MoS$_2$-Based Catalysts for N$_2$ Electroreduction to NH$_3$ – An Overview of MoS$_2$ Optimization Strategies

Liang Tian, Jinxiu Zhao, Xiang Ren, Xu Sun, Qin Wei and Dan Wu
The nitrogen reduction reaction (NRR) has become an ideal alternative to the Haber-Bosch process, as NRR possesses, among others, the advantage of operating under ambient conditions and saving energy consumption. The key to efficient NRR is to find a suitable electrocatalyst, which helps to break the strong N≡N bond and improves the reaction selectivity. Molybdenum disulfide (MoS$_2$) as an emerging layered two-dimensional material has attracted a mass of attention in various fields. In this minireview, we summarize the optimization strategies of MoS$_2$-based catalysts which have been developed to improve the weak NRR activity of primitive MoS$_2$. Some theoretical predictions have also been summarized, which can provide direction for optimizing NRR activity of future MoS$_2$-based materials. Finally, an outlook about the optimization of MoS$_2$-based catalysts used in electrochemical N$_2$ fixation are given.

1. Introduction

Ammonia (NH$_3$) not only plays a significant role in industry, agriculture and other industries related to daily work but also is a potential hydrogen storage material. In industrial production, the Haber-Bosch process is used for NH$_3$ synthesis. But the Haber-Bosch process has extremely tough requirements, including high temperature (400–500 °C) and pressure (200–250 bar). The process is also accompanied by massive CO$_2$ emission. Therefore, it is urgent to explore a NH$_3$ synthesis method that has less impact on the environment. Recently, the nitrogen reduction reaction (NRR) has attracted significant attention for artificial N$_2$ fixation because the NRR process can be performed at ambient conditions and save energy. Hence, it is regarded as an ideal alternative to the Haber-Bosch process.

However, the N≡N bond is hard to break (bond energy about 941 kJ mol$^{-1}$) and the competing hydrogen evolution reaction (HER) has a huge impact. It is thus necessary to identify suitable catalysts to improve the efficiency of ambient NH$_3$ synthesis. Noble metal catalysts show excellent activity for NRR due to their favorable conductivity and strong chemical binding with reactants. But the use of this type of catalyst has been vastly limited by its scarcity. Consequently, numbers of non-noble catalysts have been researched. In non-noble catalysts, two-dimensional materials have been widely explored in the NRR field due to the large surface area and novel electronic properties. MoS$_2$, as an emerging layered two-dimensional material, can conduct electricity like graphene. Compared to other two-dimensional materials, MoS$_2$ not only has the advantages of adjustable electronic structure, optimal N$_2$ adsorption energy and good stability in liquid media, but also has the potential of large-scale production as the preparation process is simple. Therefore, it has been largely used in the electrocatalysis field.

Recently, Sun and co-workers reported bulk MoS$_2$ nanosheets for electrochemical N$_2$ fixation. The nanosheet structure of MoS$_2$ is markedly displayed in transmission electron microscopy (TEM) images (Figure 1A). In this work, they firstly performed density function theory (DFT) calculations to verify the feasibility of MoS$_2$ for the NRR process. The calculation results showed that the energy barrier of the potential-determining step (PDS) was 0.68 eV (Figure 1B), which demonstrated MoS$_2$ was a potential NRR catalyst. The edge of MoS$_2$ was attested to be the N$_2$ adsorption site on the basis of Bard charge analysis (a large number of positive charges gather at the edge of MoS$_2$, as shown in Figure 1C). According to electrochemical experiment, the MoS$_2$ nanosheet could achieve an NH$_3$ yield of $8.08 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$ in 0.1 M Na$_2$SO$_4$ but the Faraday efficiency (FE) was only 1.17% (Figure 1D), mainly limited by the HER process. Therefore, MoS$_2$ is indeed a promising and potential NRR electrocatalyst. How to optimize MoS$_2$ to increase its NRR activity has become a hot topic among researchers.

Herein, we summarize the optimization strategies of MoS$_2$ since it was first used as a NRR catalyst, including enhancing electrical conductivity/enlarging specific surface area, taking advantage of the interaction effect between other elements and MoS$_2$ and inhibiting competitive reaction. We also summarize recent theoretical calculations on and predictions of MoS$_2$-based catalysts. In addition, some advice on how to improve the NRR progress activity of MoS$_2$-based catalysts is finally presented.

2. The Mechanism of NH$_3$ Synthesis

The NRR process can be simply divided into the following process: (1) N$_2$ is adsorbed on the active site of the catalyst surface; (2) to the N atom, hydrogen is constantly added; (3) a NH$_3$ molecule is released. The mechanism of the NH$_3$ synthesis process can involve dissociative (Figure 2A) or associative mechanisms (Figures 2B and C). During the pathway of the dissociative mechanism, the N≡N is fractured in advance, then each individual N atom gets hydrogenated. The Haber-Bosch process is thought to follow the dissociative pathway. The associative mechanism can be differentiated in the alternating (Figure 2B) and the distal pathway (Figure 2C) differing in how...
the hydrogenation proceeds. For the alternating pathway, a N atom connects with the surface of the catalyst; followingly, two N atoms are hydrogenated separately until two NH3 molecules are released. For the distal pathway, the N atom not bound to the catalyst is firstly hydrogenated to release an NH3 molecule, then the other N atom is hydrogenated and the second NH3 molecule is released. The adsorption modes of the alternating pathway and the distal pathway are called end-on adsorption.

Another mode of adsorption is called side-on adsorption (Figure 2D). In the side-on adsorption pathway, two N atoms are both bound to the catalyst surface and alternatingly hydrogenated to produce two NH3 molecules.

3. Strategies for Enhancing the NRR Activity of MoS2

3.1. Enhancing Electrical Conductivity/Enlarging Specific Surface Area

It has been demonstrated that the edges of MoS2, that is, free Mo atoms, are the N2 adsorption sites of MoS2; thus, creating more active sites to increase N2 adsorption is beneficial to the improvement of the NRR activity. After MoS2 had been used in the electrocatalytic NH3 synthesis process, Sun and co-workers further used defect-rich MoS2 nanoflowers as a catalyst for the NRR process. Thanks to the defect structure, the electronic structure of the MoS2 nanoflowers enhanced the activity of the reaction sites, which was more advantageous to the absorption of N2. The MoS2 nanoflowers could achieve a high FE of 20.48% with an NH3 yield of 29.28 μg h\(^{-1}\) mg\(_{cat}\)\(^{-1}\) in 0.1 M Na2SO4. Liao et al. reported ultra-thin MoS2 nanosheets with high specific surface area as an NRR catalyst. The large specific surface area leads to an increase in active sites. Therefore, compared with bulk MoS2, the NH3 yield of the ultrathin MoS2 nanosheets achieved a significant growth (41.66 μg h\(^{-1}\) mg\(_{cat}\)\(^{-1}\)), but the FE (1.10%) showed only little improvement due to the strong competing influence of the HER process. Chen et al. employed high temperature annealing to get porous atomic layered MoS2. Benefiting from the formation of pores, more N2 adsorption sites on the inert basal plane were exposed. The reasonable use of the inert basal plane of MoS2 provided a new concept for optimizing MoS2-base catalysts for NRR. At the same time, the multilayer structure allowed most of the N2 adsorption sites to take part in the reaction. Thus, an NH3 yield of 3405.55 μg h\(^{-1}\) mg\(_{cat}\)\(^{-1}\) and a FE of 44.36% were achieved.

In addition, it is well known that MoS2 is a semiconductor material, so taking measures to increase MoS2 electrical conductivity is also an option to optimize the NRR activity of MoS2-based catalysts. Loading MoS2 on a suitable substrate is one of the measures to tackle the lack of N2 adsorption sites and the poor electrical conductivity. As reduced graphene oxide
(rGO) has the advantages of high specific surface area, favorable electroconductibility and high stability, rGO has been widely used in electrocatalysis in recent years.\textsuperscript{57} In our recent work, we loaded MoS\textsubscript{2} nanosheets onto rGO to improve the specific surface area and electrical conductivity of MoS\textsubscript{2}.\textsuperscript{58} Having the reaction taking place in 0.1 M LiClO\textsubscript{4} furthermore had the effect of inhibiting the HER (the mechanism will be described specifically in strategy 3.3). Under the synergistic effect of the above strategies, we obtained an NH\textsubscript{3} yield of 24.82 μg h\textsuperscript{-1} mg\textsuperscript{-1}cat.\textsuperscript{1} and a FE of 4.56 \%. As MoS\textsubscript{2} nanodots has the advantages of more N\textsubscript{2} adsorption sites and larger specific surface area compared to nanosheet structures, Zhang and co-workers loaded MoS\textsubscript{2} nanodots uniformly on rGO.\textsuperscript{59} By means of X-ray photoelectron spectroscopy (XPS), the MoS\textsubscript{2} nanodots/rGO material was demonstrated to contain strong C-S-C bonds which effectively promoted electron transfer. Thus, MoS\textsubscript{2} nanodots/rGO exhibited a FE of 27.93 \% at 0.35 V versus the reversible hydrogen electrode (RHE) potential with an NH\textsubscript{3} yield of 16.41 μg h\textsuperscript{-1} mg\textsuperscript{-1}cat.\textsuperscript{1} at 0.75 V (vs. RHE).

Through a pyrolysis strategy, Zhao et al. generated MoS\textsubscript{2} grown, in situ, on a C\textsubscript{3}N\textsubscript{4} layer, which led to an NH\textsubscript{3} yield of 19.86 μg h\textsuperscript{-1} mg\textsuperscript{-1}cat.\textsuperscript{1} with a FE of 6.87 \%. The reason for the high catalytic activity is the strong interaction between C\textsubscript{3}N\textsubscript{4} and MoS\textsubscript{2}.

![Figure 1](image1.png)

Figure 1. (A) The transmission electron microscope image of MoS\textsubscript{2} nanosheets. (B) Free energy profile proposed by DFT calculations. The asterisk (*) denotes the N\textsubscript{2} adsorption site. (C) The view from atop the isosurface of deformation charge density. Red and green represent charge accumulation and drop at the edge of Mo atoms, respectively. Isosurface is 0.0025 a.u. (D) The NH\textsubscript{3} yields and FE of MoS\textsubscript{2}/CC (carbon cloth) at various potentials. Reproduced with permission from Ref. [52]. Copyright 2018 Wiley-VCH.

![Figure 2](image2.png)

Figure 2. The NRR mechanisms on the surface of catalyst: (A) dissociative pathway; (B) alternating pathway; (C) distal pathway; (D) side-on adsorption. Blue, white represent N, H atoms, respectively.
and MoS$_2$ formed by interfacial Mo–N coordination to promote electron transmission. In addition, the source of N$_2$ was also determined in electrochemical experiments. They demonstrated that C$_x$N$_y$ had no catalytic capacity for NRR, so the N source for electrocatalytic NH$_3$ synthesis only came from the N$_2$ in the air. Shao and co-workers immobilized 1T-MoS$_2$ on g-C$_3$N$_4$ (1T-MoS$_2$/g-C$_3$N$_4$) to boost NRR activity.$^{[61]}$ The 1T phase (comprised of edge-sharing [MoS$_2$] octahedra) had the advantage of more N$_2$ adsorption sites along the plane and higher electron conductivity than other phases of MoS$_2$.$^{[62]}$ Therefore, an appropriate load of 1T-MoS$_2$ was conducive to the adsorption and activation of N$_2$. 1T-MoS$_2$/g-C$_3$N$_4$ achieved a high catalytic efficiency of NRR (29.97 μg h$^{-1}$ mg$_{cat.}$$^{-1}$, 20.48%).

Mao et al. first prepared n-butyl triethyl ammonium bromide functionalized polypyrrole/graphene oxide (BTAB/PPy/GO) as a precursor,$^{[83]}$ in which the substrate polypyrrole/graphene oxide was used to enhance electroconductibility and to expand the specific surface area of the catalyst. Interestingly, BTAB/PPy/GO itself showed little NRR activity (Figure 3A), but it did affect the morphology and phase of 1T-MoS$_2$. 1T-MoS$_2$/BTAB/PPy/GO (schematic synthesis is shown in Figure 3C) thus could attain a high NRR activity (13.60 μg h$^{-1}$ mg$_{cat.}$$^{-1}$, 1.96%). However, after long-term use, the metastable 1T-MoS$_2$ could transform into Mo$_3$N due to the electrochemical reaction with N$_2$. Having formed new Mo–N bonds, this prevented the catalyst from binding N$_2$. Figure 3B shows the concentration of NH$_4^+$ versus operation time; the concentration of NH$_4^+$ stayed steady after 18 h of reaction, which indicated that the active sites of 1T-MoS$_2$/BTAB/PPy/GO had been deactivated.

Xu et al. anchored 1T-MoS$_2$ on Ti$_3$C$_2$ MXene through a hydrothermal reaction.$^{[49]}$ Because the 1T-MoS$_2$ could be fully loaded on the Ti$_3$C$_2$ MXene, in turn exposing more N$_2$ adsorption sites and the composite had high electrical conductivity, the 1T-MoS$_2$/Ti$_3$C$_2$ MXene achieved an NH$_3$ yield of 30.33 μg h$^{-1}$ mg$_{cat.}$$^{-1}$ and a FE of 10.94% in 0.1 M HCl.

### 3.2. Taking Advantage of the Interaction Effect Between Other Elements and MoS$_2$

As the NRR performance of MoS$_2$ is not satisfactory, taking advantage of the interaction effect between other elements and MoS$_2$ to enhance the NRR activity of MoS$_2$ has become a widely studied strategy. The interaction effect, including synergy effects and the addition of other elements, can change the electronic structure of MoS$_2$, thus, heteroatom doping has become the priority approach in this strategy. Zeng et al. achieved a high NH$_3$ yield of 128.17 μg h$^{-1}$ mg$_{cat.}$$^{-1}$ and a FE of 11.34% by doping bimetallic Ni-Fe in MoS$_2$.$^{[65]}$ The reason for the high activity was that the bimetallic dopant reacted with the S atoms to generate a nanohollow structure (Figure 4A), affording more N$_2$ adsorption sites because of the synergetic effect of the S-Fe-Ni system. As shown in Figure 4B, Zhao et al. doped a carefully balanced amount of Fe nanodots into MoS$_2$, using carbon cloth as a substrate, so that the Fe atoms would

---

**Figure 3.** (A) The NH$_3$ yield and FE of different catalysts at −0.49 V after electrolysis (2 h): (a) carbon cloth (CC), (b) graphene oxide (GO), (c) PPy/GO (PPy = polypyrrole), (d) BTAB/PPy/GO (BTAB = n-butyl triethyl ammonium bromide), (e) MoS$_2$, (f) MoS$_2$/GO, (g) MoS$_2$/PPy/GO and (h) 1T-MoS$_2$/BTAB/PPy/GO. (B) Time-dependent concentration of NH$_4^+$ over 30 h in 0.1 M KOH. (C) Schematic synthesis of 1T-MoS$_2$/BTAB/PPy/GO. Reproduced with permission from Ref. [63]. Copyright 2020 American Chemical Society.
not aggregate and degrade during the NRR process. The synergistic effect (Fe nanodots can regulate the chemical state of MoS$_2$) made Fe-MoS$_2$/CC afford an NH$_3$ yield of 12.5 $\mu$g h$^{-1}$ cm$^{-2}$ with a FE of 10.8%.

Most of the current MoS$_2$ synthesis processes involve ammonium ions, which leads to unclear N sources in the NRR process. Partially replacing S atoms in 2H-MoS$_2$ with Fe atoms (Figure 4C), Guo et al. used an ammonium-free hydrothermal process to grow Fe@2H-MoS$_2$ on carbon cloth, thus successfully avoiding the problem of unclear N sources. The substituted Fe atoms affected the electronic state of Mo and S atoms, which facilitated the adsorption of N$_2$. Therefore, compared with bulk MoS$_2$, the NH$_3$ production rate of Fe@2H-MoS$_2$ was increased by 10 times and the FE was increased by 5 times.

Since MoS$_2$ is a semiconductor material, which hinders the process of electron transfer, doping with a conductive metal is a potential strategy of resolving this. In addition to iron-doping, other elements have also been used to produce outstanding results with this strategy. Recently, Zhang et al. have grown ultra-small Au nanoparticles (NPs) on MoS$_2$ nanosheets to produce excellent NRR activity with an NH$_3$ yield rate of 1.14 $\times$ 10$^{-10}$ mol cm$^{-2}$ s$^{-1}$ with a FE of 17.6% (50$°$C). The high NRR activity was ascribed to the synergistic interaction between the isolated sulfur vacancies on MoS$_2$ (the hydrogenation centers) and the Au cluster (the sites of N$_2$ binding).

In addition, MoS$_2$ has also been doped with some non-metals that have also been proven to promote electron transfer. Yang et al. synthesized C/MoS$_2$ porous nanospheres by a simple one-pot hydrothermal method. Benefiting from the synergistic effect between C and MoS$_2$, the electron transfer during the N$_2$ electroreduction to NH$_3$ was significantly improved. The C/MoS$_2$ material thus achieved a FE of 8.2%. Zeng et al. reported an impressive NH$_3$ yield of 69.82 $\mu$g h$^{-1}$ mg$_{cat.}^{-1}$ and a high FE (9.14%) by doping N atoms (by using ammonium fluoride during the synthesis) into MoS$_2$ nanoflower structures. The N atoms altered the electronic structure of MoS$_2$ and produced abundant S vacancies, which promoted electron transfer.

Due to the appropriate orbital energy and symmetry, the unoccupied and occupied d orbitals of the transition metal (TM) can separately receive electrons from and feed electrons back to the N$_2$ antibonding orbitals, respectively, activating the N–N bond. Based on this mechanism, Guo et al. proposed a concept of the strong-weak electron polarization (SWEP) pair, consisting of two catalytic centers with vastly different electron acceptance and back-feeder abilities. As the d orbitals of transition metals and the p orbitals of boron show similar behavior, SWEP pairs were created by filling the S vacancy in MoS$_2$ with B atom (adjusting the electronic structure of MoS$_2$). The SWEP pair in B–MoS$_2$/CFC (CFC = carbon fiber cloth) polarized the non-polar N–N bond (Figure 5A), thus promoting...
Besides heteroatom doping, compound loading is also one of the strategies to optimize the NRR activity of MoS$_2$. Guo et al. reported FeS@MoS$_2$ under the action of independent conductive substrate carbon fiber cloth (CFC) as an NRR catalyst. The high NRR activity (NH$_3$ yield of 8.45 µg h$^{-1}$ cm$^{-2}$) of FeS@MoS$_2$/CFC was ascribed to the synergistic effect arising from FeS nanoparticles providing a large number of N$_2$ adsorption sites. Yang et al. loaded CoS$_2$ nanoparticles onto MoS$_2$ nanosheets as a heterostructured catalyst. The strong interaction between CoS$_2$ and MoS$_2$ can adjust the interface charge distribution, which effectively promoted the adsorption of N$_2$. Thus CoS$_2$/MoS$_2$ attained an NH$_3$ yield of 54.7 µg h$^{-1}$ mg$_{cat.}^{-1}$ and a FE of 20.8%.

Inspired by the role of dinitrogenase in biological NH$_3$ synthesis, Zhang et al. simulated the active site of nitrogenase by introducing Co atoms to the S vacancy of the MoS$_2$ basal plane(Figure 5C). The S vacancy could make Mo atoms below the basal plane manifest to generate more N$_2$ adsorption sites. The energy barrier of the rate-limiting step (Figure 5D), according to DFT calculations, changed from −1.62 eV (MoS$_2$) to −0.59 eV (Co–MoS$_2$), which further proved that Co-doping could enhance the activity of the NRR process. Thus the catalyst could achieve an NH$_3$ yield over 0.6 mmol h$^{-1}$ g$^{-1}$ and a FE over 10%. Similar to the work of Zhang et al., Zeng et al. also prepared Co–MoS$_2$ by making use of the positive interaction between Co and S. The difference was that they loaded Co–MoS$_2$ onto a zeolitic imidazolate framework (ZIF) as a heterojunction catalyst, which could benefit from the inhibitory effect of ZIF on the HER process. They further designed a N$_2$ diffusion cathode because N$_2$ has a low solubility in the electrolyte. Through the bidirectional optimization of the electrocatalyst and the reaction environment, the Co–MoS$_2$ could obtain a satisfactory NRR activity in 0.1 M Na$_2$SO$_4$ (127.88 µg h$^{-1}$ mg$_{cat.}^{-1}$, 11.29%).

Zheng et al. embedded Fe atoms in single-molecular layered MoS$_2$ (sMoS$_2$) which then contained a [Fe–S$_2$–Mo] motif similar to the core structure of the Fe–Mo–S cluster in nitrogenase. Benefitting from the interactions in the Fe–S$_2$–Mo motif, Fe–sMoS$_2$ could achieve an NH$_3$ yield of 24 µg cm$^{-2}$ h$^{-1}$ with a FE of 27% in 0.5 M K$_2$SO$_4$.

Due to the structure of MoS$_2$, some research has shown that heteroatom doping can also inhibit competing reactions of the NRR process; more detail will be given in the next section.

3.3. Inhibiting Competitive Reaction

As the reaction potentials of the hydrogen evolution reaction (HER) and NRR are similar to each other, HER is the biggest competitive reaction in electrocatalytic N$_2$ reduction. In the original experiment by Sun et al., it was the influence of the HER that caused the low FE of the pure MoS$_2$. Therefore, inhibition of the HER process became
one of the most effective strategies to enhance the NRR activity. Liu et al. used the interaction between Li and S to inhibit the HER process. Specifically, when S-rich MoS$_2$ nanosheets were used as NRR catalyst in a 0.1 M Li$_2$SO$_4$ electrolyte, the adsorption free energy of H was reduced (0.03 eV$-0.47$ eV) due to the interaction between Li$^+$ and the S edge site in MoS$_2$ (Figure 6A). Thus, the adsorption process of H$^*$ was inhibited. At the same time, the strong action of Li positively charged the edge site of MoS$_2$, which enhanced adsorption of N$_2$ (the N$_2$ adsorption free energy was increased from $-0.32$ eV to $-0.70$ eV). Compared to conducting the experiment in a 0.1 M Na$_2$SO$_4$ electrolyte, the Li-based electrolyte led to a high NRR activity of the S-rich MoS$_2$ nanosheets (43.4 $\mu$g h$^{-1}$mg$^{-1}$cat., 9.81%) (Figure 6B). Through electrochemical experiments, Liu et al. verified the stability of the catalyst (Figure 6C and D). In our recent work (mentioned in section 2.1), the Li–S interaction was also used to suppress the HER process. Similarly, in a 0.25 M Li$_2$SO$_4$ electrolyte, Patil et al. grew 1T-MoS$_2$ on nickel foil (1T-MoS$_2$/NF) for use in the electrochemical N$_2$ reaction also using the strong Li–S interaction to inhibit the HER process. In addition, 1T-MoS$_2$/NF featured pseudo-six-membered rings, in which the interaction between N and Li could enhance the adsorption capacity of N$_2$. This work provided researchers with a new idea to design N$_2$ fixation catalysts. 1T-MoS$_2$/NF reached a FE of 27.66% and an NH$_3$ yield of 1.05 $\mu$g min$^{-1}$ cm$^{-2}$.

In this strategy, the above-detailed reports used the action of electrolyte to inhibit the HER process. In addition, optimizing the structure of MoS$_2$ to inhibit the HER process has also been studied. Su et al. dispersed Fe atom on MoS$_2$ nanosheets to simulate nitrogenase-like NH$_3$ synthesis with superior NRR activity.
activity (8.63 µg h⁻¹ mg⁻¹, 18.8%).[82] They modified the S edge position in MoS₂ with Fe atoms, which effectively inhibited the HER process by increasing the energy barrier of HER from 0.03 eV to 0.15 eV.

It is well known that MoS₂ possesses a layered two-dimensional (2D) graphene-like structure and the decrease of MoS₂ layer spacing is beneficial to the inhibition of the HER process. By substituting S with Fe atoms in defect-rich MoS₂, Liang et al. reported F-MoS₂ as electrocatalyst for the NRR process (Figure 6E).[83] Compared with sulfur, fluorine has a smaller size and higher electronegativity, leading to a decreased layer spacing of MoS₂ and thus reduced HER activity. In addition, this work centered on defect-rich MoS₂ with marginal defects (larger specific surface area than bulk MoS₂), which further increased the number of active sites for N₂ fixation. Therefore, F-MoS₂ could achieve an NH₃ yield of 35.7 µg h⁻¹ mg⁻¹ and a FE of 20.6%.

Duan et al. prepared an NRR catalyst by completely encapsulating ball-like MoS₂ nanoflowers with a ZIF-71 coating.[84] In this MoS₂@MOF interface, the ZIF-71 coating did not only effectively concentrate N₂ through the inherent micropores, but also acted as a hydrophobic barrier to inhibit the HER process. At the same time, the ball-like MoS₂ nanoflowers provided abundant active edge sites due to the unique ultrathin subunits. Thus, MoS₂@ZIF-71 achieved an NH₃ yield of 56.69 µg h⁻¹ mg⁻¹ and a FE of 30.91%.

4. Theoretical Calculations and Predictions

Since Sun and co-workers used bulk MoS₂ as an electrocatalyst in the N₂ fixation process,[85] a large number of experimental studies on MoS₂-based catalysts have been conducted. In order to facilitate a comparison, performance parameters such as NH₃ production rate and FE were listed in Table 1. Some calculations have also been made to predict the activity of MoS₂-based catalysts, which provided researchers with ideas for enhancing their catalytic activity. So far, calculations and predictions have mainly focused on the heteroatom doping strategies.

Azofra et al. deposited Fe on MoS₂ as an electrocatalyst according to the Fe–Mo–Co structure of nitrogenase.[86] DFT calculations were employed to predict the high selectivity of Fe-MoS₂. Yang et al. used DFT calculations to investigate the NRR activity of some transition metal@MoS₂ systems.[87] By comparing the N₂ adsorption capacity and the potential-determining step (PDS) energy barrier of the selected catalysts, V@MoS₂ was predicted to have the best activity. A DFT theoretical calculation on the performance of MoS₂ doped with transition metals (3d, 4d, 5d elements) was also performed by Zhai et al.[88] Through the metal binding energy (lower than −0.5 eV), they first excluded Zn, Cd and Hg as shown in Figures 7A, B and C. Low metal binging energies indicated weak interactions between metals and substrates. After that, Zr and Ta were also excluded due to the huge distortion. According to the law of free energy variation in the proton coupling, the two highest positive free energy steps ∆G (N₂−→NH₃) and ∆G (NH₃−→NH₄⁺) needed < 0.49 eV, and only Re and Ti met the requirement as shown in

| Catalyst | Ref. | Electrolyte (Concentration [mM]) | NH₃ yield rate [µmol cm⁻² s⁻¹] | FE [%] |
|----------|------|----------------------------------|---------------------------------|--------|
| MoS₂     | [52] | Na₂SO₄ (0.1)                     | 8.08 × 10⁻¹¹ mol s⁻¹ cm⁻¹       | 1.17   |
| MoS₂ nanoflowers | [53] | Na₂SO₄ (0.1)                     | 29.28 µg h⁻¹ mg⁻¹              | 20.8   |
| Ultra-thin MoS₂ nanosheets | [54] | Na₂SO₄ (0.1)                     | 41.66 µg h⁻¹ mg⁻¹              | 1.10   |
| PLA-MoS₂ | [55] | HCl (0.1)                        | 34.55 µg h⁻¹ mg⁻¹              | 44.36  |
| MoS₂/GO  | [58] | LiClO₄ (0.1)                      | 24.82 µg h⁻¹ mg⁻¹              | 4.56   |
| MoS₂ nanodots/GO | [59] | Na₂SO₄ (0.1)                     | 16.41 µg h⁻¹ mg⁻¹              | 27.93  |
| MoS₂@g-C₃N₄ | [60] | Na₂SO₄ (0.1)                     | 19.86 µg h⁻¹ mg⁻¹              | 6.87   |
| 1T-MoS₂@g-C₃N₄ | [61] | HCl (0.1)                        | 29.97 µg h⁻¹ mg⁻¹              | 20.48  |
| 1T-MoS₂@BTAB/PPy/GO | [63] | KOH (0.1)                        | 13.60 µg h⁻¹ mg⁻¹              | 1.96   |
| 1T-MoS₂@TiC | [64] | HCl (0.1)                        | 30.33 µg h⁻¹ mg⁻¹              | 10.94  |
| NiFe@MoS₂ | [65] | Na₂SO₄ (0.1)                     | 128.17 µg h⁻¹ mg⁻¹             | 11.34  |
| Fe-MoS₂/CC | [66] | KOH (0.1)                        | 12.5 µg h⁻¹ cm⁻²              | 10.8   |
| Fe@ZIF-MoS₂ | [67] | HCl (0.1)                        | n.a.                           | n.a.   |
| Au NPs@MoS₂ | [68] | Na₂SO₄ (0.1)                     | 25 µg h⁻¹ mg⁻¹                | 9.7    |
| Ru@ZIF-MoS₂ | [69] | HCl (0.1)                        | 1.14 × 10⁻¹⁰ mol cm⁻² s⁻¹      | 17.6   |
| C/MoS₂  | [70] | Li₂SO₄ (0.1)                     | n.a.                           | 8.2    |
| Ni/MoS₂ | [71] | Na₂SO₄ (0.1)                     | 69.82 µg h⁻¹ mg⁻¹             | 9.14   |
| B–MoS₂/CF | [72] | HCl (0.1)                        | 44.09 µg h⁻¹ mg⁻¹             | 21.72  |
| FeS@MoS₂/CF | [73] | Na₂SO₄ (0.1)                     | 8.45 µg h⁻¹ cm⁻²              | 2.96   |
| CoS@MoS₂ | [74] | Li₂SO₄ (0.1)                     | 54.7 µg h⁻¹ mg⁻¹              | 20.8   |
| Co–MoS₂ | [75] | H₂SO₄ (0.01)                     | 0.6 mmoL h⁻¹ g⁻¹              | 10     |
| Co–MoS₂ | [76] | Na₂SO₄ (0.1)                     | 127.88 µg h⁻¹ mg⁻¹             | 11.29  |
| Fe–MoS₂ | [77] | HCl (0.1)                        | 24 µg h⁻¹ mg⁻¹                | 27     |
| S–rich MoS₂ | [80] | Li₂SO₄ (0.1)                     | 43.4 µg h⁻¹ mg⁻¹              | 9.81   |
| 1T-MoS₂@NF | [81] | Li₂SO₄ (0.25)                    | 1.05 µmol min⁻¹ cm⁻²          | 27.66  |
| Fe–MoS₂ | [82] | K₂SO₄ (0.5)                      | 8.63 µg h⁻¹ mg⁻¹              | 18.8   |
| F–MoS₂ | [83] | Na₂SO₄ (0.1)                     | 35.7 µg h⁻¹ mg⁻¹              | 20.6   |
| MoS₂@ZIF-71 | [84] | Na₂SO₄ (0.1)                     | 56.69 µg h⁻¹ mg⁻¹              | 30.91  |
Figure 7D. In the protonation pathway, the PDS energy barrier of Re@MoS$_2$ (0.42 eV) was found smaller than that for Ti@MoS$_2$ (0.73 eV) (Figure 7E and F). Therefore, Re@MoS$_2$ was identified as the most suitable catalyst. Moreover, the HER energy barrier of Re@MoS$_2$ was higher than that for NRR, which proved that Re@MoS$_2$ was more conducive to N$_2$ adsorption. The stability of Re@MoS$_2$ was also demonstrated by ab initio molecular dynamics simulations. Therefore, it seems reasonable to speculate that Re-doped MoS$_2$ should demonstrate high NRR activities. Zhao et al. also used DFT calculations to predict the NRR activity of some transition metal atoms embedded in MoS$_2$ nanosheets. The PDS energy barrier of Mo-doped MoS$_2$ was determined at $-0.53$ eV (Figure 8A), which was better than other systems. Thus, they regarded Mo/MoS$_2$ as a potential catalyst for the NRR process.

Although theory predicted encouraging catalytic properties of Mo/MoS$_2$, Simonov and co-workers recently demonstrated that Mo/MoS$_2$ was only partially successful in experiments, as the desorption step of NH$_3$ was not considered. They first carried out an electrocatalytic experiment in water based media (0.1 M Li$_2$SO$_4$), but Mo/MoS$_2$ showed no NRR activity under these conditions (Figure 8B). After that, they experimented with an aprotic medium (1-butyl-1-methylpyrrolidinium (trispenta-
fluoroethyl) trifluorophosphate), in which the water concentration was tightly controlled. At the initial stage of the experiment, the accumulation of NH$_3$ was stable. However, after more than 2 h of continuous operation, Mo$_2$MoS$_2$ lost its catalytic activity, because the resulting NH$_3$/NH$_4^+$ adsorbed to the surface of Mo$_2$MoS$_2$, clogging up the active sites. Therefore, it was concluded that the high NRR activity of Mo$_2$MoS$_2$ predicted by DFT calculations was not feasible in practical experiments even though, through first-principles high-throughput calculations methods, Yang et al. had also predicted the N$_2$ adsorption activity site on the top of Mo atoms had the best NRR performance (Figure 8C). In addition, they demonstrated that the N$_2$ adsorption activity site on the top of Mo atoms had the best NRR performance (Figure 8C). On this basis, other theoretical calculations were adopted to demonstrate high activity and selectivity of Mo$_2$MoS$_2$M. However, theoretical prediction lack in investigating the crucial NH$_3$ desorption step, the high activity of predicted Mo$_2$MoS$_2$M still remains to be confirmed experimentally.

Guo et al. aimed at exploring the NRR potential of a part of transition metal-doped (IIIB to IIB subgroups except for Tc and Hg) defective Mo$_2$S$_2$.

DFT calculations were carried out to affim the PDS energy barrier of each catalyst; Sc, Ti, Cu, Hf, Pt, and Zr-decorated Mo$_2$S$_2$ were considered as potential candidates for N$_2$ electroreduction to NH$_3$ due to the PDS energy barrier being smaller than $-0.7$ eV. To further screen, they tested the limiting potentials of HER [UL(HER)] versus NRR [UL(NRR)] for the six catalyst systems. As shown in Figure 8D, the HER activity of Pt- Cu-modified Mo$_2$S$_2$ was higher than N$_2$ fixation. Thus, Sc, Ti, Hf, and Zr-decorated Mo$_2$S$_2$ materials were predicted to show a decent NRR activity. Tang and Li predicted that B-doped Mo$_2$S$_2$ should have a high NRR catalytic activity, as B is difficult to combine with H under acidic conditions, which could effectively inhibit the HER process. They first contrasted the catalytic properties of B atom- and diatomic boron-doped Mo$_2$S$_2$. By calculating overpotentials (0.02 V vs. 0.30 V) and activation barriers (1.24 eV vs. 2.84 eV), they predicted that B$_2$@MoS$_2$ should have a better NRR activity. Therefore, defective Mo$_2$S$_2$ with double S vacancies was used as substrate to avoid the aggregation of B$_2$. Meanwhile, the high stability, conductivity and selectivity of B$_2$@MoS$_2$ further proved the feasibility of B$_2$@MoS$_2$ for the NRR process, predicting it to be a potentially useful electrocatalyst.

As the synergistic interactions within metal clusters contribute to improving the catalytic activity of individual metal atoms, Zhang et al. attempted to predict the NRR performance of Fe$_2$/Mo$_2$S$_2$ by theoretical calculations.

They used DFT calculations combined with the computational hydrogen electrode model,
which concluded a high catalytic activity of Fe$_2$/MoS$_2$ (the overpotential was 0.21 V and the energy barrier of PDS was $-0.37$ eV). The catalytic principle of Fe$_2$/MoS$_2$ was also proposed (the electron density loss on the Fe cluster provided a stable Lewis active site for the adsorption of N$_2$, at the same time the electron feedback from the Fe clusters to N$_2$ promoted the activation of N–N$_2$), which further indicated that Fe$_2$/MoS$_2$ had potential as a high activity NRR catalyst. Matanovic et al. explored the HER and NRR activity of defect-rich 2H-MoS$_2$ through experiments and theoretical calculations.[$^{[6]}$] By DFT calculations, they predicted that the two vacancies might have NRR selectivity, but FE might not be ideal due to the effect of the large overpotential. Therefore, it was concluded that the original 2H-MoS$_2$ has a priority role in HER reaction. Further optimization is necessary for 2H-MoS$_2$ application in the NRR process.

5. Conclusion and Outlook

MoS$_2$ is considered as a potential NRR catalyst due to the high specific surface area, adjustable electronic structure and elemental composition similar to the nitrogenase enzyme. However, due to the influence of the HER process and the defects of MoS$_2$, the NRR activity obtained by MoS$_2$ is not satisfactory. Therefore, optimization of MoS$_2$ with higher NRR catalytic activity has become a hot research direction. In this Minireview, we summarized the optimization strategies of MoS$_2$-based catalysts. Optimization strategies include enhancing electrical conductivity/enlarging specific surface area, inhibition of competing reaction and taking advantage of the interaction effect between other elements and MoS$_2$. In addition, some enhancement strategies by theoretical calculations have also been reviewed, which provides researchers with ideas for enhancing the NRR activity of MoS$_2$-based catalyst.

Despite some achievements that have been made with MoS$_2$-based catalysts, it is still a long way from replacing the Haber-Bosch process. Therefore, further optimization is necessary. As MoS$_2$ is a material with many unique characteristics, optimization research in the future can focus on the characteristics of MoS$_2$.

(1) It is well known that MoS$_2$ is a 2D-layered material. The decrease of MoS$_2$ layer spacing is conducive to inhibit the HER process. Therefore, the NRR selectivity can be improved by reducing the MoS$_2$ layer gap. Furthermore, ultra-thin mono-layer MoS$_2$ can observably increase the specific surface area. It is worth considering some other optimization measures on the basis of ultra-thin mono-layer MoS$_2$.

(2) MoS$_2$ has a variety of crystal forms (1T, 2H, 3R), among which 1T-MoS$_2$ and 2H-MoS$_2$ were widely used in the NRR process. However, the base plane of 2H-MoS$_2$ is inert, resulting in insufficient adsorption sites. The poor conductivity of 2H-MoS$_2$ also limits the activity of NRR. Compared with 2H-MoS$_2$, 1T-MoS$_2$ shows as an octahedral structure, which not only overcomes the inert base surface to expose a denser active site, but also has high electrical conductivity.
X. Chen, K. Li, X. Yang, J. Lv, S. Sun, S. Li, D. Cheng, B. Li, Y. Li, H. Zang, C. Suresh, S. Mutyala, J. Mathiyarasu, X. Zhu, Z. Liu, H. Wang, R. Zhao, H. Chen, T. Wang, F. Wang, Y. Luo, Y. X. Cheng, J. Wang, W. Xiong, T. Wang, T. Wu, S. Lu, G. Chen, S. Gao, X. F. Wang, Y. P. Liu, H. Zhang, K. Chu, J. Zhao, X. Liu, X. Ren, X. Sun, D. Tian, Q. Wei, D. Wu, J. Mater. Chem. A 2020, 8, 118984.

D. Tian, Q. Wei, D. Wu, J. Mater. Chem. A 2020, 8, 118984.

Y. Guo, Z. Yao, S. Zhan, B. J. J. Timmer, C. Tai, X. Li, Z. Xie, Q. Meng, L. Fan, F. Zhang, M. S. G. Ahlquist, M. Cuartero, G. A. Crespo, L. Sun, Nano Energy 2020, 78, 105391.

Y. Guo, Z. Yao, B. J. J. Timmer, X. Sheng, L. Fan, Y. Li, F. Zhang, L. Sun, Nano Energy 2019, 62, 282–288.

G. Yang, L. Zhang, G. Huang, Z. Liu, S. Yu, K. Wang, S. Yuan, X. Sun, L. Ni, ACS Appl. Mater. Interfaces 2021, 13, 21474–21481.

J. Zhao, X. Tian, M. Liu, H. Guo, J. Zhou, Q. Fang, Z. Liu, Q. Wu, J. Lou, J. Am. Chem. Soc. 2019, 141, 19269–19275.

L. Zhang, L. Chen, J. Shen, W. Hu, Y. Sun, J. Mater. Chem. A 2020, 8, 61029–61036.

J. Zhang, S. Wu, L. Liu, C. Huang, P. Ho, A. Kirkland, T. Sudmeier, R. Arrigo, D. Gianolio, S. C. Edman Tsang, Chem. Sci. 2021, 12, 688–695.

F. Jiao, B. Xu, Adv. Mater. 2019, 31, 180537.

T. Oshikiri, K. Ueno, H. Misawa, Angew. Chem. Int. Ed. 2016, 55, 3942–3946; Angew. Chem. 2016, 126, 4010–4014.

Y. Liu, M. Han, Q. Xiong, S. Zhang, C. Zhao, W. Gao, G. Zhang, H. Zhao, Adv. Energy Mater. 2019, 9, 1803935.

S. B. Patil, H. Chou, Y. Chen, S. H. Hsieh, C. Chen, C. Chang, S. Li, Y. C. Lee, Y. Lin, H. Li, Y. Chang, Y. Lai, D. Wang, J. Mater. Chem. A 2021, 9, 1230–1239.

H. Su, L. Chen, Y. Chen, R. Si, Y. Wu, X. Wu, Z. Geng, W. Zhang, J. Zeng, Angew. Chem. Int. Ed. 2020, 59, 20411–20416; Angew. Chem. 2020, 132, 20591–20596.

J. Zhang, S. Ma, J. Li, Y. Li, W. Jiu, Q. Zhang, Z. Liu, Y. Zhang, K. Qu, W. Cai, J. Mater. Chem. A 2020, 8, 10426–10432.

J. Duan, D. Shao, X. He, Y. Lu, W. Wang, Colloids Surf. A 2021, 619, 126529.

L. M. Azofra, C. Sun, L. Cavallolo, D. R. MacFarlane, Chem. Soc. Rev. 2017, 46, 8275–8279.

J. Zhang, Y. Chen, S. Zhang, L. Wang, Nanoscale 2020, 12, 10035–10043.
[88] J. Zhao, J. Zhao, Q. Cai, Phys. Chem. Chem. Phys. 2018, 20, 9248–9255.
[89] H.-L. Du, R. Y. Hodgetts, M. Chatti, C. K. Nguyen, D. R. MacFarlane, A. N. Simonov, J. Electrochem. Soc. 2020, 167, 146507.
[90] T. Yang, T. T. Song, J. Zhou, S. Wang, D. Chi, L. Shen, M. Yang, Y. P. Feng, Nano Energy 2020, 68, 104304.
[91] H. Guo, L. Li, X. Wang, G. Yao, H. Yu, Z. Tian, B. Li, L. Chen, ACS Appl. Mater. Interfaces 2019, 11, 36506–36514.
[92] F. Li, Q. Tang, Nanoscale 2019, 11, 18769–18778.
[93] H. Zhang, C. Cui, Z. Luo, J. Phys. Chem. C 2020, 124, 6260–6266.
[94] I. Matanovic, K. Leung, S. J. Percival, J. E. Park, P. Lu, P. Atanassov, S. S. Chou, Appl. Mater. Res. 2020, 21, 100812.
[95] Y. Song, Z. Jiang, B. Gao, H. Wang, M. Wang, Z. He, X. Cao, F. Pan, Chem. Eng. Sci. 2018, 185, 231–242.

Manuscript received: August 20, 2021
Revised manuscript received: September 28, 2021