Microstructures
Atomic modulation and phase engineering of MoS2 for Boosting N2 Reduction

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Title: Atomic modulation and phase engineering of MoS$_2$ for Boosting N$_2$ Reduction

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Abstract
Electrochemical nitrogen reduction reaction (ENRR) has been regarded as a promising alternative strategy to the traditional Haber–Bosch process for ammonia (NH$_3$) production. However, ENRR technology is still restricted by the low yield rate of NH$_3$ and low Faradic efficiency. Herein, inspired by the biomimetic catalyst, we developed Fe-modulated MoS$_2$ catalyst (named as Fe@MoS$_2$) as an efficient ENRR catalyst. Raman spectrum coupled with the X-ray absorption spectroscopy (XAS) demonstrates the introduction of Fe into the MoS$_2$ lattice and achieves partial 2H to 1T phase conversion. Benefitting from the optimal geometric structure and electronic structure, the as-constructed Fe@MoS$_2$ can achieve a high yield rate of 6.82 μg h$^{-1}$ mg$^{-1}$ at -0.6 V vs. RHE and a Faradic efficiency of ~24.5% at -0.2 V vs. RHE. Therefore, this work provides a new avenue for designing novel catalysts, eventually boosting the NRR kinetics and accelerating the ENRR application.

Keywords: Nitrogen reduction, Single atom catalyst, Molybdenum disulfide, Phase engineering

INTRODUCTION
Ammonia (NH$_3$) is one of the most in-demand chemical products in the world, playing an essential role in the production of fertilizers, plastics, and medicines$^{[1,2]}$. Furthermore, NH$_3$ is also an important carbon-free energy carrier, benefited from its high gravimetric energy density (3 kWh kg$^{-1}$) and hydrogen...
content (17.6 wt%)[1,4]. The lower liquefaction difficulty makes it more convenient for storage and transportation[5]. Currently, the artificial synthesis of NH$_3$ heavily relies on the Haber-Bosch (H-B) method. The high-purity N$_2$ and H$_2$ are transformed into NH$_3$ on the surface of catalysts under severe reaction conditions (400-600°C, ~60bar)[6-8]. The H-B process is energy-intensive, has high carbon emissions and high cost of raw materials (H$_2$)[9,10]. Therefore, it is necessary to search for a green NH$_3$ technology. Recently, electrochemical nitrogen reduction reaction (ENRR) has been developed and can realize the N$_2$ to NH$_3$ transition at ambient temperature, with H$_2$O as the hydrogen source[11,12]. The total cost and carbon footprint of NH$_3$ synthesis will be effectively reduced by driving ENRR with renewable energy sources[13]. Moreover, the simple process equipment makes flexible NH$_3$ preparation possible. Nevertheless, the ENRR process is still restricted by low yield rate and Faradaic efficiency. Thus, it is highly desirable but challenging to develop high-efficient ENRR electrocatalysts.

Mo-based nitrogenase enables N$_2$ fixation under ambient conditions[14,15], which inspired researchers to investigate biomimetic catalysts with similar elemental compositions. MoS$_2$, as a layered two-dimensional (2D) semiconductor material, possesses a large surface area and crystal phase[16-18]. Multi-variable interlayer stacking forms and tunable electronic structure make it a promising candidate in the field of electrocatalytic synthesis of NH$_3$[11,19,20]. Due to the difficulty of activating the non-polar N-N triple bond and the adsorption barrier of N$_2$, the NH$_3$ yield in ENRR is limited. Moreover, the hydrogen evolution reaction (HER) has a close reaction equilibrium potential to that of ENRR, which affects the selectivity of ENRR in aqueous phase and leading to unsatisfactory Faradaic efficiency[21,22]. Therefore, several strategies have been developed to optimize the MoS$_2$-based catalysts for improving ENRR performance, including vacancy engineering[23,24], heteroatom doping[25,26], phase engineering[27,28], etc.

The catalytic activity and stability of MoS$_2$ with different phases vary a lot in ENRR. Huang et al.[27] compared the ENRR performance of metastable phase (1T$^-$ and 1T$^-$-MoS$_2$) and stable phase (2H-MoS$_2$). Thanks to the high localized electron density around Mo-Mo, the NH$_3$ yield and Faradaic efficiency of 1T$^-$-MoS$_2$ are approximately 9 and 12 times higher than those of 2H-MoS$_2$, respectively. Besides, constructing defects on the MoS$_2$ basal plane can expose more active sites, promote the adsorption and activation of N$_2$. Chen et al.[29] successfully introduced S vacancies in natural molybdenite through one-step annealing method. The electron structure at the Mo edge was altered, which optimized the free energy barrier of the rate-limiting step. The prepared rich S-vacancy MoS$_2$ exhibited significantly improved ENRR performance compared to the raw material, with an NH$_3$ yield of 23.38 μg h$^{-1}$ mg$^{-1}$cat and a FE of 17.9% at -0.35 V vs. RHE. In addition, benefiting from the synergistic effect among different elements, superior ENRR activity can be achieved by doping heteroatoms in MoS$_2$. Zhao et al.[30] synthesized Fe-doped MoS$_2$ nanosheets (Fe-MoS$_2$/CC) using a chemical reduction method. The introduction of Fe induced the redistribution of charges on the MoS$_2$ basal plane and generated new active sites, significantly improving the NH$_3$ synthesis performance. The NH$_3$ yield was 12.5 μg h$^{-1}$ cm$^{-2}$ with FE of 10.8% at -0.1 V vs. RHE. Moreover, the average size and chemical valence state of Fe nanodots did not change significantly after long-term electrolysis, which demonstrated the excellent stability of Fe-MoS$_2$/CC.

In this work, we prepared biomimetic Fe@MoS$_2$ electrocatalysts using a one-pot hydrothermal method. The MoS$_2$ with 2H to 1T phase conversion was achieved by doping Fe atoms, thereby improving the conductivity of the material. Furthermore, the unique hydrangea-like morphology and defects on the MoS$_2$ basal plane promote the accessibility of the active site. As a result, the bionic design of Fe-Mo-S centers has a promising ENRR performance. The maximum Faradaic efficiency of 24.5% and maximum NH$_3$ yield of 6.82 μg h$^{-1}$ mg$^{-1}$ were achieved by Fe@MoS$_2$ at 0.2 V vs. RHE and 0.4V vs. RHE, respectively.

**MATERIALS AND METHODS**

**Synthesis of Materials**

MoS$_2$ was synthesized by a simple one-step hydrothermal method (Figure 1A). Briefly, 0.4 mmol Na$_2$MoO$_4$.2H$_2$O and 0.82 mmol thioacetamide dispersed in 30 mL deionized water (D.I water) and sonification for 30 min. Then the solution was transferred into a 50 mL Teflon-line stainless steel autoclave. The autoclave was heated to 190 °C for 20 h in oven and then cooled to room naturally
temperature. The MoS$_2$ was collected by filtration of reaction solution, washed with DI water and ethanol for several times and dried at room temperature. The synthesis process of Fe@MoS$_2$ were same as that of MoS$_2$, except for the addition of 0.004 mmol FeCl$_3$.

Electrochemical Measurement

The ENRR performance evaluation were carried on an electrochemical workstation (VMP) under ambient environment (25 ℃, 1 atm). The Pt wire, Ag/AgCl (saturated KCl solution) electrode, and 0.25 M LiClO$_4$ serve as the counter electrode, reference electrode, and electrolyte, respectively. The working electrode was prepared by catalysts. Firstly, 2 mg of catalyst was dispersed into 1 mL NaFon/ISO/DI water solution (with the volume ration: 1:9:40) with the sonication for 30 min. Then, 100 μL catalyst inks (MoS$_2$ and Fe@MoS$_2$) were drop-casted on carbon paper (1 cm$^2$) with 0.2 mg cm$^{-2}$ and dried in the ambient environment. Before the ENRR test, the electrolyte was bubbled with N$_2$ gas (purity, 99.99%) for 20 min. During the ENRR test, the N$_2$ flow was continuously inputted with the flow rate of 20 sccm.

Determination of NH$_3$

The quantification of NH$_3$ was determined by the salicylic acid-based colorimetric method$^{[31]}$. To obtain the calibration curve, a series of standard NH$_4$Cl solution with different concentration of 0.0, 0.2, 0.5, 1.0, 2.0, 4.0 g mL$^{-1}$ in the electrolyte were first prepared. Then, 50 μL oxidation solution (0.75 M NaOH and sodium hypochlorite (pCl = 4 – 4.9)), 500 μL coloring solution (0.4 M sodium salicylate and 0.32 M sodium hydroxide), and 50 μL of catalytic solution (0.1 g Na$_2$[Fe(NO)(CN)$_5$]·2H$_2$O diluted in 10 mL deionized water) were mixed with the 10 mL standard NH$_4$Cl solution, and standing for 1h for color development. Next, the ultraviolet-visible (UV-Vis) spectrophotometer was used to measure the absorbance ($\lambda = 655$ nm) with different concentration of NH$_4$Cl. Finally, we got the calibration curve with a good linear relationship (Supplementary Figure 1). The standard curve was used to calculate the concentration of NH$_3$ in reacted electrolyte.

And the NH$_3$ formation rate can be calculated using the following equation:

$$R_{NH3} (\mu g \ h^{-1} \ mg^{-1}) = \frac{x(ppm) \times 10^{-3} \ (g/mg) \times V(L)}{t(h) \times m(mg)}$$

Where

- $x$ (ppm): calculated concentration of NH$_4^+$.
- $V$(L): volume of reacted electrolyte.
- $t$ (h): reaction time in hour.
- $m$ (mg): mass of catalyst on the carbon paper.
- $R_{NH3}$ (mg): the formation rate of NH$_3$.

And the NH$_3$ Faradic efficiency can be calculated using the following equation:

$$FE_{NH3} (%) = \frac{3 \times R_{NH3} (mol \ h^{-1} \ mg^{-1}) \times t(h) \times m(mg) \times F}{I(A) \times t(h)} \times 100\%$$

Where

- $x$ (ppm): calculated concentration of NH$_4^+$.
- $M$ (NH$_4^+$): 18 (g/mol).
- $V$ (L): the volume of reacted electrolyte.
- $I$ (A): the average current during the reaction.
- $F$: the Faraday constant 96485 mol$^{-1}$.
- $R_{NH3}$ (mg): the formation rate of NH$_3$.

Operando attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS)
The electrochemical operando ATR-SEIRAS was measured by INVENIO R FTIR spectrometer (Bruker) equipped with a mercury–cadmium–telluride (MCT) detector. Ag/AgCl electrode was employed as the reference electrode and a Pt foil was used as the counter electrode. During spectrum collection, the optical path was continuously purged with N₂ gas. The electrolyte was N₂-saturated electrolyte containing 0.1 M Li₂SO₄. The background spectrum of the catalyst electrode was acquired at an open-circuit potential before each measurement. Afterwards, the spectra at different potentials were collected. All collected spectra were given by the absorbance (-log(R/R₀)) with a spectral resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

Material Characterization

For prepared Fe@MoS₂, Fe is expected to replace the Mo and bond with S, and simultaneously introduces S vacancies on MoS₂ plane (Figure 1B). X-ray diffraction (XRD) patterns of MoS₂ and Fe@MoS₂ are shown in Figure 1C. The diffraction peaks at 32.5°, 35.8° and 57.2° could be indexed to (100), (102), and (110) planes of standard MoS₂ phase (PDF #37-1492)[32-34], respectively. The diffraction peaks of Fe@MoS₂ do not change significantly compared to MoS₂, and no FeS or FeS₂ phases were observed, which indicates that traces of Fe element did not form new sulfide. Scanning electron microscopy (SEM) image (Figure 1D) shows that the synthesized Fe@MoS₂ is assembled from many 2D nanosheets and ultimately exhibits a hydrangea-like morphology. The high specific surface area exposes more active sites, which is beneficial to its catalytic activity. There is no recognizable nanoparticles or clusters observed in transmission electron microscopy (TEM) image (Figure 1E), indicating that Fe was inserted into the MoS₂ plane rather than deposited on the surface. Raman spectra (Figure 1F) were employed to further investigate the effect of Fe insertion on MoS₂. The results suggest that synthesized MoS₂ exhibits distinct 2H phase signals, with two peak positions at 376.5 cm⁻¹ and 403 cm⁻¹ corresponding to the E₁²g vibrational peak and A¹g vibrational peak of 2H-MoS₂, respectively[32,35,36]. However, Fe@MoS₂ is a mixed 1T/2H-MoS₂ phase, two new 1T phase characteristic peaks of J₁ (146 cm⁻¹) and J₃ (334 cm⁻¹) are also clearly observed, indicating that the doping of Fe atoms triggers a phase transition from 2H-MoS₂ to 1T-MoS₂[37,39].

Figure 1. Schematic illustration of (A) synthesis process and (B) atomic structure, (C) XRD patterns of MoS₂ and Fe@MoS₂, (D) SEM image of Fe@MoS₂, (E) TEM image of Fe@MoS₂, (F) Raman spectra of MoS₂ and Fe@MoS₂.
High-resolution transmission electron microscopy (HRTEM) image (Figure 2A) shows the same results as those obtained from TEM images, with no impurities or other Fe-based structures observed in Fe@MoS\(_2\). Further, with the help of dark field transmission electron microscopy (STEM) characterization (Figure 2B and Supplementary Figure 2), it is seen that defects are present on the surface of the 2D structure. Atomic level Fe replaces some Mo atoms and distributes the surface of the 2D MoS\(_2\) plane. To explore the distribution of different elements in the catalysts, corresponding EDS elemental mapping was carried out to characterize Fe@MoS\(_2\). Figure 2C shows that Mo, S, and Fe are uniformly distributed in Fe@MoS\(_2\). Strong signals were observed for Mo and S, while weaker signals from Fe.

**Figure 2. Material Characterization.** (A) HRTEM image of Fe@MoS\(_2\). (B) STEM image, and (C) the corresponding EDS elemental mappings of Fe@MoS\(_2\). (D) Fe K-edge XANES Fe K-edge of Fe foil, FeO, Fe\(_2\)O\(_3\), and Fe@MoS\(_2\). (E) FT-EXAFS spectra of the Fe K-edge in Fe foil, FeO, and Fe@MoS\(_2\). (F) XAFS fitting result of Fe@MoS\(_2\). Inset: Atomic illustration of Fe@MoS\(_2\) (Mo atoms, purple; S atoms, yellow; Fe atoms, red).

X-ray absorption near edge structure (XANES) spectra and Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectra further revealed the coordination structure and coordination number of Fe atom in Fe@MoS\(_2\). As shown in Figure 2D, the absorption edge of Fe@MoS\(_2\) is located between FeO and Fe\(_2\)O\(_3\), indicating that the valence state of Fe lies between +2 and +3. In the FT-EXAFS spectra (Figure 2E), a peak can be observed at 1.87 Å for Fe@MoS\(_2\) corresponding to the first coordination\(^{[40,41]}\). There is no Fe-O and Fe-Fe observed in Fe@MoS\(_2\), indicating that the atomically dispersed Fe may dope within Mo-based vacancy and bond with S atoms. Fitting curve (Figure 2F and Supplementary Figure 3) of the Fe K-edge EXAFS spectra of Fe@MoS\(_2\) indicates that the Fe-S coordination number is about 5.5, implying that Fe mainly replaces the five-fold unsaturated coordinated Mo atoms near the S vacancy in MoS\(_2\)\(^{[42]}\). X-ray Photoelectron Spectroscopy (XPS) reveals the valence changes of the Mo and S elements after Fe doping. Similar S 2p spectra (Figure 3A) and Mo 3d spectra (Figure 3B) are demonstrated for MoS\(_2\) and Fe@MoS\(_2\). The core-level peaks of Mo 3d and S 2p experienced a positive shift for MoS\(_2\), indicating an increase in S and Mo valence states in Fe@MoS\(_2\), which is well in line with the previous reported research\(^{[42]}\).
Figure 3. (A) S 2p and (B) Mo 3d XPS of MoS$_2$ and Fe@MoS$_2$.

Electrochemical measurements

The ENRR performance of the Fe@MoS$_2$ is evaluated in H-type cell equipped with 3-electrodes system. (Figure 4A). The linear scan voltammetry (LSV) was first performed to compare the response current density under Ar- or N$_2$- saturated electrolyte of Fe@MoS$_2$. As shown in Figure 4B, the current density in N$_2$ is higher than that in Ar, which indicates the possibility of the Fe@MoS$_2$ towards N$_2$ reduction. The subsequent ENRR performance was evaluated by chronoamperometry method in N$_2$-saturated electrolyte for 3 hours. The response current density under different potentials were recorded in Figure 4C. The reacted electrolyte was collected and the concentration of NH$_3$ was determined by the indophenol blue method$^{31}$. Ultraviolet-visible (UV-Vis) absorption spectra of the reacted solution are collected. The yield rate and Faradaic efficiency can be calculated according to the UV-vis absorption spectra using the equation.

Figure 4. Electrochemical performance evaluation. (A) Schematic illustration of the reactor for electrochemical N$_2$ reduction. (B) LSV curves of Fe@MoS$_2$ in Ar and N$_2$-saturated 0.25 M LiClO$_4$ at a scan rate of 10 mV s$^{-1}$. (C) Chronoamperometric curves of Fe@MoS$_2$ at different applied potentials. NH$_3$ yield rate and Faradic efficiency of (D) MoS$_2$, and (E) Fe@MoS$_2$. The picture of the reacted solution of (F) MoS$_2$ and (G) Fe@MoS$_2$.

Obviously, the yield rate and FE of NH$_3$ over the electrocatalyst Fe@MoS$_2$ is higher than that of the pristine MoS$_2$ electrocatalyst, which indicated the optimization of the introduction of Fe element in the pristine MoS$_2$ plane. As shown in Figure 4D, the MoS$_2$ can achieve the yield rate of NH$_3$ ~ 4 μg h$^{-1}$ mg$^{-1}$ between the potential of -0.2 V to -0.8 V vs. RHE, while the Fe@MoS$_2$ can achieve the yield rate of NH$_3$
larger than 4.5 µg h⁻¹ mg⁻¹. As shown in Figure 4F, 4G, the color of the reacted electrolyte of Fe@MoS₂ and MoS₂ is green and yellow, respectively, suggesting the Fe@MoS₂ generate more NH₃ than that of MoS₂. The highest yield rate of 6.82 µg h⁻¹ mg⁻¹ is obtained at -0.4 V vs. RHE, which is about two times higher than that of MoS₂. The highest Faradaic efficiency of ~24.5% is obtained at -0.2 V vs. RHE (Figure 4E). The Faradaic efficiency dramatically decrease with the increasing of the applied potentials, which suggest the reaction is dominated by side-reaction HER.

Figure 5. Mechanism study. Operando ATR-SEIRAS of (A) MoS₂, (B) Fe@MoS₂.

To identify the reaction intermediates and study the reaction mechanism, the operando attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) was performed. Figure 5 recorded the ATR-SEIRAS spectra of MoS₂ and Fe@MoS₂ under different potentials during ENRR process. As shown in Figure 5A, there is no obvious peak can be observed for pristine MoS₂, indicating no intermediates generated. In contrast, some peaks gradually increase with the increasing potentials for Fe@MoS₂ (Figure 5B). Some peaks attributed to N-H stretching located at 3361 cm⁻¹ and 3286 cm⁻¹ [43,44]. The peak at 3112 cm⁻¹ and 1650 cm⁻¹ is corresponding to the O-H stretching and bending mode of H₂O, respectively[45,46]. The bending vibration absorption peak of -N-H at 1552 cm⁻¹ gradually strengthened[47], indicating strong N₂ reduction reaction over the Fe@MoS₂. These results clearly demonstrate that the introduction of Fe can accelerate the ENRR kinetics.

CONCLUSIONS

In conclusion, an inspired-biomimetic electrocatalyst of Fe@MoS₂ is designed and successfully prepared by a one-step hydrothermal method. The introduction of atomic-level of Fe achieves the geometric and electronic structure modulation of MoS₂, and modulate the 2H-phase MoS₂ into 1T-phase MoS₂. Benefitting from the optimized atomic structure and increased electrical conductivity of Fe@MoS₂, the kinetics is greatly accelerated, thus leading to the enhanced ENRR performance. Compared with the pristine 2H MoS₂, the prepared Fe@MoS₂ boost the NRR kinetics and exhibits superior NRR performance with yield rate of 6.82 µg h⁻¹ mg⁻¹ at -0.4 V vs. RHE and a Faradic efficiency of ~24.5% at -0.2 V vs. RHE. This work provides a new insight for designing efficient ENRR catalyst by the synergistic doping and phase engineering.

DECLARATIONS

Authors’ contributions

Synthesis and testing of materials, data collection, original manuscript writing:
Validation and original manuscript revision:
Data collection: Jia Y, Shao G, Li Y, Yang R
Data analysis: Jia Y, Li Y, Shao G
Writing, review, and editing: Jia Y, Li Y, Shao G

Supervision: Li Y, Huang M

Funding acquisition: Li Y, Huang M

All authors have read and agreed to the published version of the manuscript.

Availability of data and materials

According to reasonable requirements, all of the data examined in this research can be obtained from the correspondents.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

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Dear Editor,

We are pleased to submit this manuscript entitled “Atomic modulation and phase engineering of MoS$_2$ for Boosting N$_2$ Reduction” as a Research Article to the upcoming special issue of Microstructures, titled “2D Functional Materials: Microstructure, Properties and Applications”. We declare that this manuscript is not under consideration for publication in any other journals. The following is a brief introduction to the work.

Ammonia (NH$_3$) is one of the most in-demand chemical products in the world, playing an essential role in the production of fertilizers, plastics, and medicines. The electrochemical nitrogen reduction reaction (ENRR) is a mild and energy-efficient method for ammonia synthesis compared to the conventional Haber-Bosch process. However, the restricted NH$_3$ yield and low selectivity place higher demands on catalyst materials and electrochemical systems. MoS$_2$ with 2D layered structure shows great potential in the field of electrochemical catalysis, due to its unique electronic structure, conductivity, large specific surface area and good chemical stability. Furthermore, the adjustable stacking structure, electronic configuration, and crystalline phase of MoS$_2$ render its modulation readily feasible. This feature facilitates the enhancement of its ENRR catalytic performance.

In our work, we posit a comprehensive strategy to optimize the catalytic activity of MoS$_2$. Fe atom doping induces a 2H to 1T phase transition in MoS$_2$, optimizing the electrical conductivity. The unique hydrangea-like morphology and defects on the MoS$_2$ basal plane promote the accessibility of the active site. Meanwhile, the bionic design of Fe-Mo-S centers has a promising ENRR performance.

Highlights include:

1. **A combined strategy of atom doping, vacancy engineering and phase transition for the development of high performance ENRR catalysts is presented.** Two new 1T phase characteristic peaks of J$_1$ (146 cm$^{-1}$) and J$_3$ (334 cm$^{-1}$) are clearly observed in Raman spectrum, indicating Fe@MoS$_2$ is a mixed 1T/2H-MoS$_2$ phase. Furthermore, with the help of STEM characterization, it is seen that defects and atomic-level Fe are present on the surface of the 2D
structure.

2. **ENRR performance over the Fe@MoS₂ is significantly improved.** The maximum Faradaic efficiency of 24.5% and maximum NH₃ yield of 6.82 μg h⁻¹ mg⁻¹ were achieved by Fe@MoS₂ at 0.2 V vs. RHE and 0.4V vs. RHE, respectively. However, at the similar potential (between 0.2 V to 0.8 V vs. RHE), the NH₃ yield of MoS₂ was only ~4 μg h⁻¹ mg⁻¹.

3. **In-situ and electrochemical characterizations demonstrated Fe doping accelerated the ENRR kinetics.** The operando attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) spectra shows that there is no obvious peak can be observed for pristine MoS₂. In contrast, some peaks gradually increase with the increasing potentials for Fe@MoS₂, indicating strong N₂ reduction reaction over the Fe@MoS₂.

Thank you very much for your kind consideration.

Sincerely,

Li Yang

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Supplementary Material: Atomic modulation and phase engineering of MoS$_2$ for Boosting N$_2$ Reduction

Supplementary Figure 1. Standard curves. (A) UV-Vis absorption spectra of NH$_3$ standard solutions; (B) Calibration curve for colorimetric NH$_3$ assay using salicylic acid.

Supplementary Figure 2. STEM image of A) Fe@MoS$_2$, and B) the corresponding Fourier transform.
Supplementary Figure 3. The corresponding EXAFS fitting curves of Fe@MoS$_2$.

Supplementary Table 1. Fe K-edge EXAFS curve Fitting Parameter.

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<td>Fe@MoS$_2$</td>
<td>Fe-S</td>
<td>5.5±0.4</td>
<td>2.29±0.05</td>
<td>3.3±0.7</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Fe-Mo</td>
<td>0.7±0.1</td>
<td>2.83±0.025</td>
<td>1.9±0.5</td>
<td></td>
</tr>
</tbody>
</table>
Highlights

1. A combined strategy of atom doping, vacancy engineering and phase transition for the development of high performance ENRR catalysts is presented. Two new 1T phase characteristic peaks of J₁ (146 cm⁻¹) and J₃ (334 cm⁻¹) are clearly observed in Raman spectrum, indicating Fe@MoS₂ is a mixed 1T/2H-MoS₂ phase. Furthermore, with the help of STEM characterization, it is seen that defects and atomic-level Fe are present on the surface of the 2D structure.

2. ENRR performance over the Fe@MoS₂ is significantly improved. The maximum Faradaic efficiency of 24.5% and maximum NH₃ yield of 6.82 µg h⁻¹ mg⁻¹ were achieved by Fe@MoS₂ at 0.2 V vs. RHE and 0.4V vs. RHE, respectively. However, at the similar potential (between 0.2 V to 0.8 V vs. RHE), the NH₃ yield of MoS₂ was only ~4 µg h⁻¹ mg⁻¹.

3. In-situ and electrochemical characterizations demonstrated Fe doping accelerated the ENRR kinetics. The operando attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) spectra shows that there is no obvious peak can be observed for pristine MoS₂. In contrast, some peaks gradually increase with the increasing potentials for Fe@MoS₂, indicating strong N₂ reduction reaction over the Fe@MoS₂.
Graphical Abstract

Na$_2$MoO$_4$·6H$_2$O
Thioacetamide
FeCl$_3$

Hydrothermal 190 °C, 20h

S  Mo  Fe