Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information (SI) for:

Coupling NiFe-MOF nanosheets on Ni_3N microsheet arrays for efficient electrocatalytic water oxidation

Boran Wang,†[a] Duo Chen,†[c] Shihui Jiao, [a] Qi Zhang, [a] Wenwen Wang, [a] Mengjie Lu, [c] Zhenxing Fang, [b] Guangsheng Pang*[a] and Shouhua Feng [a]

Experimental section

Preparation of NiFe-MOF@Ni_3N/NF

In a typical procedure for the preparation of $Ni(OH)_2$/NF, 4 mmol $Ni(NO_3)_2{\cdot}6H_2O$ (98%, Sinopharm Chemical Reagent Co.,Ltd), 20 mmol of $CO(NH_2)_2$ (99.5%, Aladdin), and 12 mmol NH_4F (99.99%, Aladdin) were dissolved in 50 mL deionized water under stirring. The reaction solution and blank Ni foam (1×5 cm^2) were transferred to a 100 mL autoclave and maintained at 120 °C for 6 h. After being cooled down to room temperature, the product on Ni foam ($Ni(OH)_2$/NF) was washed with deionized water and ethanol, and dried in a vacuum overnight. Ni_3N/NF was obtained by annealing $Ni(OH)_2$/NF at 380 °C for 2 h with a heating rate of 2 °C min^{-1} under an NH_3 atmosphere. The loading amount of Ni_3N on the Ni foam was 2.8 mg cm^{-2}.

To prepare NiFe-MOF@Ni_3N/NF, the prepared Ni_3N/NF was immersed into a homogenous solution of 1 mmol $FeCl_2{\cdot}4H_2O$ (99%, Sinopharm Chemical Reagent Co.,Ltd), 1 mmol 1,4-H_2BDC (TPA, 99%, Sinopharm Chemical Reagent Co.,Ltd), 28 mL DMF, 2 mL ethanol and 2 mL deionized water. The mixture was transferred to a 50 mL autoclave and maintained at 125 °C for 10 h. After being cooled down to room temperature, the product on Ni foam (NiFe-MOF@Ni_3N/NF) was washed with deionized water and ethanol, and dried in a vacuum overnight. The loading amount of NiFe-MOF@Ni_3N on the Ni foam was 4.5 mg cm^{-2}.

Similarly, NiFe-MOF/NF was prepared by replacing Ni_3N/NF with blank Ni foam. The loading amount of NiFe-MOF on the Ni foam was 2.3 mg cm^{-2}.

Preparation of IrO_2/NF

20 mg IrO_2 was dispersed in 950 μL isopropanol and 50 μL Nafion to form a homogeneous ink by sonication for 40 minutes. Then, the prepared ink was dropped onto Ni foam with a mass loading of 4.5 mg cm^{-2} to serve as a working electrode.

Structural Characterization

X-ray diffraction (XRD) measurement was carried out on a Rigaku D/Max 2550 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscope (SEM) image and energy dispersive spectrometer (EDS) was obtained with a JEOL JSM 6700F electron microscope. The transmission electron microscope (TEM) image was obtained with a Tecnai G2 F30 S-Twin microscope equipped with a field emission gun operating at 200 kV. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic X-ray source (Al Kα hυ = 1486.6 eV). The contact angle was measured by Kruss DSA 100 system.

Electrochemical measurements

Electrochemical measurements were performed on a CHI 660e electrochemical station with a three-electrode system. The obtained products were directly used as the working electrodes (1 × 0.3 cm^2). A graphite rod and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. 1 M KOH aqueous solution was used as the electrolyte. The polarization curves were characterized by linear sweep voltammetry at a scan rate of 2 mV s^{-1}. And all curves were corrected with iR-compensation. The electrochemical impedance spectroscopy (EIS) was collected at 1.48 V (vs. RHE). The frequency range was 100 kHz to 0.01 Hz and the amplitude of the applied voltage was 5 mV. The cyclic voltammetry (CV) measurement was carried out to assess the electrochemical double-layer capacitance (C_{dl}). The scan rates were in the range of 30-80 mV s^{-1}. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) by the formula: $E_{vs.\ RHE} = E_{vs.\ Hg/HgO} + 0.098 + 0.059$ pH.

TOF calculations

According to the references (Nat. Commun., 2018, **9**, 5309; Nano Energy, 2018, **53**, 492-500), we have carried out the TOF calculation using the following formula (1)

$$TOF_{per\ site} = \frac{\#\ Total\ Oxygen\ Turn\ Overs/cm^2 geometric\ area}{\#\ Surface\ Sites\ /cm^2\ geometric\ area}$$

(1)

The number of total oxygen turn overs was calculated from the current density by the following equation (2):

$$\#_{O_2} = \left(j\frac{mA}{cm^2}\right)\left(\frac{1C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ O_2}{4\ mol\ e^-}\right)\left(\frac{6.022\ \times 10^{23}\ O_2\ molecules}{1\ mol\ O_2}\right) = \times 10^{15}\frac{O_2/s}{cm^2} per \frac{mA}{cm^2}$$

(2)

The total number of effective surface sites was calculated based on the following equation (3):

$$\frac{\#\ Surface\ sites}{cm^2\ geometric\ area} = \frac{\#\ Surface\ sites\ (flat\ standard)}{cm^2\ geometric\ area} \times Roughness\ factor$$

(3)

In the equation (3), the roughness factor (R_f) can be determined by the double-layer capacitance (C_{dl}) from Fig. 3d of the main text. The specific capacitance can be converted into an electrochemical active surface area using the specific capacitance value for a flat standard with 1 cm^2 of surface area. According to the reference (Energy Environ. Sci., 2015, **8**, 3022-3029), we assumed 60 μF cm^{-2} for a flat electrode and the surface sites of 2 × 10^{15} for the flat standard electrode. Thus, the number of surface active sites for catalyst was estimated to be: $\frac{C_{dl} \times 10^3}{60} \times 2 \times 10^{15}$

surface sites/cm^2 = $\frac{C_{dl}}{30}$ × 10^{18} surface sites/cm^2.

Therefore, the TOF_{OER} per site for the catalyst at different overpotentials (η) was calculated as follows:

$$TOF_{OER} = \frac{1.56 \times 10^{15}}{\frac{C_{dl}}{30} \times 10^{18}} \times j$$

(4)

j corresponds to the current density at different overpotentials.

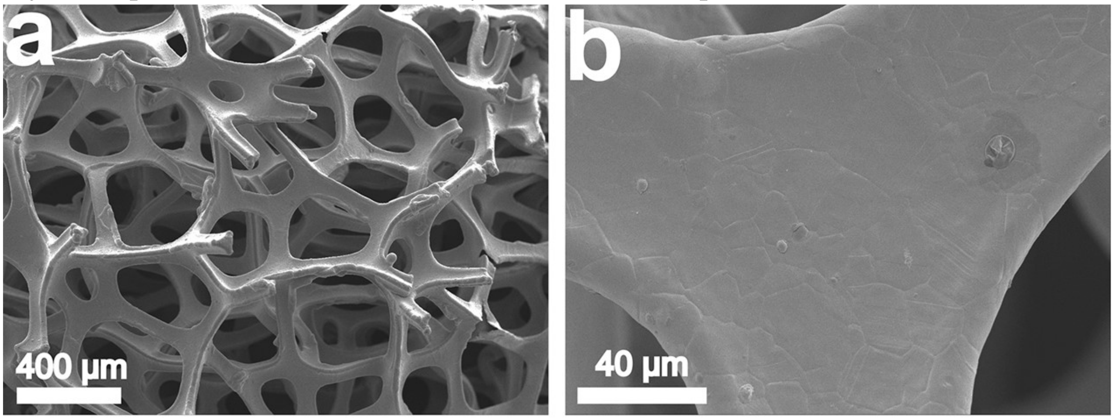

Fig. S1 (a, b) SEM images of blank Ni foam.

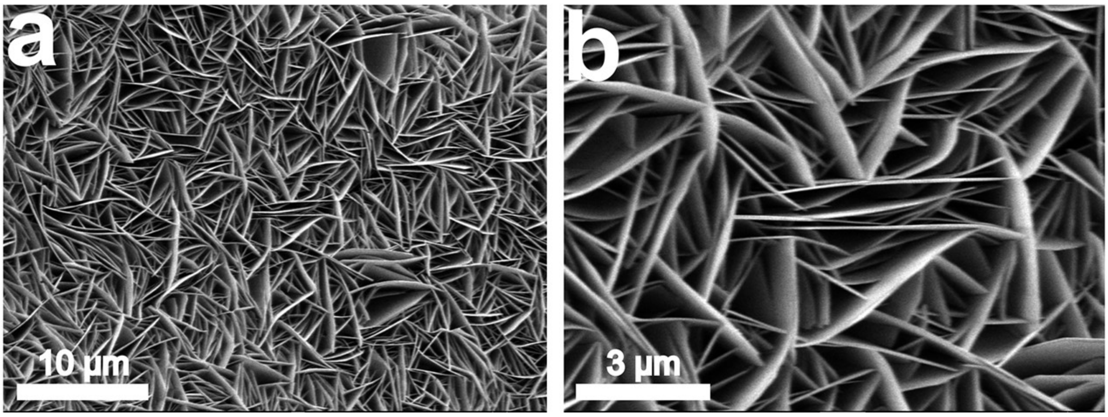

Fig. S2 (a, b) SEM images of $Ni(OH)_2$/NF.

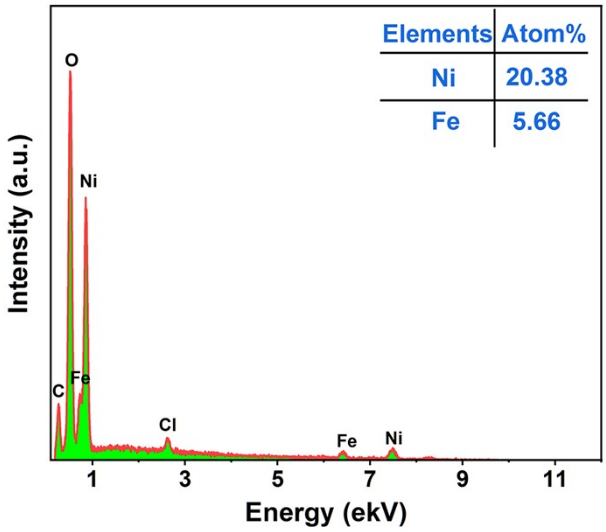

Fig. S3 EDS spectrum of NiFe-MOF@Ni_3N/NF based on the element mapping.

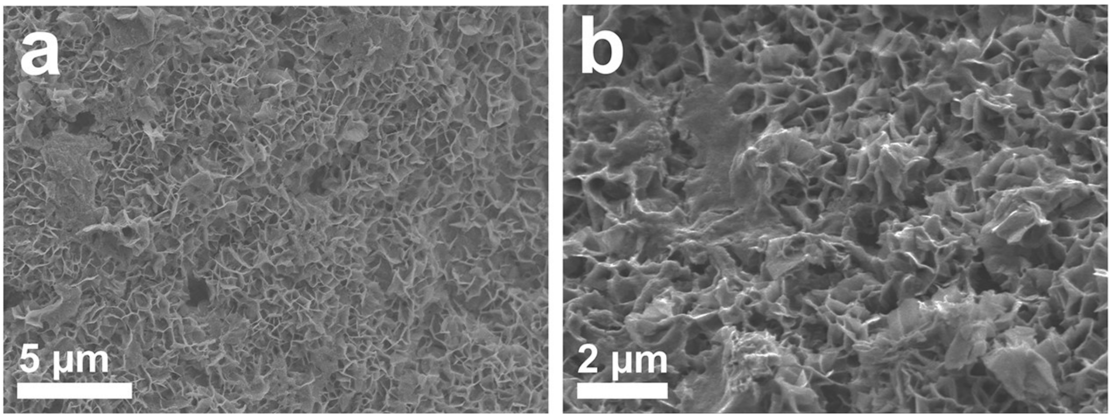

Fig. S4 (a, b) SEM images of NiFe-MOF/NF.

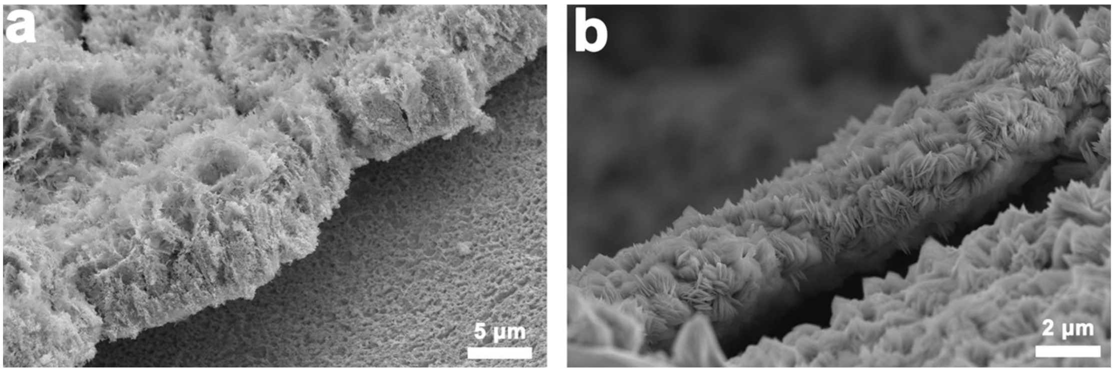

Fig. S5 Cross-section SEM images of (a) NiFe-MOF@Ni_3N/NF and (b) NiFe-MOF /NF.

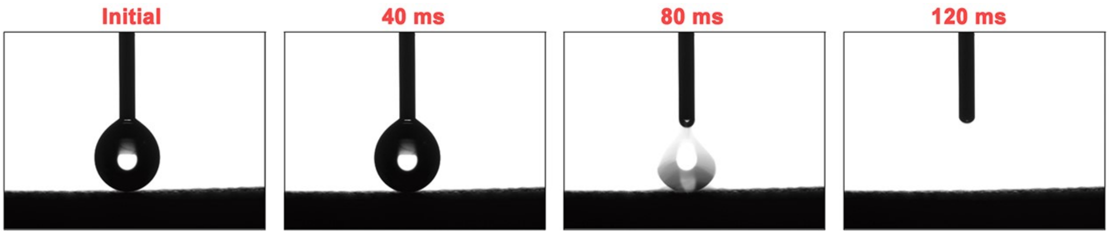

Fig. S6 Penetration process of water droplet on the NiFe-MOF@Ni_3N/NF.

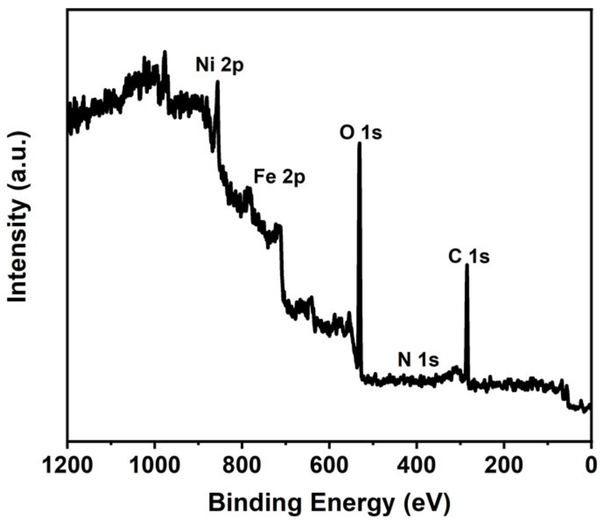

Fig. S7 XPS survey spectrum for NiFe-MOF@Ni_3N/NF.

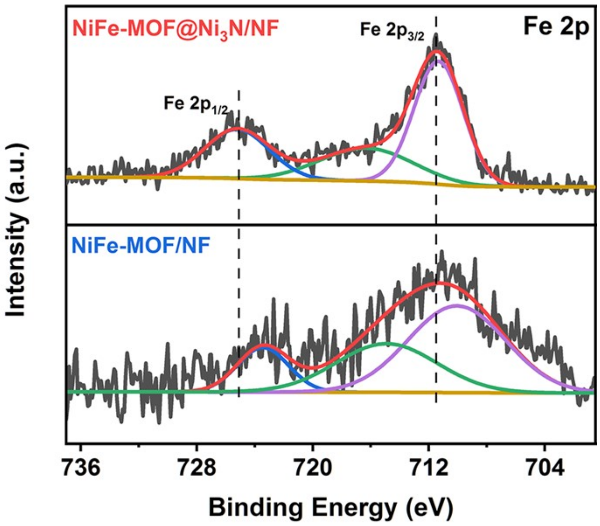

Fig. S8 XPS spectra of Fe 2p for NiFe-MOF/NF and NiFe-MOF@Ni_3N/NF.

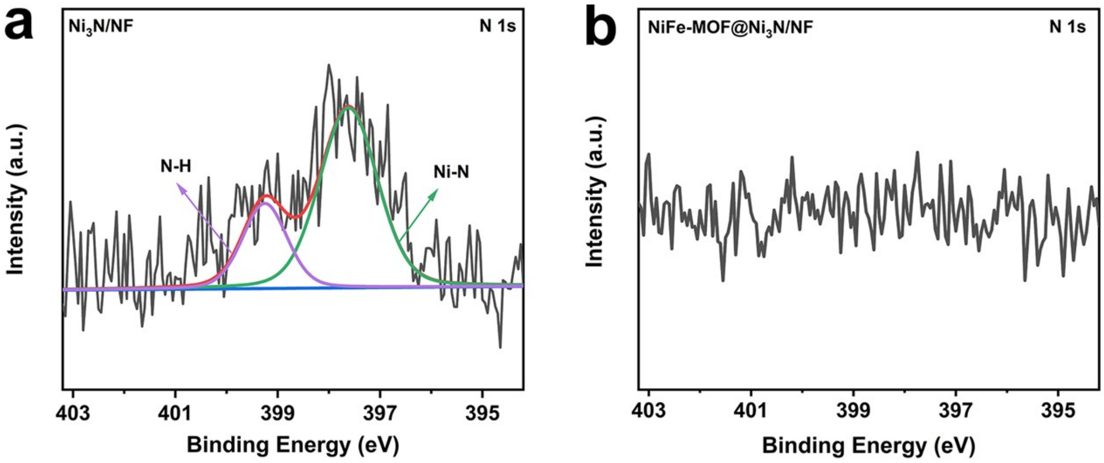

Fig. S9 XPS spectra of N 1s for (a) Ni_3N/NF and (b) NiFe-MOF@Ni_3N/NF.

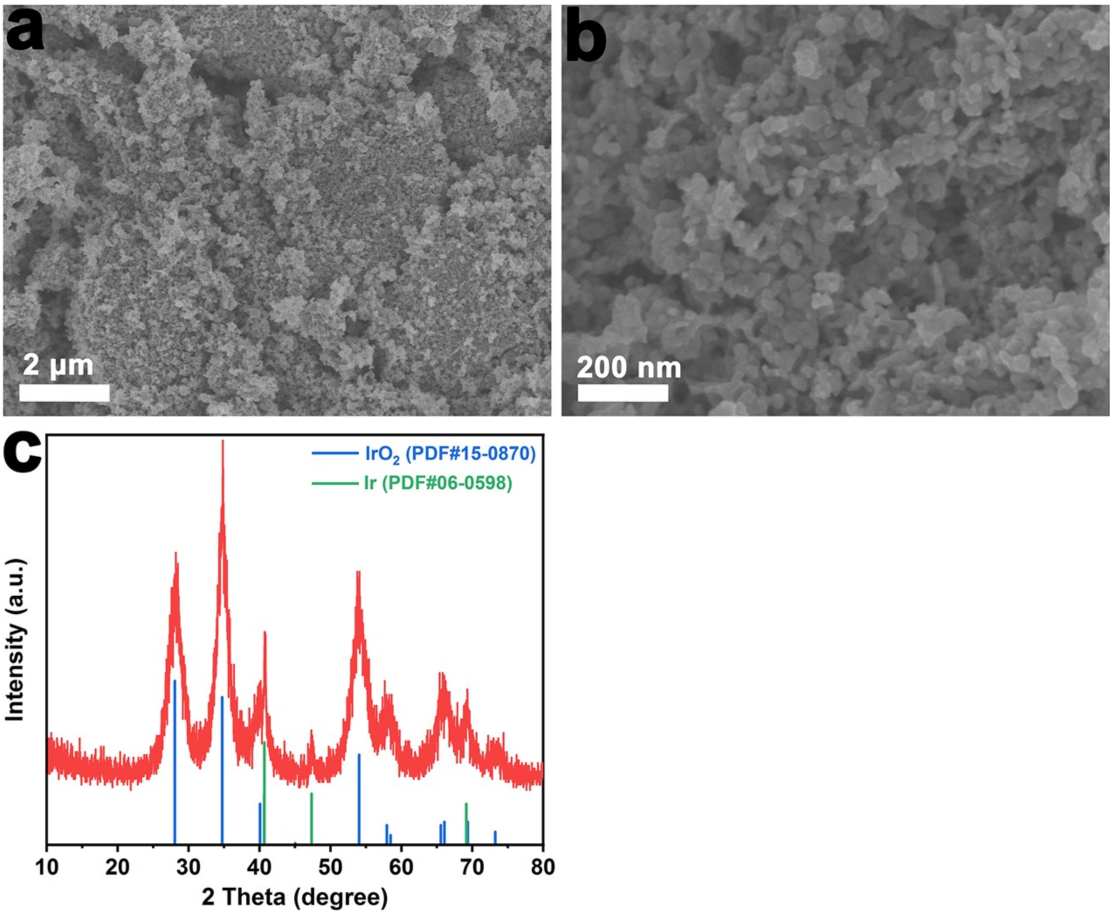

Fig. S10 (a, b) SEM images and (c) XRD pattern of IrO_2.

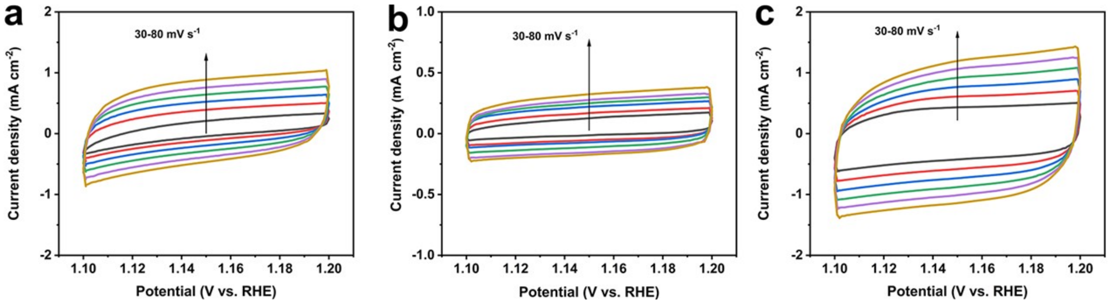

Fig. S11 CV curves of (a) Ni_3N/NF; (b) NiFe-MOF/NF and (c) NiFe-MOF@Ni_3N/NF.

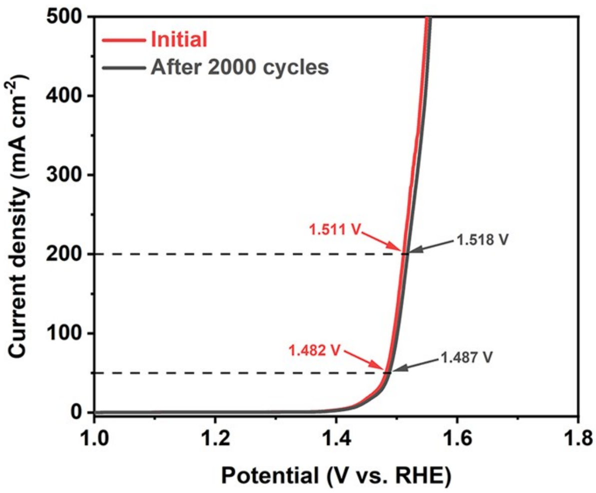

Fig. S12 Polarization curves for NiFe-MOF@Ni_3N/NF obtained before and after 2000 CV cycles.

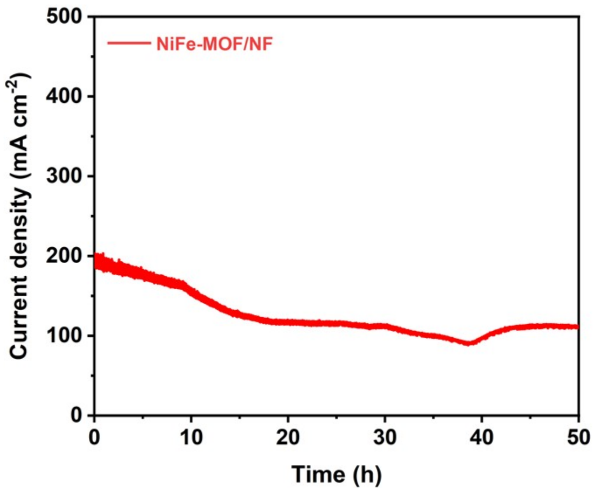

Fig. S13 Stability test of NiFe-MOF/NF at the current density of 200 mA cm^{-2}.

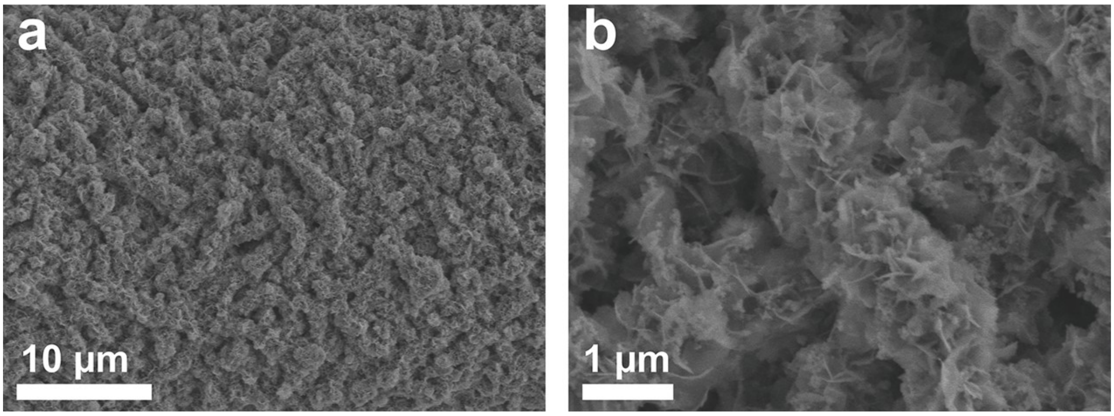

Fig.S14 (a, b) SEM images of NiFe-MOF@Ni_3N/NF after stability test.

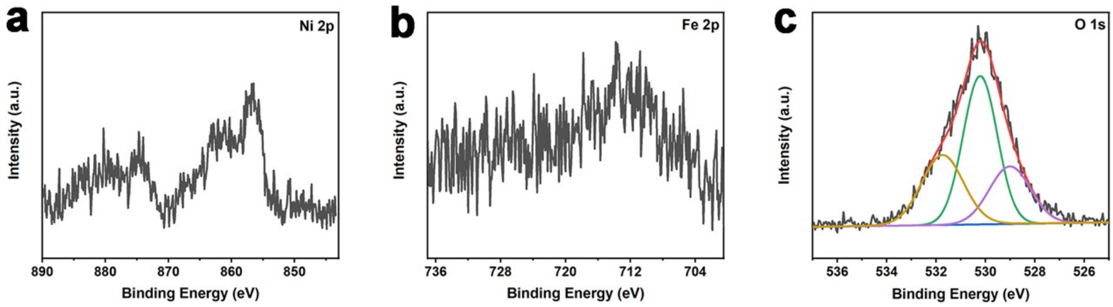

Fig. S15 High-resolution XPS spectra of (a) Ni 2p; (b) Fe 2p and (c) O 1s for NiFe-MOF@Ni_3N/NF after stability test.

Table S1 OER performance of some recently reported MOFs based OER electrocatalysts and NiFe-MOF@Ni_3N/NF in this work.

Reference	Electrocatalyst	*j* (mA cm^{-2})	*η* (mV)
This work	NiFe-MOF@Ni_3N/NF	50 200	252 281
ACS Appl. Mater. Interfaces, 2019, **11**, 41595-41601.	Ni-BDC@NiS	20	330
ChemSusChem, 2020, **13**, 5647.	$Mn_{0.52}Fe_{0.71}$Ni-MOF-74	10 100	245 462
J. Mater. Chem. A, 2020, **8**, 14574-14582.	Ni_3S_2/MIL-53(Fe)	100	251
J. Mater. Chem. A, 2020, **8**, 16908-16912.	NiFe-MOF/$NiSe_x$/NF	100	230
J. Power Sources, 2020. **451**, 227295.	Ni_3S_2@MIL-53(NiFeCo)	50	236
Nanoscale, 2019, **11**, 14785-14792.	Ni–S/MIL-53(Fe)	10 100	256 298
Nanoscale, 2020, **12**, 67-71.	MIL-53(Co–Fe)	100	262
Adv. Funct. Mater., 2018, **28**, 1801554.	Ni-MOF@Fe-MOF	10	265
Nat. Commun., 2017, **8**, 15341.	NiFe-MOF	10	240

Table S2 TOF values for different samples at the overpotential of 250 and 300 mV, respectively.

	Electrocatalyst	η = 250 mV	η = 300 mV
TOF (s^{-1}) for OER	Ni_3N/NF	0.0121	0.0285
	NiFe-MOF/NF	0.0487	0.391
	NiFe-MOF@Ni_3N/NF	0.144	1.04

Table S3 Comparison of the TOF values of our electrocatalyst with recently reported ones.

Reference	Electrocatalyst	TOF (s^{-1}) for OER
This work	NiFe-MOF@Ni_3N/NF	0.144 at 250 mV; 1.04 at 300 mV
Nat. Commun., 2018, **9**, 2014.	NiFe/Ni-P	0.13 at 250 mV
Adv. Mater., 2018, **30**, 1705516.	Co-Ni_3N	0.0134 at 350 mV
Nat. Commun., 2018, **9**, 1809.	IFONFs-45	0.2141 at 370 mV
Nano Energy, 2019, **63**, 103880.	NiFe-LDH/MXene/NF	0.82 at 300 mV
Small, 2020, **16**, 1906564.	D-Ni-MOF NSAs	0.440 at 300 mV
Adv. Funct. Mater., 2020, **31**, 2006484.	Ni_2P-Fe_2P/NF	0.925 at 300 mV
Appl. Catal. B-Environ., 2020, **270**, 118889.	Ni_2Co-N	0.012 at 270 mV
Adv. Mater., 2020, **32**, 1905679.	W_2N/WC	0.15 at 370 mV