Supporting Information

Mo-doped FeP Nanospheres for Artificial Nitrogen Fixation

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Reference.

Experimental section

Materials Iron (II) sulfate heptahydrate (FeSO₄·7H₂O), 2-methylimidazole (2-MIM), polyvinylpyrrolidone (PVP), sodium molybdate dehydrate (Na₂MoO₄), sodium hypophosphite monohydrate (NaH₂PO₂), sodium citrate (C₆H₅Na₃O₇), sodium hydroxide (NaOH), salicylic acid (C₇H₆O₃), methanol, sodium hypochlorite (NaClO), pare-(dimethylamino) benzaldehyde (C₉H₁₁NO), hydrochloric acid (HCl), hydrazine (N₂H₄), and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd (China). Sodium nitroferricyanide (C₅FeN₆Na₂O) and Nafion 211 membrane were provided by Sigma-Aldrich. Ammonium chloride-¹⁵N (¹⁵NH₄Cl) were purchased from Aladdin Ltd. Dimethyl Sulfoxide-D6 (DMSO-*d*₆, 99.9%) was purchased from Adamas Reagent, Ltd. All reagents were analytical reagent grades and used as received without further purification. Ultrapure water used through all experiments was purified through a Millipore system.

Preparation of Fe-ZIF The iron-based metal-organic framework (Fe-ZIF) was prepared according to the previous report with some modifications.¹ In a typical process, a methanolic solution (25 mL) of 2-MIM (328 mg) and PVP (K-30, 0.3 g) was added into a methanolic solution (25 mL) of $FeSO_4 \cdot 7H_2O$ (278 mg) drop by drop slowly. The whole reaction process was kept at room temperature with agitated stirring. After being stirred for 5 min, the resulting mixture was aged at room temperature without any interruption for 24 h. The obtained solids were washed with methanol for five times and finally dried under oven at 60 °C for 12 h.

Preparation of Fe-Mo intermediates A 40 mg of Fe-ZIF was added into an ethanol/water solution (1:4 in volume, 100 mL) containing Na_2MoO_4 (0.2 g). After reaction at 85 °C for 60 min, the product was collected by centrifugation, washed with ethanol and water repeatedly, and dried at 60 °C over night.

Preparation of Mo-FeP Typically, the as-prepared Fe-Mo intermediates and NaH_2PO_2 with a mass ratio of 1:10 were placed in different porcelain boats, which were put into a tube furnace with NaH_2PO_2 at the upstream side. The tube furnace was flushed with Ar, then heated up to 350 °C with a heating rate of 2 °C/min, and kept for 2 h. After phosphorization, the resulting catalyst was collected after the furnace

was cooled to room temperature under an Ar atmosphere.

Preparation of working electrode A 5 mg of catalyst and 20 μ L of Nafion solution (5 wt %) were dispersed in 980 μ L mixed solution containing 700 μ L ethanol and 280 μ L water by 1 h sonication to form a homogeneous ink. Then, 20 μ L catalyst ink was loaded on a carbon paper (CP) with area of 1×1 cm² and dried under vacuum condition, the catalyst loading mass was 0.1 mg cm⁻².

Characterizations The X-ray diffraction analysis (XRD) was performed on a Bruker D8 Advance X-ray diffractometer with Cu K α (α = 1.5405 Å) radiation. The size and morphology of nanomaterials were observed on a transmission electron microscope (TEM, JEM-2010, JEOL) and a scanning electron microscope (SEM, Quanta 200). X-ray photoelectron spectroscopy (XPS) characterizations were measured on a VG Multilab 2000X instrument (Thermal Electron, USA). Fourier transform infrared spectra (FT-IR) were collected on a FT-IR spectrometer (ALPHA, Bruker). The absorbance data of spectrophotometer were measured on an UV-2450 spectrophotometer (Shimadzu, Japan).

Electrochemical measurement The reduction of N₂ gas (99.99%) was carried out in a two-compartment cell under ambient condition, which was separated by a Nafion 211 membrane. Prior to the NRR experiments, the membrane was protonated by first boiling in ultrapure water for 1 h, then treating in H₂O₂ (5%) aqueous solution at 80 °C. Finally, the membrane was treated in 0.5 M H₂SO₄ at 80 °C for 3 h and in water for 6 h. All electrochemical measurements were performed at room temperature using an Iviumstat electrochemical workstation (Eco Chemie, Netherlands) in a standard three-electrode electrochemical system with Mo-FeP coated carbon paper as working electrode, Ag/AgCl (saturated KCl electrolyte) as reference electrode and a graphite rod as counter electrode. All potentials are referenced to the reversible hydrogen electrode (RHE) according to Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.256 \text{ V}$. For NRR test, the cathode chamber was first purged with N₂ for 30 min before measurement to form N₂-saturated solution, then conducted in 0.1 M HCl with continuous N₂ bubbling. The volume of the electrolyte in the anode and cathode chambers was 40 mL for each. **Determination of NH**₄⁺ The concentration of the produced NH₄⁺ during NRR was determined by the indophenol blue method.² Typically, 2 mL HCl electrolyte was taken from the cathodic chamber, and then 2 mL of 1 M NaOH solution containing 5 wt % C₇H₆O₃ and 5 wt % C₆H₅Na₃O₇ were added into this solution. Subsequently, 1 mL 0.05 M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were added into the above solution in turn. Absorbance measurements were performed after 2 h at λ = 655 nm. The concentration-absorbance curves were calibrated using the standard NH₄Cl solution with a series of NH₄⁺ concentrations (0~0.3 µg mL⁻¹). The fitting curve (Figure S3, y = 0.343x + 0.008, R² = 0.998) shows good linear relation of the absorbance value with NH₄⁺ concentration by three times independent calibrations.

Determination of N₂H₄ The concentration of N₂H₄ in the electrolyte was determined by the method proposed by Watt and Chrisp.³ In detail, the p-C₉H₁₁NO (5.99 g), concentrated HCl (30 mL), and C₂H₅OH (300 mL) were mixed and the resulting mixture was used as a color reagent. Then, 5 mL electrolyte after electrolysis was added into 5 mL prepared color reagent with stirring at room temperature for 20 min. The absorbance of the resulting solution was measured by an UV-vis spectrophotometer at a wavelength of 455 nm. The concentration-absorbance curve was calibrated using standard N₂H₄ solutions with a series of concentrations (0~0.6 μ g mL⁻¹). The fitting curve (Figure S4, y = 0.893x + 0.025, R² = 0.999) shows good linear relation of the absorbance value with N₂H₄ concentration by three times independent calibrations.

¹⁵N isotopic labeling experiment ¹⁵N₂ (Sigma-Aldrich, 98 atom % ¹⁵N₂) was used as the feeding gas to perform the isotopic labeling experiment in 0.1 M HCl electrolyte. Before the measurement, the gas purified by subsequently passing through 1 mM H₂SO₄ solution and an ultrapure water trap to remove NO_x and NH₃ contamination in the gas.⁴ Purified Ar was first passed through the cathode chamber for 30 min to remove ¹⁴N₂ present in the system. Afterwards, the reactor was filled with ¹⁵N₂. After electrochemical reduction reaction at –0.3 V (vs. RHE) for 6 h with a ¹⁵N₂ gas flow rate of 0.5 mL/min, the electrolyte was taken out and a known quantity of DMSO-*d*₆ was added. The ammonia produced was quantified by 1H nuclear magnetic resonance (NMR) on a Bruker Avance III 600 MHz spectrometer.

Calculation of NH_4^+ yield and Faradaic efficiency (FE) NH_4^+ yield rate is calculated using the following equation:

$$\nu_{NH_4^+} = \frac{c_{NH_4^+} \times V}{t \times m_{cat}} \tag{S-1}$$

Assuming three electrons were needed to produce one NH_4^+ molecule, the FE could be calculated as follows:

$$FE = \frac{3 \times F \times c_{NH_4^+} \times V}{18 \times Q}$$
(S-2)

where $c_{NH_4^+}$ is the measured NH₄⁺ concentration, V is the volume of the cathodic reaction for NH₄⁺ collection, t is the reduction reaction time (2 h), m_{cat} is the loaded mass of catalyst, F is the Faraday constant, and Q is the quantity of applied electricity.



Figure S1. (A) IR spectra of (a) the 2-methylimidazolate linker and (b) the resulting Fe-ZIF precursor. (B) XRD pattern of the as-prepared Fe-ZIF precursor.



Figure S2. XPS survey spectra of (A) Mo-FeP and (B) FeP.



Figure 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^+ ion concentrations.



Figure S4. (A) UV-vis curves of various concentrations of N_2H_4 stained with p-C₉H₁₁NO indicator and incubated for 40 min at room temperature. (B) A calibration curve used to calculate the concentrations of N_2H_4 .



Figure S5. NH_4^+ yield rates of Mo-FeP with different amount of Na_2MoO_4 added.



Figure S6. (A) UV-vis absorption spectra of HCl electrolyte stained with indophenol indicator after electrolysis at -0.3 V for different interval times. (B) The corresponding curve of NH₄⁺ amounts vs reaction time at -0.3 V.



Figure S7. 1H NMR spectra of the standard samples of ${}^{14}NH_4^+$, ${}^{15}NH_4^+$ and the post-electrolysis electrolytes with ${}^{14}N_2$, ${}^{15}N_2$ and Ar as the feeding gas.



Figure S8. (A) 1H NMR spectra of ${}^{15}\text{NH}_4^+$ standard samples with different concentrations. (B) Calibration curve for ${}^{15}\text{NH}_4^+$ concentrations *vs.* NMR signal integration values of standard samples. The star represents the concentration of ${}^{15}\text{NH}_4^+$ in the electrolyte after 6 h electrochemical reduction reaction at -0.3 V. According to the calibration curve, the concentration of ${}^{15}\text{NH}_4^+$ can be determined to be 13.5 μ M. This value is very close to the value measured by the indophenol blue method (13.34 μ M).



Figure S9. (A) Chronoamperometry curve at -0.3 V in N₂-saturated 0.1 M HCl. (B) Corresponding UV-vis absorption spectrum of the electrolyte stained with indophenol indicator after electrolysis.



Figure S10. UV-vis absorption spectra of 0.1 M HCl electrolyte stained with indophenol indicator after cycling stability test at -0.3 V for 2 h.



Figure S11. XRD spectrum of Mo-FeP after durability test.



Figure S12. SEM and TEM spectra of Mo-FeP after durability test.



Figure S13. XPS high resolution spectra of Mo-FeP and FeP in the P 2p region.

Catalyst	Electrolyte	FE/%	Yield	Ref.
Transition-metal based electrocatalysts				
Mo-FeP/CP	0.1 M HCl	7.49	13.1 μg h ⁻¹ mg ⁻¹	This work
			1.31 μg h ⁻¹ cm ⁻²	
CoP hollow nanocages	1.0 M KOH	7.36	10.78 μg h ⁻¹ mg ⁻¹	5
MoC/C	0.5 M Li ₂ SO ₄	7.8	11.3 μg h ⁻¹ mg ⁻¹	6
Mo nanofilm	0.01 M H ₂ SO ₄	0.72	1.89 μg h ⁻¹ cm ⁻²	7
Fe ₂ O ₃ -CNT	0.1 M KHCO ₃	0.03	0.22 μg h ⁻¹ cm ⁻²	8
Fe/Fe ₃ O ₄	0.1 M PBS pH7.2	8.29	0.19 μg h ⁻¹ cm ⁻²	9
WO ₃ (V _o)	0.1 M HCl	6.8	4.2 μg h ⁻¹ mg ⁻¹	10
Noble-metal based electrocatalysts				
Pd/C	0.1 M PBS	8.2	4.5 μg h ⁻¹ mg ⁻¹	11
Ag-Au@ZIF	THF-based electrolyte	18	0.61 μg h ⁻¹ cm ⁻²	12
Pd _{0.2} Cu _{0.8} /rGO	0.1 M KOH	4.5	2.8 μg h ⁻¹ mg ⁻¹	13
Metal-free electrocatalysts				
PCN-NVs	0.1 M HCl	11.59	8.09 μg h ⁻¹ mg ⁻¹	14
B ₄ C/CPE	0.1 M HCl	15.95	26.57 μg h ⁻¹ mg ⁻¹	15
Li+-PEBCD/C	0.5 M Li ₂ SO ₄	2.91	2.01 μg h ⁻¹ cm ⁻²	16

Table S1. Comparison of the electrocatalytic N_2 reduction performance for Mo-FeP nanospheres with other recently reported electrocatalysts under ambient conditions.

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