Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Bimetallic sulfide particles incorporated in Fe/Co-based metal-organic framework ultrathin nanosheets toward boosted electrocatalysis of the oxygen evolution reaction

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1. Experimental Section

1.1 Chemical reagents

N, N-dimethylformamide (DMF, reagent, 99.5%) was bought from Aladdin. $Co(NO_3)_2{\cdot}6H_2O$ (99.99%) was purchased from Shanghai Macklin Biochemical. KOH (analytical reagent), $Ni(NO_3)_2{\cdot}6H_2O$ (≧98.5%), $Cu(NO_3)_2{\cdot}3H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ (≧98.6%), Terephthalic acid (TPA, 99%), isopropanol (C_3H_8O, >99.7%) and ethanol (C_2H_5OH) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Thioacetamide (TAA, 99%) was bought from J&K Scientific Ltd., AEF. Nafion (5 wt%) was bought from Sigma-Alirich. All reagents were directly employed without extra additional handling.

1.2 Synthesis of CoM(M=Fe, Ni, Cu)-MS/MOF, CoFe-MOF and (Fe)-Co_3S_4

In the preparation of CoFe-MS/MOF, TPA (66.5 mg), $Co(NO_3)_2 \cdot 6H_2O$ (111.65 mg), $Fe(NO_3)_3 \cdot 9H_2O$ (38.784 mg), and TAA (50 mg) were dispersed in 10 mL of DMF and 4 mL ethanol, subsequently stirred for 20 min to yield a homogeneous solution. The solution was transferred to a Teflon autoclave to heat at 150 °C for five hours. The resultant substances were rinsed with distilled water, centrifuged, and subsequently dried in an oven at 60 °C to yield CoFe-MS/MOF. For comparison, other CoFe-MS/MOF electrocatalysts with different Fe/Co ratios were synthetized as well. The synthesis procedures for CoNi-MS/MOF and CoCu-MS/MOF were similar to those for CoFe-MS/MOF except changing $Fe(NO_3)_3 \cdot 9H_2O$ to $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, respectively. CoFe-MOF and (Fe)-Co_3S_4 were synthesized using the similar procedures as that of CoFe-MS/MOF in the absence of TAA and TPA, respectively.

1.3 Fabrication of Pt/C and RuO_2 Electrodes

1 mg of Pt/C (20wt%) or 6 mg RuO_2 powder (≧75.2%) was dispersed in the mixture of isopropanol (1.0 mL) and Nafion solution (5 wt%, 25 μL), respectively. After ultrasonic treatment for 30 min to obtain a homogeneous ink, 20 μL of ink was dropped on the glassy carbon electrode and dried at 60 °C. At this point, Pt/C and RuO2 electrodes were successfully fabricated.

1.4 Material Characterizations

The phase composition and purity of the samples were analyzed by powder X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.54 Å). Scanning electron microscopy (SEM) was operated at 15 kV. Further morphological characterizations of samples were conducted by transmission electron microscope (TEM) operated at 120 kV and high-resolution TEM (HRTEM) using a TecnaiG2F20 TEM operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was conducted by Thermo Scientifc's EXCALAB 250 XI system. Raman spectra were recorded under ambient conditions by XploRA Plus micro-Raman spectrometer from Horiba Jobin Yvon.

1.5 Electrochemical characterization

All electrochemical tests were conducted on CHI660 workstation (Chenhua, Shanghai) by employing the three-electrode system, in which the glassy carbon (GC), Ag/AgCl and carbon rod served as the working electrode, reference electrode and counter electrode in 1 M KOH, separately. To fabricated working electrodes, 4 mg catalysts and 2mg toners were dispersed in hybrid solution containing 1.0 mL of isopropanol and 30 μL Nafion. After 30-minute ultrasound, the appropriate amount of catalyst ink was dripped onto the GC electrodes (diameter: 5 mm, area: 0.196 cm^2). Polarization curves were obtained by linear sweep voltammetry (LSV) measurements at a scan rate of 5 mV s^{-1} without iR compensation. The Tafel slopes were derived from polarization curves. CV test is performed at sweep rates ranging from 10 to 50 mV/s. Electrochemical impedance spectroscopy (EIS) was conducted in the frequency region from 1 Hz to 500 kHz. Chronopotentiometry measurement was conducted at the current density of 10 mA cm^{-2}. The i-t curve was tested at a potential of 1.5 V (vs. RHE). Electrochemical water splitting was measured by employing a dual-electrode system.

2. Supporting Figures and Tables

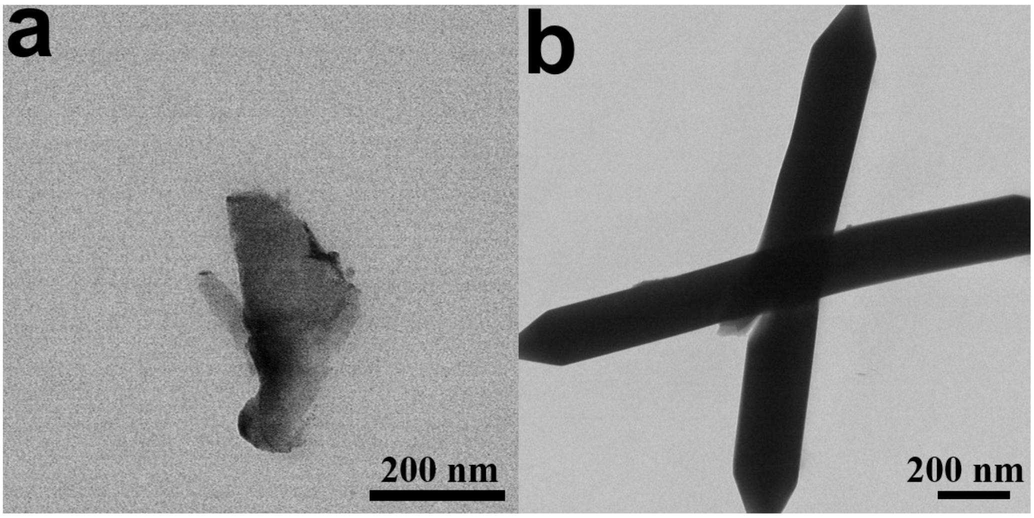
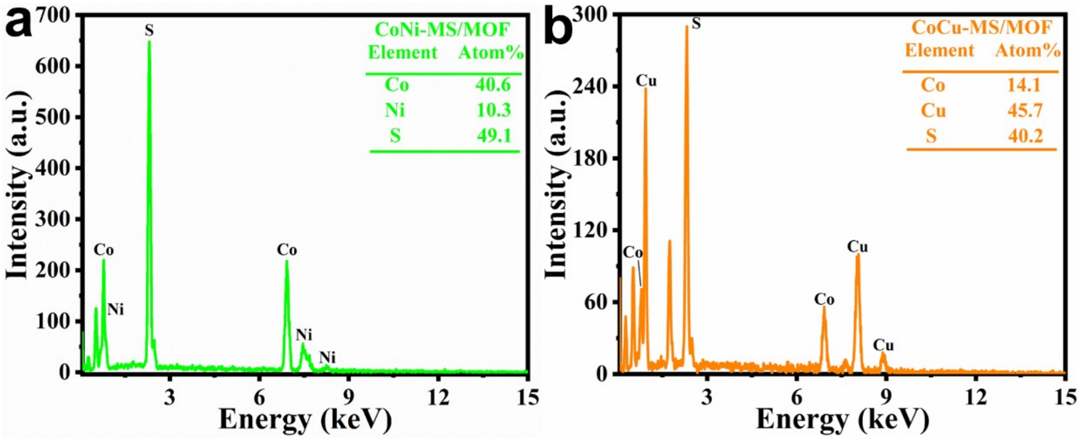


Fig.S1 TEM images of (a) CoNi-MS/MOF, (b) CoCu-MS/MOF.



CoNi-MS/MOF

Element	Atom%
Co	40.6
Ni	10.3
S	49.1

CoCu-MS/MOF

Element	Atom%
Co	14.1
Cu	45.7
S	40.2

Fig.S2 EDX spectrum and atomic percentages of (a) CoNi-MS/MOF and (b) CoCu-MS/MOF.

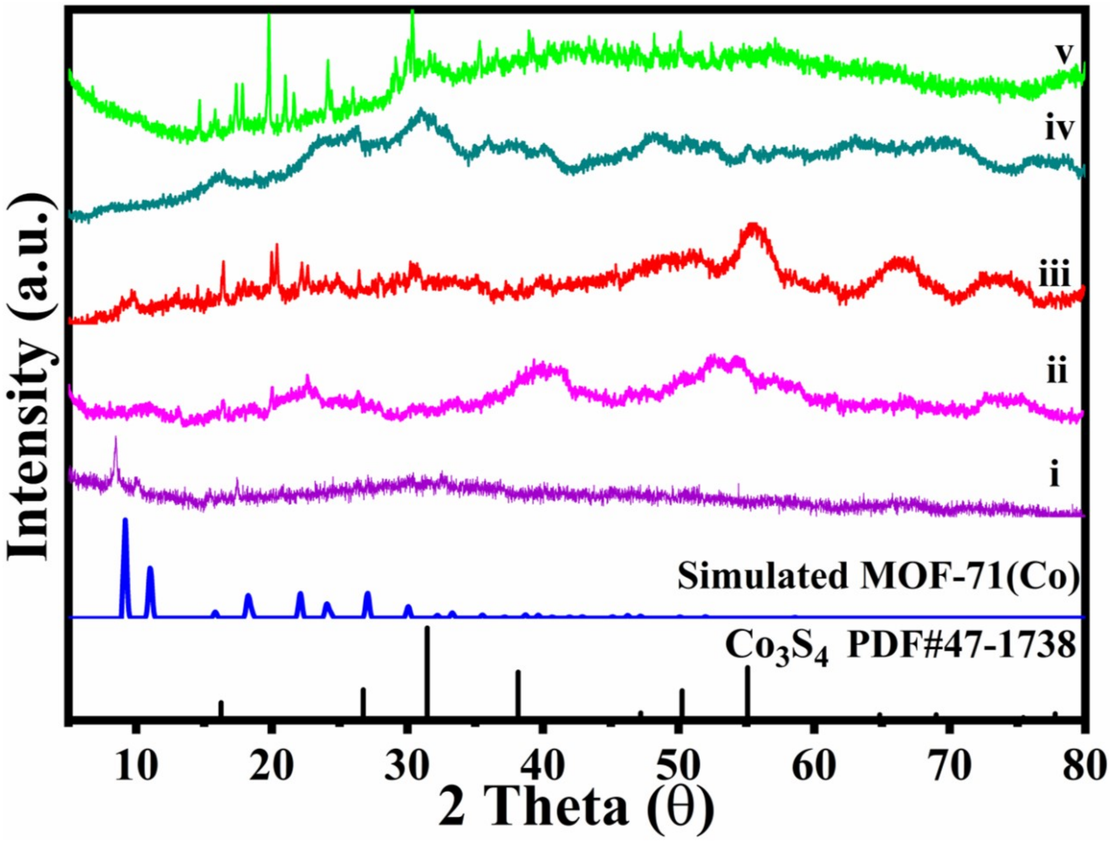


Fig.S3 XRD patterns of (i) CoFe-MOF, (ii) (Fe)-Co_3S_4 and different CoFe-MS/MOF samples synthesized with different mount of TAA (iii) 0.05 g, (iv) 0.08 g, and (v) 0.11 g.

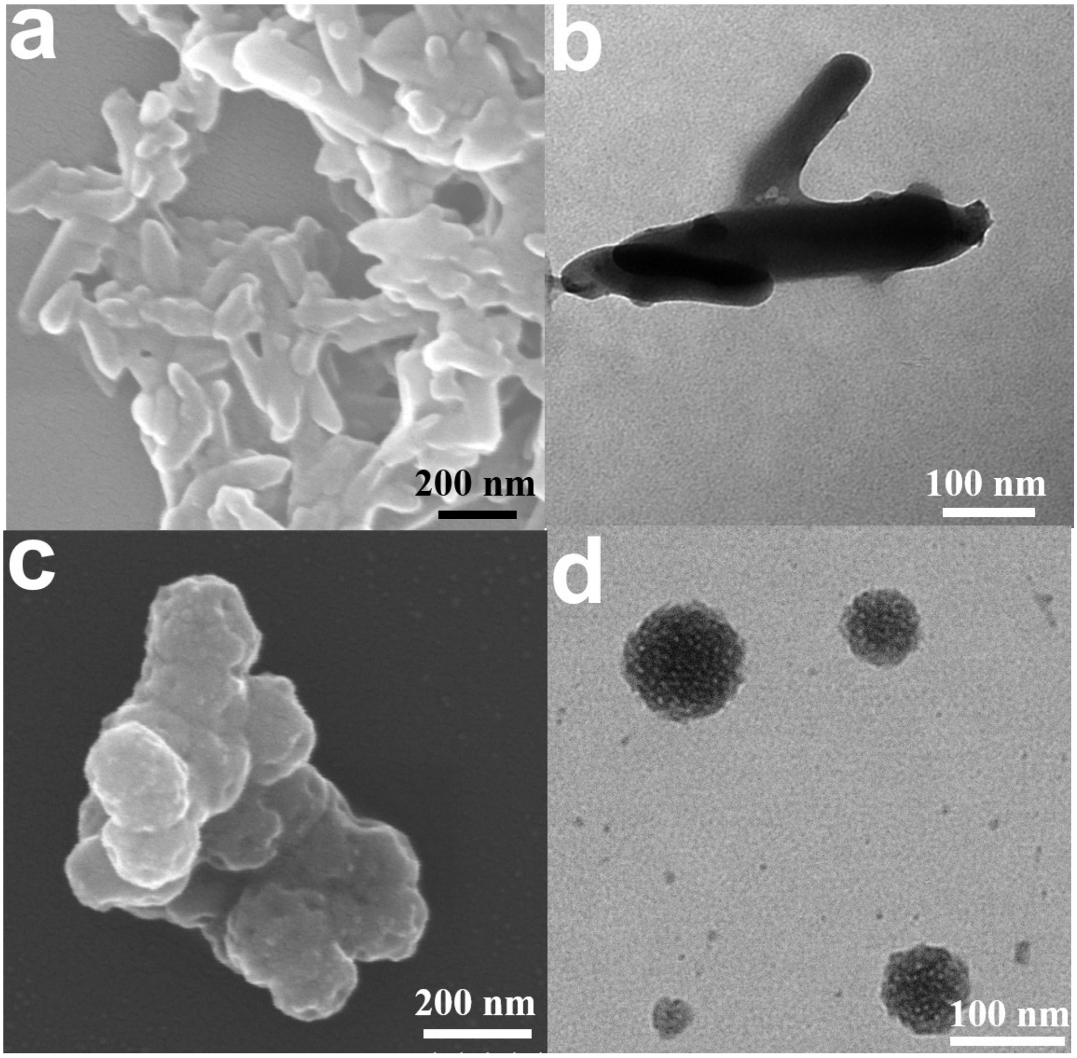


Fig.S4 (a) SEM image and (b) TEM image of CoFe- MOF. (c) SEM image and (d) TEM image of (Fe)-Co_3S_4.

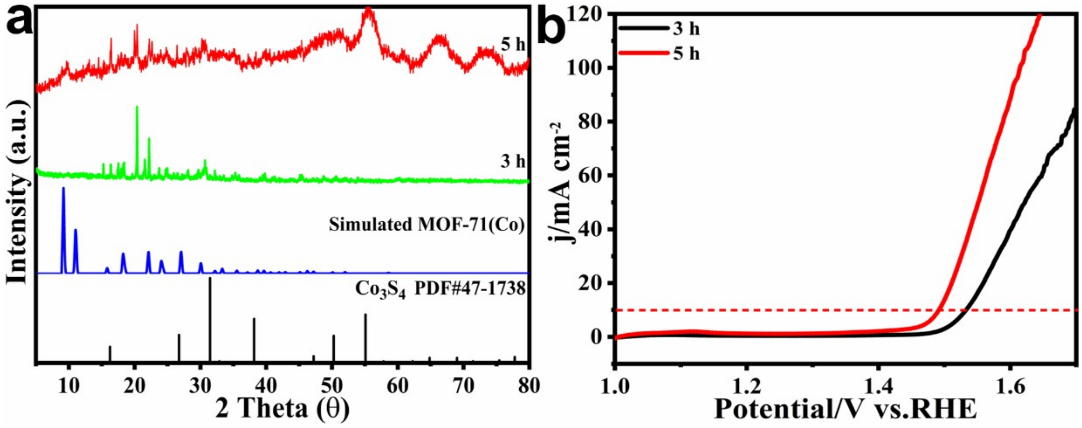


Fig.S5 (a) XRD patterns of CoFe-MS/MOF synthesized with 3 and 5 h reaction; (b)

OER polarization curves of CoFe-MS/MOF electrodes synthesized with 3 h and 5 h reaction time without iR compensation.

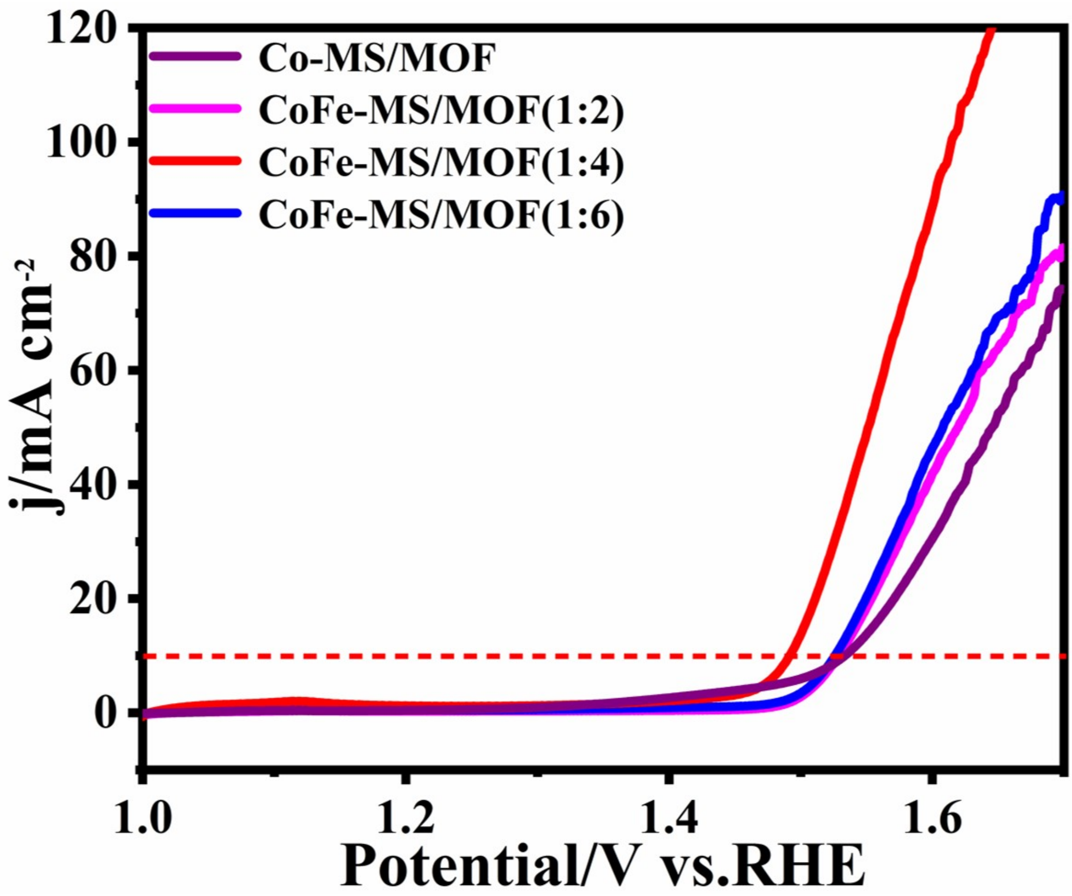


Fig.S6 OER polarization curves of a batch of CoFe-MS/MOF electrodes synthesized with different Fe/Co dosage ratios without iR compensation.

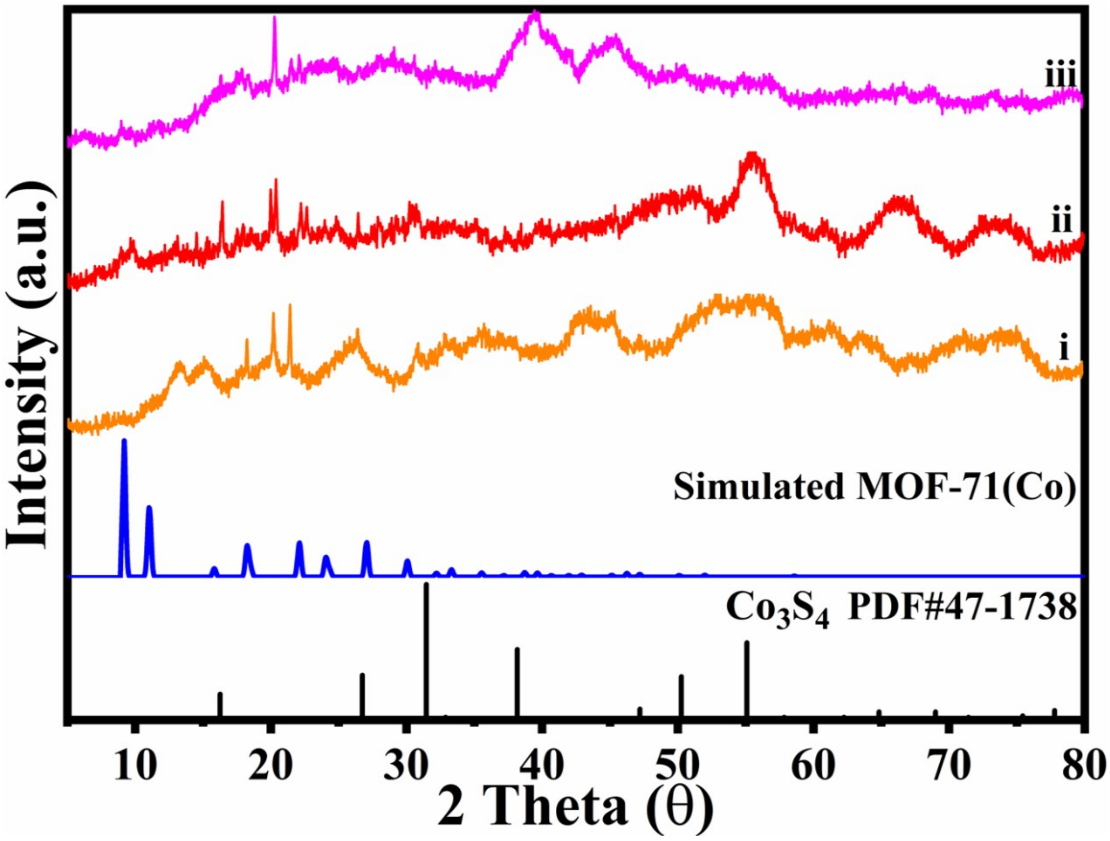


Fig.S7 XRD patterns of CoFe-MS/MOF samples synthesized with different Fe/Co dosage ratio of (i) 1:2, (ii) 1:4, (iii) 1:6.

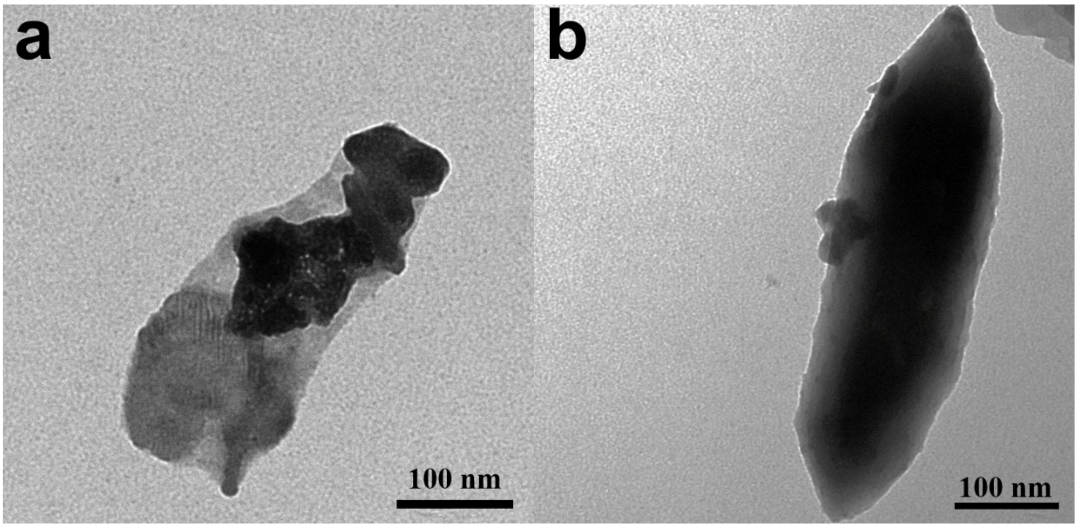


Fig.S8 TEM images of CoFe-MS/MOF synthesized with Fe/Co dosage ratio of (a) 1:2 and (b) 1:6.

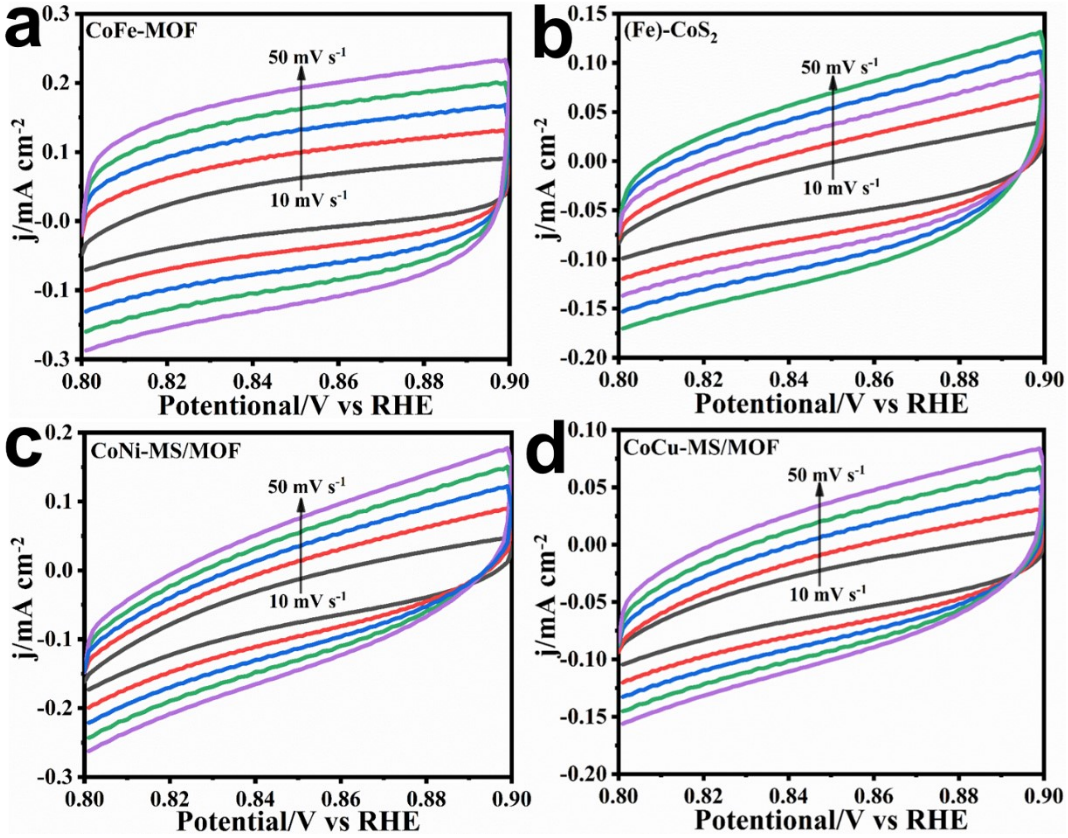


Fig.S9 CV curves of (a) CoFe-MOF, (b) (Fe)-Co_3S_4, (c) CoNi-MS/MOF, and (d) CoCu-MS/MOF with scan rates ranging from 10 to 50 mV s^{-1}. By plotting the capacitive currents (ΔJ, $(J_a-J_c)/2$) against the scanning rate and following with a linear fit, the C_{dl} was estimated as the slope.

Table S1 The transfer resistances obtained from Nyquist plots in 1.0 M KOH solution.

samples	CoFe-MS/MOF	CoFe-MOF	(Fe)-Co_3S_4	CoNi-MS/MOF	CoCu-MS/MOF
R_s	5.85	6.16	6.21	5.21	6.37
R_{ct}	9.50	51.8	10.10	72.92	14.60

Table S2 Comparison of the electrocatalytic OER performance of the as-prepared catalysts at 10 mA cm^{-2} in 1.0 M KOH.

catalysts	Overpotential (mV)	Tafel slope (mV dec^{-1})	C_{dl} (mF cm^{-2})
CoFe-MS/MOF	261	60.3	7.71
CoFe-MOF	312	73.6	2.94
(Fe)-Co_3S_4	305	67.1	1.64
CoNi-MS/MOF	304	111.8	1.94
CoCu-MS/MOF	298	130.2	1.22