

Supporting Information

NiFe₂O₄ nanoflowers with Mo doping for self-powered hydrogen production at large current density

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1. Material and Experimental Instruments

1.1 Materials used in the experiment

Pt/C (20 wt%) and oxalic acid was obtained from Macklin Ltd. (Shanghai, China). $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, urea, RuO_2 , KOH and $\text{Zn}(\text{OAc})_2$ were supplied by Beijing Chemical Reagents Company. Iron foam (IF) was gained from Guangjiayuan New Materials Co., Ltd. (Jiangsu, China).

1.2 Experimental Section

1.2.1 Preparation of the IF

Immerse the IF in 1.0 M oxalic acid solution for 10 minutes to remove the oxide layer. Remove surface reactants from the IF by ultrasonic treatment in deionized water and anhydrous ethanol for 15 seconds. At last, dry the treated IF at 60 °C vacuum for further use.

1.2.2 Preparation of the Mo-NiFe₂O₄/IF

First, dissolve 40 mmol $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 0.28 mmol $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 280 mmol urea into 50 ml deionized water under magnetic stirring at room temperature to form a light green solution; then, place IF (2 * 4 cm²) into the solution; later, poured the above solution and IF into a 100 ml Teflon-lined stainless-steel autoclave and maintained at 220 °C for 5 hours; last, washed the gained Mo-NiFe₂O₄/IF with deionized water and anhydrous ethanol for several times, dried at 60 °C for 12 hours. The loading capacity is approximately 3.23 mg cm⁻². Additionally, the molar ratio of Mo and Ni is about 1:10.

As for the comparison samples, we labeled the catalyst without adding $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as NiFe₂O₄/IF. Weighted Pt/C and RuO_2 with the same loading capacity as the Mo-NiFe₂O₄/IF and gained the RuO_2 /IF (OER), Pt/C/IF (HER) and Pt/C+ RuO_2 /SSM (OWS and air-cathode) as comparison samples.

1.2.3 Basic Phase Characterizations

X-ray diffraction (XRD) experiment was tested on a Rigaku D-Max 2550 diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) images were obtained on a JEOL-6700 scanning electron microscope. Transmission electron microscope (TEM), high resolution TEM

(HRTEM) images were obtained with microscopy of Philips-FEI Tecnai G2S-Twin, equipped with a field emission gun operating at 200 kV. X-ray photoelectron spectra (XPS) analysis was performed on a VG Scienta R3000 spectrometer with Al K α (1486.6 eV) as the X-ray source.

1.2.4 Electrochemical Measurements

Electrochemical measurements were conducted using the three-electrode system with the electrochemical workstation (CHI 760e). The as-prepared electrodes were directly used as the work electrodes; meanwhile, graphite rod and Hg/HgO electrode were served as counter and reference electrodes, respectively. 1.0 M KOH solution was used as electrolyte for OER. Potentials were normalized versus the standard hydrogen electrode (RHE) according to formula below :

$$E_{(RHE)} = E_{(Hg/HgO)} + 0.098 \text{ V} + 0.591 \text{ pH}$$

Here, “ $E_{(Hg/HgO)}$ ” was the potential we directly measured during the experiment. We applied the 1.0 M KOH throughout the OER and HER processes, thus, corresponding pH for OER and HER is 14.

Polarization curves were performed via sweeping potentials at a scan rate of 2.0 mV s⁻¹. Corresponding stabilities were examined through current-time curves at the constant potentials.

Tafel slope:

Tafel slope can be plotted by the gained linear sweep voltammetry (LSV) curves, which is obtained from the follow equation:

$$\eta = a + b \log j$$

Where, “ η ” refers to the overpotential; “ j ” is the current density; “ a ” relates to the exchange current density (j_0) and can be reflected by the intercept; “ b ” is the Tafel slope we need to acquire.

The electrochemical active surface area (ECSA) is calculated by the formula below:

$$ECSA = A * C_{dl} / C_s$$

Here “ A ” refers to the area of the working electrode, and we set the electrode area to 0.25 cm² throughout the electrocatalytic testing; “ C_s ” relates to the electrolyte and $C_s = 0.04 \text{ mF cm}^{-2}$, “ C_{dl} ” is the abbreviation of double layer capacitance and calculated

from a series of CV curves that tested within the non-Faraday potential range (0.9254 - 1.0254 V vs. RHE), scan rate changed from 10 to 100 mV s⁻¹, increased with 10 mV s⁻¹ each time.

1.2.5 Assembly and Testing of the Zn-Air Battery (ZAB)

As for the liquid ZAB, to avoid electrolyte leakage, we physically compounded the IF-based catalyst with the waterproof/breathable carbon film, and then assembled the complex as the air-cathode of the ZAB. The exposed cathode-area is 0.19625 cm² (diameter of the circle is 0.5 cm).

Both the charge and discharge curves were measured by the CHI 760e, the power density was calculated from the data of the discharge curve. Charge-discharge curves at current density of 10 mA cm⁻² in this work were measured by the Land battery test system.

3. Supplementary Figures and Tables

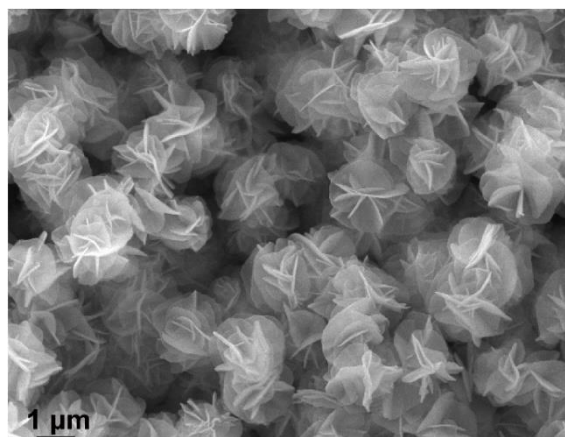


Fig. S1. SEM image of the pure NiFe₂O₄/IF.

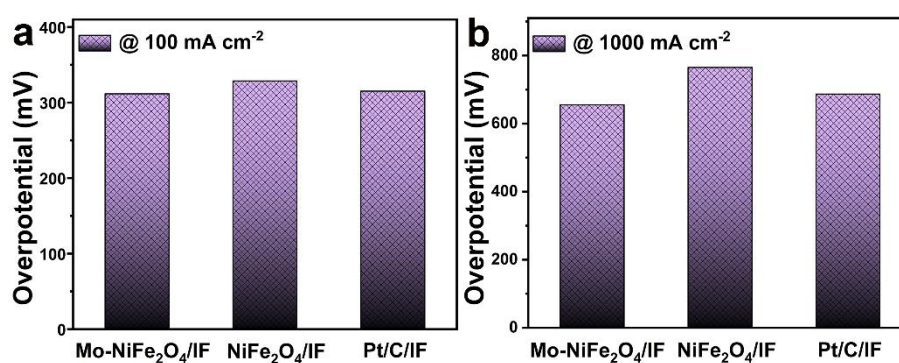


Fig. S2. The bar graphs of Mo-NiFe₂O₄/IF, NiFe₂O₄/IF and commercial ones that between overpotential and current density at (a) 100 and (b) 1000 mA cm⁻², respectively.

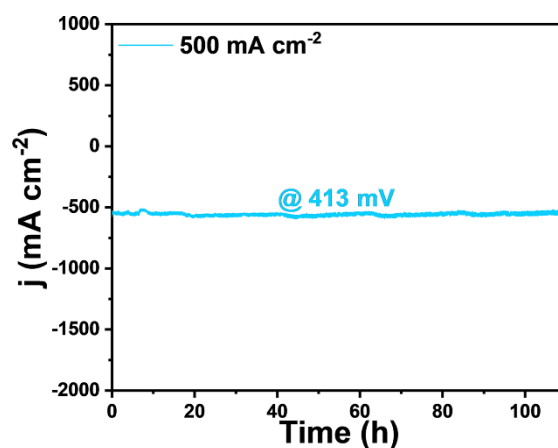


Fig. S3. The i-t behavior of Mo-NiFe₂O₄/IF during the HER process when the provided overpotential is 413.2 mV.

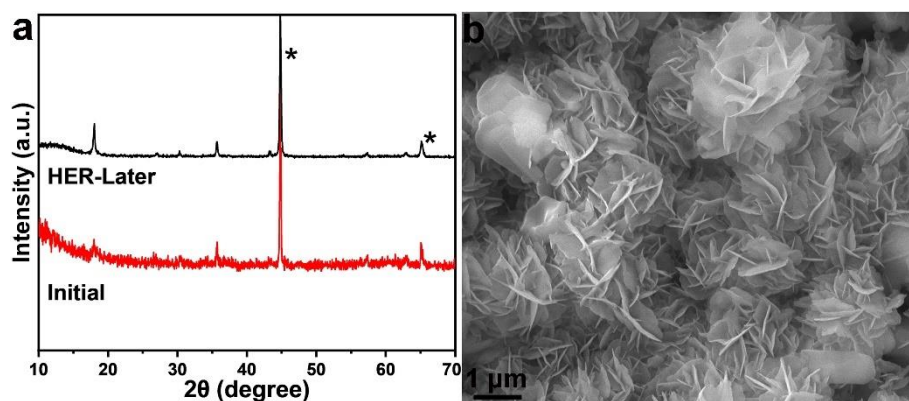


Fig. S4. The (a) XRD and (b) SEM result of Mo-NiFe₂O₄/IF that HER test later.

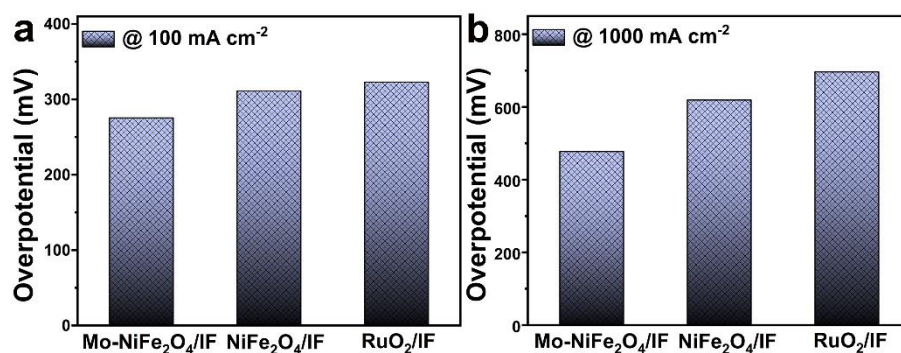


Fig. S5. The bar graphs of Mo-NiFe₂O₄/IF, NiFe₂O₄/IF and commercial ones that between overpotential and current density at (a) 100 and (b) 1000 mA cm⁻², respectively.

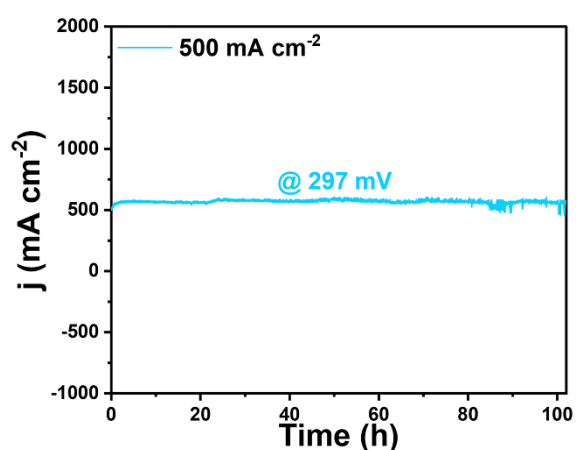


Fig. S6. The i-t behavior of Mo-NiFe₂O₄/IF during the OER course when the provided overpotential is 297.4 mV.

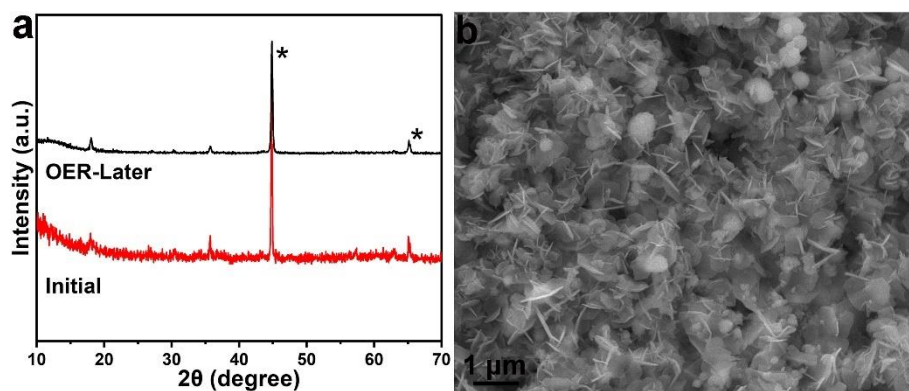


Fig. S7. The (a) XRD and (b) SEM result of Mo-NiFe₂O₄/IF that OER test later.

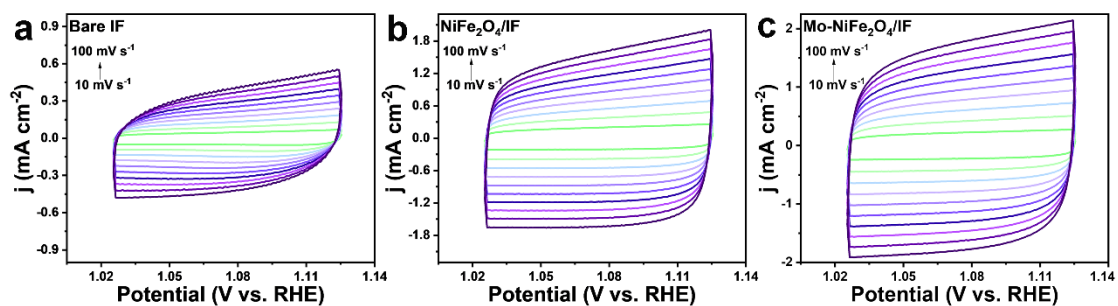


Fig. S8. The CV curves at different scan rates of (a) Bare IF, (b) NiFe₂O₄/IF, and (c) Mo-NiFe₂O₄/IF.

Table S1. Electrochemical activity conclusion of recently reported bifunctional catalysts.

Catalyst	η_{100} (mV) for HER	η_{100} (mV) for OER	E_{10} (V) for OWS	Reference
Mo-NiFe ₂ O ₄ /IF	311.7	275.4	1.69	This work
NiFe ₂ O ₄ /IF	328.6	311.2	1.72	This work
Ru-Cu ₃ (PO ₄) ₂ /CF	405.6	557.4	1.762	<i>J. Mater. Chem. C</i> , 2024 , 12, 17128- 17134.
CoFe NPs	290.0	406.0	1.92	<i>Catal. Today</i> , 2020 , 351, 44-49.
Cr ₂ CTx/NiFe ₂ O ₄	--	--	1.69	<i>Surf. Interfaces</i> , 2024 , 52, 104849
CoO _x /CoN _x NSs	464.0	517.0	1.562	<i>ACS Appl. Nano Mater.</i> , 2024 , 7: 22738-22751.
CoNiC/CoNibc/SSM	340.6	340.4	1.65	<i>ACS Appl. Nano Mater.</i> , 2024, 7, 27620-27627.
NiCoP@CoNi- LDH/SSM	245.6	327.4	1.579	<i>Green Chem.</i> , 2024 , 26, 6713.
NGQD/NiCo-MOF-5	218.0	359.0	1.62	<i>ACS Appl. Nano Mater.</i> , 2024 , 7, 2086-2099.
CoPONPCNTs/CTs	191.1	349.1	1.66	<i>Small</i> , 2024 , 20: e2310012.
NiCo ₂ S ₄ NA/CC	305	340	1.68	<i>Nanoscale</i> , 2015 , 7, 15122-15126.

Ni₃S₂/Cu–NiCo LDH/NF	304	218	1.75(η_{100})	<i>J. Mater. Chem. A</i> , 2021 , 9, 27639- 27650.
FeCo-Ni(OH)₂/NM-2	224	324	1.73(η_{50})	<i>Electrochim. Acta</i> , 2024 , 496, 144484.

Table S2. C_{dl} , ECSA and related data of bare IF, NiFe₂O₄/IF and Mo-NiFe₂O₄/IF.

Catalyst	C_{dl} (mF cm ⁻²)	C_s (mF cm ⁻²)	A (cm ²)	ECSA (cm ²)
Bare IF	1.94	0.04	0.25	12.12
NiFe ₂ O ₄ /IF	7.3	0.04	0.25	48.06
Mo-NiFe ₂ O ₄ /IF	13.09	0.04	0.25	53.56

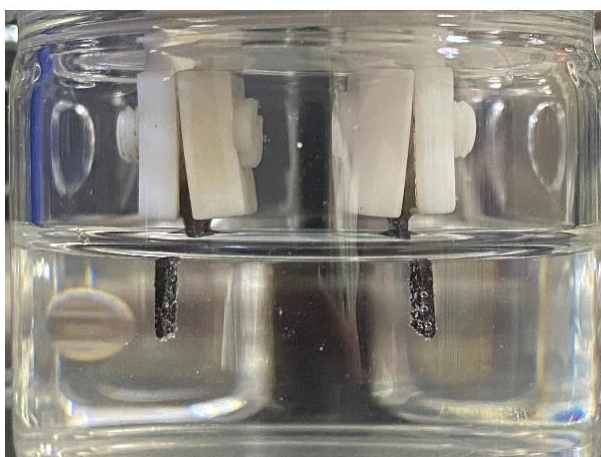


Fig. S9. The enlarged photograph of the water splitting cell during the self-powered water splitting experiment.