Semi-metal 1T' phase MoS2 nanosheets for promoted electrocatalytic nitrogen reduction

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Abstract

Herein, we constructed urchin-like TiO2 hollow nanospheres (HNSs) by hydrothermal targeted etching, and used it as a substrate to load semi-metal 1T'-MoS2 nanosheets as effective nitrogen reduction reaction (NRR) electrocatalysts. 1T'-MoS2/TiO2 HNSs composites display outstanding NRR activity with the highest NH3 yield of 29.62 μg h⁻¹ mg⁻¹ cat. at −0.75 V versus RHE. Besides, the highest FE of 24.9% is obtained at −0.65 V. The remarkable NRR performance is attributed to the high conductivity of 1T'-MoS2 and the urchin-like structure of TiO2 hollow nanospheres. DFT calculations display that the 1T'-MoS2 in 1T'-MoS2/TiO2 makes the activation and further reduction of *N2 more thermodynamically favorable than pristine TiO2, contributing to better NRR catalytic activities. 15N isotopic labeling experiment reveals that N in produced NH3 comes from N2 of electrolyte.

KEYWORDS
electrocatalytic nitrogen reduction, MoS2, semi-metal 1T' phase, TiO2 hollow nanosphere, urchin-like
1 | INTRODUCTION

Ammonia (NH₃), as one of the most important chemicals of industrial production, is not only widely used in the synthesis of fertilizers, fibers, and explosives, and so forth,¹-³ but is considered as a hopeful carbon-free energy carrier, so it can be used as a possible substitute to hydrogen.⁴-⁷ Till now, the industrial-scale ammonia synthesis is dominated by the Haber-Bosch process with high temperature and pressure.⁹,¹⁰ Hence, develop and design a high-performance, cost-effective, and environmentally friendly alternative technology for the production of NH₃ is necessary.

Up till now, several strategies have been developed toward ammonia synthesis under ambient condition, including biological nitrogen fixation,¹¹,¹² photochemical nitrogen reduction,¹³-¹⁵ and electrochemical nitrogen reduction (NRR).¹⁶,¹⁷ Among them, electrochemical NRR, as a novel ammonia synthesis route, has a higher ammonia yield than biological nitrogen fixation. Compared with photochemical nitrogen reduction reaction, it also has higher Faradaic efficiency (FE) and NH₃ yield. This is because, for the photochemical NRR, not all of the photos can be utilized efficiently due to multiple wavelengths and fast charge carrier recombination.¹⁶ In addition, compared with the Haber-Bosch method, the electrochemical NRR has many advantages, such as using renewable solar, wind, or hydro energy-driven electricity, reducing the energy input by about 20%, decreasing the CO₂ emission, simplifying the reactor design, and easing the complicacy of ammonia production.¹⁶ Despite many advantages of electrochemical NRR, achieving efficient NRR has been proved to be extremely challenging in practice. Among them, the grand challenge is that the catalyst surface that catalyzes the reduction of N₂ in the aqueous electrolyte also has a strong activity for the reduction of H₂O to H₂. More importantly, most of the protons and electrons in the electrochemical reduction system tend to shift toward the HER rather than the NRR, causing lower NH₃ yields and Faradaic efficiencies (FEs).¹⁸ Therefore, developing a suitable catalyst for achieving efficient electrochemical NRR is needed.

Since 2016, noble metals (Au, Ag, Ru, Rh, etc.), transition metals and their derivatives (Ti, Nb, Bi, etc.), metal-free materials (organic conducting polymers and carbonaceous catalysts), single-atom catalysts, and their hybrids, have been developed as potential catalysts for electrochemical NRR.¹⁹ Among them, noble metals have outstanding catalytic activity for electrocatalytic NRR. El-Sayed et al. reported that the Au nanocages can achieve a FE of 30.2% in 0.5 M LiClO₄ aqueous solution,²⁰ but their low abundance and high cost limit the possibility of its large-scale application. In contrast, low-cost and earth-abundant transition metals and their derivatives are studied as NRR electrocatalysts.⁹ Considering the fact that in nature, the nitrogenase enzymes with FeMo cofactor as catalytic active sites can achieve electron efficiency of 70% under room temperature and pressure,²¹ therefore Mo-based nanomaterials are promising NRR electrocatalysts.

Molybdenum sulfide (MoS₂), as a typical layered two-dimensional transition metal sulfide, has been widely used in industry as a hydrodesulphurization catalyst. With the rise of the field of electrocatalytic NRR, its performance in the direction of NRR began to be explored. Sun et al. demonstrated firstly that 2H-MoS₂ was active for NRR under ambient condition but presented a lower Faradaic efficiency (1.17%). The density functional theory (DFT) calculations display that the edge of MoS₂ is active for N₂ molecules.²² Subsequently, defect-rich MoS₂ nanoflowers with excellent selectivity were developed to boost electrocatalytic N₂ reduction to NH₃, which can attain a FE of 8.34% and a NH₃ yield of 29.28 μg h⁻¹ mg⁻¹cat. in 0.1 M Na₂SO₄ aqueous electrolyte.²³ In addition, Liu and coworkers introduced orbital hybridization by introducing S vacancies at the basal plane of MoS₂, which activated the basal plane’s catalytic activity and promoted the dissociation of N≡N bonds. Furthermore, the substitution of Mo atoms by Co doping reduces the Gibbs free energy of N₂ adsorption step and hydrogenation intermediate, thereby achieving a FE exceeding 10%.²⁴ Considering that the phase structure of the catalyst will affect its catalytic performance, our group previously loaded 1T-MoS₂ nanodots onto g-C₃N₄ nanosheets, achieving a FE of 20.48% and a NH₃ yield of 29.97 μg h⁻¹ mg⁻¹cat.²⁵ 1T-MoS₂, as a derivation of 1T-MoS₂, not only retains the physical and chemical properties of 1T-MoS₂, but also has better stability. However, its performance on NRR has not been studied.

TiO₂, as a common semiconductor functional material, has huge potential in the field of catalysis,²⁶,²⁷ electrochemical energy storage,²⁸,²⁹ and solar cell,³⁰ and so forth owing to its exceptional electronic and optical properties. In recent years, since Nb₂O₅,³¹ Bi₅V₂O₁₁/CeO₂,³² MoO₃,³³,³⁴ Fe₃O₄,³⁵ and more transition metal oxides as NRR electrocatalysts were developed, and the performance of TiO₂ in NRR began to be explored. Sun’s group reported that the TiO₂ nanosheets array is efficient for electrochemical NRR with a FE of 2.50% at ambient condition.³⁶ Then, TiO₂ nanoparticles were loaded on the rGO with high conductivity, which presented a FE of 3.3% with the corresponding NH₃ yield of 15.13 μg h⁻¹ mg⁻¹cat. in 0.1 M Na₂SO₄.³⁷ In addition, Xu and coworker prepared the TiO₂ nanoparticles on Ti₃C₂Tₓ nanosheets for NRR, achieving a FE of 16.07% and the NH₃ yield of 32.17 μg h⁻¹ mg⁻¹cat.³⁸ Thus, TiO₂ based NRR electrocatalysts that simultaneously
achieve a large NH₃ yield and a high FE are still worthy of our research.

Herein, we report that 1T'-MoS₂ nanosheets loaded on urchin-like TiO₂ hollow nanospheres (HNSs) can achieve effectively the electrochemical conversion of N₂ to NH₃. In 0.1 M Na₂SO₄, the catalyst exhibits excellent NRR electrocatalytic performance with the highest NH₃ yield of 29.62 μg h⁻¹ mg⁻¹ cat. at −0.75 V versus RHE. Besides, the highest FE of 24.9% is achieved at −0.65 V versus RHE for 1T'-MoS₂/TiO₂ HNSs composites. Notably, 1T'-MoS₂/TiO₂ HNSs electrocatalyst also displays outstanding selectivity and stability to NH₃, without the formation of by-products such as N₂H₄. ¹⁵N isotopic labeling test is investigated to confirm the nitrogen source of produced NH₃.

## RESULTS AND DISCUSSION

The preparation of 1T'-MoS₂/TiO₂ HNSs composites is described in Scheme 1. Firstly, TiO₂ SNSs were synthesized by direct hydrolysis of titanium isopropoxide in an ethanol-acetonitrile mixed solution containing trace of H₂O and NH₃ (Scheme 1A), where NH₃ acts as an aggregation driver and morphological controller to conduct titanium isopropoxide to assemble spherical agglomerates. Subsequently, the prepared TiO₂ SNSs were fluorinated through ligand exchange between surface hydroxyl groups and F⁻, after the F⁻ are evenly distributed throughout the spheres, PVP was introduced into the suspension of TiO₂ SNSs and coated TiO₂ SNSs. Then, the F-TiO₂/PVP was targeted etched by hydrothermal reaction, assembling an urchin-like hollow nanosphere structure (Scheme 1B). Finally, 1T'-MoS₂ nanosheets were loaded on the nanothorns by the hydrothermal reaction on TiO₂ HNSs as the substrate, forming 1T'-MoS₂/TiO₂ HNSs composites (Scheme 1C).

The phase composites and crystal structure of TiO₂ SNSs, urchin-like TiO₂ HNSs and 1T'-MoS₂/TiO₂ HNSs composites with various amount of 1T'-MoS₂ (1, 3, 5, 7, and 10 wt%) were studied by XRD (Figure 1A). The XRD pattern of TiO₂ SNSs obtained by hydrolysis using TTIP

**SCHEM E 1** Schematic illustration of the preparation of 1T'-MoS₂/TiO₂ HNSs composites
as a precursor does not show any diffraction peaks, indicating that the TiO$_2$ SNSs structure is amorphous. After hydrothermal targeted etching and calcination, the obtained urchin-like TiO$_2$ HNSs show excellent crystallinity, and the strongest diffraction peak at $\sim$25.32° can be attributed to the (101) plane of TiO$_2$. Other peaks at $\sim$37.85°, $\sim$48.12°, $\sim$54.09°, $\sim$55.11°, $\sim$62.74°, $\sim$68.93°, $\sim$70.27°, and $\sim$75.16° can be assigned to (004), (200), (105), (211), (204), (116), (220), and (215) crystal plane of TiO$_2$ (JCPDS No.21–1272), consistent with the previously reported anatase TiO$_2$.

After loading the 1T'-MoS$_2$ nanosheets by hydrothermal reaction, the diffraction pattern did not change significantly. In addition, all of the 1T'-MoS$_2$/TiO$_2$ HNSs composites do not present obvious signals that can be assigned to MoS$_2$, which may be caused by a small amount and highly dispersed of 1T'-MoS$_2$.

As shown in Figure 1B, the fully scanned XPS spectrum of 1T'-MoS$_2$/TiO$_2$ HNSs composites indicates the existence of Ti, Mo, O, S, and trace impurities C in

**FIGURE 1** (A) XRD patterns of TiO$_2$ SNSs, urchin-like TiO$_2$ HNSs and 1T'-MoS$_2$/TiO$_2$ HNSs composites (1.0, 3.0, 5.0, 7.0, and 10.0 wt% 1T'-MoS$_2$). XPS spectra of 1T'-MoS$_2$/TiO$_2$ HNSs composites (7.0 wt% 1T'-MoS$_2$): (B) fully scanned spectra; (C) Ti 2p; (D) O 1s; (E) Mo 3d and (F) S 2p.
the composites. For the Ti 2p spectrum (Figure 1C), the two peaks at ~458.85 eV (Ti 2p\textsubscript{3/2}) and ~464.55 eV (Ti 2p\textsubscript{1/2}) can be attributed to the Ti-O bond of TiO\textsubscript{2}.\textsuperscript{41} Regarding the O 1 s spectrum, the two peaks at ~530.08 and ~531.65 eV can be assigned to the Ti-O band and the –OH adsorbed on the surface of TiO\textsubscript{2} (Figure 1D).\textsuperscript{42} The Mo 3d spectrum can be divided into five peaks (Figure 1E). The two main peaks located at ~232.2 and ~228.9 eV can be ascribed to the Mo 3d\textsubscript{3/2} and Mo 3d\textsubscript{5/2} of 1T\textsuperscript{0}-MoS\textsubscript{2}, indicating the formation of 1T\textsuperscript{0} phase MoS\textsubscript{2}.\textsuperscript{43} Furthermore, the two small peaks at ~233.2 and ~230.3 eV correspond to Mo 3d\textsubscript{3/2} and Mo 3d\textsubscript{5/2} of 2H-MoS\textsubscript{2}, respectively.\textsuperscript{44} The extra peak at ~235.3 eV corresponds to Mo\textsuperscript{6+} of MoO\textsubscript{3}.\textsuperscript{33} Similarly, the two main peaks located at ~162.7 and ~161.3 eV are attributed to S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2} of 1T\textsuperscript{0}-MoS\textsubscript{2} (Figure 1F), respectively. While the two weak peaks at ~163.8 and ~162.3 eV are assigned to S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2} of 2H-MoS\textsubscript{2}, respectively.\textsuperscript{45} The proportion of 1T\textsuperscript{0} phase in the MoS\textsubscript{2} component is calculated ~63.6% on the basis of the deconvolution of the XPS spectra, indicating the 1T\textsuperscript{0} phase in the composite is a major phase.

The microstructures and morphologies of TiO\textsubscript{2} SNSs, urchin-like TiO\textsubscript{2} HNSs and 1T\textsuperscript{0}-MoS\textsubscript{2}/TiO\textsubscript{2} HNSs composites are attained using SEM and TEM (Figures 2 and 3). The prepared TiO\textsubscript{2} SNSs exhibit the uniform sphere and the size is around 500 nm. The surface of TiO\textsubscript{2} SNSs is rough and granular protrusions can be clearly seen, indicating that TiO\textsubscript{2} SNSs are composed of smaller size nanoparticles (Figure 2A,B). As shown in Figure 2C,D, after TiO\textsubscript{2} SNSs are targeted etched by hydrothermal reaction, the microstructure of TiO\textsubscript{2} SNSs is transformed into a hollow structure. In addition, the surface of the TiO\textsubscript{2} HNSs exhibits an urchin-like morphology due to the spontaneous reorganization of the structure during the reaction, which is conducive to the MoS\textsubscript{2} loading and the contact of N\textsubscript{2} molecules. After loading 1T\textsuperscript{0}-MoS\textsubscript{2} with urchin-like TiO\textsubscript{2} HNSs as the substrate, the hollow

**FIGURE 2** SEM images of (A, B) TiO\textsubscript{2} SNSs; (C, D) urchin-like TiO\textsubscript{2} HNSs and (E, F) 1T\textsuperscript{0}-MoS\textsubscript{2}/TiO\textsubscript{2} HNSs composites (7.0 wt% 1T\textsuperscript{0}-MoS\textsubscript{2})
structure of TiO$_2$ HNSs did not collapse, but the nanothorns on the surface changed to granular or sheets shape (Figure 2E,F). In addition, the EDS mapping images of 1T'-MoS$_2$/TiO$_2$ HNSs composites show the MoS$_2$ are homogeneously distributed on urchin-like TiO$_2$ HNSs (Figure S1).

Figure 3A,B show that the TiO$_2$ HNSs exhibits typical hollow structure characteristics, and a number of nanothorns grow on the surface. The whole displays a good urchin-like hollow structure, which can improve significantly TiO$_2$ specific surface area. The TEM images of 1T'-MoS$_2$/TiO$_2$ HNSs composites are displayed in Figure 3C, D. As shown in Figure 3C that TiO$_2$ HNSs still maintain a hollow structure after loading 1T'-MoS$_2$, but the urchin-like morphologies changes to a sheet shape. A closer scrutiny of the surface morphologies image clearly shows the size of MoS$_2$ nanosheets is 20 ~ 30 nm (Figure 3D). The HRTEM images of 1T'-MoS$_2$/TiO$_2$ HNSs composites are shown in Figure 3E,F. The internal composition of nanosheets is TiO$_2$ (Figure 3E) and the lattice spacing of 0.35 and 0.28 nm can assign to the (101) and (111) planes of TiO$_2$, respectively. In addition, the typical fold-like morphology attributed to MoS$_2$ can be observed at the edge position. The typical triangle arrangement of Mo atoms indicates the presence of 1T'-MoS$_2$ (Figure 3F).

The electrocatalytic nitrogen fixation activity of 1T'-MoS$_2$/TiO$_2$ HNSs composites was measured in an H-type cell. The quantities of the produced NH$_3$ and possible by-product N$_2$H$_4$ were measured by the indophenols blue and Watt/Chrisp method (Figure S2). In order to preliminary test the electrocatalytic NRR performance of 1T'-MoS$_2$/TiO$_2$ HNSs composites, the LSV curves are recorded in N$_2$- and Ar-saturated 0.1 M Na$_2$SO$_4$ electrolytes (Figure S3a). There is a difference in current density between the LSV curves obtained under the two test
conditions in the potential range of −0.65 to −0.95 V versus RHE, which indicates that 1T'-MoS2/TiO2 HNSs exhibit NRR catalytic activity in this potential range. Similar to previous studies,25,47 two LSV curves recorded in Ar- and N2-saturated electrolyte gradually coincide owing to the drastic HER dominant the cathode reaction. Figure 4A shows the UV–Vis absorption spectra of electrolytes attained at various potentials, indicating the nitrogen fixation effect of 1T'-MoS2/TiO2 HNSs composites reaches the best at −0.75 V. The specific results are displayed in Figure 4B. The highest NH3 yield of 29.62 μg h⁻¹ mg⁻¹ cat. and corresponding FE of 12.4% is obtained at −0.75 V for 7.0 wt% 1T'-MoS2/TiO2 HNSs composites. Besides, the NH3 yield of 12.50 μg h⁻¹ mg⁻¹ cat. and corresponding highest FE of 24.9% is obtained at −0.65 V for 7.0 wt% 1T'-MoS2/TiO2 HNSs composites. With the applied potential becomes more negative, both NH3 yield and FE decrease sharply to 6.94 μg h⁻¹ mg⁻¹ cat. and 0.49% (−0.90 V), which can also be attributed to the intense HER at lower applied potential, consisting with the results of LSV curves.48

In order to prevent the cathode electrolyte from being affected by NH3 escape and atmosphere during the reaction, an in-line acid trap is installed outside of the cathode chamber and tests the NH3 concentration. The results show that the presence of NH3 could not be detected in-line acid trap (Figure S4a). Furthermore, considering that there may be slight NH3 in the supplied gas, we also test the NH3 content in the electrolyte before NRR. The corresponding UV–Vis absorption spectrum showed that NH3 is not generated in the electrolyte after supplying N2 for 30 min, indicating that the experimental results were hardly interfered by the supplied gas (Figure S4b). Furthermore, to verify that the NH3 detected in the cathode chamber is produced by electrocatalytic NRR, the reaction is performed in Ar-saturated electrolyte at −0.75 V and in N2-saturated electrolyte at open circuit potential, respectively. Figure S4c and d compare the UV–Vis absorption spectra of the electrolyte solutions acquired under the above two test conditions. The results show that the presence of NH3 is not detected under the above two conditions, indicating that the previously detected NH3 originated from electrocatalytic nitrogen reduction of 1T'-MoS2/TiO2 HNSs composites. In view of the fact that electrocatalytic nitrogen fixation is a multi-electron reaction, it is possible to produce other products except for NH3, therefore, we also examine the possible by-products N2H4, and the results indicate that 1T'-MoS2/TiO2 HNSs composites have the excellent selectivity (Figure S5).

Stability is another important parameter to evaluate the property of catalysts, which was investigated through recycling and chronoamperometric measurements. Time-dependent current density curves at different potentials in N2-saturated 0.1 M Na2SO4 are presented in Figure S6. Remarkably, the current densities keep steady under higher potential (−0.65 to −0.80 V), demonstrating 1T'-MoS2/TiO2 HNSs composites have the excellent chemical stability. The NH3 yield and corresponding FEs at −0.75 V during the recycling test is shown in Figure 5A, the results show the NH3 yield and corresponding FEs do not decline obviously after eight recycling tests, which also indicates the prepared 1T'-MoS2/TiO2 HNSs composites has admirable chemical stability. In addition, no obvious current density loss can be found during the long-term electrochemical nitrogen reduction for 24 h at −0.75 V (Figure 5B), which further displays the good stability of 1T'-MoS2/TiO2 HNSs composites. The NH3 yield increases proportionally with time (Figure S7), demonstrating the efficient NRR activity of 1T'-MoS2/TiO2 HNSs composites. In addition, XRD analysis confirms that 1T'-MoS2/TiO2 HNSs composites present no
observable crystalline phase change (Figure S8) and SEM image shows the structure of 1T\textsuperscript{-}MoS\textsubscript{2}/TiO\textsubscript{2} HNSs composites remain stable after NRR electrolysis (Figure S9).

The effect of 1T\textsuperscript{-}MoS\textsubscript{2} content on the property of electrocatalytic nitrogen fixation was further explored. As shown in Figure 6A, the NH\textsubscript{3} yield and FE of pure TiO\textsubscript{2} HNSs are only 9.26 μg h\textsuperscript{-1} mg\textsuperscript{-1}cat. and 5.76%, significantly smaller than 1T\textsuperscript{-}MoS\textsubscript{2}/TiO\textsubscript{2} HNSs composites, indicating that 1T\textsuperscript{-}MoS\textsubscript{2} plays an important role in the NRR. As the loading of 1T\textsuperscript{-}MoS\textsubscript{2} increases from 0 to 10.0 wt\%, the electrocatalytic NRR activity of 1T\textsuperscript{-}MoS\textsubscript{2}/TiO\textsubscript{2} HNSs composites is expressively improved, and the highest NH\textsubscript{3} yield and FE are simultaneously attained at a loading of 7.0 wt% 1T\textsuperscript{-}MoS\textsubscript{2}. In addition, we also explored the influence of N\textsubscript{2} flow rate on the NRR performance (Figure 6B). The NH\textsubscript{3} yield and corresponding FE are stable with no change in different N\textsubscript{2} flow rates, which shows that N\textsubscript{2} diffusion is not the rate-determining step in the NRR. To confirm NH\textsubscript{3} production originating from N\textsubscript{2}, \textsuperscript{15}N isotopic labeling experiment is measured (Figure S10). \textsuperscript{1}H NMR displays a triplet coupling for \textsuperscript{14}NH\textsubscript{4}\textsuperscript{+} and a doublet coupling for \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+} with \textsuperscript{14}N\textsubscript{2} and \textsuperscript{15}N\textsubscript{2} as feeding gas, which powerfully indicates that NH\textsubscript{3} is yield from NRR by 1T\textsuperscript{-}MoS\textsubscript{2}/TiO\textsubscript{2}.

DFT calculation is tested to explore the origin of the enhanced activities of 1T\textsuperscript{-}MoS\textsubscript{2}/TiO\textsubscript{2} toward NRR. The most stable configurations of reaction intermediates on the 1T\textsuperscript{-}MoS\textsubscript{2}/TiO\textsubscript{2} surface are shown in Figure 7A, and the corresponding structures on the pristine TiO\textsubscript{2} surface are included in Figure S11. The NRR activity can be evaluated through the Gibbs free energy diagram, where the most favorable reaction pathway is the alternating pathway for both structural models. The distal pathway is also investigated and shown in Figure S12 for comparison. To comply with the experimental conditions, free energies were calculated at pH = 7 and
As shown in Figure 7B, the reduction of $N_2$ to $NNH$ is the potential-determining step (PDS) for both structural models. However, the energy barrier for the reduction of $N_2$ on the $1T'$-MoS$_2$/TiO$_2$ surface ($0.84$ eV) is lower than that on the pristine TiO$_2$ surface ($1.48$ eV), which indicates that the $1T'$-MoS$_2$ on the $1T'$-MoS$_2$/TiO$_2$ surface makes the activation and further reduction of $N_2$ more thermodynamically favorable than pristine TiO$_2$, contributing to better NRR catalytic activities.

The excellent electrocatalytic NRR performances of $1T'$-MoS$_2$/TiO$_2$ HNSs composites are mainly attributed to the following points: Firstly, $1T'$-MoS$_2$ nanosheets retain the high electrical conductivity of $1T$-MoS$_2$, which is favorable to the electron transfer in the process of nitrogen fixation. In addition, there are abundant active sites at the edge position and plane, which can be used to activate nitrogen molecules. Besides, the urchin-like structure of TiO$_2$ HNSs provides a large specific surface area, which is helpful in the adsorption of nitrogen molecules during the reaction. Finally, the semiconducting properties of TiO$_2$ can effectively inhibit the HER during nitrogen fixation (Figure 8).
3 | CONCLUSION

In summary, we constructed urchin-like TiO2 HNSs by hydrothermal targeted etching, and used it as a substrate to loading 1T-MoS2 nanosheets as an effective NRR electrocatalyst. The 1T-MoS2/TiO2 HNSs composite attains the highest NH3 yield of 29.62 µg h⁻¹ mg⁻¹cat. and corresponding FE of 12.4% at −0.75 V. Besides, the NH3 yield of 12.50 µg h⁻¹ mg⁻¹cat. and corresponding highest FE of 24.9% is achieved at −0.65 V for 1T-MoS2/TiO2 HNSs composites. Meanwhile, the 1T-MoS2/TiO2 HNSs composites also display excellent selectivity and stability. DFT calculation reveals that the 1T-MoS2 on the surface of 1T-MoS2/TiO2 makes the activation and further reduction of △N2 more thermodynamically favorable than pristine TiO2, contributing to better NRR catalytic activities. 15N isotopic labeling experiment indicates that NH3 is yield from NRR by 1T-MoS2/TiO2.

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CONFLICT OF INTEREST

The authors declare that we have no conflicts of interest to this work.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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