Highly Efficient Electrocatalytic N₂ Reduction to Ammonia over Metallic 1T Phase of MoS₂ Enabled by Active Sites Separation Mechanism

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The 1T phase of MoS₂ has been widely reported to be highly active toward the hydrogen evolution reaction (HER), which is expected to restrict the competitive nitrogen reduction reaction (NRR). However, in this work, a prototype of active sites separation over 1T-MoS₂ is proposed by DFT calculations that the Mo-edge and S atoms on the basal plane exhibit different catalytic NRR and HER selectivity, and a new role-playing synergistic mechanism is also well enabled for the multistep NRR, which is further experimentally confirmed. More importantly, a self-sacrificial strategy using g-C₃N₄ as templates is proposed to synthesize 1T-MoS₂ with an ultrahigh 1T content (75.44%, named as CNMS, representing the composition elements of C, N, Mo, and S), which yields excellent NRR performances with an ammonia formation rate of 71.07 μg h⁻¹ mg⁻¹ cat. at −0.5 V versus RHE and a Faradic efficiency of 21.01%. This work provides a promising new orientation of synchronizing the selectivity and activity for the multistep catalytic reactions.

1. Introduction

Ammonia (NH₃) synthesis is one of the most important processes for all life forms because it supplies valuable chemicals for the agricultural industries as well as others.[1–3] To date, NH₃ is predominantly produced by the traditional Haber-Bosch process in which the harsh reaction conditions of high pressure and temperature are inevitably required, causing heavy energy consumption,[2,4] together with significant CO₂ emission.[5] Thus, an environmentally benign and sustainable alternative route for NH₃ production is urgently desired.

The electrochemical conversion approach offers a promising cost-efficient and environmentally friendly strategy for artificial NH₃ synthesis at the ambient temperature and pressure, but it requires the identification of electrocatalysts with high activity for the NRR.[6–9] Among the catalysts for NRR, Mo-based complex catalysts have emerged as promising candidates.[10–13] Besides, many efforts have been devoted to Mo-based catalysts including single-Mo atoms,[14] molybdenum sulfides,[15] molybdenum nitrides,[16,17] and molybdenum carbides.[18] Among them, MoS₂ plays a significant role in NRR owing to the similar constituent elements compared to natural nitrogenase.[19] Sun et al. initially reported that the MoS₂ nanosheets possessed good electrocatalytic performance toward the NRR with a NH₃ yield of 13.09 μg h⁻¹ mg⁻¹ cat. and Faradic efficiency (FE) of 1.17% under the ambient conditions.[20] Then they designed defect-rich 2H-MoS₂ nanoflower and obtained a boosted NH₃ yield rate of 29.28 μg h⁻¹ mg⁻¹ cat. at −0.4 V versus RHE.[21] However, its catalytically inert basal planes and poor conductivity limit the large-scale applications.[22] Compared to 2H-MoS₂, metallic 1T-MoS₂ offers interesting benefits for electrocatalysis with more active sites along the basal surface as well as superior electronic conductivity.[23,24] Though the 1T-MoS₂ exhibits excellent HER performance, which serves as a competitive reaction of NRR, it is also considered as a promising NRR catalyst with amazing intrinsic catalytic activity and conductivity.[25–27] Most recently, 1T MoS₂-based modified electrodes have been attempted as NRR electrocatalysts, such as 1T-MoS₂-NDs/g-C₃N₄,[28] 1T-MoS₂-Ni,[29] and SV-1T-MoS₂@MoO₃,[30] all of which possess decent performances confirmed experimentally due to the existence of 1T phase. Nonetheless, the specific competition of the HER and NRR over 1T-MoS₂ has never been discussed, which is urgently demanded to be further investigated.

In this work, we first proposed the prototype of active sites separation over 1T-MoS₂ that the Mo-edge and S atoms on the basal plane are selective to NRR and HER, respectively, which was further confirmed experimentally and theoretically. Moreover, the contents of 1T phase in MoS₂ were regulated using g-C₃N₄ nanosheets as self-sacrificial templates, and their
evolution relation with the corresponding NRR performances has been clarified.

2. Results and Discussion

The scanning electron microscopy (SEM) image and transmission electron microscopy (TEM) image (Figure 1a,b) reveal well-defined nanoflower morphology of as-prepared CNMS. The interplanar distance is determined from the HRTEM images (Figure 1c), which is 0.74 nm, significantly larger than that of bulk 2H-MoS$_2$ (0.61 nm), implying the existence of intercalation ions or molecules.$^{[31–33]}$ The high-resolution TEM (HRTEM) image (Figure 1d) demonstrates the coexistence of the octahedral 1T phase and the trigonal prismatic 2H phase in CNMS, and a clear view over the detailed microstructures of 1T and 2H phases can be clearly observed from Figure 1e,f, respectively.$^{[34,35]}$ The TEM mapping images in Figure 1g affirm the uniform distribution of Mo, S, C, and N in CNMS.

Figure 2a presents the XRD pattern of CNMS, in which the (002) characteristic peak separates into two diffraction peaks locating at 8.7° and 17.5°, indicating an expanded interlayer distance due to the inserted species.$^{[36]}$ And there are no typical diffraction peaks of g-C$_3$N$_4$, suggesting the complete decomposition of g-C$_3$N$_4$ during the hydrothermal treatment.$^{[37]}$ As compared in Figure S1 (Supporting Information). Besides, to verify the key role of inserted species and investigate the phase transformation, the CNMS was annealed at 800 °C for 2 h in Ar (named as A-CNMS). As compared in Figure 2a, all the diffraction peaks
can be well indexed to the standard pattern of hexagonal MoS$_2$ (PDF cards: 37–1492) in A-CNMS, which verifies that the g-C$_3$N$_4$ triggers the remarkable lattice expansion. After annealing, the (002) plane of A-CNMS moves back to 14.1°, indicating the phase transformation from metastable 1T-MoS$_2$ to thermodynamically stable 2H-MoS$_2$ with a decreased interlayer distance. Besides, several new graphite characteristic peaks appear after annealing, as illustrated in the region enclosed by the red rectangle of Figure 2a, which is due to the graphitization of inserted small carbon molecules after high-temperature calcination. In addition, Fourier transform infrared spectra (FTIR) demonstrates the decomposition of the ring structure of g-C$_3$N$_4$ and the formation of small carbonic molecules (Figure S2, Supporting Information), while differential scanning calorimetry-thermogravimetric curve (DSC/TGA) further proves that carbonic molecules mentioned above are inserted into the interlayers of MoS$_2$ (Figure S3, Supporting Information).

Figure 2b shows the Raman spectra, presenting three distinct peaks at 148, 212, and 335 cm$^{-1}$ for MS and CNMS, consistent with $J_1$, $J_2$, and $J_3$ vibrational modes of 1T-MoS$_2$. The additional peak $E_{1g}$ (282 cm$^{-1}$) of metallic MoS$_2$ can also be observed in MS and CNMS, certainly demonstrating the existence of 1T phase MoS$_2$. In comparison, there are only two typical peaks at 376 and 402 cm$^{-1}$ corresponding to the $E_{2g}$ and $A_{1g}$ vibrational modes of 2H-MoS$_2$ in A-CNMS, demonstrating the successful conversion from 1T phase to 2H phase after calcination. Note that characteristic signals of 1T phase are also found over the as-prepared MS, but are much weaker than that of CNMS. As a result, it can be concluded that the 1T phase can also be synthesized without g-C$_3$N$_4$ with lower contents, which should be attributed to the insertion of other small molecules.

To further verify the formation of 1T phase and determine the corresponding contents, the X-ray photoelectron spectroscopy (XPS) spectrum of CNMS was collected, demonstrating the
The coexistence of Mo, S, C, and N elements (Figure S4, Supporting Information). To give a direct comparison, the Mo 3d spectra of various samples are presented in Figure 2c, and two dominant peaks of Mo 3d3/2 and Mo 3d5/2 located at 233 and 230 eV in A-CNMS can be ascribed to the 2H phase of MoS2.[13] As for CNMS and M5S, the other two characteristic peaks at 229 and 232 eV are allocating to Mo 3d3/2 and Mo 3d5/2 of the 1T phase of MoS2.[31,40,41] According to the peak area ratios of deconvoluted Mo 3d peaks, the phase contents are calculated and presented in Figure S5, Supporting Information. It can be seen that the relative content of 1T phase in CNMS reaches up to 75.44%, much larger than that of M5S (40.56%), implying the vital role of the sacrificial g-C3N4 template in the phase transformation from 2H to 1T. Besides, in Figure 2d, two peaks appearing at 163 and 164 eV are attributed to S 2p3/2 and S 2p1/2 of 2H-MoS2.[36] The other two peaks at binding energies around 162.1 and 163.4 eV are in agreement with the 1T-MoS2, further demonstrating the formation of metallic MoS2.[36] In addition, the element contents attained from XPS and EDX have been presented in Table S1 (Supporting Information). The results from both XPS and EDX exhibit a similar tendency: the atomic ratio of C and N is far from the theoretical value of g-C3N4, indicating that the g-C3N4 templates have decomposed into carbolic molecular under the hydrothermal conditions.

To clarify the operation mechanism of g-C3N4 sacrificial templates, the effect of hydrothermal temperature was explored. In the preparation, some white flocs attached to the black MoS2 plates, the effect of hydrothermal temperature was explored. In Figure S6a, the g-C3N4 suspension changes to a colloidal solution with the increased temperatures from 220 °C to 280 °C, demonstrating its catalytic activity for NRR. The time-dependent current density curves in Figure S13b (Supporting Information), indicate there is almost no fluctuation at a series of potentials ranging from −0.4 to −0.8 V, demonstrating superior durability in the catalytic process. It is worth mentioning from Figure S3a,b that when the applied potential moves lower than −0.5 V, both the NH3 yield rates and FEs of as-obtained catalysts at various potentials. The CNMS exhibits a remarkable NH3 yield rate of 71.07 μg h−1 mg−1cat. and FE of 21.01% at −0.5 V versus RHE, much higher than that of (NH2) yield rate: 21.93 μg h−1 mg−1cat. (FE: 9.72%) and A-CNMS (NH3 yield rate: 13.08 μg h−1 mg−1cat. (FE: 4.88%), implying that the 1T phases of MoS2 are main active sites for the electrocatalytic NRR. Linear sweep voltammetry (LSV) curves of CNMS in N2 and Ar-saturated 0.1 M Na2SO4 solutions are provided in Figure S13a (Supporting Information). Note that the CNMS exhibits a higher catalytic current density under the N2 atmosphere, demonstrating its catalytic activity for NRR. The time-dependent current density curves in Figure S13b (Supporting Information), indicate there is almost no fluctuation at a series of potentials ranging from −0.4 to −0.8 V, demonstrating superior durability in the catalytic process. It is worth mentioning from Figure S3a,b that when the applied potential moves lower than −0.5 V, both the NH3 yield rates and FEs of catalysts significantly decrease due to the competing HER. To double-check the production of NH3 from CNMS, Nessler’s tests and ion chromatography (IC) methods were also employed to determine the production rate of NH3. The comparable results obtained by the Nessler’s reagent are shown in Figure S14 (Supporting Information), confirming the reliability of the detection results of the indophenol blue method. As shown in Figure S15 (Supporting Information), the Na+ peak (in 4.10 min) is so high because of the Na2SO4 electrolyte, which almost covers the NH3+ peak (in 4.8 min), resulting in the unsuitability of the IC method in this case. Besides, the quantified nuclear magnetic resonance (NMR) experiments have been operated and are shown in Figure S16 (Supporting Information). One can see that the produced 14NH3+ in the electrochemical reaction over CNMS for 1 h and 2 h by feeding 14N2 is a diploid relationship, in which the produced 14NH3+ for 2 h is close to that by indophenol blue method (Figure S16d, Supporting Information), further indicating the reliability of the ammonia detection by the indophenol blue method. Thus, the performance of CNMS compares favorably to the NRR behaviors of most reported 1T-MoS2 electrocatalysts operated under ambient conditions, such as 1T-MoS2/g-C3N4 (29.97 μg h−1 mg−1cat., 20.48%), 1T-MoS2 @Ti3C2 (30.33 μg h−1 mg−1cat., 10.94%), 1T-MoS2/CTAB/Py/GO (7.05 μg h−1 mg−1cat., 5.88%) and many other aqueous-based NRR electrocatalysts, including
Fe-N/C-CNTs (34.83 μg h⁻¹ mg⁻¹ cat., 9.28%), Pd-Co/CuO (10.04 μg h⁻¹ mg⁻¹ cat., 2.16%), and Au/TiO₂ (21.40 μg h⁻¹ mg⁻¹ cat., 8.11%). A more detailed comparison is summarized in Table S2 (Supporting Information). Moreover, the performance of CNMS was also evaluated in 0.1 M HCl and 0.1 M KOH solution (Figure S17, Supporting Information), and lower NH₃ yield rates and smaller FEs are obtained in the above electrolytes compared to the neutral Na₂SO₄ solution, resulting from the sharply promoted competitive HER.[33,36,38]

To validate the reaction product indeed originating from the NRR catalyzed by CNMS, the potential nitrogen source contaminant caused by the incomplete dissolution of g-C₃N₄ in CNMS should be clarified. First, we can see from Figure S7d (Supporting Information) that there is no peak at 402.3 eV in all samples,[33] demonstrating that no NH₄⁺ ion exists in the catalysts, but other N species. Second, as shown in Table S1 (Supporting Information), the atomic percent of N element in MoS₂ obtained from the EDX analysis is 7.5%, and the corresponding catalyst mass loaded on the electrode is about 0.015 mg. Assuming that the N species in the catalysts are completely converted to NH₄⁺, the NH₃ yield rate of the potential nitrogen source contaminant should be about 3.98 μg h⁻¹ mg⁻¹ cat., which is much lower than that of 71.07 μg h⁻¹ mg⁻¹ cat., indicating that the N-contamination caused by the incomplete dissolution of g-C₃N₄ in CNMS is much lower than N₂ for the reductive production of ammonia. Moreover, an isotopic labeling experiment was further conducted using ¹⁵N₂. And the products were measured by the ¹³N NMR spectroscopy. As shown in Figure 3c, the ¹³N NMR spectra display a doublet coupling for ¹⁵NH₄⁺ and a triplet coupling for ¹⁴NH₄⁺ with ¹⁴N₂ and ¹⁵N₂ as feeding gas, corresponding to the spectra of their standard substances, respectively. What’s more, almost no NH₃ was detected when the NRR was conducted at open circuit potential, in an Ar-saturated 0.1 M Na₂SO₄ solution, or using a bare GCE as the working electrode without CNMS (Figure S18, Supporting Information). Figure S19 (Supporting Information), demonstrates bare g-C₃N₄ has almost no catalytic activity for the NRR, eliminating the effect of the incomplete dissolution of g-C₃N₄. For the reaction catalyzed by CNMS at −0.5 V with switching 2 h cycles between N₂- and Ar-saturated 0.1 M Na₂SO₄ solution (Figure 3d), the NH₃ can only be detected in the electrolysis process of the N₂-saturated solution. The results above powerfully indicate that the generated ammonia indeed originates from N₂ fixation by CNMS. After the electrolysis, N₂H₄ is not detected at the optimum potential, as revealed in Figure S20 (Supporting Information), proving that CNMS possesses excellent selectivity toward NH₃ production.

The stability is also evaluated and the corresponding results are shown in Figure 3e. After 24 h electrolysis, the CNMS still maintains good electrochemical durability with only a slight fluctuation of current density at −0.5 V, as well as both the NH₃ yield rate and the FE (Figure S21, Supporting Information). Moreover, both NH₃ yield rates and FEs of CNMS have negligible changes after six times cycling electrolysis, as revealed in Figure 3f. Besides, the linear correlation between the NH₃ yield and reaction time during the NRR catalytic process is also presented in Figure S22 (Supporting Information), demonstrating a stable production of NH₃. The XRD patterns (Figure S23, Supporting Information) affirm the MoS₂ nature without remarkable changes and XPS spectra (Figure S24, Supporting Information) prove that the CNMS presents no obvious change over valence states and
crystalline phases after the NRR. Furthermore, the TEM image (Figure S25a, Supporting Information) proves the preservation of nanoflower features, and the HRTEM image (Figure S25b, Supporting Information) reveals that the 1T phase of MoS2 is well-maintained after the long-term electrolysis. Consequently, it is convincingly exemplified that the CNMS catalyst possesses extraordinarily electrochemical catalytic activity, selectivity and stability for the NRR.

We further explored the improvement mechanism of the superior catalytic performance of CNMS toward the electrocatalytic NRR. The electrochemical active surface area (ECSA) was collected to estimate the number of active sites (Figure S26 and Table S3, Supporting Information). Note that the ECSA of CNMS is 30.2 cm$^{-2}$, much larger than those of MS (13.5 cm$^{-2}$) and A-CNMS (11.0 cm$^{-2}$), indicating more exposure of active sites. As depicted in Figure S27a (Supporting Information), the charge transfer resistance ($R_{ct}$) of the CNMS is much smaller than those of MS and A-CNMS, implying the outstanding nitrogen adsorption ability, consistent with the results of ECSA. Considering the competitive relationship between HER and NRR, HER tests were also conducted in Ar-saturated 0.1 M Na$_2$SO$_4$ solution to understand the evolution of the intrinsic activities. We can see from Figure 4a,b and Figure S28 (Supporting Information) that the evolution of TOF$_{NRR}$ and TOF$_{HER}$ are highly consistent with the evolution of 1T contents (Figure S5, Supporting Information), indicating that the presence of 1T phase can accelerate both NRR and HER.

To get an optimized parameter, the influence of preparation temperature was also investigated. Figure S29 (Supporting Information) displays the NRR performances of all the catalysts prepared at various temperatures. One can see that with the increased preparation temperatures, the NRR performances are gradually increased and reach the maximum at 220 °C and then...
decrease at higher temperatures. The ECSA tests (Figure S30 and Table S4, Supporting Information) clearly show that the CNMS-220 shows a significantly larger ECSA value than other counterparts, providing more active sites. And the CNMS-260 shows a remarkably decreased ECSA value, which can be ascribed to the absence of 1T phase. In addition, electrochemical impedance spectroscopy (EIS) was also acquired, as exhibited in Figure S31a (Supporting Information). The $R_p$ is gradually decreased with the increased temperature and achieves the minimum value over CNMS-220, and then rises up. Based on the $N_2$-TPD spectra (Figure S31b, Supporting Information), we can see that the CNMS-220 exhibits the highest signal, indicating the strongest adsorption ability on $N_2$ molecules due to the highest content of 1T phase. Moreover, the evolution of the TOF$_{\text{NRR}}$ and TOF$_{\text{HER}}$ versus the hydrothermal temperatures are depicted in Figure 4c,d and Figure S32 (Supporting Information). It is obvious that both the TOF$_{\text{NRR}}$ and TOF$_{\text{HER}}$ are enlarged with the increased hydrothermal temperatures and reach maximum at CNMS-220, and then get down, consistent with the evolution of 1T content versus hydrothermal temperatures (Figure S8, Supporting Information), further demonstrating the leading function of 1T phase in the NRR and HER processes.

Subsequently, we further attempted to figure out the role of the g-C$_3$N$_4$/MoS$_2$ ratio in NRR. It can be observed from Figure S33 (Supporting Information) that the evolution of NRR properties with increased g-C$_3$N$_4$ contents shows a “volcano” trend. Note (Supporting Information) that the evolution of NRR properties (Figure S36b, Supporting Information) display that the CNMS-5 possesses the minimum $R_p$, suggesting more rapid charge transfer due to the highest 1T content. Moreover, when the g-C$_3$N$_4$/MoS$_2$ ratio achieves 5, the obtained CNMS-5 shows the highest $N_2$ adsorption ability (Figure S36b, Supporting Information). Furthermore, we also conducted the evolution of the TOF$_{\text{NRR}}$ and TOF$_{\text{HER}}$ versus the g-C$_3$N$_4$/MoS$_2$ ratio (Figure 4e,f and Figure S37, Supporting Information). Obviously, the evolution of TOF$_{\text{NRR}}$ and TOF$_{\text{HER}}$ are highly consistent with the evolution of 1T contents versus the g-C$_3$N$_4$/MoS$_2$ ratio (Figure S10, Supporting Information), further suggesting the dependence of the NRR and HER properties with the 1T content.

In addition, we collected the NH$_3$ yield rate at $-0.5$ V in $N_2$ saturated 0.1 m Na$_2$SO$_4$ as NRR performance and the current density measured at $-0.5$ V in Ar-saturated 0.1 m Na$_2$SO$_4$ as HER performance of all samples and plotted the evolution of them versus the 1T content, as shown in Figure 4g,h, respectively. It can be seen that both the NH$_3$ yield rate and the current density at $-0.5$ V are positively related to the content of 1T phase, demonstrating that the 1T phase plays an active role in both NRR and HER. Finally, the FE evolution of NRR and HER are plotted in Figure 4i, in which the FFs of NRR are increased with the enlarged 1T content, while the FFs of HER are on the contrary, which suggests that the selectivity toward NRR is also directly proportional to the 1T content, and the performance growth of NRR (Figure 4g) with the increase of 1T content is faster than that of HER (Figure 4h). Hence, it can be concluded that the 1T phase can synchronize the selectivity and activity in the NRR process.

First principle calculations based on density functional theory (DFT) were performed to figure out the likely mechanism of the overall NRR on the combined entity of 1T and 2H phases of MoS$_2$. Figures S38–S42 (Supporting Information) summarize the optimized atomic structures along several feasible NRR pathways as well as others considered. The optimal one was chosen to compare with 2H-MoS$_2$ in consideration of both $N_2$ adsorption energy and the potential-determining step (PDS), and the obtained Gibbs free energy diagrams are illustrated in Figure 5a. One can see that the 1T-MoS$_2$ is able to absorb the inert $N_2$ more remarkably than the 2H phase at Mo-edge with $\Delta G_{1T-MoS_2}$ ($N_2\rightarrow N_2^*$) = $-1.28$ eV and $\Delta G_{1T}$,Mo$_S_2$ ($N_2\rightarrow N_2^*$) = $-0.11$ eV, respectively. The PDS is the hybrid step containing the hydrogenation of $N_2^*$ to $N^*$, to generate $N^*$–NH$_3$ and the desorption of the first NH$_3$ for 1T-MoS$_2$ ($U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$) = $-0.36$ V), while it is only the first hydrogenation of $N^*$ to produce $N^*$–NH$_3$ for 2H-MoS$_2$ ($U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$) = $-0.58$ V). Furthermore, from the charge density difference (Figure S43, Supporting Information), it can be clearly seen that more electrons tend to accumulate around the edge Mo atoms of 1T phase than that of 2H phase, indicating the change of electronic structure and more intensive $N_2$ adsorption and activation ability, which is in coincidence with the XPS (Figure 2c) and TPD (Figure S27b, Supporting Information) results. All the results above suggest that the Mo-edge of 1T phase is more catalytically active toward NRR than that of 2H phase.

It is well known that the HER is the major competing reaction against NRR. Hence, the HER activities on the Mo-edge of 1T and 2H phases were also investigated, as exhibited in Figure 5b. Analogous to NRR, the hydrogen atom can be bound to the Mo-edge of 1T phase with the hydrogen desorption/combination as the PDS ($U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$) = $-0.38$ V). According to previous studies,[43–47] the selectivity of an electrocatalyst between NRR and HER can be qualitatively judged by comparing the change of Gibbs free energy for the first step (NRR: $N_2 \rightarrow N_2^*$; HER: $H^* + e^- \rightarrow H^0$) and the PDS. When an electrode potential of $U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$ is applied, $\Delta G$ ($N_2 \rightarrow N_2^*$) = $-1.28$ eV is still more negative than $\Delta G$ ($H^* + e^- \rightarrow H^0$) = $-0.74$ eV, as well as $\Delta G$ ($H_2O \rightarrow H_2O^*$) = $-0.03$ eV (Figure S44, Supporting Information), suggesting that the Mo-edges of 1T phase are covered by the nitrogen, rather than hydrogen and water adsorbates. Besides, considering the limiting potential, $U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$, implies that on the Mo-edges of 1T phase the barrier for hydrogen desorption/combination cannot be overcome at $U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$. Therefore, the Mo-edge of 1T phase favors the NRR. As for 2H-MoS$_2$, when an electrode potential of $U_{\text{lim}}^{\text{NRR}}$ $\rightarrow$ $U_{\text{lim}}^{\text{HER}}$ is applied, $\Delta G$ ($H^* + e^- \rightarrow H^0$) = $-0.41$ eV is negative than $\Delta G$ ($N_2 \rightarrow N_2^*$) = $-0.11$ eV, indicating that the Mo-edge of 2H phase tends to be covered by hydrogen adsorbates. Besides, $U_{\text{lim}}^{\text{HER}}$ $\rightarrow$ $U_{\text{lim}}^{\text{NRR}}$ suggests that the Mo-edge of 2H-MoS$_2$ prefers the HER.
Generally, the basal plane of 1T-MoS$_2$ is also considered as active sites for the HER [36,38]. In the basal plane, the calculated free energy of hydrogen adsorption ($\varepsilon G_{\text{Hbasal plane}}^H$) as a function of surface H coverage in the absence of water and a bias potential is shown in Figure S45 (Supporting Information). The adsorption geometries at different H coverages are provided in Figure S46 (Supporting Information). At a low H coverage (<25%) in the initiation of catalysis, the $\varepsilon G_{\text{basal plane}}^H$ value (−1.90 eV) is more negative than that of $\varepsilon G_{\text{Mo-edge}}^H$ (−0.38 eV), indicating the adsorbed H prefers binding to S atoms in the basal plane, thus making the N$_2$ adsorption easier on the Mo-edge. In addition, when an electrode potential of $U_{\text{NRR limiting}}$−1T−MoS$_2$ is applied, the barrier for hydrogen desorption/combination on the edge S atoms of the basal plane cannot be overcome, thus the HER will not happen and the adsorbed H will remain on the edge S atoms of the basal plane. In this case, the hydrogenated S atoms can provide a fundamental role in the NRR mechanism as a H-provider because the formed *H can be transferred directly to nearby bound N$_2$ or to the nitrogen reduction intermediates, significantly accelerating the NRR process, as shown in Figure 5c, which is similar to previous studies [48–50].

At a high H coverage, we can see from Figure S45 (Supporting Information) that the free energy becomes close to zero (the $\varepsilon G_{\text{Hbasal plane}}^H$ value is between −0.02 and 0.27 eV around 37.5–50% H coverage). Therefore, it is most likely that the HER process occurs at the later stage of H coverage on the basal plane of 1T-MoS$_2$. Separation of the active sites can partially result in the separation of the space occupied by the adsorbed species. Though the 1T phase can accelerate both the NRR and HER, to a certain degree, it will reduce the competition between HER and NRR due to the active sites separation, thus synchronizing the selectivity and activity for the NRR, as exhibited in Figure 4g.i. Evidently, the site separation analysis based on the DFT calculations is in good agreement with the previous experimental results.

3. Conclusions

With the addition of g-C$_3$N$_4$, the hybrid 1T/2H MoS$_2$ with a high 1T phase content (75.44%) has been successfully produced by a facile hydrothermal route and verified as a highly active and selective NRR electrocatalyst. The optimized CNMS catalyst exhibits a high NH$_3$ yield rate of 71.07 μg h$^{-1}$ mg$^{-1}$cat. and a large FE of 21.01% at −0.5 V versus RHE in 0.1 m Na$_2$SO$_4$. The 1T phase of MoS$_2$ plays several vital roles: 1) serving as active sites...
rationally associated with a lower energy barrier of PDS, as well as promoting the interfacial charge transfer from catalysts to N₂ molecules with a smaller resistance. DFT calculations suggest that the enhanced NRR performance of the Mo-edge in 1T-MoS₂ compared with 2H-MoS₂ should be rationally associated with a lower energy barrier of PDS, as well as more profitable adsorption of N₂ molecules due to the presence of 1T phase. Meanwhile, the separation of active sites over 1T phase can reduce the competition between HER and NRR, which contributes to higher Faradaic efficiency toward the NRR, thus achieving the synchronization of selectivity and activity. The present study demonstrates a new strategy on the active sites separation to synchronize the selectivity and activity over 1T phase of MoS₂ for the multistep catalytic reactions.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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