# **Supplementary Information**

# Activation of MoS<sub>2</sub> Monolayer Electrocatalysts *via* Reduction and Phase Control in Molten Sodium for Selective Hydrogenation of Nitrogen to Ammonia

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### Sample preparation

Commercial  $MoS_2$  powder (Sigma-Aldrich) was used directly as the staring material. 100 mg of bulk  $MoS_2$  were transferred to an Ar-filled glovebox and mixed with 1000 mg of metallic Na in a crucible. The crucible was heated to 120°C for 10 mins using a hotplate, and then the mixture was cooled to room temperature naturally. The solidified mixture was taken from the glovebox and was immersed in ethanol to leach off Na and its related species. The catalyst powder was collected via vacuum filtration, washed repeated using water and vacuum dried. Catalysts of different 1T contents and junction densities were prepared using the same procedure.

### Sample characterization

**Physical characterizations:** X-ray diffraction (XRD) patterns were recorded on a Bruker D8 powder Xray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried on an Escalab250 X-ray photoelectron spectrometer using Al Kα radiation. The position of C1s peak at 284.5 eV, was used to calibrated the binding energies. The microstructures of the electrocatalysts were analysed using a Transmission electron microscopy (JEOL JEM-2100F TEM) and a High-resolution TEM (HRTEM) microscope operated at an accelerating voltage of 200 kV. The Raman spectra were collected on Renishaw inVia Raman Microscope with a 514 nm laser. Nitrogen sorption isotherms was performed on a Micromeritics ASAP 2020 system. And before measurements, the sample were degassed at 100 °C for 10 h under vacuum. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface. The pore size distribution was based on the Barrett-Joyner-Halenda (BJH) method. The UV-Vis absorbance spectra were measured on Techcomp UV1000 spectrophotometer. In situ Fourier transform infrared (FT-IR) spectra of the electrochemical cell were collected on a Nicolet 8700 FT-IR spectrometer (Thermo Fisher). The atomic ratio was conducted by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 7300DV (ICP).

**Electrochemical measurements:** Electrochemical measurements were carried out with an electrochemical workstation (Interface 1010E, Gamry) in a three-electrode system in. The saturated calomel reference electrode (SCE) electrode and a graphite rod were used as the reference and counter electrodes, respectively.

Typically, to prepare the working electrode (WE), 10 mg active material and 40 µL Nafion solution (5 wt%) were dispersed in the solution containing 240 µL deionized water and 720 µL isopropanol solution. Then, sonicating for 30 min to form a homogeneous catalyst ink. Finally, 30 µL of ink was loaded onto a carbon paper to prepare a working electrode, mass loading was about 0.3 mg cm<sup>-2</sup>. And the WE was soaked in 25 mL of 0.1 M Na<sub>2</sub>SO<sub>4</sub> (Adamas) for 30 min to eliminate the contamination before the test. The electrochemical nitrogen reduction eaction test was performed in an H-type electrolytic cell was separated by Nafion 211 membrane. Before the test, The Nafion 211 membrane was pretreated in H<sub>2</sub>O<sub>2</sub> 5% aqueous solution at 80 °C for 1 h, ultrapure water at 80 °C for 1 h, 0.5 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 3 h and finally in ultrapure water at 80 °C for another 4 h. The feeding gas was flowed through the whole system for more than 30 min. All potentials were calibrated to the reversible hydrogen electrode (RHE) reference scale using E (vs. RHE) = E (vs. SCE) + 0.242 V + 0.0591 × pH. The potentiostatic tests were conducted in a N<sub>2</sub>-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> at different potentials.

**Determination of ammonia:** The concentration of produced  $NH_3$  in the electrolyte was determined by the Indophenol blue method.<sup>1</sup> The calibration curves were obtained by using different concentrations the standard  $NH_4Cl$  solution (Adamas) in 0.1 M  $Na_2SO_4$ . Typically, 2 mL of reaction electrolyte was mixed with 2 mL 1 M NaOH solution containing 5wt% salicylic acid and 5 wt% sodium citrate, 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt % sodium nitroferricyanide ( $C_5FeN_6Na_2O$ ) aqueous solution. After standing at room temperature in the dark for 2 h to form indophenol blue. The absorbance of the solution at 650 nm was measured by UV-Vis absorption spectroscopy.

**Determination of hydrazine hydrate:** The concentration of hydrazine hydrate in electrolyte was estimated by the method of Watt and Chrisp.<sup>2</sup> The calibration curves were obtained by using the different concentrations standard  $N_2H_4$  solution in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. A mixture of para-(dimethylamino) benzaldehyde (5.99 g) with 30 mL concentrated HCl (Sigma-Aldrich) and 300 mL was used as a color reagent. In brief, 2 mL electrolyte after the electrocatalytic reaction was mixed 2 mL color reagent and kept for 30 min at room temperature before measurement. Finally, the absorbance of the resulting solutions was measured at 455 nm. <sup>15</sup>N<sub>2</sub> isotope labeling experiments<sup>3</sup>: <sup>15</sup>N<sub>2</sub> gas (Wuhan Newradar Special Gas Co. Ltd 99 atom% <sup>15</sup>N) was served as feeding gas for isotope labeling experiments in order to clarify the source of ammonia. <sup>15</sup>N<sub>2</sub> passes through 0.05 M H<sub>2</sub>SO<sub>4</sub> and deionized water to remove possible impurities in the gas and then enters the cathode electrolytic cell. The electrochemical reactor is sealed, degassed and filled with Ar 3 times, and then filled with <sup>15</sup>N<sub>2</sub> gas. The reactions were carried out at -0.4 V vs. RHE in 0.1 M Na<sub>2</sub>SO<sub>4</sub>, and the nitrogen flow rate was maintained at 5 ml/min. After the reaction, 0.9 ml of the concentrated electrolyte was taken out and mixed with 0.1 ml of D<sub>2</sub>O for the <sup>1</sup>H nuclear magnetic resonance (NMR) (Bruker DRX 600 MHz) measurement to identify the produced <sup>15</sup>NH<sub>4</sub><sup>+</sup>.

**Calculations of NH<sub>3</sub> yield and FE:** The Faradaic efficiency for NRR was defined as the amount of electric charge used for synthesizing  $NH_3$  divided the total charge passed through the electrodes during the electrolysis. The total amount of  $NH_3$  was measured using colorimetric methods. The Faradaic efficiency and mass-normalized yield rate of  $NH_3$  was calculated as follows:

$$FE(NH_3, C mol^{-1}) = [3F \times c(NH_3) \times V]/Q$$
  
Yield Rate<sub>mass</sub>  $(NH_3, \mu g h^{-1} mg_{cat.}^{-1}) = [17 \times c(NH_3) \times V]/(t \times m)$ 

where F is the Faraday constant (96485 C mol<sup>-1</sup>), t is the electrolysis time, m is the loading mass of the catalyst, Q is the total charge passed through the electrode, V is the volume of the electrolyte and  $c(NH_3)$  is the measured ammonia concentration.

#### **DFT** calculation details

The DFT was employed as implemented in the Vienna Ab initio simulation package (VASP) for calculations.<sup>4-6</sup> The exchange-correlation potential is calculated by the generalized gradient approximation in Perdew-Burke-Ernzerhof (GGA-PBE). The projector augmented-wave (PAW) method is used to analyse interactions between ion cores and valence electrons and ion cores. The plane-wave cutoff energy was set to 500 eV. The structures were relaxed when the Hellmann–Feynman forces and the change in energy lower than -0.02 eV/Å and 10<sup>-5</sup> eV. During the calculation, the Brillouin zone was demonstrated by a  $\Gamma$  centered k-point of 2×2×1. A vacuum layer with 20 Å was used to eliminate the spurious interlayer interaction. The

free energy ( $\Delta G$ ) calculations of each step were based on the standard hydrogen electrode model, which can be obtained as:  $\Delta G = \Delta E + \Delta EZPE - T\Delta S - neU$ , where  $\Delta E$  and  $\Delta S$  are the reaction energy and entropy change;  $\Delta EZPE$  is the difference in zero point energy between the adsorbed and the gas; U is the applied bias and n is the electron transfer number in the reaction (U = 0 V for free energies diagrams).

Electrocatalysts		C <sub>s</sub> (mg L <sup>-1</sup> )	C <sub>Mo</sub> (mg L <sup>-1</sup> )	Atomic ratio of S/Mo
Commercial MoS <sub>2</sub>	MoS <sub>2</sub> -H	4.346	6.519	2:1
(MoS <sub>2</sub> -Na, reaction 2 min)	MoS <sub>1.92</sub> -H/T	5.105	7.977	1.92:1
(MoS <sub>2</sub> -Na, reaction 5 min)	MoS <sub>1.85</sub> -H/T	3.774	6.121	1.85:1
(MoS <sub>2</sub> -Na, reaction 10 min)	MoS <sub>1.79</sub> -H/T	4.676	7.837	1.79:1
(MoS <sub>2</sub> -Na, reaction 20 min)	MoS <sub>1.66</sub> -H/T	3.998	7.225	1.66:1
(MoS <sub>2</sub> -Na, reaction 30 min)	MoS <sub>1.59</sub> -H/T	4.797	9.051	1.59:1

**Table S1.** ICP-AES data and the atom ratio of Mo/S of different  $MoS_x$  samples.



Figure S1. TEM image of the commercial bulk  $MoS_2$  powder.



Figure S2. N<sub>2</sub> adsorption/desorption and the comparison of BET surface areas of different samples.



Figure S3. CVs of (a)  $MoS_2$ -H and (b)  $MoS_{1.79}$ -H/T samples.



Figure S4. EIS comparison for the different MoS<sub>2</sub>-based catalysts in terms of Nyquist plots.



Figure S5. Schematic and photograph of H-type electrochemical setup.



**Figure S6.**  $NH_3$  quantification using indophenol blue method. (a) Optical images and (b) UV-vis spectra of indophenol assays with  $NH_4^+$  ions. (b) Calibration curve for the estimation of  $NH_4Cl$ .



Figure S7. Chronoamperometric curves at different electrode potentials (vs. RHE) for 1 h.



**Figure S8.** Optical images of the  $0.1 \text{ M Na}_2\text{SO}_4$  electrolyte detected using indophenol blue method after a 1 h NRR test at at varied potentials and the corresponding UV-vis absorption spectra of electrolytes after the nitrogen reduction test.



Figure S9. UV-Vis spectra of electrolyte before and after nitrogen reduction for colorimetric  $N_2H_4$  assay using Watt and Chrisp method.



**Figure S10.** (a) ECSA normalized LSV curves and (b) comparison of ammonia yield rate of different  $MoS_x$  samples at -0.4 V vs RHE.



**Figure S11.** Durability of the  $MoS_{1.79}$ -H/T catalyst as revealed from the relationship between ammonia content and electrolysis duration for 30 h (at -0.4 V vs RHE).



**Figure S12.** The top and front view of the 2H-MoS<sub>2</sub> with and without NRR intermediates adsorbed along the bridge enzymatic-alternating-hybrid pathway and corresponding Gibbs free energies calculation.



**Figure S13.** The top and front view of the 1T-MoS<sub>2</sub> with and without NRR intermediates adsorbed along the bridge enzymatic-alternating-hybrid pathway and corresponding Gibbs free energies calculation.

## References

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