\text{NH}_3}$). The detailed threshold values are listed in Fig. 4b, and these steps theoretically require a large energy input and are usually the PLS of the NRR (Table 1). A total of 97 ASCs were selected in the first step (Fig. 4c) because they strongly interact with $\text{N}_2$ and can hydrogenate $\text{N}_2$ to $\text{N}_2\text{H}$ with high performance (red region), while 10 highly active ASCs were selected in the second step (Fig. 4d). Among the ASCs, W$_1$C$_3$ exhibited the best NRR performance with a $U_L$ value of $-0.25$ V through the enzymatic mechanism (Fig. 4e). This benchmarking work provided an example of high-throughput DFT calculations that accelerated the discovery of NRR ASCs.

### 2.2.2 Machine Learning

Even though the above-mentioned high-throughput DFT method can reduce the time cost for screening NRR ASCs, further optimization of the screening process is indispensable when the dataset contains hundreds or thousands of systems. Machine learning (ML), an interdisciplinary approach, has been widely used in screening energy materials, including lithium-ion conducting materials [120, 121], perovskites [122], and CO$_2$RR/HER electrocatalysts [123]. Specifically, for electrocatalyst design, ML approaches can build the relationship between catalytic performance and intrinsic structural/electronic/bonding properties by analyzing the feature importance. Kim and coworkers used the deep neural network (DNN) ML approach for the high-throughput screening of NRR ASCs on boron-doped graphene [71]. They first narrowed down the number of key features for describing results for TMs supported on N-doped graphene, and e NRR free energy diagram of the enzymatic mechanism for W$_1$C$_3$ at different applied potentials. Reprinted with permission from Ref. [62]. Copyright © 2018, Wiley-VCH
NRR performance to seven (including electronegativity, the atomic number, and the atomic radius) by DNN and used them to select eligible candidates for the NRR by the criteria described in Ref. [62] (Fig. 5a). Then, after training the data with a light gradient boosting machine (LGBM) model, the ML results were similar to the DFT-calculated adsorption energy values (Fig. 5b). Furthermore, by analyzing the correlations between the features (Fig. 5c), the authors found that the most important features are the TM coordination number and number of hydrogen atoms in the DNN and LGBM models, respectively. Finally, among ASCs screened out by DFT and ML, CrB$_2$C$_3$ showed the smallest overpotential of 0.13 V (Fig. 5d). The authors also extended their methodology to the NRR on TM borides, defective 2D materials, and ASCs on π-conjugated polymers for fast screening and descriptor discovery [124]. These pioneering works pave the way for combining DFT with ML to reduce the computational cost of screening NRR ASCs, but more effort in analyzing different ML models and further refinement of the screening procedure are necessary.

2.3 Activity Descriptors of NRR ASCs

Activity descriptors play a significant role in understanding the reaction mechanisms and constructing the relationships between geometric structure, electronic properties, and catalytic activity. Therefore, developing activity descriptors is an urgent task for catalyst design [125]. To this end, descriptors of hydrogen and oxygen electrocatalysts have been intensively investigated since Hammer and Nørskov came up with the d-band theory in the 1990s [126], and more sophisticated descriptors such as surface distortion, d-band shape, and generalized/orbitalwise coordination number have been developed for the HER, oxygen evolution reaction (OER), and ORR [125, 127]. The well-defined active sites of the ASCs provide an ideal platform for developing accurate structure–activity relationships and descriptors. For

![Fig. 5](image-url)  
**Fig. 5** Design of NRR ASCs by machine learning approaches. a Artificial neural network architecture for the screening of NRR ASCs, b plot of predicted performance by DFT calculations versus ML results, c feature-feature correlation map, and d NRR free energy diagram of the distal mechanism of CrB$_2$C$_3$ ASCs at different applied potentials. Reprinted with permission from Ref. [71]. Copyright 2020, the Royal Society of Chemistry
instance, a universal descriptor $\varphi$ based on valence electrons in the d orbital and electronegativity was proposed to describe HER/OER/ORR activity of ASCs supported on N-doped graphene [128]. However, unlike hydrogen/oxygen electrocatalytic reactions, the NRR is a more complicated process with a much larger number of possible intermediates and pathways, making the discovery of activity descriptors a more challenging task.

2.3.1 Adsorption Energy Descriptors

As proven by many reports [73, 83, 99], similar to those of other catalytic reactions, such as the OER, ORR, and CO$_2$RR, the adsorption energies of *N$_x$H$_y$ NRR intermediates on ASCs may also follow linear scaling relations. In this case, the NRR activity descriptor based on the adsorption energy of only one intermediate (instead of a complicated multiple-parameter problem) is possible, so the rational design of NRR ASCs can be greatly simplified. For example, for ASCs supported on Ti$_{3-x}$C$_{2}O_{y}$ and Ti$_{2-x}$CO$_{y}$ MXenes, the limiting potential and adsorption energy of *NNH satisfy a linear relationship [105]. The descriptors of different substrates may also vary in their $\Delta E_{NN}$ (ASCs on PtS$_2$[101] and graphdiyne (GDY) [76]) and $\Delta G_{NNH}$ (ASCs on MoS$_2$ [99] and with MB$_{s}$/MC$_{2}$/MN$_{4}$ coordination [73]). A systematic study by Qiao et al. built a system for describing the NRR activity of ASCs based on the scaling relations between the adsorption energies of *NNH, *NNH$_2$, *NH, *NH$_2$, and *N [83]. By plotting the NRR limiting potential as a function of $\Delta E_{NN}$ (Fig. 6a, b), the authors showed that $\Delta E_{NN}$ can act as a facile descriptor for predicting the NRR limiting potential, since the DFT-calculated data points (scatter plots) and predicted limiting potential (line graphs) agreed well. When the $\Delta E_{NN}$ value is located in different regions, the PLS and limiting potential for the NRR change accordingly. Furthermore, based on the scaling relations, the authors provided a more intuitive contour plot of the NRR limiting potential as a function of the Gibbs free energies of *NNH and *NH$_2$ (Fig. 6c). Ru@g-C$_3$N$_4$, which was located very close to the center of the red region due to the scaling relations, had the lowest limiting potential of −0.33 V (Table 1). However, the adsorption energy descriptors heavily depend on the type of TM elements; for example, for the early TM elements (Fig. 6a) and late TM elements

![Figure 6](image-url)
Another important descriptor correlating the intrinsic properties of ASCs with their catalytic performance is electronic structure. In many systems, the well-known d-band center and the highest peak position of the density of states (DOSs) below the Fermi level have a poor linear relationship with NRR performance [83]. Thus, there has been a search for more sophisticated electronic structure descriptors. For example, in Qiao’s work, following the limiting potential-ΔΔG∞ relationship free energy of N2 and *H further exhibits a linear relationship to the integrated crystal orbital Hamiltonian population (ICOHP) (Fig. 6d) [83]. Increased ICOHP suggests increased filling of the antibonding orbital population and decreased *N adsorption, and thus, a linear relation is formed. Wu et al. used the percentage of empty d orbitals as an electronic structure descriptor, and a higher proportion of empty d orbitals led to a lower NRR overpotential [94]. In another work, Cai et al. [101] correlated the ΔG of the NRR PLS with the integral of the unoccupied d states (UDs) and found that the Ru on PtS2, which had a high UDS integral value, exhibited the best NRR performance (Fig. 6e). In summary, the electronic structure of ASCs, especially the overlapping bonding/antibonding metal-nitrogen orbitals, plays a decisive role in the adsorption strength of the NRR intermediates and in the overall activity.

2.3.3 Other Descriptors

In addition to those mentioned above, other descriptors combining electronic structure and atomic structure parameters were also explored. According to Xu and Chen et al., an integrated NRR descriptor EL(θ, Z) = (l + sinθ)² × √Z² − Z² for ASCs on metal diborides was identified by high-throughput DFT calculations and mathematical regression technology (Fig. 6f) [113]. Here, l, θ, Z₃₂, and Z₄ n denote the metal–nitrogen bond length, the metal–nitrogen–boron bond angle, the atomic number of adsorbed metal, and the atomic number of boron, respectively. EL(l, θ, Z) exhibited a linear relationship with the ΔG of the PLS, proving its effectiveness in predicting NRR performance. Li and coworkers used the dipole moment of the N≡N triple bond as a descriptor and found that N≡N dipole moments have a similar trend to that of the N₂ adsorption energy on TMs anchored on Pc [114]. Nevertheless, all the above-mentioned activity descriptors are only applicable to one group of ASCs, and more universal activity descriptors for NRR ASCs are still lacking.

2.4 Selectivity Descriptors for NRR ASCs

The selectivity of NRR ASCs is greatly affected by the HER side reaction, and the active sites for the NRR can be poisoned by adsorbed hydrogen (*H), leading to poor NRR selectivity. The prevailing theoretical selectivity descriptor is the adsorption Gibbs free energy difference between *H and *N₂ or *NNH, depending on whether N₂ adsorption or NNH formation is the first step of the NRR [73]. For example, in Fig. 7a, the ASCs located in the blue regions exhibit negative ΔGN₂–ΔGₜₜ, indicating that the adsorption of N₂ is more favorable. Hence, they have higher NRR selectivity [62]. In contrast, Xiao et al. [73] considered the concerted mechanism where N₂ + H⁺ + e⁻ → *NNH is the first step of NRR, and the corresponding selectivity descriptor is ΔG[N₂ (g) + H⁺ + e⁻ → *NNH] − ΔG[H⁺ + e⁻ → *H] (Fig. 7b). In a simplified model where the HER is the only competing reaction of the NRR and the mass and electron transfer are not rate-determining factors, the Faradaic efficiency (FE) for the NRR can be estimated by the Boltzmann distribution [63, 83]: f_{NRR} = 1/[1 + exp(−δG/k_B T)], where δG is the difference between the HER and NRR PLS and k_B and T represent the Boltzmann constant and temperature, respectively.
2.5 Perspective and Challenges for Theoretical Design of NRR ASCs

Despite all the progress, there are several challenges in the theoretical design approaches to NRR ASCs. First, the reliability of the DFT-calculated limiting potential should be carefully examined. Even for the same system, different conclusions are sometimes drawn in different studies. For example, for ASCs supported on g-C₃N₄, at the same level of theory (GGA-PBE with van der Waals correction), different authors reported that Ti \((U_L = -0.51 \text{ V})\) [81], W \((U_L = -0.35 \text{ V})\) [82], Ru \((U_L = -0.33 \text{ V})\) [83], and Pt \((U_L = -0.24 \text{ V})\) [84] on g-C₃N₄ are the best systems for the NRR (Table 1), leading to questions about the standardization of such Gibbs free energy calculations. The origins of this discrepancy may include the use of slightly different initial geometric structures and input parameter settings for the DFT calculations. Second, the neglect of several complex factors in the theoretical calculations may result in a large gap between calculations and experiments; such factors include the following:

1. **Kinetic analysis.** Most works only focus on thermodynamic analysis, while kinetic analysis has long been overlooked because of the difficulty in the computation of electrochemical activation barriers. In a pioneering work by Azofra et al. [26], Janik’s DFT methodology was used in NRR calculations to estimate the activation barrier for species \(*A: G_{act}(U) = G_{act}^0 + \beta F (U - U_\beta)*\), where \(G_{act}^0\) is the activation barrier for \(*A hydrogenation, U\) and \(U_\beta\) are the applied electrode potential and energy of \(*A + *H reactants to *A + H^+ + e^-\), respectively, \(\beta\) is set as 0.5, and \(F\) is the Faraday constant [129]. Another solution is Nørskov’s charge-extrapolation method, in which the total charge of a system remains constant and the potential can change during an electrochemical step [130, 131]. These methods can also be used to estimate the kinetic energy barriers of ASCs in the NRR, as such barriers play an important role in NRR activation [73, 81, 105]. For instance, \(*N_2 \rightarrow *N_H\) which has the highest activation barrier of 1.12 eV, is the rate-determining step for Mo@Ti₃−ₓC₂O₇ ASCs (Fig. 8a), and this value is much larger than the corresponding thermodynamic barrier (0.44 eV) [105].

2. **Simulation of the NRR catalytic performance under realistic conditions.** A turnover frequency (TOF) map can be calculated at different temperatures and pressures by microkinetic modeling, providing a prediction of the NRR reactive performance of ASCs under realistic conditions. For example, within the pressure range of 1–100 bar (1 bar = 100 000 Pa) and temperature range of 300–1 000 K, the TOF of Mo-BHT ASCs increases with both temperature and pressure, and the high TOF of \(2.8 \times 10^{-5} \text{ s}^{-1}\) per site (700 K, 100 bar) is comparable to those of benchmarking Fe catalysts (Fig. 8b) [117].

3. **Charge effects.** Most theoretical NRR works follow the constant charge model (CCM), which uses the simplifying assumption that the total number of electrons in an electrochemical system is constant. However, this is not the case in a real electrochemical environment where the catalysts can accept electrons from (or donate electrons to) the electrodes to match the Fermi level of the catalysts with the applied potential. As illustrated by Liu and coworkers, charges have a strong impact on electrochemical reactions on 2D materials (which is usually the case for the computational NRR) [132]. A recent work by Ji et al. suggested that the calculated NRR limiting potentials for Ru–N₃ and Ru–N₄ ASCs depend on whether charge effects are considered. In CCM, the limiting potential for Ru–N₃ ASCs \((-1.19 \text{ V})\) is lower than that for Ru–N₃ \((-1.02 \text{ V})\). However, if the constant potential model (CPM) and grand canonical DFT are used, the order is reversed, and Ru–N₄ is the better ASC \((-0.66 \text{ V})\) (Fig. 8c, d) [70]. As such, the calculation results of the CCM should be reexamined with the CPM for the NRR to consider the charge effects and simulate more realistic situations.

4. **Solvation effects.** Solvation corrections are also needed to narrow the gap between theoretical calculations and experimental conditions, and applying the implicit solvation model to correct DFT calculation results can supplement the current calculations [133]. Solvation effects are usually neglected in theoretical modeling of the NRR because their changes are usually smaller than 0.1 V [14], but explorations are needed to obtain more accurate results. Recently, Carter’s group employed a mixed implicit/explicit solvation model to study the NRR performance of a single TM atom-doped g-GaN monolayer, where explicit H₂O molecules were added in the first solvation shell, and the implicit solvation model was also applied for the long-range solvation effects [134]. Their results suggest that the solvation effect in the NRR should not be neglected for more rigorous theoretical investigations.

These are only some of the urgent challenges for the theoretical design of NRR ASCs. Fortunately, with the development of computing power and new approaches, the gap between theory and experiments is rapidly becoming narrower.
In this section, we review the current progress in the experimental realization of TM ASCs in the NRR. Based on the type of TM elements (active sites), we divide the cases into three categories: noble metal (Au, Ag, Pt, and Ru) ASCs; nonprecious metal (Fe, Co, Ni, Cu, and Mo) ASCs; and rare-earth metal (Y and Sc) ASCs. The metal content, electrolyte, and key NRR performance indicators (NH₃ yield rate and FE) for each ASC are summarized in Table 2 for comparison. Since DFT calculations are effective and common in the design of ASCs and reveal the origin and mechanism of their NRR performance, the theoretical limiting potential and PLS values (at the DFT-GGA level) for the best samples in experiments are also listed in Table 2. Unless specified otherwise, all the potential values in this review are referenced to the reversible hydrogen electrode (RHE).

It is noteworthy that most of the synthesized ASCs are supported on nitrogen–doped (porous) carbon materials (NC or NPC) through metal–nitrogen (M–Nₓ) coordination bonds due to the outstanding electrical conductivity, abundant active sites with high porosity, and good mechanical strength and stability [135–137], and the corresponding synthetic strategies, including wet-chemistry methods, spatial confinement, and coordination site construction strategies (especially stabilizing ASCs by MOFs and their derivatives), are used in fabricating ASCs on NC [50, 138]. Very recently, other support materials for ASCs have been developed for the NRR, including Pt on WO₃ [139], Fe on nitrogen-free lignocellulose-derived carbon [140], Fe on MoS₂ [141], and Mo on GDY [142], and the family of NRR ASCs has been enriched by these processes.

### 3 Practical Applications of TM ASCs in the NRR

In this section, we review the current progress in the experimental realization of TM ASCs in the NRR. Based on the type of TM elements (active sites), we divide the cases into three categories: noble metal (Au, Ag, Pt, and Ru) ASCs; nonprecious metal (Fe, Co, Ni, Cu, and Mo) ASCs; and rare-earth metal (Y and Sc) ASCs. The metal content, electrolyte, and key NRR performance indicators (NH₃ yield rate and FE) for each ASC are summarized in Table 2 for comparison. Since DFT calculations are effective and common in the design of ASCs and reveal the origin and mechanism of their NRR performance, the theoretical limiting potential and PLS values (at the DFT-GGA level) for the best samples in experiments are also listed in Table 2. Unless specified otherwise, all the potential values in this review are referenced to the reversible hydrogen electrode (RHE).

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### 3.1 Noble Metal ASCs

Catalysts based on noble metals such as Au, Ag, Pt, and Ru usually exhibit superior catalytic performance. For instance, Pt is an ideal catalyst for the HER and ORR, while the noble metal oxides RuO₂ and IrO₂ exhibit high OER activity [168].
## Table 2
Summary of the experimentally realized TM ASCs for the NRR. The sign wt % means percentage in weight ratio and at% means the atom number percentage

| Catalyst | Metal content/wt % | Potential/V versus RHE | Electrolyte (1 M = 1 mol L⁻¹) | NH₃ production rate | Faradaic efficiency/% | Theoretical limiting potential /V (PLS) | Year of publication |
|----------|-------------------|------------------------|-------------------------------|---------------------|-----------------------|----------------------------------------|-------------------|
| **Noble metal ASCs** | | | | | | | |
| Au/C₃N₄ | Au 0.15 | −0.10 | 5 mM H₂SO₄ | 1.305 μg h⁻¹ mg⁻¹ Au (NH₄⁺) | 11.1 | −1.33 (*N₂ → *N₂H) | 2018 [143] |
| AuSAs–NDPCs | Au 0.205 | −0.20 | 0.1 M HCl | 2.32 μg h⁻¹ cm⁻² | 12.3 | N.A | 2018 [144] |
| SA Ag–NC | Ag 0.39 | −0.65 | 0.1 M HCl | 270.9 μg h⁻¹ mg⁻¹ cat/69.4 m g h⁻¹ mg⁻¹ Ag | 21.9 (−0.6 V) | −1.88 (*N₂ → *N₂H) | 2018 [145] |
| Pt@WO₃ | Pt 0.5 | −0.20 | 0.1 M K₂SO₄ | 342.4 μg h⁻¹ mg⁻¹ Pt | 31.1 | −0.78 (*N₂ → *N₂H) | 2020 [139] |
| Ru SAs/N–C | Ru 0.18 | −0.20 | 0.05 M H₂SO₄ | 120.9 μg h⁻¹ mg⁻¹ cat | 29.6 | −0.73 (*N₂ → *N₂H) | 2018 [146] |
| Ru@ZrO₂/NC | Ru 0.14 | −0.21 | 0.1 M HCl | 7.48 μg h⁻¹ mg⁻¹ cat | 56.55 | 14.1 | 2021 [148] |
| Ru SAs@CuₓOᵧ | N.A | 0.05 | 0.1 M NaOH | 42.4 μg h⁻¹ mg⁻¹ cat | 14.1 | ~ −1.0 (*N₂ → *N₂H) | |

| **Nonprecious metal ASCs** | | | | | | | |
| Fe₅₈N₄–C | Fe 1.09 | 0 | 0.1 M KOH | 7.48 μg h⁻¹ mg⁻¹ | 56.55 | −0.28 (*H₂O–N₂ → *H₂O–NNH) | 2019 [149] |
| Fe/NC | Fe 4.2 | −0.40 | 0.1 M PBS | (62.9 ± 2.7) μg h⁻¹ mg⁻¹ cat | 18.6 ± 0.8 | −1.69 (*N–N → *N–*NH) | 2019 [150] |
| Co–MoS₂ | Co 0.95 | −0.90 | 0.05 M Na₂SO₄ | 16.9 μg h⁻¹ mg⁻¹ cat | 18.8 | −0.59 (*N–N → *N–*NH) | 2020 [157] |
| FeTPPCI | N.A | −0.30 | 0.1 M KOH | (18.28 ± 1.6) μg h⁻¹ mg⁻¹ cat | 16.76 ± 0.9 | −0.84 (*N₂ → *N₂H) | 2021 [155] |
| Co SA/NPC | Co 1.4 | −0.20 | 0.05 M Na₂SO₄ | 0.86 μmol cm⁻² h⁻¹ | 10.5 | −0.53 (* + N₂ → *N–NH) | 2019 [156] |
| Co–SAs/NC (laser-irradiation) | Co 0.98 | −0.25 | 0.005 M H₂SO₄ | 16.9 μg h⁻¹ mg⁻¹ cat | 18.8 | −0.59 (*N–N → *N–*NH) | 2020 [157] |
| Co–Nₓ–C | Co 0.95 | −0.90 | 0.05 M H₂SO₄ | 37.6 μg h⁻¹ mg⁻¹ | 17.6 (−0.3 V) | 0.97 (*N₂ → *N₂H) | 2020 [158] |
| Ni–Nₓ–C | Ni 0.5 | −0.80 | 0.5 M LiClO₄ | 115 μg h⁻¹ cm⁻² | 21 ± 1.9 (−0.2 V) | −0.79 (*NH₂ → * + NH₃) | 2020 [159] |
| SA-Mo/NPC | Mo 9.54 | −0.30 | 0.1 M KOH | (34.0 ± 3.6) μg h⁻¹ mg⁻¹ cat | 14.6 ± 1.6 | N.A | 2019 [160] |
| Mo/GDY | Mo 7.5 | −1.20 | 0.1 M Na₂SO₄ | 145.4 μg h⁻¹ mg⁻¹ cat | 21 | −1.29 (*NNH → *NNH₂) | 2019 [142] |
| MoSAs–MoₓC/NCNTs | N.A | −0.25 | 0.005 M H₂SO₄ | 16.1 μg h⁻¹ cm⁻² cat | 7.1 | −0.37 (*NH → *NH₃) | 2020 [161] |
ASCs showed stable NH$_3$ production and much-improved metal-free NPC for the NRR, and they concluded that Au et al. NRR tested Au ASCs and Au NPs on NPC as well as that for Au NPs due to the high AUE of ASCs. Oschatz mentions. Based on Luo et al.’s calculations, the end-on N$_2$ tions can greatly reduce the cost of trial-and-error experi-

FE [144].

The rational design of ASCs based on theoretical calculations can greatly reduce the cost of trial-and-error experiments. Based on Luo et al.’s calculations, the end-on N$_2$ adsorption configuration and oblique *NNH admolecules favor high NRR performance. Thus, Ag–N$_4$ ASCs on NC (SA–Ag/NC) were designed, and their instability inhibited the side-on *NNH configuration [145]. The fabricated Ag ASCs showed a high NH$_3$ yield rate of 270.9 µg h$^{-1}$ mg$^{-1}$ cat and FE of 21.9% at −0.65 and −0.6 V, respectively, as well as long-term (60 h) stability. This work highlighted the importance of theoretical calculations in the targeted design of novel ASCs for NRR.

Conventionally, Pt-based catalysts are considered unsuitable for the NRR due to their high HER activity, which suppresses the NRR [31, 169]. However, a different story was depicted by Shen et al., who downsized Pt NPs to iso-
lated atoms supported on a WO$_3$ substrate (Pt SAs/WO$_3$), which exhibited excellent NRR activity [139]. Pt SAs/WO$_3$ were prepared by in situ photodeposition combined with a hydrothermal method, and the atomic dispersion could be observed by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. 9a). Diffuse reflectance infrared Fourier transform spectroscopy using CO (CO-DRIFTS) exhibited a CO adsorption band at 2 114 cm$^{-1}$, which can be attributed to the CO top adsorption configuration, further proving the CO adsorption band at 2 114 cm$^{-1}$, which can be attributed to the CO top adsorption configuration, further proving the formation of Pt SAs/WO$_3$ (Fig. 9b). At −0.2 V, Pt SAs/WO$_3$ showed an optimized production rate of 342.4 µg h$^{-1}$ mg$^{-1}$ cat and an FE of 31.1%, which are more than 10 times higher than those of the NRR-inert Pt NP catalysts (Pt NPs/WO$_3$). DFT calculations suggested that N$_2$ adsorption on the Pt–3O site may be less hindered by *H adsorption, leading to suppressed HER. This work provides another example in which the rational design of ASCs can lead to the entirely different scenario of an NRR with high efficiency and selectivity.

Unlike Ag and Pt, Ru metal is conventionally identified as a second-generation catalyst for ammonia synthesis after Fe [14, 170–173]. However, the NH$_3$ production rate and FE for Ru NRR catalysts are still not satisfactory [170]. In 2018, Zeng’s group reported the synthesis of Ru ASCs sup-
ported on N–C (Ru SAs/N–C) by high-temperature pyrolysis of a Ru-containing zeolite imidazolate framework (ZIF-8) (Fig. 9c) and investigated their applications in the NRR [146]. Extended X-ray absorption fine structure (EXAFS) spectra showed that compared with Ru NPs/N–C, the only peak for Ru SAs/N–C can be attributed to Ru–N bonds, and no peaks corresponding to Ru metal and oxides were

### Table 2 (continued)

| Catalyst | Metal content/wt % | Potential/V versus RHE | Electrolyte | NH$_3$ production rate | Faradaic efficiency/% | Theoretical limiting potential /V (PLS) | Year of publication |
|----------|--------------------|------------------------|-------------|------------------------|-----------------------|---------------------------------------|-------------------|
| NC–Cu SA | Cu 5.31            | −0.35                  | 0.1 M KOH/HCl | 53.3 (KOH)/49.3 µg h$^{-1}$ mg$^{-1}$ cat | 13.8 (KOH)/11.7 (HCl) | −1.573 (*N$_2$ → *NH$_3$) | 2019 [162] |
| Mn–N–C  | Mn 2.82            | −0.45                  | 0.1 M NaOH    | 21.43 µg h$^{-1}$ mg$^{-1}$ cat | 32.02 | −0.53 (*N$_2$ → *NH$_3$) | 2021 [163] |
| Y$_2$/NC and Sc$_2$/NC | 0.38/Sc 1.24 | −0.10                  | 0.1 M HCl | Y 21.8/Sc 19.2 µg h$^{-1}$ cm$^{-2}$ | 12.1 (Y)/11.2 (Sc) | Y − 0.979 (*N$_2$ → *N$_2$H)/Sc − 1.355 (*NH$_2$ → *+NH$_3$) | 2020 [164] |

**Double-atom catalysts**

| Catalyst | Metal content/wt % | Potential/V versus RHE | Electrolyte | NH$_3$ production rate | Faradaic efficiency/% | Theoretical limiting potential /V (PLS) | Year of publication |
|----------|--------------------|------------------------|-------------|------------------------|-----------------------|---------------------------------------|-------------------|
| FeMoNC   | Fe 0.007; Mo 0.002 | −0.40                  | 0.25 M LiClO$_4$ | 14.95 µg h$^{-1}$ cm$^{-2}$ | 41.7 (-0.2 V) | −0.906 (*NH$_3$ → *+NH$_3$) | 2019 [165] |
| PdCu/NC  | Pd 2.23; Cu 2.32  | −0.45                  | 0.05 M H$_2$SO$_4$ | (69.2 ± 2.5) µg h$^{-1}$ mg$^{-1}$ cat | 24.8±0.8 | −0.78 (*NH$_3$ → *NH$_4$) | 2020 [166] |
| Zn/Fe–N–C | Zn 0.29; Fe 0.34 | −0.30                  | 0.1 M PBS | 30.5 µg h$^{-1}$ mg$^{-1}$ cat | 26.5 | −0.79 (*N$_2$ → *N$_2$H) | 2020 [167] |
observed, indicating that Ru SAs/N–C are atomically distributed (Fig. 9d). The designed Ru ASCs could achieve an FE of 29.6% (Fig. 9e) and a record-high NH3 production rate of 120.9 µg h−1 mg−1 cat. (Fig. 9f). In a recent publication, Ma et al. used a theoretical simulation-directed strategy to design Ru ASCs supported on Cu oxides; this strategy involved weak single atom-substrate interactions that led to improved N2 adsorption and reduced alkaline HER (compared to Ru–N ASCs), which was further proven by experiments [148]. They also proposed two descriptors—water dissociation energy and d-band center—for NRR and alkaline HER activities to accelerate ASC screening. In another work by Sun et al., the addition of ZrO2 was shown to dramatically increase the NRR FE of Ru ASCs from 9% to 21% (Table 2) [147]. DFT calculations revealed that while Ru supported on NC exhibited high theoretical NRR performance, Ru@ZrO2 can provide high NRR/HER selectivity due to the less hindered N2 adsorption by H (Fig. 9g, h), in line with experimental results. Therefore, Ru@ZrO2/NC ASCs have the bifunctional capability to simultaneously enhance the NH3 production rate and FE. The low Ru loading (< 0.2%) and outstanding NRR activity (Table 2) endow Ru ASCs with great potential in NRR applications. However, the relatively low yield of Ru single sites and difficulty in the synthesis [147] appeal for more research into this area.

### 3.2 Non-Precious Metal ASCs

Substituting noble metal elements with nonprecious metal elements can reduce the cost of ASCs. Among the nonprecious metal elements, Fe and Mo attract attention because they act as active centers in natural FeMo nitrogenases (FeMo-co) [7, 9, 174], and Fe/Mo ASCs may also exhibit high NRR activity. For example, Yan and coworkers prepared Fe ASCs by modulating polypyrrrole-iron complexes [149]. The synthesized Fe3N–N–C can achieve striking FE of 56.55% at 0 V (Fig. 10a), which is the highest among all reported ASCs for the NRR to date (Table 2), and the
competing HER can be suppressed (Fig. 10b). Molecular dynamics (MD) simulations indicated that the FeSA–N–C structure can attract N₂ molecules with a considerably small energy barrier of 2.38 kJ mol⁻¹ (Fig. 10c), promoting subsequent NRR thermodynamics. In another work, Liu and coworkers reported Fe ASCs with high NRR performance in a neutral environment (0.1 M phosphate buffer solution) [150]. The EXAFS and DFT results ascribed the performance to the Fe–N₄ configuration, which can effectively activate N₂.

In addition to ASCs supported on NC, Zeng’s group used Fe single atoms to decorate HER-active MoS₂ edge sites, and the Fe–MoS₂ ASCs with lower PLS (0.37 eV) for NRR (0.50 eV for MoS₂) and higher HER barrier resulted in much-improved NRR reactivity [141]. Zhao et al. reported the facile synthesis of Fe ASCs with a new nitrogen-free coordination environment (Fe on lignocellulose-derived carbon, Fe SAs/LCC) [140]. X-ray absorption near edge structure (XANES) spectroscopy implied the atomically dispersed nature of Fe by the absence of Fe–Fe bonds, and it indicated the presence of Fe–O bonds (Fig. 10d). Additionally, the EXAFS fitting results proved that the Fe single atoms formed a novel Fe–(O–C₂)₄ bond (Fig. 10e), while DFT calculations suggested that such a structure can promote N₂ activation through a back-donation mechanism. Consequently, electrochemical tests with ASCs immobilized on a glassy carbon electrode showed near-record NRR performance (yield rate of 307.7 µg h⁻¹ mg⁻¹ cat. and FE of 51.0%). Most recently, Fe ASCs on N,O-doped porous carbon were designed and fabricated, and their outstanding NRR activity originated from the optimized charge transfer between Fe and

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**Fig. 10** Nonprecious metal ASCs for the NRR. a FE and NH₃ yield rates at different potentials for FeSA–N–C, b H₂ selectivity for FeSA–N–C and N–C at different potentials, and c potential of the mean force (PMF) for N₂ adsorption on FeSA–N–C in 0.1 M KOH (the inset: MD snapshots). Reprinted with permission from Ref. [149]. Copyright 2019, Nature Publishing Group. d k¹-weighted Fe K-edge EXAFS of Fe SAs/LCC, Fe foil, and Fe₂O₃, and e EXAFS fitting curve. Reprinted with permission from Ref. [140]. Copyright 2020, Wiley-VCH. f 3D spatial contour plot for the HOMO and the LUMO near the Fermi level for Mo⁰/GDY. Reprinted with permission from Ref. [142]. Copyright 2019, American Chemical Society. g NH₃ yield rate and FE of Mo SAs/Mo₂C/NCNTs, Mo₂C/NCNTs, and Mo SAs/NCNTs at different potentials, and h NH₃ yield rate with increasing cycle numbers at −0.25 V potential. Reprinted with permission from Ref. [161]. Copyright 2020, Wiley-VCH.
adjacent O atoms [154]. This work highlighted the influence of the local coordination environment and the ligands on the NRR performance of ASCs.

In 2019, cost-effective and highly efficient Mo ASCs (SA-Mo/NPCs) were first utilized in NRRs [160]. Owing to the highly exposed active sites with the designed hierarchical porous carbon framework, SA-Mo/NPC exhibited a high NH₃ yield rate of 34.0 µg h⁻¹ mg⁻¹ cat. and FE of 14.6% as well as high stability. Li’s group designed zerovalent Mo ASCs on graphdiyne (Mo₀/GDY), which can be synthesized through a facile and scalable method, and the Mo ASCs have novel bifunctional NRR/HER applications that are not reported elsewhere [142]. Compared with traditional ASCs, zerovalent ASCs with excellent stability and performance can accelerate fundamental investigations of the electrocatalytic mechanisms [44]. Calculations suggested that the Mo sites close to the corner of the alkyne ring serve as electron-rich centers for catalysis (Fig. 10f) with prominent electronic structure and NRR energetics. The XANES spectra of the Mo⁰/GDY and Mo references are almost identical, confirming the zerovalent nature of the ASCs. M Na₂SO₄, Mo⁰/GDY exhibited outstanding performance under ambient conditions, while in the non-N₂-saturated electrolytes, high HER activity was also achieved. This work was the first to apply GDY-based ASCs to a bifunctional NRR/HER in different environments.

Assembling Mo ASCs with Mo₂C nanoparticles on nitrogen-doped carbon nanotubes (Mo SAS-Mo₂C/NCNTs) can improve the NRR activity and selectivity more than either the nanoparticles or nanotubes alone due to the synergistic mechanism, as confirmed by Wang et al.’s theoretical calculations and experiments [161]. DFT calculations suggested that the Mo₂C(101) surface is more catalytically active for the NRR, while Mo ASCs show higher HER reactivity. Following the newly proposed surface hydrogenation mechanism [175], hydrogen coverage of Mo ASCs can reinforce N₂ activation on the surrounding Mo₂C, providing a cooperative effect between Mo ASCs and Mo₂C. Electrochemical NRR tests verified the theoretical calculations that Mo SAS-Mo₂C/NCNTs exhibited NRR performance several times as high as that of either Mo SAS/NCNTs or Mo₂C/NCNTs alone (Fig. 10g) and a small amount of decay during the reusability test (Fig. 10h). As illustrated by this work, the synergistic effect between ASCs and other types of active sites may enhance the NRR performance. In addition to Fe and Mo, nonprecious metal Co [156–158], Ni [159], Cu [162, 176], and Mn [163] ASCs have also been examined as catalysts for the NRR.

3.3 Rare-Earth Metal ASCs

Catalysts based on rare-earth metal elements are conventionally considered ineffective because the multi-shell nature of electrons from rare-earth elements may lead to strong binding with reactant molecules that are difficult to release [164]. Nevertheless, after nitrogen and carbon coordination, electronic structure modulation can endow rare-earth metal ASCs with greatly enhanced catalytic performance compared with rare-earth metal NPs, as proven by Shui’s group [164]. Y₁/NC and Sc₁/NC ASCs were synthesized by using Y/Sc-doped ZIF-8, followed by 1 000 °C pyrolysis. Both DFT calculations (Fig. 11a) and Fourier transform EXAFS (FT-EXAFS) spectra (Fig. 11b) confirmed the six-coordinate structures (Y₁–NC, preferably with N₃C₃ and Sc₁–NC with N₆ coordination), which are different from the prevailing TM–N₄ coordination structures of other TM-based ASCs because of the large atomic radii of rare-earth elements. The synthesized Y and Sc ASCs exhibit high ammonia production rates of 21.8 and 19.2 µg h⁻¹ cm⁻² (Fig. 11c, d) and outstanding FE of 12.1% and 11.2% at −0.1 V, respectively, even under strict experimental control, indicating that the coordination environment can greatly enhance the inert nature of rare earth metal-based catalysts. Finally, DFT calculations further proved that Sc and Y ASCs have lower N₂ activation barriers than the corresponding oxides (Fig. 11e). This interesting work extended the current family of ASCs to the rare-earth elements (Fig. 11f).

3.4 Perspectives and Challenges

In our closing remarks, we summarize the current reports on NRR ASCs categorized by the element type (Fig. 11f). Nearly half of the reports are focused on nonprecious Fe ASCs, and among them, Fe₅₄–N–C exhibits the highest FE of 56.55% [149] and Fe SAS/LCC or Fe–(O–C₄)₄ shows the highest NH₃ yield rate of 307.7 µg h⁻¹ mg⁻¹ cat [140]. Considering the lower cost than noble-metal-based catalysts and stability, Fe ASCs are among the most promising next-generation electrocatalysts for the NRR. In addition, Mo, Co, and Ru ASCs have attracted the attention of researchers. The coordination environment also has a significant influence on the catalytic activity, and the rational design of ASCs based on the coordination environment calls for the combination of theoretical calculations and characterization techniques (e.g., XANES and EXAFS), which is particularly important for ASCs (with electrocatalytic activity very sensitive to the local coordination environment) compared with other electrocatalysts.

A more urgent task for the development of the electrocatalytic NRR (not only with ASCs as the electrocatalysts but also with other electrocatalysts) is the identification and suppression of false positives caused by other nitrogen.
resources in the experiments, such as nitrogen-containing compounds in the gas stream, environment, or even the electrocatalysts themselves. Standard experimental procedures to eliminate false positives have been suggested [48, 49, 177]. Nevertheless, according to Choi et al.’s [178] evaluation, only two of 127 papers on the aqueous NRR up to April 2020 could satisfy two of the three criteria they set (sufficiently high NH₃ yield rate; sufficient and reliable ¹⁵N experiments; rigorous control and quantification of NOₓ), and none met all three criteria due to the neglect of key experimental controls (especially NOₓ contamination), leading scientists to doubt the reproducibility and reliability of the reported NRR electrocatalysts and the true catalytic origin. Therefore, standardization of experimental protocols is very important for the healthy development of this newly emerging field, and similar to other fields, establishing internationally recognized certification laboratories for electrocatalytic NRR may also be a solution.

With respect to the theoretical design prior to experiments, the comparison between the adsorption of N₂ and that of O, NH₃, and NOₓ is seldom reported, which is also a long-overlooked yet necessary approach to evaluating the N₂ adsorption ability with the influence of those contaminants before experimental realization. In addition, the thermodynamic stability of the catalysts can also be predicted by theoretical calculations. All these challenges must be sufficiently addressed before the electrocatalytic NRR can reach the level of industrial ammonia synthesis.

Fig. 11 Rare-earth metal ASCs for the NRR. (a) Different active site structures for Y₁/NC and the corresponding adsorption energy, (b) FT-EXAFS fitting in R-space of Y₁/NC, NH₃ yield at different potentials on e Y₁/NC and d Sc₁/NC ASCs, and e DFT-calculated free energy diagrams of Y₁/NC and Sc₁/NC (the distal pathway). Reprinted with permission from Ref. [164]. Copyright 2020 American Chemical Society. (f) Schematic presentation of the periodic table based on experimentally realized NRR-active TM ASCs. Elements are colored based on the number of publications on NRR ASCs associated with them.
4 Rational Design of Double-Atom Catalysts

Despite all the advantages of the atomically dispersed nature of single-atom catalysts, they also suffer from structural simplicity; that is, single sites may not provide both an ideal yield rate and FE [56]. For complicated multielectron-transfer reactions such as the NRR, tuning the adsorption strength of intermediates on active sites is an urgent issue for the rational design of highly efficient catalysts with high selectivity. Specifically, for the NRR, scaling relations between the adsorption energy of *N*₂H₄ radicals hinder the optimization of theoretical NRR overpotential [83], so the circumvention of scaling relations is one of the most significant tasks.

Double-atom catalysts (DACs), or atom-pair catalysts, such as metal dimers supported on substrates have emerged as a newly extended group of ASCs with practical applications in the HER [179, 180], OER [181, 182], ORR [182–186], and CO₂RR [187–189]. Theoretically, metal dimer sites, unlike single atomic sites, may break the intrinsic scaling relations and optimize the adsorption behavior of intermediates, thus surpassing the theoretical limit of the catalysts, as revealed by the pioneering theoretical works in OER/ORR [190] and CO₂RR [191]. However, for the NRR, both experimental and theoretical benchmarking investigations about the rational design of DACs are scarce, possibly due to the difficulty in controlling their synthesis and the complexity of the NRR mechanism.

Li et al. [165] synthesized FeMo dimers supported on N-doped graphene (FeMo@NG) by an in situ sacrificial template anchoring method. The NH₃ yield rate of 14.95 µg h⁻¹ mg⁻¹ at −0.4 V and FE of 41.7% at −0.2 V were recorded in an electrochemical test (Table 2), and they were much superior to those of the corresponding single-atom Fe and Mo catalysts (Fe@NG and Mo@NG). DFT calculations indicated that FeMoN₆ structures act as the active sites for the NRR and have a lower limiting potential (−0.906 V) than Fe@NG and Mo@NG. A very recent publication highlighted the importance of incorporating Cu into Pd/NC ASCs to form PdCu/NC DACs in electrocatalytic NRR [166]. DFT calculations indicated that the incorporation of Cu can shift the partial density of states of Pd toward the Fermi level and promote d-2π* coupling between Pd and N₂, leading to much-improved N₂ adsorption and protonation with suppression of the HER. The experimental results validated the conclusion that PdCu/NC [(24.8 ± 0.8)% FE and (69.2 ± 2.5) µg h⁻¹ mgcat⁻¹] outperformed Pd/NC in the NRR.

These works laid a solid foundation for utilizing synergy of DACs to enhance the activity and selectivity for the NRR. However, more experimental efforts into the controllable synthesis of DACs are still in great demand to gain more fundamental insights into the mechanisms for the enhanced NRR performance, while theoretical design can compensate for the deficiency in experimental results (Table 3) [19].

In a comparative study, Jiang et al. [193] concluded that TM₂–C₂N DACs were more suitable for the NRR than TM–C₂N single-atom catalysts, and Mn₂–C₂N exhibited the lowest limiting potential of −0.23 V. Huang and coworkers screened homonuclear and heteronuclear DACs supported on 2D phthalocyanine (M₂–Pc and MM’–Pc, Fig. 12a) by high-throughput DFT calculations using *N*₂H adsorption energy ΔEₙ₂H* as a simple descriptor for NRR activity [56]. They first screened 30 M₂–Pc structures with thermodynamic and electrochemical stability for their N₂ adsorption properties and found that eight of them can achieve N₂ chemisorption and activation. Among them, Ti₂–Pc, V₂–Pc, and Re₂–Pc exhibited outstanding NRR potential as a function of Gibbs free energy changes of the key elementary steps to screen for DACs with outstanding U₅ (Fig. 12b), superior to the Ru(0001) benchmark (U₅ = −0.98 V) with the highest theoretical NRR activity among metal surfaces [59]. ΔEₙ₂H* was selected as a descriptor to obtain a volcano-like relationship between NRR U₅ and ΔEₙ₂H* (Fig. 12c), and obviously, V₂–Pc, which had the best U₅ among all the DACs, was located near the top of the volcano. The authors further extended the relationship toward heteronuclear DACs MM’–Pc (Fig. 12d), and in a selectivity investigation performed by using ΔG(H*)−ΔG(N₂H*) as a descriptor (Fig. 12e), five DACs, Ti₂–Pc, V₂–Pc, TiV–Pc, VCr–Pc, and VTa–Pc, were found to simultaneously achieve both high NRR activity and selectivity. Deng et al. [203] studied the NRR performance of homonuclear DACs TM₂–N₆@G (Fig. 12f). They constructed a contour plot of limiting potential as a function of Gibbs free energy changes of the key elementary steps to screen for DACs with outstanding U₅ (Fig. 12g). The author further used the d-band center of 0–2 eV as a descriptor and found a volcano-like relationship between U₅ and the d-band center and further related them to ICOHP. Wang et al. [195] proposed a pull–pull effect in which dual-metal sites can maximize N₂ activation by pulling the two lone pair electrons of N₂ at both ends (Fig. 12h, i). The constructed donor–acceptor couples can circumvent the scaling relations by synergistic effects that promote high NRR activity (Fig. 12j). The FeMoₙ₃–C₃N₄ DAC has a low limiting potential of −0.23 V and high selectivity, while TiMo, NiMo, and MoWₙ₃–C₃N₄ are promising NRR photocatalysts. These theoretical works paved the way for designing DACs for high-performance NRRs.

In addition to DACs, several theoretical investigations proved that triple-atom catalysts such as Fe₃/Al₃O₃(010) [209] and Fe₃–GDY/Gra [210] are NRR-active. The synthesis of Ru₃ triple-atom catalysts was reported with a confined pyrolysis method within MOFs [211], and the application of
double- or triple-atom catalysts for the NRR in the laboratory is promising. In summary, replacing single-atom catalysts with DACs might be a potential solution to improve the theoretical NRR activity and selectivity. Nevertheless, the reported double-atom electrocatalysts for the NRR are relatively rare compared with those for the ORR, water splitting, and CO2RR [19], and their NH3 yield rate and FE do not show a pronounced improvement compared with those for single-atom catalysts. Currently, the discovery of DACs for the NRR is still driven by theoretical design, appealing for more efforts in this field.

5 Rational Design of Boron-Based Metal-Free ASCs

As stated above, metal-based catalysts, including TM ASCs, remain the most widely applied catalysts for the NRR. Despite recent progress, metal-based catalysts still suffer from relatively low efficiency because of the competition between the formation of metal–N and metal–H bonds. Since the d-orbital electrons in TM centers are usually more inclined to form metal–H bonds [212, 213], the FE of the NRR is greatly compromised. Metal-based catalysts may also raise stability, economic, and environmental concerns. Designing a new group of metal-free catalysts is therefore of great significance for the development of electrocatalytic and photocatalytic NRRs [214–217]. Pioneering works suggested that NPC [218] and B4C nanosheets [215] are superior NRR catalysts, but until now, metal-free NRR catalysts have generally been far less explored than metal-based catalysts.

5.1 Theoretical Design

For a typical TM-based NRR catalyst, TM elements with both empty and occupied d orbitals exhibit high N2 activation ability, and the origin of effective N2 activation can be ascribed to the “acceptance-donation” mechanism (also known as the “σ donation–π* back-donation” mechanism): TM atoms accept lone-pair electrons from N2 and donate the d electrons to the antibonding orbital so that the inert N≡N bonds can be weakened (Fig. 13a).
In a pioneering work by Légaré et al. [219], the d-block element boron was found to be NRR-active, and since N₂ is a weak Lewis base, boron atoms with empty orbitals can act as Lewis acid active sites for the NRR [219, 220]. For sp²-hybridized boron atoms, N₂ can be activated through a B₂N₂ motif with an end-on adsorption.
configuration [219]. Similarly, sp$^3$-hybridized boron atoms can also activate N$_2$ effectively, as they can have one occupied and one empty sp$^3$ orbital for bonding via the “acceptance-donation” mechanism (Fig. 13b), and the possibility of adopting a side-on adsorption pattern may induce different behavior in the NRR [214]. Following this concept, Wang et al. designed metal-free boron SASCs, i.e., B/g–C$_3$N$_4$ through DFT calculations, where N$_2$ can be activated in both end-on and side-on configurations through the “acceptance-donation” mechanism, as illustrated by the negative adsorption energy as well as charge accumulation and depletion around the boron atom and N$_2$ (Fig. 13c, d) [214]. Detailed energetics analysis confirmed that through the side-on adsorption configuration and enzymatic NRR pathway, a very low onset potential of 0.20 V can be achieved (Fig. 13e).

Such design principles for boron-based metal-free ASCs can also be applied to NRR electrocatalysts. Sun’s group designed 21 conceptual single-boron catalysts, including adsorbed (A), substituted (S), and lattice (D) boron on graphene, boron nitride, boron sulfide, black phosphorus, g–C$_3$N$_4$, and MoS$_2$ (Fig. 13f) [221]. By using the N adsorption energy on Ru$_{E(N^*)}$ as a reference [59], a volcano-shaped plot of the maximum Gibbs free energy change for the NRR elementary steps $\Delta G_{\text{max, NRR}}$ versus $E_{\text{NRR}}$ was constructed (Fig. 13g), and boron adsorbed on graphene (G-A), boron nitride (BN-A), and substituted on h-MoS$_2$ (h-S1) were identified as the most promising NRR ASCs with $\Delta G_{\text{max, NRR}}$ values of 0.31, 0.45, and 0.46 eV, respectively. For selectivity issues, the authors compared $\Delta G_{\text{max, HER}}$ with $\Delta G_{\text{max, NRR}}$ (Fig. 13h) and concluded that G-A and h-S1 have high NRR selectivity. By correlating $\Delta G_{\text{max, HER}}$ and
Δ$G_{\text{max}}$ NRR with the Bader charge $\delta$ on boron (Fig. 13i), they found that a small or negative charge on boron favors the NRR and a positive charge favors the HER, so the charge on boron can act as a descriptor for the design of boron ASCs for the NRR.

Another question for boron-based ASCs is whether the optimized boron species for the NRR are sp$^2$-hybridized [222, 223] or sp$^3$-hybridized [214]. Yin et al. [224] provided theoretical insight by designing NRR ASCs with boron on C$_2$N. Boron adsorbed on C$_2$N is sp$^3$-hybridized (denoted as B/C$_2$N-a), while substituted boron is sp$^2$-hybridized (denoted as B/C$_2$N-s); thus, C$_2$N is an ideal platform for analyzing the hybridization. B/C$_2$N-s exhibited better activity for the NRR (all the steps along the alternating pathway are exothermic, Table 4) and higher HER suppression ability so that more sp$^2$-hybridized boron sites can enhance the NRR ability. This work provides guidance for NRR catalyst design and is in line with experimental results [222, 223]. More theoretical progress in the rational design of boron-based ASCs is summarized in Table 4.

### 5.2 Experimental Evidence

Experimentally, boron-doped graphene (BG) was first applied as sp$^2$-hybridized NRR boron ASCs by Zheng et al. [222]. BG was fabricated by H$_3$BO$_3$/graphene oxide thermal reduction in H$_2$/Ar mixed gas, and according to B 1s X-ray photoelectron spectroscopy (XPS) results, four structures, including BC$_4$ (lattice defect of graphene), BC$_3$ (B replacing a carbon atom in graphene framework), BC$_2$O, and BCO$_2$ (B replacing edge/defect site carbon), could be observed after boron doping (Fig. 14a). The temperature-programmed desorption (TPD) curve indicated that boron doping at different levels (BG-1, BG-2) can significantly enhance N$_2$ chemisorption (Fig. 14b), and further electrochemical tests suggested that at a doping level of 6.2% (BG-1), boron ASCs exhibited NH$_3$ yield rates of 9.8 µg h$^{-1}$ cm$^{-2}$ and 10.8% FE (in 0.05 M H$_2$SO$_4$), which were several times higher than those for undoped graphene (Fig. 14c, d). DFT calculations proved that the NRR is prohibited on graphene due to large energy barrier, and compared with those of BC$_2$O (1.04 eV) and BCO$_2$ (1.30 eV), the BC$_3$ structure has the PLS (*N$\rightarrow$*NH with the lowest energy barrier (0.43 eV), contributing to the high NRR activity of B ASCs (Fig. 14e). Boron-doped nanostructured diamond also performed well in the electrocatalytic NRR with an NH$_3$ yield rate of 9.8 µg h$^{-1}$ cm$^{-2}$ and an FE of 21.2%, and DFT calculations illustrated that boron atoms are active sites that can facilitate charge accumulation and reduce the free energy barrier of the PLS [234].

### 5.3 Perspective and Challenges

Apart from B-doped ASCs, S- [235], O- [236], and F-doped [237] carbon materials can also improve the NRR activity of pristine carbon because the electronegativity differences between S, O, F and C can create Lewis acid sites for activating N$_2$ and repelling H. All these examples open up a new avenue for the rational design of metal-free ASCs for the electrocatalytic NRR. There are also several challenges for the design of metal-free ASCs, including:

1. Experimental synthesis and characterization of non-metal atomic sites: Compared with metal-based ASCs, the control and characterization of nonmetal ASCs are difficult, so the atomically dispersed nature cannot be
firmly verified. Nevertheless, with the aid of theoretical calculations, the NRR-active or NRR-inactive local structure of metal-free ASCs can be identified so that it can be determined whether single atomic sites act as active sites [222].

(2) Exploration of the interaction between boron, substrate, and N$_2$ molecules: While some studies have investigated the interaction between boron and carbon or N-doped carbon [214, 222, 224–228], the interplay between other substrates and boron has not yet been fully illustrated. Additionally, whether substrates and ligands can affect the NRR activity of metal-free ASCs remains unclear and requires more attention. In addition, the effects of strain-, defect-, or doping-tailored electronic structures on the performance of metal-free NRR ASCs have not yet been revealed.

(3) Design of metal-free ASCs other than those that are boron-based, such as F-doped carbon materials [237]: Recently, nonmetal single-phosphorus-atom catalysts were fabricated for the HER [238], and more evidence is needed for their applications in the NRR.

6 Conclusion and Outlook

In this review, we comprehensively summarized the recent progress in the theoretical and experimental design of ASCs for the NRR. The computational schemes, activity and selectivity descriptors, and experimental design were subsequently introduced, and corresponding progress was highlighted. Furthermore, the use of metal dimers instead of single-atom sites can synergistically improve the NRR activity, and boron-based ASCs can be a typical example of metal-free catalysts with similar or even superior NRR activity. Despite the vast progress that has occurred in recent years (Fig. 15), several challenges that may hinder the effective design of NRR ASCs with high activity and selectivity still remain; they include but are not limited to:

(1) Standardization of the experimental and computational setup. As we discussed in Sect. 3.4, the nitrogen-containing compounds in catalysts, electrodes, and environments may cause false positives in the detection of ammonia and induce accuracy and reliability issues in
the design of ASCs for the NRR [48, 49, 177]. Therefore, standardization of the control experiments is necessary for the elimination of contamination, and benchmarking protocols proposed by Anderson et al. [48] can be applied to ASCs as a solution; in particular, quantitative isotope measurements of $^{15}$N$_2$ gas were used to increase the reliability and reduce the cost. In computational experiments, standardization is also important to ensure that the simulated activity and selectivity can reflect the real situations in experiments to a greater extent.

(2) Developing and applying advanced theoretical approaches to narrow the gap between theory and experiments. These approaches include analysis of the kinetic energy barrier in the NRR [26], introduction of the charge effect [70] and the solvation effect, and microkinetic simulation of the TOF map at different temperatures and pressures [117]. In addition, more rigorous functional and van der Waals (vdW) corrections for the calculations of adsorption energy should be developed and applied. For example, the Bayesian error estimation functional with vdW (BEEF-vdW) can lead to a more accurate description of the energetics of catalytic reactions [239, 240].

(3) Advanced instrumentation of experimental characterization and design of NRR ASCs. In situ and operando characterization of ASCs plays a significant role in understanding the underlying origins of NRR activity. For example, in situ XANES and EXAFS can be applied to detect the role of local coordination environments and electronic structures of active sites in the NRR process, and in situ DRIFTS or surface-enhanced infrared absorption spectroscopy (SEIRAS) [31, 173] can be used to measure the intermediate species during NRR, both contributing to a more comprehensive mechanistic understanding. Further utilization of other advanced dynamic characterization approaches can be a great opportunity for the rational design of NRR ASCs.

(4) Mechanistic investigation. Although most current theoretical investigations adopt a concerted PCET mechanism and CHE model in the calculations, there are controversies regarding whether concerted PCET or sequential PCET can better describe the proton and electron transfer process. For the CO$_2$RR, Koper concluded that pH plays an important role in the competition between concerted and sequential PCET mechanisms [241]. For the NRR, more mechanistic investigations are needed. In addition, for the (111) facets of TM nitrides, a lattice-nitrogen-related Mars-van Krevelen mechanism is also possible for NRR [25]; thus, similar investigations of nitrogen-containing ASCs are needed.

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