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Electronic Supplementary Information

Experimental Section

Materials: Mo powder (99.9%), and hydrogen peroxide (30%) were purchased from Sigma Aldrich (UK). Ethanol was purchased from Beijing Chemical Corp. Nafion (5 wt%) were purchased from Sigma-Aldrich. All chemical regents were used as received without further purification. Deionized water was made by the Millipore system and used in all experiments.

Synthesis of MoO₃ nanosheet: a solution was obtained by dissolving 0.24 g molybdenum metal powder and 3.4 g 30% H_2O_2 aqueous solution in 30 ml anhydrous ethanol solvent, which was magnetically stirred for about 1 hour. The solution turned from dark green to yellow during the stirring process and was subsequently transferred into the Teflon vessel (50 ml), which was then sealed in stainless steel autoclave. The autoclave was heated to a certain temperature ranging from 140–180°C for 20 hour. After the autoclave cooled to room temperature, the supernatant was discarded and the residual product in the bottom of Teflon vessel was collected by centrifugation, rinsed with ethanol several times and dried at 60°C in a vacuum.

Preparation of working electrode: GCE (3 mm diameter) was first polished with 0.5, 0.1 and 0.03 mm alumina slurries, followed by rinsing with copious amounts of water. Then the electrode was further cleaned via brief sonication with ethanol and water. To prepare the working electrode, 5 mg of the catalyst and 10 μ L 5 wt% Nafion solution were dispersed in 990 μ L water/ethanol (V:V = 1:1) followed by 30 min sonication to form a catalyst ink. 14 μ L of the catalyst suspension was loaded onto a GCE (mass loading 1.0 mg cm⁻²) and dried at room temperature.

Characterizations: XRD data were collected on a Rigaku X-ray diffractometer equipped with a Cu Ka radiation source. XPS data were collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. SEM measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. e). In order to reduce the influence of ferromagnetic materials on scanning electron microscopy and to make the sample acquire conductive property, it is necessary to spray Pt on sample for 20 min. TEM measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. A gas chromatograph (SHIMADZU, GC-2014C) equipped with MolSieve 5A column and Ar carrier gas was used for H₂ quantifications. Gas-phase product was sampled every 1000 s using a gas-tight syringe (Hamilton). ¹H NMR spectra were collected on a superconducting-magnet NMR spectrometer (Bruker AVANCE III HD 500 MHz) and dimethyl sulphoxide was used as an internal to calibrate the chemical shifts in the spectra.

Electrocatalytic measurements: The N_2 reduction experiments were carried out in a twocompartment cell under ambient condition, which was separated by Nafion 211 membrane. The membrane was protonated by first boiling in ultrapure water for 1 h and treating in H_2O_2 (5%) aqueous solution at 80 °C for another 1 h, respectively. And then, the membrane was treated in 0.5 M H_2SO_4 for 3 h at 80 °C and finally in water for 6 h. The electrochemical experiments were carried out with an electrochemical workstation (CHI 660E) using a three-electrode configuration with prepared electrodes, graphite rod and Ag/AgCl electrode (saturated KCl electrolyte) as working electrode, counter electrode and reference electrode, respectively. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.256 V and the presented current density was normalized to the geometric surface area. For electrochemical N₂ reduction, chrono-amperometry tests were conducted in N₂-saturated 0.1 M HCl solution.

Determination of NH₃: Concentration of produced NH₃ was spectrophotometrically determined by the indophenol blue method.¹ Typically, 2 mL HCl electrolyte was taken from the cathodic chamber, and then 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. Subsequently, 1 mL of 0.05 M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were add into the above solution. After standing at room temperature for 2 h, the UV-Vis absorption absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH₄Cl solution with a serious of concentrations. The concentration-absorbance curve used for estimation of NH₃ was calibrated using standard NH₄Cl solution with NH₄⁺ concentration with NH₄⁺ concentration by five times independent calibrations.

Determination of N₂H₄: The N₂H₄ in the electrolyte was estimated by the method of Watt and Chrisp. A mixture of $p-C_9H_{11}NO$ (5.99 g), HCI (concentrated, 30 mL) and C₂H₅OH (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent and stirring 10 min at room temperature. The absorbance of the resulting solution was measured at 455 nm.

Determination of FE: The FE for N_2 reduction 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 produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH_3 molecule, the FE could be calculated as follows:

$$FE = \frac{3F \times [NH_3] \times V}{17 \times Q}$$

The rate of NH₃ formation was calculated using the following equation:

$$v_{NH_3} = \frac{[NH_3] \times V}{t \times m_{cat.}}$$

Where F is the Faraday constant, $[NH_3]$ is the measured NH_3 concentration, V is the volume of the HCl electrolyte for NH_3 collection, t is the reduction time and mcat. is the catalyst mass.

Calculation details: Spin-polarized first-principles calculations based on the Density Functional Theory (DFT) were performed using the Vienna Ab initio Simulation Package (VASP).²⁻⁴ The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁵ within the generalized gradient approximation (GGA) was used to describe the exchange-correlation energy. The projector-augmented-wave (PAW)⁶ method was adopted for the pseudopotentials. The energy cutoff for the plane wave basis expansion was set to 450 eV. The force on each atom smaller than 0.02 eV/Å was set for convergence criterion. In order to investigate the N₂ Reduction Reaction (NRR) on the MoO₃ (011) surface, a 2×1×1 supercell was built with a vacuum layer of 20 Å. The sampling in the Brillouin zone was performed with 3×3×1 by the Monkhorst-Pack⁷ method. The free energies of the NRR reaction steps were calculated using the equation, ${}^8\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S$, where ΔE_{DFT} is the DFT calculated binding energy, the difference in zero-point energy correction ΔE_{ZPE} was obtained by vibration analysis, and the T ΔS term is gotten from the database (Computational Chemistry Comparison and Benchmark Database. http://cccbdb.nis.gov/).



Fig. S1. EDX spectrum of MoO₃.



Fig. S2. Schematic diagram to sillustrate the electrochemical setup for NRR test.



Fig. S3. (a) UV-Vis absorption spectra of indophenol assays with NH_{4^+} ions after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_{4^+} (Error bar = SD, n=5).



Fig. S4. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator before and after electrolysis at a series of potentials for 2 h and other conditions.



Fig. S5. UV-Vis spectra of the electrolyte stained with indophenol indicator before and after 2 h electrolysis at open circuit conditions.



Fig. S6. UV-Vis spectra of the electrolyte stained with indophenol indicator before and after 2 h electrolysis at the potential of -0.40 V under Ar atmosphere on the MoO₃/GCE electrode.



Fig. S7. Amount of NH₃ generated for MoO₃/GCE under different conditions.



Fig. S8. ¹H NMR spectra of ¹⁵NH₄⁺ calibration solution and after electrolysis at the potential of -0.40 V under ¹⁵N₂ atmosphere on the MoO₃/GCE electrode.



Fig. S9. UV-Vis spectra of the electrolyte stained with indophenol indicator before and after electrolysis in N_2 atmosphere at the potential of -0.40 V using bare GCE and MoO₃/GCE as the working electrode, respectively.



Fig. S10. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt-Chrisp before and after 2 h electrolysis in N_2 atmosphere at -0.40 V at room temperature.



Fig. S11. Chrono-amperometry curve at potential of -0.40 V using MoO₃/GCE.



Fig. S12. NH₃ yield rates after charging at -0.40 V for 2 h (Initial) and 24 h.

Table S1. Comparison of the electrocatalytic N_2 reduction performance for MoO_3/GCE with other aqueous-based NRR electrocatalysts under ambient conditions.

Catalyst	Electrolyte	$V_{ m NH3}$	FE (%)	Ref.
MoO ₃	0.1 M HCl	$\frac{29.43 \ \mu g \ h^{-1} \ mg^{-1}{}_{cat.}}{4.80 \times 10^{-10} \ mol \ s^{-1} \ cm^{-2}}$	1.9	This work
MoS ₂ /CC	0.1 M HCl	$8.08 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	1.17	9
Mo nanofilm	0.01 M H ₂ SO ₄	$3.09 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	0.72	10
Pd/C	0.1 M PBS	4.5 μ g h ⁻¹ mg ⁻¹ _{cat.}	8.2%	11
Ru/C	Solid Polymer electrolyte	$3.44 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2}$	0.28	12
Au nanorods	0.1 M KOH	$6.042 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	4	13
α-Au/CeO _x -RGO	0.1 M HCl	8.31 μ g h ⁻¹ mg ⁻¹ _{cat.}	10.1	14
TA-reduced Au/TiO ₂	0.1 M HCl	21.4 μ g h ⁻¹ mg ⁻¹ _{cat.}	8.11	15
Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	23.21 μ g h ⁻¹ mg _{cat.} ⁻¹	10.16	16
Fe ₂ O ₃ -CNT	KHCO ₃	$3.58 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2}$	0.15	17
NPC	0.1 M HCl	23.8 μ g h ⁻¹ mg ⁻¹ _{cat.}	1.42	18

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