

## **Electronic Supplementary Information**

### **MoFe Nitrogenase-Mimic Electrocatalyst for Nitrogen Fixation with High Faradaic efficiency**

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## **Experimental section**

### **Preparation of MoO<sub>2</sub>/FeS<sub>2</sub>/GA:**

First, GO solution was prepared by dispersing 40 mg of GO powder in 20 mL of deionized water by ultrasonication. Next, 0.25 mmol Na<sub>2</sub>MoO<sub>4</sub>, 1.75 mmol FeCl<sub>3</sub> and 2.25 mmol Na<sub>2</sub>S were added to the above solution. Then, the mixture was vigorously stirred at room temperature for 1 h. The whole solution was transferred into a 40 mL Teflon-lined stainless-steel autoclave, and placed in an electric oven at 180°C for 12 h. After that, the autoclave was cooled down to room temperature naturally. A 3D MoO<sub>2</sub>/FeS<sub>2</sub>/GA was formed by the hydrothermal reaction. The MoO<sub>2</sub>/FeS<sub>2</sub>/GA product was collected and freeze-dried for further application. As a comparison, GA, MoO<sub>2</sub>/GA and FeS<sub>2</sub>/GA were also prepared by a similar procedure.

### **Preparation of GA-CP, MoO<sub>2</sub>/GA-CP, FeS<sub>2</sub>/GA-CP and MoO<sub>2</sub>/FeS<sub>2</sub>/GA-CP:**

Carbon paper (CP) was cleaned via brief sonication with ethanol and water for several times. 5 mg sample and 20 μL 5 wt% Nafion solution were dispersed in 960 μL water/ethanol (V : V = 1 : 3) followed by 1-h sonication to form a homogeneous ink. 20 μL ink was loaded onto a CP (1 × 1 cm<sup>2</sup>) and dried under ambient condition.

**Characterizations:** The XRD patterns were measured on a Bruker D2 PHASER diffractometer using Cu-Kα radiation ( $\lambda = 0.1542$  nm). The XPS was carried out by Thermo Scientific Escalab 250Xi. The SEM images were obtained with a Hitachi SU8010 scanning electron microscope (Japan). The TEM and HRTEM images were measured using a JEOL JEM-2100F transmission electron microscope operated at 200 kV. The absorbance signals of the system spectra were all gained from a Mapada UV 6300 spectrophotometer (Shanghai, China).

**Electrochemical measurements:** All the electrochemical experiments were conducted on an electrochemical workstation (CHI 760E) using MoO<sub>2</sub>/FeS<sub>2</sub>/GA-CP (GA-CP, MoO<sub>2</sub>/GA-CP or FeS<sub>2</sub>/GA-CP), Ag/AgCl electrode (saturated KCl electrolyte) and Pt foil as the working, reference and counter electrodes, respectively. The electrochemical NRR tests were performed using an H-cell system that was isolated by Nafion 211 membrane. For NRR experiments, the potentiostatic test was carried out at different potentials (−0.45 to −0.2 V) in the N<sub>2</sub>-saturated 0.1 M HCl

solution (40 mL). High-pure N<sub>2</sub> was successively introduced into the cathodic portion for 30 min before the measurement.

**Determination of NH<sub>3</sub>:** NH<sub>3</sub> concentration was detected by the indophenol blue method. In detail, 2 mL electrolyte was obtained from the cathodic chamber, and then 2 mL of 1 M NaOH solution (contains 5 wt% salicylic acid and 5 wt% sodium citrate) was added into this solution. Subsequently, 1 mL of 0.05 M sodium hypochlorite and 0.2 mL of sodium nitroferricyanide (1 wt%) were added into the above solution. After standing at room temperature for 2 h, the UV-vis absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH<sub>4</sub>Cl solution (0.1 M HCl solution as mother solution) with a series of concentrations. The fitting curve ( $y = 0.449x + 0.0381$ ,  $R^2 = 0.999$ ) shows good linear relation of absorbance value with NH<sub>3</sub> concentration by three times independent calibrations.

**Determination of N<sub>2</sub>H<sub>4</sub>:** The N<sub>2</sub>H<sub>4</sub> present in the electrolyte was determined by the method of Watt and Chrisp. The mixture of C<sub>9</sub>H<sub>11</sub>NO (5.99 g), HCl (30 mL), and C<sub>2</sub>H<sub>5</sub>OH (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. Moreover, the absorbance of the resulting solution was measured at a wavelength of 460 nm. The concentration absorbance curves were calibrated using standard N<sub>2</sub>H<sub>4</sub> solution with a series of concentrations. The fitting curve ( $y = 0.522x + 0.064$ ,  $R^2 = 0.999$ ) shows good linear relation of absorbance value with N<sub>2</sub>H<sub>4</sub> concentration.

**Calculations of NH<sub>3</sub> yield and FE:** NH<sub>3</sub> yield was calculated using the following equation:

$$\text{NH}_3 \text{ yield} = [\text{NH}_4^+] \times V / (m_{\text{cat.}} \times t)$$

FE was calculated according to following equation:

$$\text{FE} = 3 \times F \times [\text{NH}_4^+] \times V / (17 \times Q)$$

Where [NH<sub>4</sub><sup>+</sup>] is the measured NH<sub>4</sub><sup>+</sup> concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; m<sub>cat.</sub> is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of charge in Coulombs.

**$^{15}\text{N}_2$  isotope labeling experiments:** An isotopic labeling experiment used  $^{15}\text{N}_2$  (99 atom %  $^{15}\text{N}$  purchased from Qingdao Dehai Weiye Technology Co., Ltd. CAS: 29817-79-6) as the feed gas. After the electrolytic reaction for 24 h at  $-0.25$  V, the obtained 40 mL electrolyte after NRR was concentrated to 4 mL. And then, the electrolyte was determined by  $^1\text{H}$  nuclear magnetic resonance (NMR, 600 MHz). Similarly, the standard curves were calibrated using standard  $^{15}\text{NH}_4\text{Cl}$  solution at concentrations of 1 mM in 0.1 M HCl. All NMR measurements were carried out with water suppression and 4000 scans.

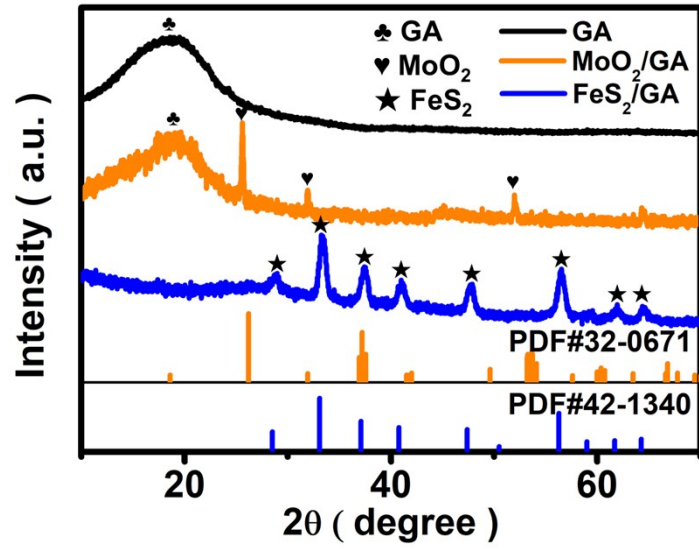
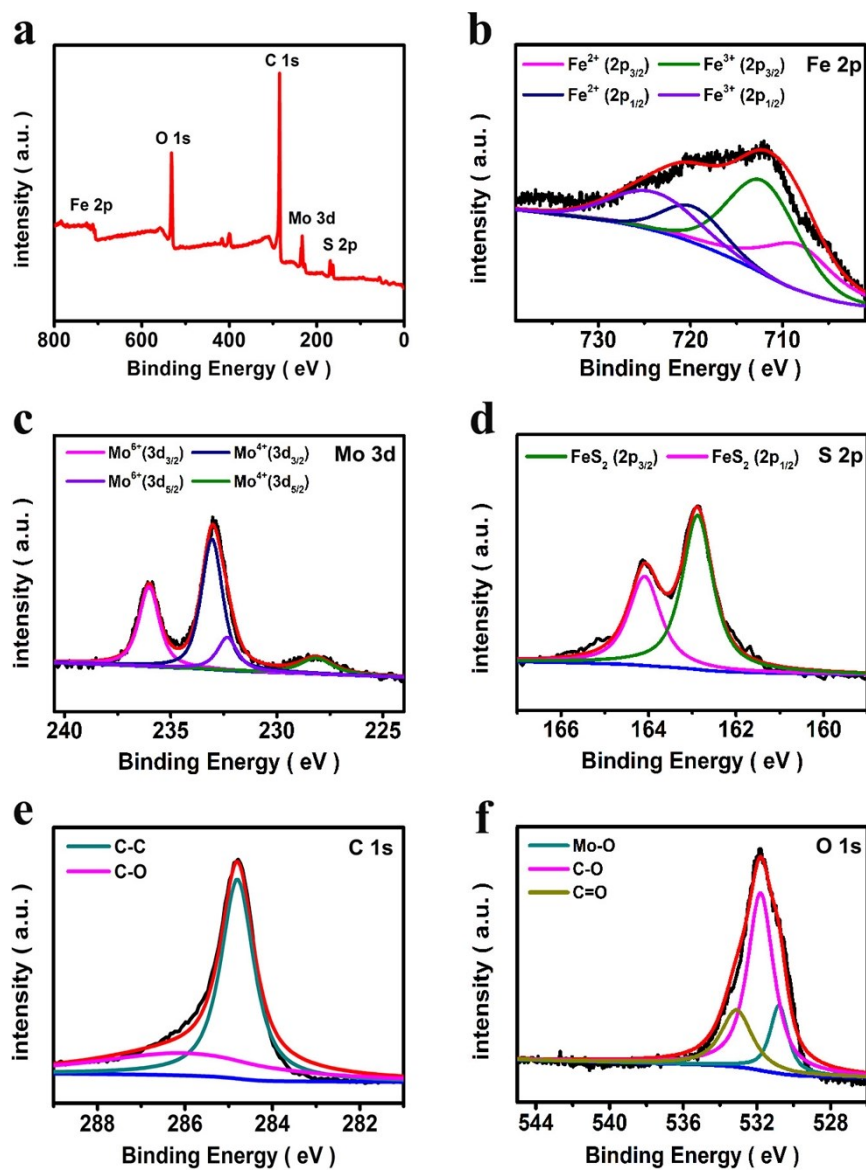
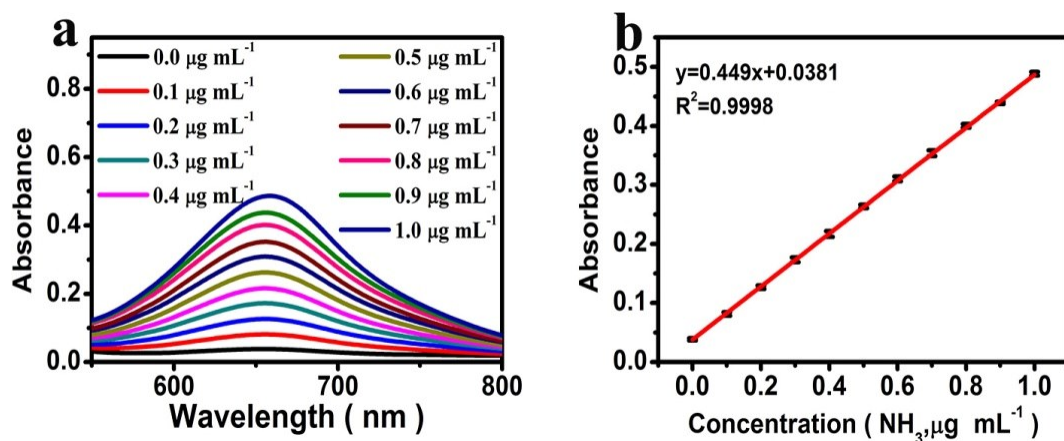


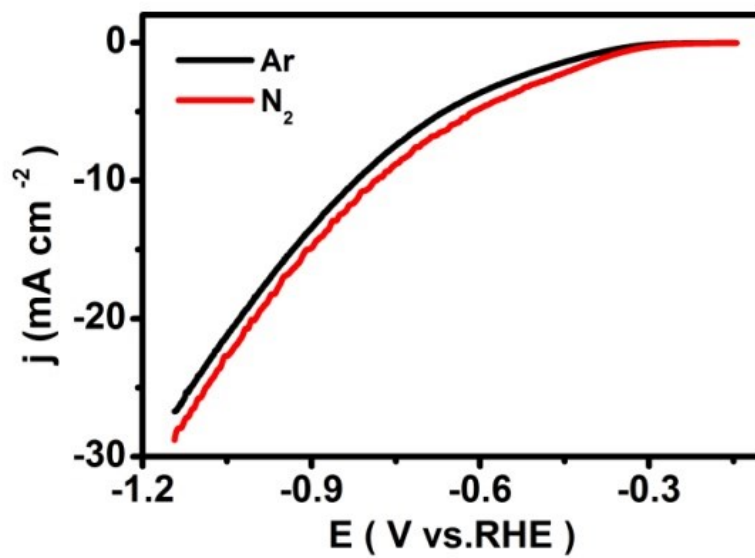
Fig. S1. (a) XRD pattern of GA、MoO<sub>2</sub>/GA and FeS<sub>2</sub>/GA.



**Fig. S2.** The survey XPS spectra (a) and the narrow scan spectra of (b) Fe 2p, (c) Mo 3d, (d) S 2p, (e) C 1s and (f) O 1s of MoO<sub>2</sub>/FeS<sub>2</sub>/GA.

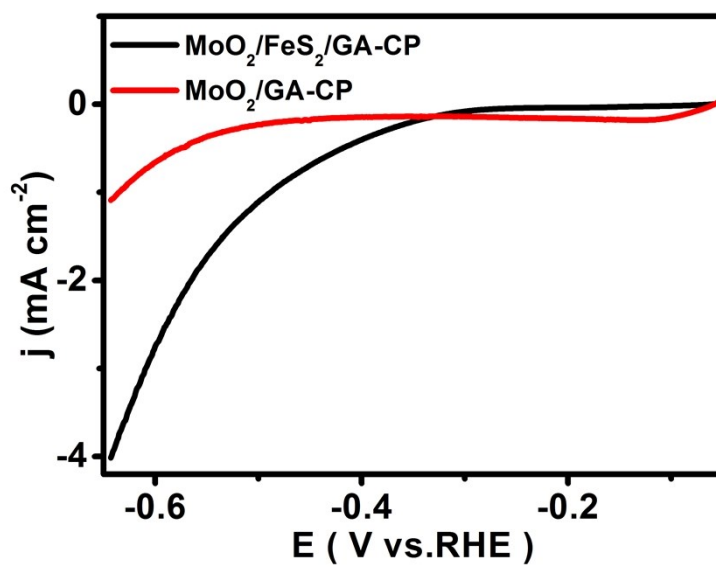


**Fig. S3.** (a) UV-vis absorption spectra of various  $\text{NH}_3$  concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of  $\text{NH}_3$  concentrations. (error bar=SD, n=3).

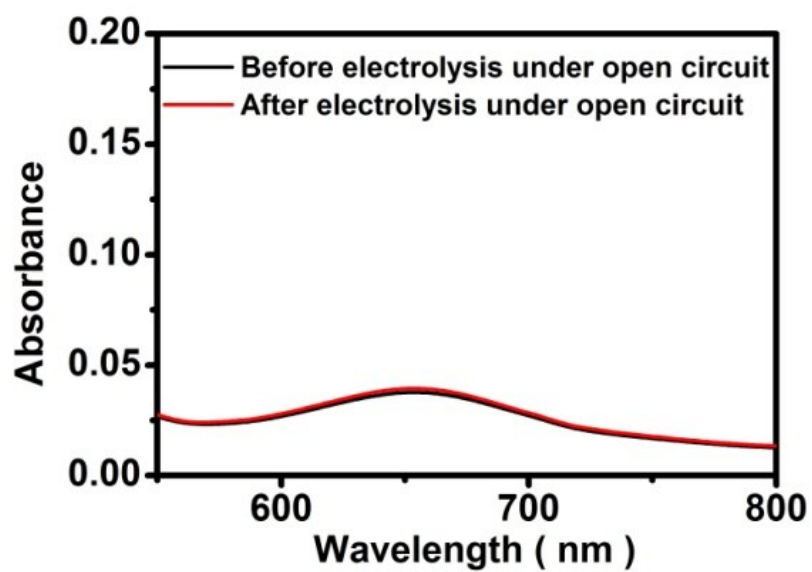


**Fig. S4.** LSV curves of MoO<sub>2</sub>/FeS<sub>2</sub>/GA-CP in Ar- and N<sub>2</sub>-saturated 0.1 M HCl.

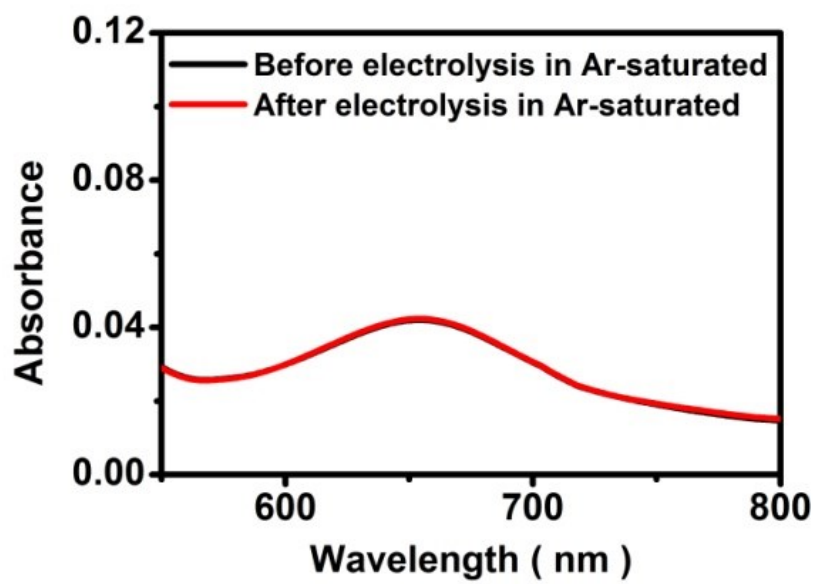




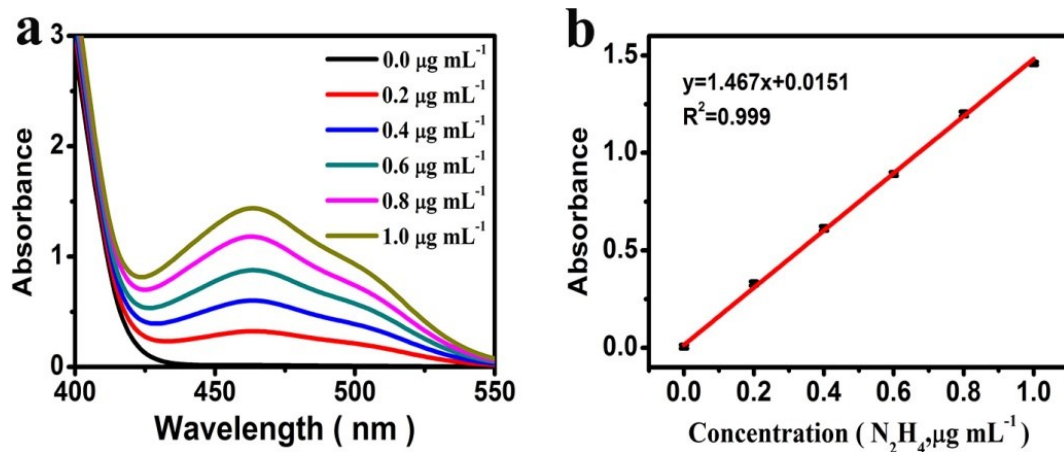
**Fig. S5.** LSV curves of  $\text{MoO}_2/\text{GA-CP}$  and  $\text{MoO}_2/\text{FeS}_2/\text{GA-CP}$  in  $\text{N}_2$ -saturated 0.1 M HCl.



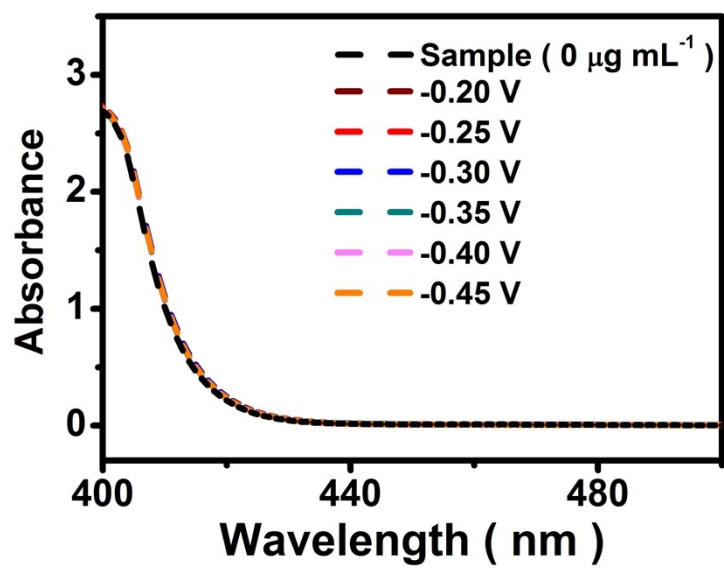
**Fig. S6.** UV-vis absorption spectra of the electrolytes stained with indicator before and after 2 h electrolysis under open circuit conditions.



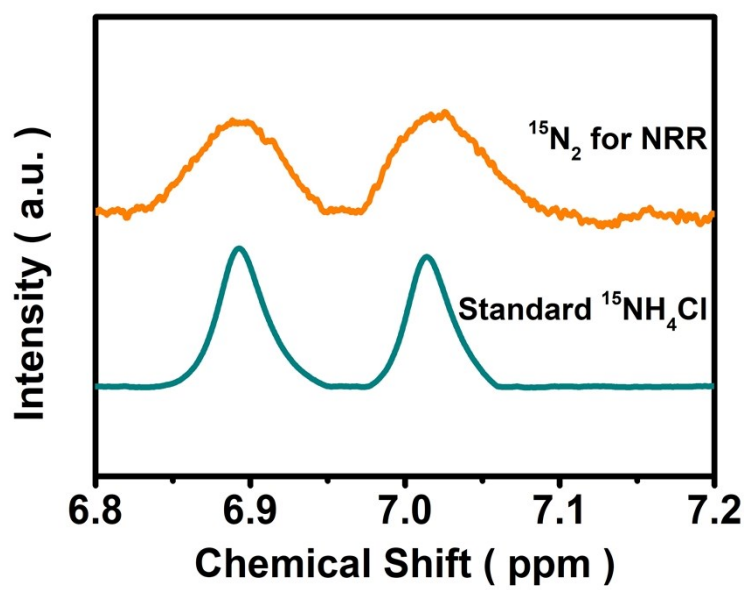
**Fig. S7.** UV-vis absorption spectra of the electrolyte stained with indicator before and after 2 h electrolysis at the potential of  $-0.25$  V under Ar-saturated solution.



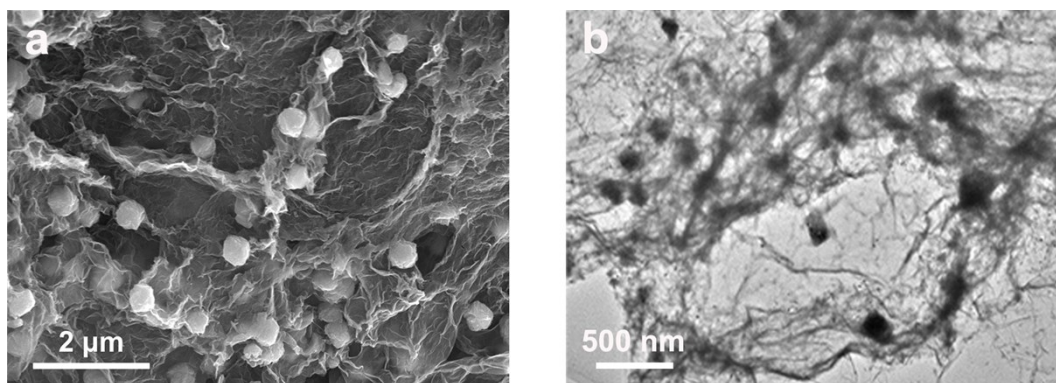
**Fig. S8.** (a) UV-vis absorption spectra of various  $N_2H_4$  concentrations after incubated for 20 min at room temperature. (b) Calibration curve used for calculation of  $N_2H_4$  concentrations. (error bar=SD, n=3).



**Fig. S9.** UV-vis absorption spectra of N<sub>2</sub>H<sub>4</sub> before and after 2 h electrolysis in N<sub>2</sub> atmosphere at different potential.



**Fig. S10.**  $^1\text{H}$  NMR spectra (600 M) of standard samples of  $^{15}\text{NH}_4^+$ , and the electrolyte produced from the NRR reaction using  $^{15}\text{N}_2$  as the isotopic  $\text{N}_2$  source.



**Fig. S11.** The SEM (a) and TEM (b) patterns for MoO<sub>2</sub>/FeS<sub>2</sub>/GA after stability test.

**Table S1.** Comparison of the NH<sub>3</sub> electrosynthesis activity for MoO<sub>2</sub>/FeS<sub>2</sub>/GA with other aqueous-based NRR electrocatalysts at ambient conditions.

Catalyst	Electrolyte	Potential (V) vs. RHE	NH <sub>3</sub> yield	FE(%)	Ref.
MoO <sub>2</sub> /FeS <sub>2</sub> /GA	0.1 M HCl	-0.25 V	40.18 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	37.44	This work
Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.6 V	18.16 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	9.1	1
Mo(IV) doped FeS <sub>2</sub>	0.1 M KOH	-0.2 V	25.15 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	14.41	2
FeS@MoS <sub>2</sub> /CFC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.5 V	6.34 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	2.96	3
Fe <sub>3</sub> S <sub>4</sub> nanosheets	0.1 M HCl	-0.4 V	75.4 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	6.45	4
OVs-MoO <sub>2</sub>	1.0 M KOH	-0.15 V	12.20 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	8.2	5
MoO <sub>3</sub>	0.1 M HCl		29.43 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub> (-0.5 V)	1.9 (-0.3 V)	6
MoS <sub>2</sub>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.4 V	29.28 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	8.34	7
Pd <sub>0.2</sub> Cu <sub>0.8</sub> /rGO	0.1 M KOH		2.8 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub> (-0.2 V)	- (0 V)	8
oxygen-doped carbon nanosheet	0.1 M HCl	-0.6 V	20.15 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	4.97	9
α-Au/CeO <sub>x</sub> -rGO	0.1 M HCl	-0.2 V	8.3 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	10.1	10
Au nanorods	0.1 M KOH	-0.2 V	6.04 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	4.02	11
γ-Fe <sub>2</sub> O <sub>3</sub>	0.1 M KOH	0 V	0.21 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	1.9	12
MnO	0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.39 V	7.92 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	8.02	13
Nb <sub>2</sub> O <sub>5</sub> nanofiber	0.1 M HCl	-0.55 V	43.6 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	9.26	14
MnO <sub>2</sub> -Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.1 M HCl	-0.55 V	34.12 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	11.39	15



R-WO <sub>3</sub> NSs	0.1 M HCl	-0.3 V	17.28 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	7	16
black P nanosheet	0.01 M HCl		31.37 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$ (-0.7 V)	5.07 (-0.6 V)	17
TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.1 M HCl		32.17 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$ (-0.55 V)	16.07 (-0.45 V)	18
$\beta$ -FeOOH nanorod	0.5 M LiClO <sub>4</sub>		23.32 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$ (-0.75 V)	6.7 (-0.7 V)	19
polymeric carbon nitride	0.1 M HCl	-0.2 V	8.09 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	11.59	20
Au/TiO <sub>2</sub>	0.1 M HCl	-0.2 V	21.4 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	8.11	21
Au flowers	0.1 M HCl	-0.2 V	25.7 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	6.05	22
S-doped carbon nanosphere	0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.7 V	19.07 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	7.47	23

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