Supplementary Information

Structural Insight of [Fe-S2-Mo] Motif in Electrochemical Reduction of N_2 over Fe₁ supported Molecular MoS₂

1. Materials Used

Reagents used for synthesis were: MoS_2 (Sigma-Aldrich); iron acetate (reagent grade, Alfa Aesar); $FeCl_3 \cdot 6H_2O$ (reagent grade, Alfa Aesar); $FeCl_2$ (reagent grade, Sigma-Aldrich); nbutyllithium/hexane (reagent grade, Sigma-Aldrich); Polyvinylpyrrolidone (PVP, reagent grade, Sigma-Aldrich); Potassium acetate (reagent grade, Sigma-Aldrich); hydrazine (puriss. p.a., absolute $\geq 99.8\%$ (GC), Sigma-Aldrich); Isopropanol (99.9%, Sigma-Aldrich); para-(dimethylamino) benzaldehyde (reagent grade, Sigma-Aldrich); H₂SO₄ ($\geq 98\%$, Sigma-Aldrich); HCl ($\geq 98\%$, Sigma-Aldrich). HAuCl₄ 3H₂O (reagent grade, Sigma-Aldrich); Ru acetate (reagent grade, Sigma-Aldrich); Cu acetate (reagent grade, Sigma-Aldrich); Co acetate (reagent grade, Sigma-Aldrich); Ni acetate (reagent grade, Sigma-Aldrich); Manganese acetate (reagent grade, Sigma-Aldrich); Sodium chlorite (25%, Sigma-Aldrich); ¹⁵N₂ (98%+, CK isotopes); HNO₃ (5 M, diluted from 70%, Sigma-Aldrich); Cu powder (Sigma-Aldrich).

2. Methods

Synthesis of few-layered MoS₂ (fMoS₂) and single-layered MoS₂ (sMoS₂)

Few-layered MoS_2^{1} . 6 g of bulk MoS_2 (bMoS₂) powder was added into 400 mL of water/isopropanol (1:3, v/v), followed by adding 4 mL of hydrazine monohydrate. The solution mixture was then placed into a sonication bath for 12 hours and centrifuging to exfoliate the layers. The supernatant collected was then filtered by vacuum filtration, followed by washing with deionized water. The exfoliated product was finally dried under vacuum for 24 hours.

Single-layered MoS₂^{2,3}. 0.5 g of bulk MoS₂ powder was firstly soaked in 4 mL of 1.6 M nbutyllithium/hexane under inert nitrogen for 48 hours. The obtained solid Li_xMoS₂ was then isolated using vacuum filtration, followed by washing with n-hexane to remove the excess nbutyllithium. Afterwards, the dried product was immersed into 250 mL of deionized water and placed into a sonication bath for 12 hours and then centrifuged at 5000 rpm for 15 minutes. The supernatant collected was then filtered by vacuum filtration, followed by washing with deionized water. The exfoliated product was finally dried under vacuum for 24 hours.

Synthesis of single Fe atom doped bMoS₂/fMoS₂/sMoS2². Transition-metals (Mn, Fe, Co, Ni, Cu, Au, Ru) precursor solution was freshly prepared by dissolving 0.2 mM metal ions into 1 mL of 0.5 mM thiourea solution and kept for overnight to form the corresponding metal complex. The metal complex solution was then mixed with 30 mL of colloid solution, which was prepared by dispersing 30 mg of sMoS₂ (bMoS₂ or fMoS₂) into 30 mL of water/isopropanol (1:3, v/v) with the aid of 30 mg of PVP (stabiliser). The mixture was then transferred to an

autoclave and heated at 160 °C for 24 hours. Finally, the precipitate was washed with deionized water and dried under vacuum for 12 hours to obtain the solid product.

3. Characterization

High-angle annular dark field scanning transition electron microscopy (HAADF-STEM). The samples were firstly ground and dispersed in ethanol. After sonicating half an hour, the solution was dropped and dried on a holey carbon coated Cu-TEM grid for STEM analysis. The analysis was performed by JEOL-ARM300 Aberration-Corrected Transmission Electron Microscope at Diamond Light Source (Diamond, UK). A low voltage of 60 kV to avoid beam excitation and damage was applied for the imaging. An off-axis annular detector imaging was employed for Dark-field (Z-contrast) imaging and atomic-resolution imaging.

Inductively coupled plasma (ICP). The samples were dissolved in 5 wt.% HCl and filtered to get the dissolved Fe for ICP analysis. The analysis was conducted by ICP optical emission spectroscopy (Optima2100DV, PerkinElmer). The doped-metal content was controlled at around 2.8 wt. % with error \pm 0.5 (Fe 2.8 wt. %, Co 3.0 wt. %, Ni 3.5 wt. %).

X-ray diffraction (XRD). XRD patterns were collected on a PANalytical X'Pert Pro diffractometer, which is operated at 40 kV and 30 mA. Samples were grounded and pressed onto a glassy slide. The scan rate is at 0.000267°/s with 15s per step.

Electron paramagnetic resonance (EPR). Continuous-wave EPR spectra were performed by an X-band (9.4 GHz) Bruker EMX EPR spectrometer. All measurements were conducted at room temperature. For each measurement, 10 mg of powder was weighed and put into a glassy EPR tube (0.60 i.d. and 0.84 o.d.). Then X-Band spectra were performed over a 300 Gauss field range and 15 scans were collected. Signal intensity and electron spin numbers were calculated from the double integral of a defined peak range of the spectra.

Synchrotron-radiation X-ray absorption fine structure (srXAFS). EXAFS measurements at the Fe K-edge were performed on beamline B18 at Diamond Light Source (Diamond, UK) to obtain information about the local structure of the metal (the nearest-neighbor interatomic distances and coordination number). The Diamond installation comprises a 3 GeV electron storage ring with typical currents of 200 mA. The B18 is a bending magnet beamline which has been designed to deliver monochromatic X-rays in the energy range of 2 to 35 keV. A Si (311) double crystal monochromator was used for energy selection with a resolution of 1 eV. X-ray absorption spectroscopy data were collected at ambient temperature in fluorescence mode using optimized ionization chambers as detectors. Fluorescence spectra were acquired using I₀ and a high count rate fluorescence 9-element Ge detector. The EXAFS data analysis was performed using IFEFFIT 1 with Horae packages 2 (Athena and Artemes). To confirm the reproducibility of the experimental data, at least 2 scan sets were collected and compared for each sample. The spectra were calibrated with Fe and Mo foil as reference. The amplitude

reduction factor was obtained from analysis of the Fe and Mo foil, which was used as a fixed input parameter to allow refinement in the coordination number and bond distance of the absorption element. The curve-fitting analyses were done a range of R = 3-12Å. The best fit was selected according to the lowest R factor throughout EXAFS analysis.

Operando experiments were performed with an electrochemical cell, allowing the X-ray beam to incident on the sample. A platinum coil counter electrode and an Ag|AgCl (0.1 M HCl) reference electrode were used in this study. To prepare the working electrode, 1 mg of the electrocatalyst will be dispersed in 1 ml of water/ethanol (4:1 v/v) and then followed by 30 min sonication to create a homogeneous ink. The ink was then drop-coated onto the surface of a carbon cloth with exposed surface area of 1 cm². The carbon paper was dipped in the 0.1 M H⁺ electrolyte. The EXAFS spectra were collected under a flow of N₂/Ar at open circuit or a potential.

Simulations of the XANES spectra were conducted in JFEFF 9.0. A (3×3) supercell of 2H-MoS₂ with a Fe atom atop Mo site was selected to simulate Fe-sMoS₂. The model of N₂ adsorption on Fe-sMoS₂ is optimised by DFT calculation (see below). To simulate the catalyst under potential, an ion parameter of 0.2 was applied to Fe. All the simulated results are obtained after convergence.

Isotopic study. Isotopic N₂ was used to prove that the obtained ammonia derives from N₂ gas rather than some other sources. The feed gas was purified by passing through 0.2 M NaClO₂ and 1 mM H₂SO₄ double traps to remove any possible NO_x and NH₃ contamination. NMR and LCMS measurements were used to detect the product. For NMR measurement, 10 ml of the electrolyte was taken out, and its pH was adjusted to 3 by adding 0.5 M H₂SO₄. Then, 0.9 ml of the resulting liquid was taken out, followed by adding 0.1 ml of D₂O as an internal standard. The ¹H NMR signal of ¹⁵NH₄⁺ is split by the nuclear spin of ¹⁵N into a doublet (~73 Hz) in the region near 7.0 ppm. A calibration curve, Figure S10, has been obtained as a function of concentration using standard solutions made up from ¹⁵NH₄⁺, pH was adjusted to 3 by adding 0.5 M H₂SO₄. A known quantity of d⁶-DMSO was added as an internal standard.

Indophenol assays were prepared by adding 0.5 mL of aliquot solution after 1-h reaction to 0.1 mL of 1% phenolic solution in 95% ethanol/water. Stepwise, 0.375 mL of 1% NaClO in alkaline sodium citrate solution and 0.5 mL of 0.5% Na[Fe(CN)₅NO] solution were mixed. The assayed aliquots were then aged overnight before testing on a Xevo LCMS-ESI system.

Electrochemical Measurement. A three-electrode system controlled by IviumSoft potentiostat (Ivium Technologies B. V.) was applied in a single cell to carry out all electrochemical measurements. A platinum coil counter electrode and an Ag|AgCl reference electrode were used in this study. The electrolyte is 0.1 M HCl with a pH of around 1. To prepare the working electrode, 1 mg of the electrocatalyst will be dispersed in 1 ml of water/ethanol (4:1 v/v) and then followed by 30 min sonication to create a homogeneous ink. The ink was then drop-coated onto the surface of a carbon cloth with exposed surface area of

1 cm², affording the working electrode with a catalyst density of 1 mg/cm². Before tests, highpurity N₂ (99.99%) or Ar (99.99%) was purified by two traps filled with 0.2 M NaClO₂ and 1 M H₂SO₄ prior to bubbling to the reaction cell at a flow rate of 10 mL/min. In another way, the gas was purified by a VARIAN filter (Agilent, CP17973), which contained two gas-clean fillers for stepwise moisture and oxygen removals, following by flowing into the 1 M H₂SO₄ trap. For each measurement of N₂ reduction, controlled experiment was first performed using Ar and without catalyst. The obtained solutions did not give ammonia with more than 0.01 ppm before carrying out the subsequent ammonia synthesis. A three-electrode system controlled by μ -AUTOLAB III potentiostat (Eco-Chemie, Netherlands) was applied to carry out all the Linear Sweep Voltammetry (LSV) measurements with a scan rate of 5 mV s⁻¹. A platinum coil counter electrode and an Ag|AgCl (1 mol L⁻¹ KCl) reference electrode were used in this study.

All measurements were calibrated with respect to the reversible hydrogen electrode (RHE) by the following equation:

 $E_{RHE} = E_{Ag|AgCl} + 0.197V + 0.059pH.$

For the measurement of ammonia yields, the obtained solution was taken out and the concentration was monitored by colorimetry with the UV-vis spectrometer. To ensure the accuracy, all the reactions were tested and measured for at least three times. In addition, a specialized highly sensitive ammonia detector was used (Thermo SicentifcTM OrionTM Ammonia Gas Sensing ISE Electrode). The selective ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. Liquid does not penetrate the membrane holes. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample the partial pressure of ammonia will be proportional to its concentration. The potential of the electrode sensing element with respect to the internal reference element is described by the Nernst equation: $E = E_0 - S \log [NH_3]$, where E is measured electrode potential; E₀ is the reference potential; NH₃ is the ammonia concentration in solution; S is the electrode slope. Prior to each test, the pH of all standards and samples is adjusted above 11. The ammonia electrode responds to the partial pressure of dissolved ammonia gas. The partial pressure of dissolved ammonia gas is related to the ammonia concentration by Henry's Law: $K_h = [NH_3]aqueous/P_{NH3} = 56$ moles/liter-atm. (25 °C). The amount of electron consumed was calculated based on the current density and Faradaic efficiency assuming no heat generated during the test.

DFT Theoretical Calculation. All calculations were conducted by first-principles density of functional theory (DFT) using Vienna ab initio simulation packages (VASP)⁴, the exchange-correlation energy functional was described by generalized gradient approximation through

Perdew-Burke-Ernzerhof (PBE) functional⁴, and the ion-electron interaction was treated by the projector-augmented wave (PAW) method⁵ at a plane-wave cutoff energy of 400 eV. Single-layered MoS₂ (sMoS₂) was simulated by a (3×3) supercell of 2H-MoS₂ under periodic boundary conditions.15 Å of vacuum in the *z*-direction was used to separate the neighboring single-layered MoS₂ sheet. The Brillouin zone has been sampled with an 8×8×4 and a 2×2×1 Monkhorst-Pack⁶ grid of k-points for orbital analysis calculations and geometry optimizations, respectively. Both atomic positions and lattice constants were relaxed until the forces on atoms were less than 0.02 eV Å⁻¹ and the total energy change was less than 1.0×10⁵ eV. To rationalize the different performances of transition metal doped sMoS₂ and sMoS₂ in electro-chemical ammonia synthesis, density of states and frontier orbitals topology analysis were conducted at the PBE/PAW level of theory.

4. Results



Figure S1. Proposed *e*HB processes integrating ammonia synthesis over photo-/electro-/thermo- pathways and electricity produced by wind energy.

Several new technologies have been developed to replace Habor-Bosch progress (see Figure S1).⁷ For example, small pilot plants are built up to convert the solar/wind/tidal power into electricity for ammonia synthesis. Another option is to use solar energy or electricity from renewable energy to directly synthesize ammonia from nitrogen and water as reported in this work.



Figure S2. Schematic diagram of energy potentials of nitrogen reduction, hydrogen evolution and water oxidation at 1 M H⁺ solution.⁸



Figure S3. X-ray diffraction (XRD) patterns of MoS_2 with different layers and $sMoS_2$ supported transition metals.



Figure S4. Atomic force microscopy (AFM) image analyses for the chemically exfoliated $sMoS_2$. **a**, AFM image of spin-coated $sMoS_2$ and **b**, It can be seen that the step heights of individual layers of 0.6-0.7 nm. This value is comparable to ca. 0.65 nm of a single layer of the S-Mo-S building block.



Figure S5. DFT optimized geometries of Fe binding configurations and an atomic model FeMo cluster in FeMo cofactor. Top, side and perspective views (left to right) of the DFT calculated geometries for Fe on the Mo atop site (a),S substitution (b), and FeMo cluster (c). The values are the calculated bond lengths with the unit of Å. The [Fe-S₂-Mo] four member rings are circled.



Figure S6. Mass spectra of NO_x in a N₂ flow with/without the NaClO₂ and H₂SO₄ traps. NO_x were produced from the reaction of Cu powder (1mmol) and 5 M HNO₃ (7.5 mL) at 5 min. As shown, NO_x were trapped as signals of NO_x dropped to the background level if the mixed gas was passed through the two traps almost instantly.



Figure S7. UV-vis spectra of standard 0-1 ppm and reaction assay. Reaction conditions: FesMoS₂, -0.1 V vs RHE, 1 h.



Figure S8. Calibration curve of UV-vis spectra of standard 0-1 ppm and reaction assay. Reaction conditions: Fe-sMoS₂, -0.1 V vs RHE, 1 h.



Figure S9. Calibration curve of ammonia selective electrode method of standard 0-1 ppm and reaction assay. Reaction conditions: Fe-sMoS₂, -0.1 V versus RHE, 1 h.



Figure S10. Current density at different applied potential over Fe-sMoS₂.



Figure S11. Tafel Plot for Fe-sMoS₂ based on the linear sweep voltammetry under a flow (10 mL/min) of Ar. *b* is the Tafel slope.



Fig. S12. N₂ reduction activity to NH₃ and Faradaic efficiency over bulk MoS_2 (bMoS₂), few layered MoS_2 (fMoS₂), single layered MoS_2 (sMoS₂), respectively at -0.10 V. Each point was taken by the average of at least 3 measurements with the given error bars.



Fig. S13. N₂ reduction activity to NH₃ and Π FE over sMoS₂ with different transition metals at -0.10 V. Each activity point was taken by the average of at least 3 measurements with the given error bars.



Figure S14. Proton NMR spectra under controlled conditions either in Ar, or without Fe-sMoS₂, or under open circuit.



Figure S15. Proton NMR spectra of ¹⁵NH₄⁺ standard 0-1 ppm and reaction assay. Reaction conditions: Fe-sMoS₂, -0.1 V vs RHE, 1 h.



Figure S16. Mass spectroscopy chart of indophenols in the solutions obtained by the reaction of (A) ${}^{14}N_2$ and (B) ${}^{15}N_2$.

As shown in Fig. S9, the aliquot solution (a) obtained by the reaction with ${}^{14}N_2$ shows indophenol anion at m/z 198. In contrast, the aliquot solution (b) obtained by the reaction with indicates strong

¹⁵N-labelled indophenol anion at m/z 199 with relative intensity significantly higher than the natural abundance ratio of ¹⁴N. ¹⁵N nuclei. This result clearly confirmed that gas N₂ is fixed into NH₃.



Figure S17. Stability test for nitrogen reduction over Fe-sMoS₂ at -0.1 V.



Figure S18. DFT optimized geometries of Fe binding configurations with a N_2 molecule absorbed. The values are the calculated bond lengths of Fe-N bond and Fe-S bond with the unit of Å.



Figure S19. The energy plot of N_2 adsorption on Fe-sMoS₂ from DFT calculations with the reference to the energies of Fe-sMoS₂ and free N_2 molecule. N_2 is absorbed on single Fe atom atop Mo site spontaneously.

Bond species	Bond length (Å)			
_	FeMoco	Calculation		
Fe-S1	2.248	2.137		
Fe-Mo	2.666	2.539		
Fe-S2	2.213	2.136		
Mo-S1	2.356	2.542		
Mo-S2	2.336	2.542		

Table S1. The bond lengths of $[Fe-S_2-Mo]$ in FeMoco and Fe-sMoS₂ on basis of EXAFS experiments in comparison with optimised DFT calculations.

Table S2. Comparison of the catalytic performances of Fe-sMoS₂ with reported Fe-based NRR catalysts at ambient conditions.

Catalyst	Potential (V)	NH ₃ yield	$ \Pi_{\text{FE}}(\%) $	Ref.	
Fe-sMoS ₂	-0.1	27.45 µg h ⁻¹ mg ⁻¹ _{cat}	27.0	This work	
Fe-TiO ₂	-0.4	25.47 µg h ⁻¹ mg ⁻¹ _{cat}	25.6	9	
Fe ₂ O ₃ -CNT	-2	$0.22 \ \mu g \ h^{-1} \ cm^{-2}$	0.15	10	
Fe _{SA} -N-C	0	7.48 µg h ⁻¹ mg ⁻¹ _{cat}	56.55	11	
Fe ₂ O ₃ nanorod	-0.8	15.9 μg h ⁻¹ mg ⁻¹ _{cat}	0.94	12	
γ-Fe ₂ O ₃	0.0	$0.0125 \ \mu g \ h^{-1} \ mg^{-1}_{cat}$	1.9	13	
Fe ₃ O ₄ /Ti	-0.4	3.63 μg h ⁻¹ cm ⁻²	2.6	14	
β-FeOOH	-0.7	23.32 µg h ⁻¹ mg ⁻¹ _{cat}	6.7	15	
Fe/Fe ₃ O ₄	-0.3	0.19 μg h ⁻¹ cm ⁻²	8.29	16	
FeO(OH,F) nanorod	-0.6	42.38 µg h ⁻¹ mg ⁻¹ _{cat}	9.02	17	
Fe ₃ S ₄	-0.4	$75.4 \ \mu g \ h^{-1} \ m g^{-1} \ cat$	6.45	18	

Table S3. Electronic structure of N_2^* adsorption on atop site of Fe of Fe-sMoS₂ and Fe₃S₄. The Bader charge is reported for Fe, Mo, N bound to the surface (Ns), and the terminal N bound to the first (Nt). The Bond length on internal N-N bond length and Ns to Fe (in Angstrom) are also reported (also see Fig. 5).

Bader Charge (n _{electrons}))	Bond length (Å)		
	Nt	Ns	Fe	Мо	N-N	Fe-N	
N ₂	-	-	-	-	1.1	-	
N ₂ -Fe-sMoS ₂	-0.01	-0.28	0.71	0.52	1.14	1.85	
N_2 -Fe ₃ S ₄	0.23	-0.43	0.82	-	1.13	1.82	

5. References

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