

**Ni/Fe complex incorporated into covalent organic framework as
single-site heterogeneous catalyst for efficient oxygen evolution
reaction**

Xuefeng Feng, Zhi Gao*, Longhui Xiao, Zhenqin Lai, and Feng Luo*

State key Laboratory of Nuclear Resources and Environment, School of Biology, Chemistry
and Material Science, East China University of Technology, Nanchang, Jiangxi 330013,
China

*Corresponding author

E-mail: gaozhi910201@163.com (Z. Gao); ecitluofeng@163.com (F. Luo)

EXPERIMENTAL SECTION

Material Synthesis

2,4,6-triformylphloroglucinol, 2,5-diaminobenzenesulfonic acid, COF-SO₃H and NH₄@COF-SO₃ were synthesized according to our previous work [17]. In a typical synthesis of (Cyclen@Ni_xFe_{1-x})@COF-SO₃ (x = 0, 0.2, 0.5, 0.8, 1.0), cyclen (18.9 mg), x mL NiCl₂·6H₂O (Ni²⁺, 1000 ppm in aqueous solution) and (1-x) mL FeCl₂·4H₂O (Fe²⁺, 1000 ppm in aqueous solution) were mixed into 5 mL glass bottle under vigorous stir for 1 h at room temperature to form Cyclen@Ni_xFe_{1-x} complex. Afterwards, 20 mg of NH₄@COF-SO₃ powder was put into above solution under continuous stirring for 1 h. Finally, the resulting products was collected by filtration, washed with deionized water to pH = 7.0 and dried in a vacuum oven at 60 °C for 12 h overnight. The final sample was denoted as (Cyclen@Ni_xFe_{1-x})@COF-SO₃. cyclen/NH₄@COF-SO₃ was prepared by grinding the mixture of cyclen (18.9 mg) and NH₄@COF-SO₃ (20 mg). 10 mg of (Cyclen@Ni)@COF-SO₃ and 10 mg of (Cyclen@Fe)@COF-SO₃ were mixed uniformly by grinding to obtain (Cyclen@Ni)@COF-SO₃/(Cyclen@Fe)@COF-SO₃.

Electrochemical measurements

All the electrochemical tests were performed in a standard three-electrode system using 1 M KOH aqueous solution as electrolyte at room temperature on a CHI660E electrochemical workstation (CH Instruments Inc., Shanghai). Carbon electrode, saturated calomel electrode and the as-prepared catalyst were served as counter electrode, reference electrode and working electrode, respectively. The area of working electrode immersed into the electrolyte is 1 cm × 1 cm. Before measurement, a mixture of 3 mg sample and 3 mg carbon powder was added to 1 mL solution composed of 0.95 mL ethyl alcohol and 50 μL Nafion solutions under ultrasonication for 30 min to obtain a homogeneous catalyst ink. Finally, 50 μL of above ink was loaded on the carbon paper and then dried at room temperature. All the potentials were

referenced to a reversible hydrogen electrode (RHE). The linear sweep voltammetry (LSV) was recorded in an O₂-saturated 1.0 M KOH at a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements of (Cyclen@Ni_xFe_{1-x})@COF-SO₃ (x = 0, 0.2, 0.5, 0.8, 1.0) were carried out over a frequency range from 100 kHz to 0.1 Hz at the overpotential of 308 mV. The electrochemically active surface area (ECSA) of different catalysts was determined based on the double-layer capacitance (C_{dl}) using a simple cyclic voltammetry method in a non-Faradic potential range of 1.23-1.33 V vs RHE. By plotting the capacitive density at 1.28 V vs RHE against the scan rate, a linear trend was observed. The slope of the fitted line was the twice of C_{dl}. Turnover frequency (TOF) value of catalysts was calculated based on the equation: $TOF = (J \times A) / (4 \times F \times n)$, where J (mA/cm²) is the current density at an overpotential of 300 mV; A is the surface area of electrode (1 cm²); F is the Faraday constant (96485 C/mol); n is molar number of active sites on the electrode. Both Ni and Fe in (Cyclen@Ni_xFe_{1-x})@COF-SO₃ (x = 0, 0.2, 0.5, 0.8, 1.0) (x = 0, 0.2, 0.5, 0.8, 1) samples are regarded as active sites. The Faradaic efficiency was determined by comparing the experimentally produced gas volume with the theoretically calculated one by the equation of Faradaic efficiency = $V_{experimental} / V_{theoretical}$. The experiment volume of O₂ ($V_{experimental}$) was obtained by experimental data and the theoretical volume of O₂ ($V_{theoretical}$) can be calculated by the formula of $V_{theoretical} = J \cdot t \cdot V_m / n \cdot F$, where J is the current density; t is the measured time; V_m is the molar volume of O₂ in 1/mol; n is the number of electrons required for one molecule O₂ and F is the Faraday constant (96485 C/mol).

Characterizations

The samples were tested by X-ray diffraction (XRD) on a Bruker AXSD8 Discover powder diffractometer with Cu K α radiation ($\lambda = 0.154$ nm). Mercury 1.4 was used to determine the simulated powder patterns. Infrared spectra (IR) of samples were investigated on a Bruker VERTEX70 spectrometer. Low temperature N₂ adsorption-desorption isotherms were recorded on a Belsorp-max. SEM images were obtained on a Hitachi S-4800 microscope. X-

ray photoelectron spectra (XPS) spectra were collected by Thermo Scientific ESCALAB 250 Xi spectrometer. Transmission electron microscopy (TEM) was taken using a JEOL 2100 microscope operated at an accelerating voltage of 200 kV. Metal content in samples was determined by a Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer (ICP-AES).

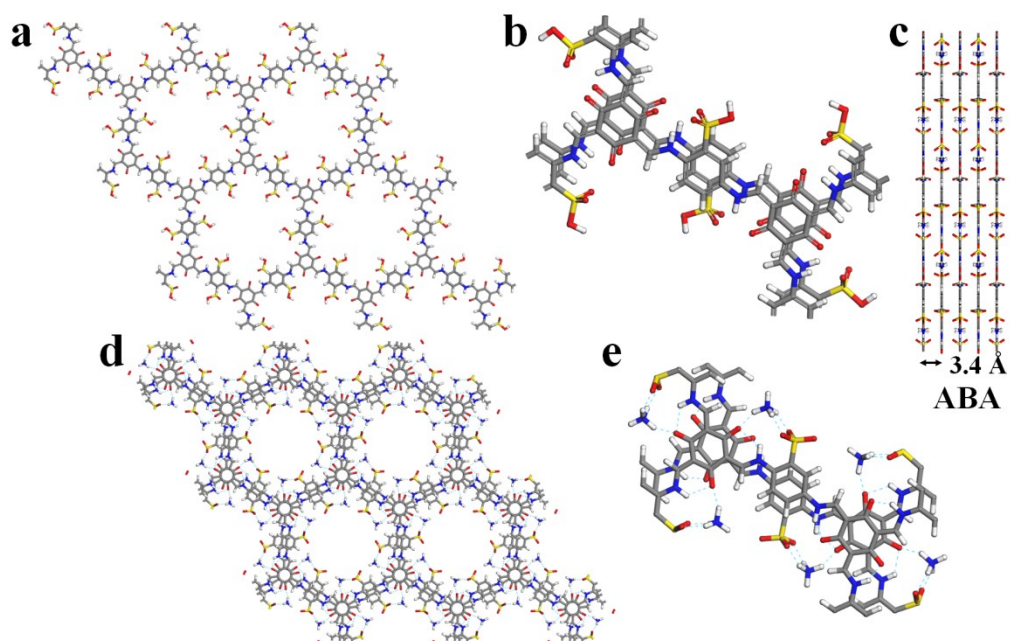


Figure S1 The structure of COF-SO₃H (a-c) and NH₄@COF-SO₃H (d, e).

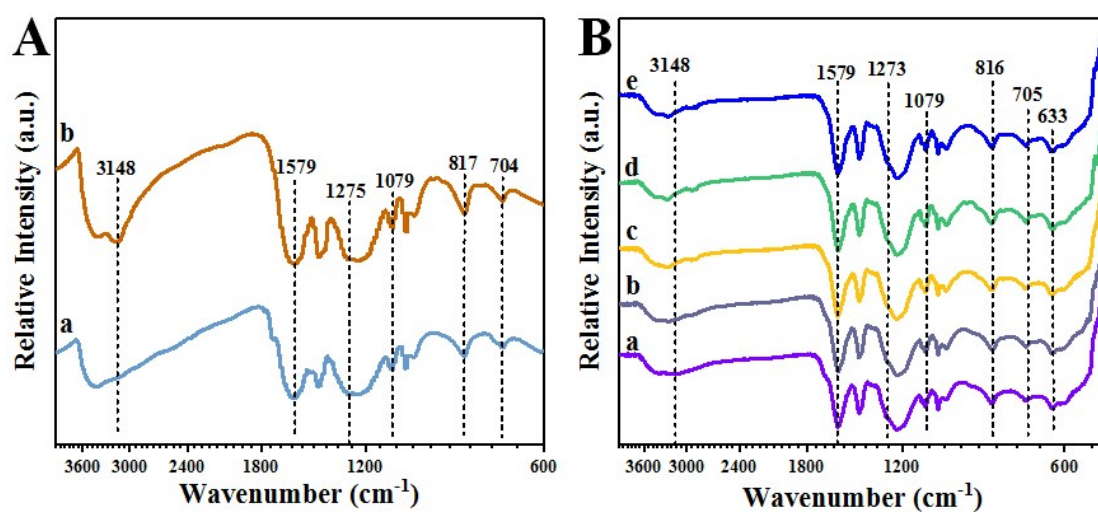
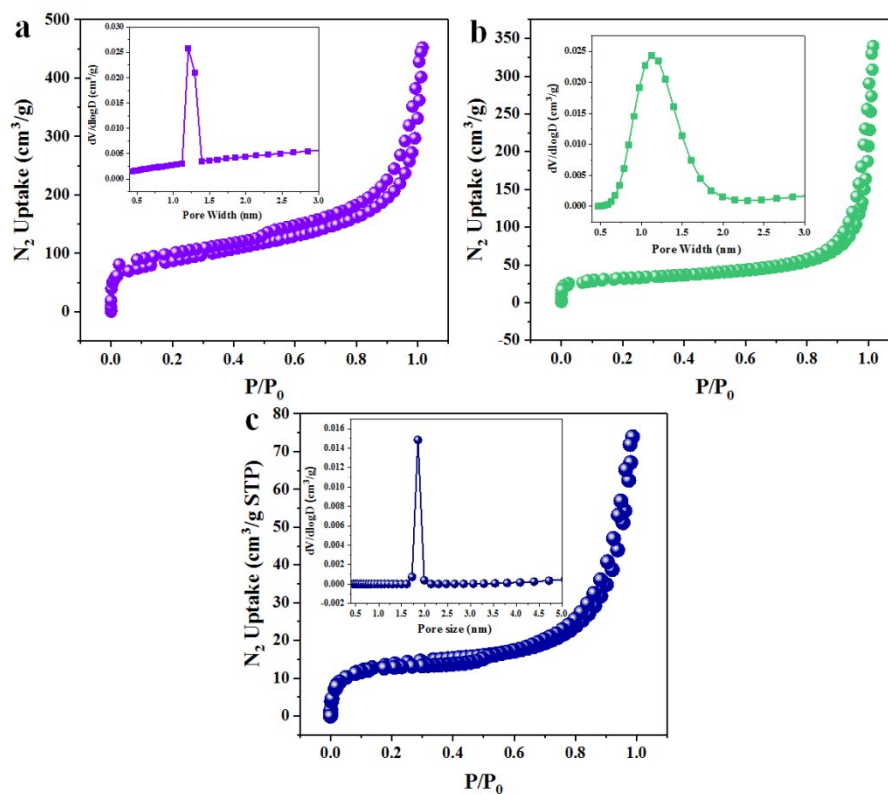
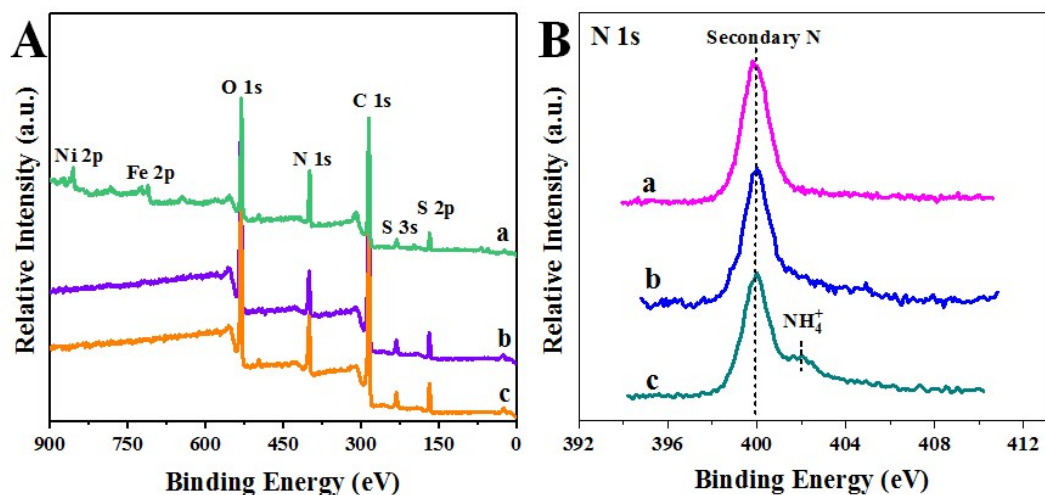


Figure S2 A) IR spectrum of COF-SO₃H (a) and NH₄@COF-SO₃ (b). B) IR spectrum of (Cyclen@Fe)@COF-SO₃ (a), (Cyclen@Ni_{0.2}Fe_{0.8})@COF-SO₃ (b), (Cyclen@Ni_{0.8}Fe_{0.2})@COF-SO₃ (c), (Cyclen@Ni)@COF-SO₃ (d) and (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ (e).



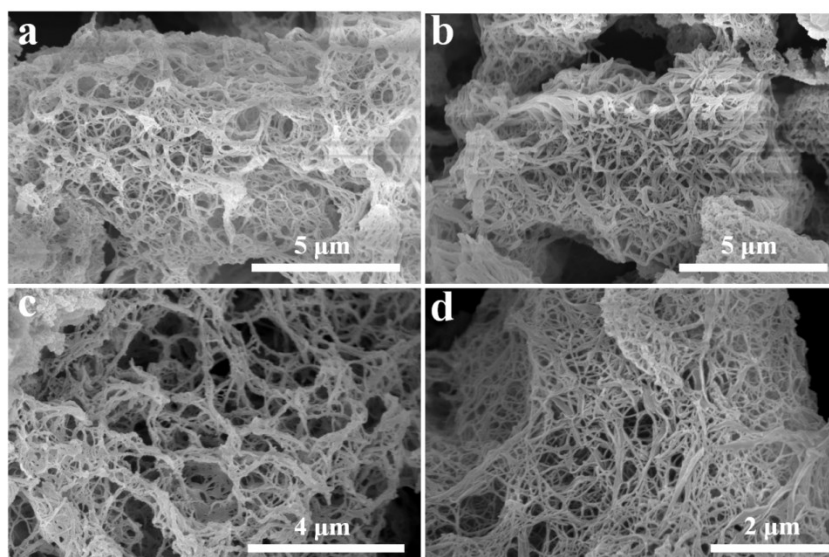


Figure S5 SEM images of (Cyclen@Ni)@COF-SO₃ (a), (Cyclen@Ni_{0.2}Fe_{0.8})@COF-SO₃ (b), (Cyclen@Ni_{0.8}Fe_{0.2})@COF-SO₃ (c) and (Cyclen@Fe)@COF-SO₃ (d).

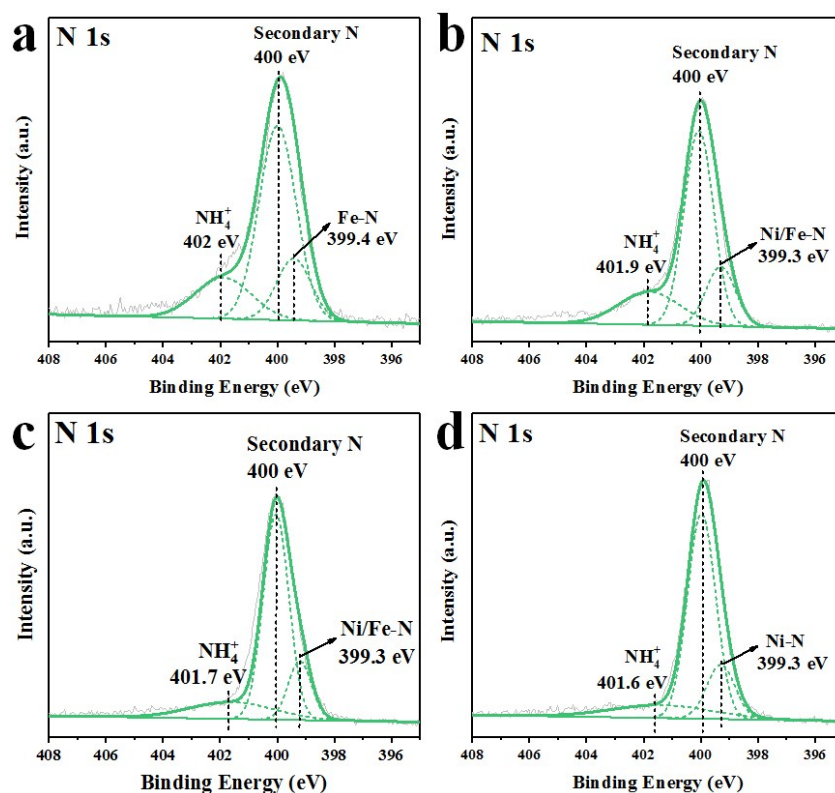


Figure S6 XPS spectra of high-resolution N 1s region in (Cyclen@Fe)@COF-SO₃ (a), (Cyclen@Ni_{0.2}Fe_{0.8})@COF-SO₃ (b), (Cyclen@Ni_{0.8}Fe_{0.2})@COF-SO₃ (c) and (Cyclen@Ni)@COF-SO₃ (d).

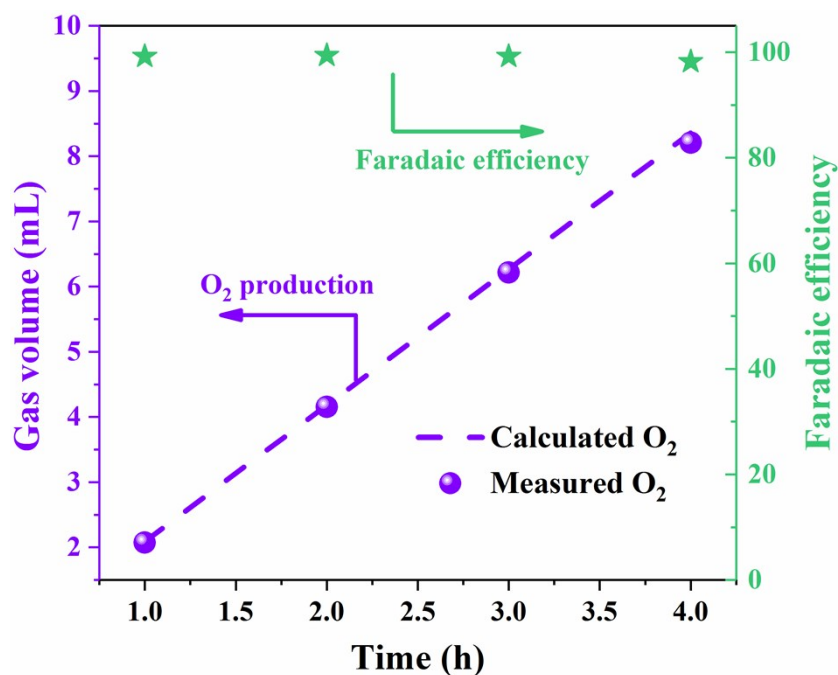


Figure S7 Faradaic efficiency of (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ for oxygen production.

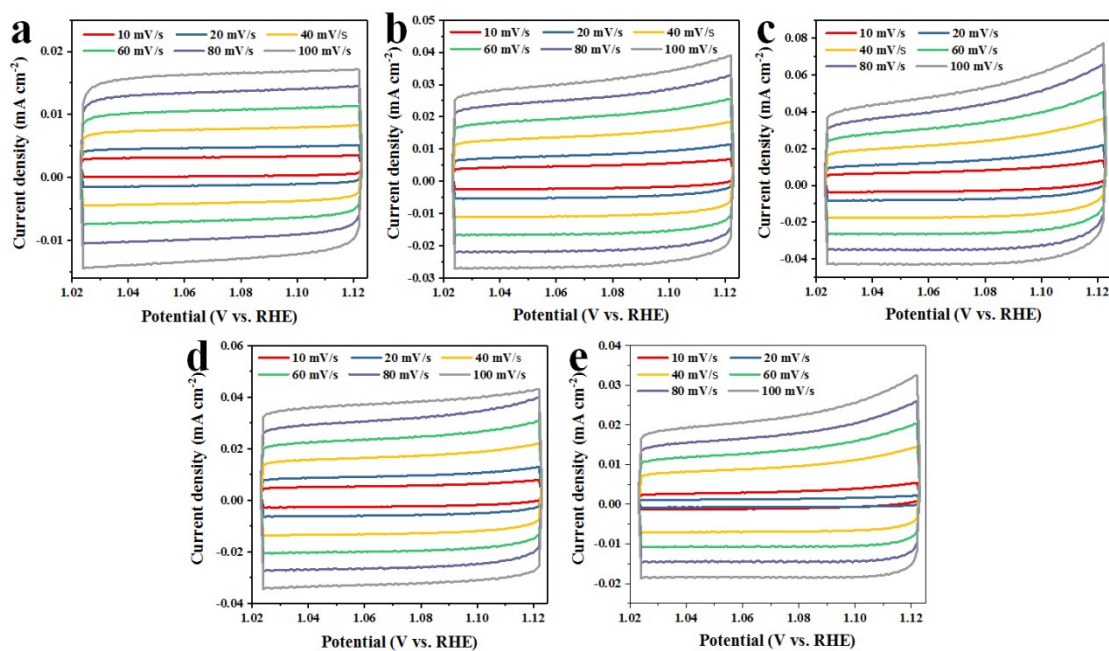


Figure S8 CV plots of (Cyclen@Fe)@COF-SO₃ (a), (Cyclen@Ni_{0.2}Fe_{0.8})@COF-SO₃ (b), (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ (c), (Cyclen@Ni_{0.8}Fe_{0.2})@COF-SO₃ (d) and (Cyclen@Ni)@COF-SO₃ (e) tested at various scan rates from 10 to 100 mV s⁻¹.

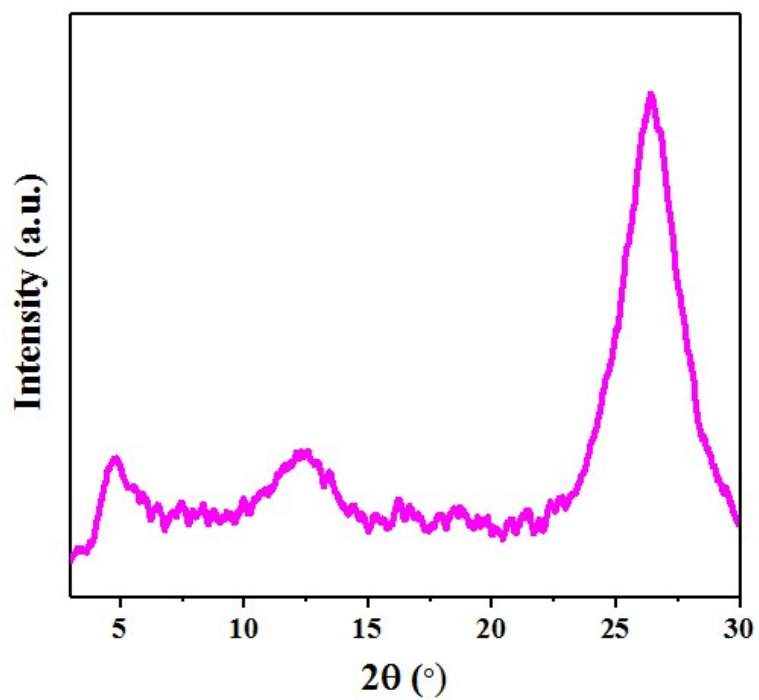


Figure S9 PXRD image of (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ after chronoamperometric measurement.

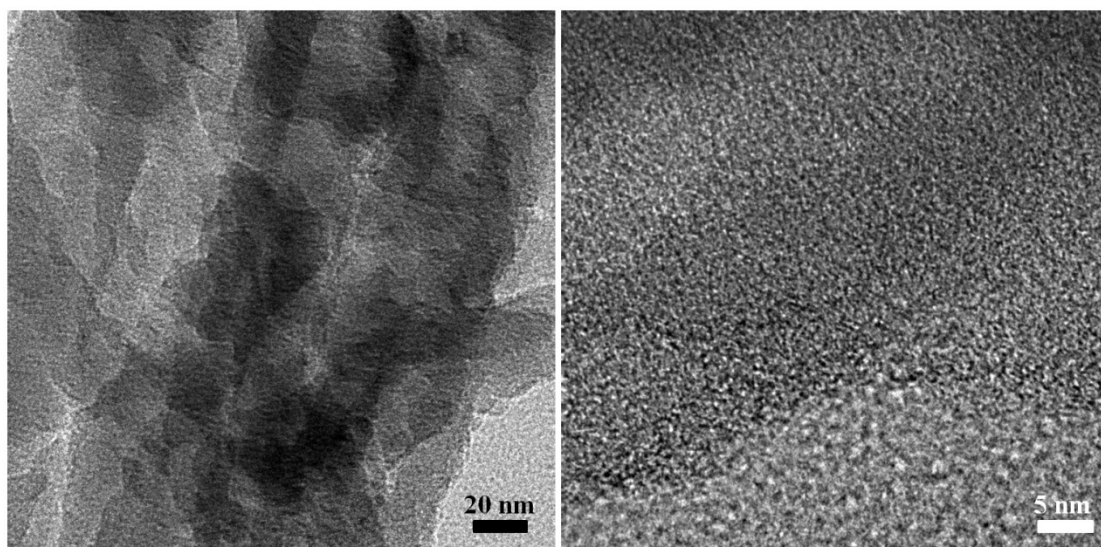


Figure S10 TEM and HRTEM image of (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ after chronoamperometric measurement.

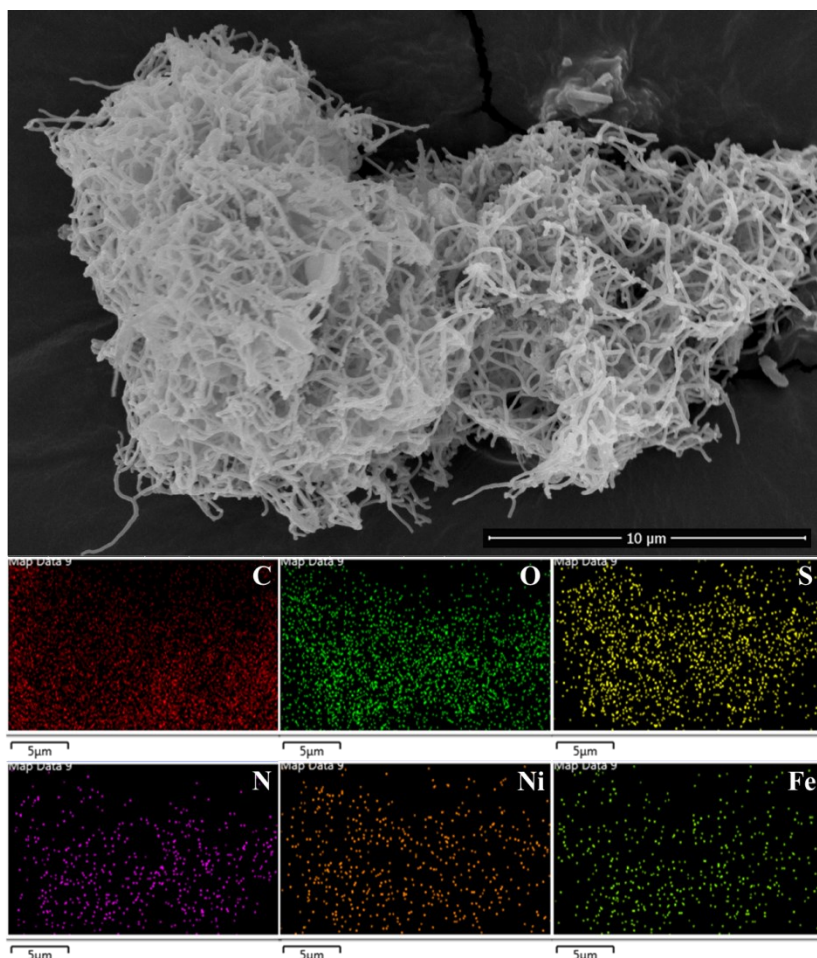


Figure S11 SEM image and SEM-EDS mapping of (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ after OER stability test.

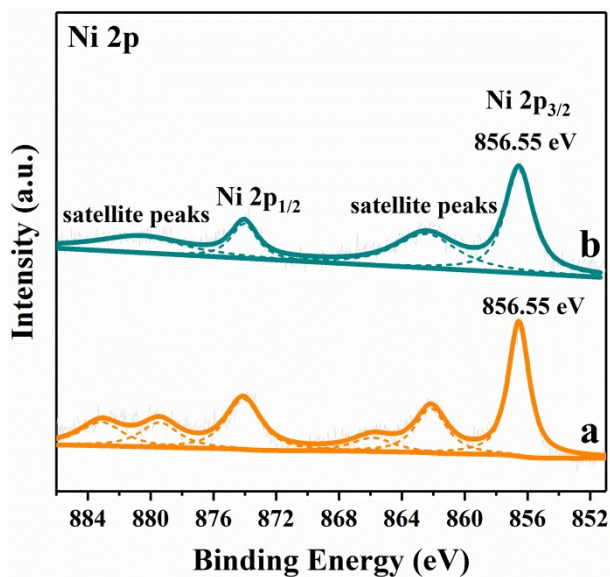


Figure S12 XPS spectra in the fine Ni 2p region for (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ before (a) and after OER stability test (b).

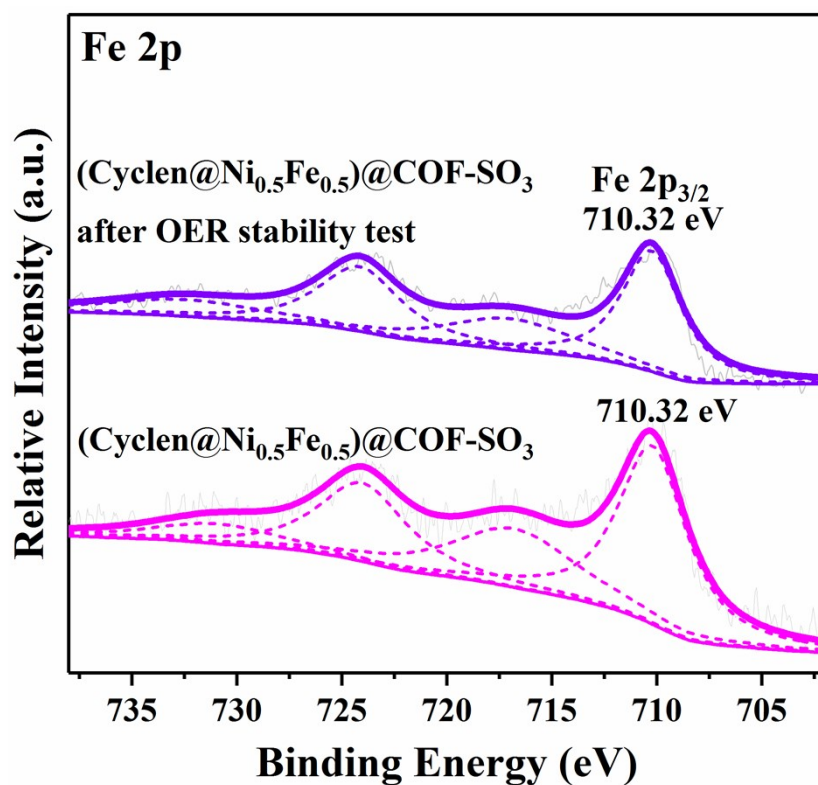


Figure S13 XPS spectra in the fine Fe 2p region for (Cyclen@Ni_{0.5}Fe_{0.5})@COF-SO₃ before and after OER stability test.

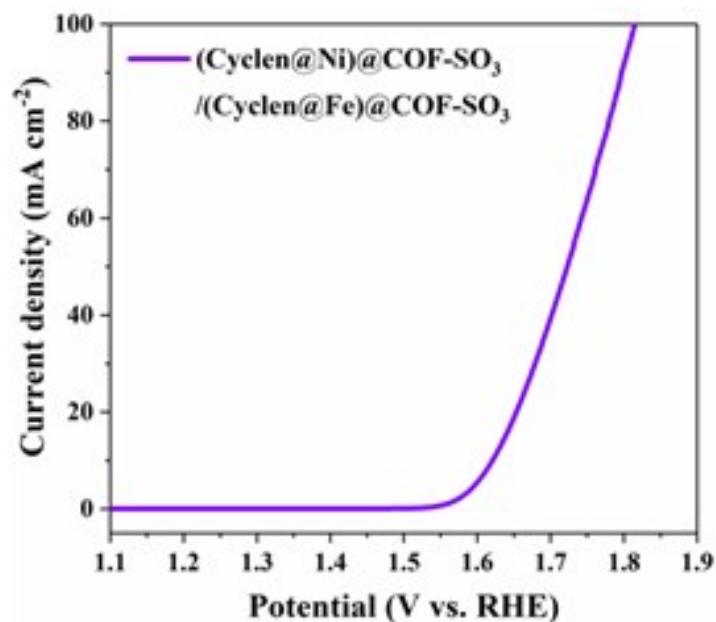


Figure S14 LSV curve of the mechanical mixture of (Cyclen@Ni)@COF-SO₃/(Cyclen@Fe)@COF-SO₃.

Table S1 ICP-AES results of different COFs.

Catalyst	Content (wt.%)		Ni/Fe mass ratio
	Ni	Fe	
(Cyclen@Ni)@COF-SO ₃	4.97	0	4.97/0
(Cyclen@Fe)@COF-SO ₃	0	5.12	0/5.12
(Cyclen@Ni _{0.2} Fe _{0.8})@COF-SO ₃	1.03	4.32	0.2/0.84
(Cyclen@Ni _{0.5} Fe _{0.5})@COF-SO ₃	2.53	2.47	0.5/0.49
(Cyclen@Ni _{0.8} Fe _{0.2})@COF-SO ₃	4.14	1.06	0.8/0.21

Table S2. Comparison of the OER activities of recently reported highly active catalysts in 1.0 KOH.

Catalysts	Overpotential at 10 mA cm ⁻² (mV vs. RHE)	Tafel slope (mV dec ⁻¹)	Mass loading (mg cm ⁻²)	Substrate	TOF (10 ⁻² s ⁻¹) at overpotential of 300 mV	Reference
(Cyclen@Ni _{0.5} Fe _{0.5})@C	276	43	0.15	carbon	69	This work
OF-SO ₃				cloth		<i>Adv. Energy Mater.</i>
Fe ₃ Co ₇ -B/CNT	265	30	0.3	GC	43	2019 , 9, 1901503
Fe ₁ Ni ₂ -BDC	260	35	0.255	GC	36@330 mV	<i>ACS Energy Lett.</i> 2019 , 4, 285–292
MIL-53(FeNi)/NF	233 at 50 mA cm ⁻²	31.4	2.63	Ni foam	40@252 mV	<i>Adv. Energy Mater.</i> 2018 , 8, 1800584
MAF-X27-OH	303	83	0.21	Cu Foil	1.9	<i>J. Am. Chem. Soc.</i> 2016 , 138, 8336.
CoO _x -ZIF	318	70.3	0.04	GC	8.2@320 mV	<i>Adv. Funct. Mater.</i> 2017 , 27, 1702546
CTGU-10c2	240	58	0.14	GC	5.378@240 mV	<i>Angew. Chem. Int. Ed.</i> 2019 , 58, 4227-4231.
0.1 KOH				Carbon		<i>Angew. Chem. Int. Ed.</i>
NNU-23	376	77.2	1	Carbon	3@400 mV	2018 , 57, 9660.
0.1 KOH				cloth		<i>Nat. Energy</i> 2016 , 1, 16184.
NiCo-UMOFNs	250	42	0.2	GC	86	<i>ACS Nano</i> 2015 , 9, 1977.
NiFeLDH/GO	210	42	0.25	GC	10	<i>Science</i> 2016 , 352, 333.
G-FeCoW	217 (±2)	37 (±2)	0.21	GC	46(±8)	<i>Nat. Commun.</i> 2014 , 5, 4477.
LDHNiFe	300	40	0.07	GC	7	<i>J. Am. Chem. Soc.</i> 2014 , 136, 16481.
CoMn LDH	324	43	0.142	GC	7.5	<i>J. Am. Chem. Soc.</i> 2017 , 139, 1778.
Fe ₃ -Co ₂	225	48	0.2	Ni foam	182	
0.1 M KOH						