

## Electronic Supplementary Information

### **3D Flower-like Bimetallic Ni-Co Metal-Organic Framework as Electrocatalyst for Oxygen Evolution Reaction**

*Chao Shuai*<sup>\*a,b iD</sup>, *Chao Kong*<sup>a,b</sup>, *Yingying Li*<sup>a,b</sup>, *Liang Zhang*<sup>a,b</sup>, *Caiju Qi*<sup>a</sup>, *Zunli Mo*<sup>\*b,c iD</sup>

<sup>a</sup>*College of Petroleum and Chemical Engineering, Longdong University, Qingyang 745000, China. E-mail: shuai\_xc@163.com*

<sup>b</sup>*Gansu Key Laboratory of Efficient Utilization of Oil and Gas Resources in Longdong, Qingyang, 745000, China*

<sup>c</sup>*Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, People's Republic of China. E-mail: mozlwnnu@126.com*

## Experimental Section

### Chemicals

Nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99 %), cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99 %), 1,3,5-Benzenetricarboxylic acid (BTC, 98%) and Commercial  $\text{RuO}_2$  were bought from Aladdin Ltd. Methanol (analytical grade) was bought Sinopharm Chemical Reagent Co., Ltd. All Chemicals and reagents were used without further purification.

### Synthesis of Materials

Preparation of flower-like bimetallic (F-Ni<sub>1</sub>Co<sub>4</sub>-BTC) MOFs: In a typical method,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.88 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (3.52 mmol) and BTC (2.4 mmol) were dissolved in 50 mL absolute methanol. The mixture was stirred until forming clear solution, and then transferred to a 100 mL PTFE-lined stainless-steel autoclave. The autoclave was heated at 170 °C for 24 h. After cooling to room temperature, the precipitates were obtained by centrifugation, washed several times with methanol, then dried at 60 °C overnight under vacuum. The similar fabrication procedure was adopted for the preparation of F-Ni-BTC, F-Co-BTC and other bimetallic F-NiCo-BDC except using different molar ratios of Nickel (II) chloride and cobalt (II) chloride at the beginning (4.4 mmol was total metal ions), the details in Table S1.

F-Ni<sub>1</sub>Co<sub>4</sub>-BTC grown on Carbon Cloth (F-Ni<sub>1</sub>Co<sub>4</sub>-BTC/CC): The fabrication procedure employed the equal metal concentration and same

reaction conditions as the above method. A piece of carbon cloth (CC, 1×1 cm) was pre-treated with sonication in 2.0 M HCl and ethanol for 4 h, respectively. The treated carbon cloth was placed in the precursor solution and was transferred in a 100 mL autoclave. The obtained CC substrate was washed with ethanol and dried in a flowing N<sub>2</sub> gas.

### **Material characterization**

Thermogravimetric analyzer (AutoTGA 2950HR V5.4A, TA Instruments) was used to obtain pyrolysis temperature by using platinum pans at a heating rate of 5 C min<sup>-1</sup> in a N<sub>2</sub> atmosphere. The surface morphology and detailed microstructure of the as-prepared materials were analyzed by scanning electron microscope (SEM, JEOL JSM6510LV) and transmission electron microscope (TEM, Hitachi, HITACHI H-8100). The elemental distributions were measured by using energy-dispersing X-ray spectroscopy (EDS). The X-ray diffraction (XRD, Shimadzu D-6000) with Cu K $\alpha$  radiation ( $\lambda=0.15418$  nm) was employed to investigate the phase structure of the materials. The chemical-state analysis was carried out by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C). N<sub>2</sub> adsorption/desorption tests were applied at 77 K by a gas adsorption analyzer (Micromeritics ASAP 2020M). Fourier transform infrared spectrophotometer (FTIR, AVTA-TAR, 370) was conducted to decide the functional groups on the as-prepared materials over a range of 400 to 4000 cm<sup>-1</sup>.

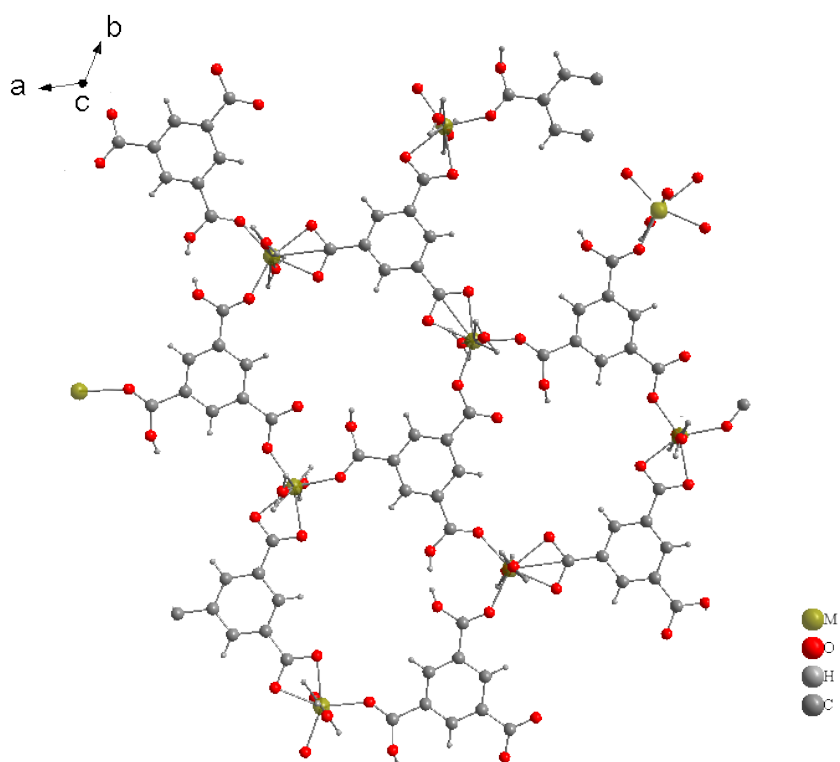
## Electrochemical Characterizations

A conventional three-electrode system (CHI 660D, CH Instruments, Inc. Shanghai) was employed for OER measurements at room temperature using 1.0 M KOH as the electrolyte. Among a Pt foil and a Hg/HgO electrode were used as the counter and reference electrode, respectively. The glassy carbon electrode (GCE, the diameter of 3 mm) was modified catalysts as the working electrodes (area: 0.071 cm<sup>2</sup>). For the preparation of the working electrode. Typically, the GCE was polished with Al<sub>2</sub>O<sub>3</sub> slurry (0.3 μm) before use. 5 mg of the as-synthesized catalyst was sonicated in a mixed solvent of water (600 μL), ethanol (400 μL) and 10 μL 10 wt% Nafion, then forming a homogeneous ink. Next, 5 μL of the ink was drop-casted onto the GCE, leading to the mass loading of catalyst (about 0.35 mg cm<sup>-2</sup>). The F-Ni<sub>1</sub>Co<sub>4</sub>-BTC grown directly on carbon cloth were used as the working electrode without further processing (about 0.3 mg cm<sup>-2</sup>). In this work, the electrolyte solution was purged with high-purity O<sub>2</sub>, and magnetically stirred to remove bubbles attached to the electrode surface. Polarization curves were recorded with the scan rate of 5 mV s<sup>-1</sup>. The working electrodes were cycled several times with 100 mV s<sup>-1</sup> until the signals were stabilized before the data were collected. All reported potentials were referenced to the reversible hydrogen electrode (RHE), and were corrected for iR at 95%. In 1.0 M KOH (pH = 14), E (RHE) = E (Hg/HgO) + 0.924 V - 95% iR. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10 mHz to 100 kHz

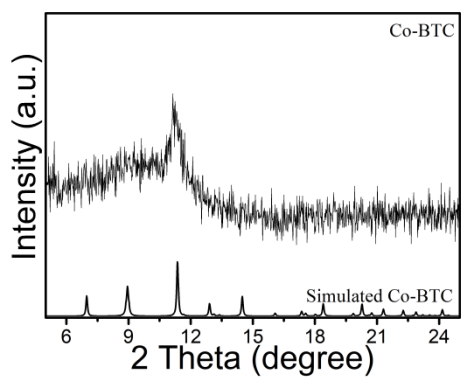
with an AC amplitude of 10 mV. Chronopotentiometry responses and LSV curves were obtained to evaluate the catalyst durability.

**Table S1.** Experimental condition and the chemical compositions for F-Ni<sub>x</sub>Co<sub>y</sub>-BTC samples.

samples	Ni mmol	Co mmol	Ni:Co	BTC mmol	EDS analysis [Atom%]			
					Ni	Co	O	C
F-Ni-BTC	4.4	0	1:0	2.4	33.1	—	32.8	34.1
F-Co-BTC	0	4.4	0:1	2.4	—	34.5	30.4	35.1
F-Ni <sub>2</sub> Co <sub>1</sub> -BTC	2.93	1.46	2:1	2.4	21.8	10.4	31.7	36.1
F-Ni <sub>1</sub> Co <sub>1</sub> -BTC	2.2	2.2	1:1	2.4	16.8	17.3	30.9	35.0
F-Ni <sub>1</sub> Co <sub>2</sub> -BTC	1.46	2.93	1:2	2.4	11.3	23.2	31.7	33.8
F-Ni <sub>1</sub> Co <sub>4</sub> -BTC	0.88	3.52	1:4	2.4	7.4	27.3	30.9	34.4
F-Ni <sub>1</sub> Co <sub>6</sub> -BTC	0.63	0.37	1:6	2.4	4.6	29.1	32.4	33.9

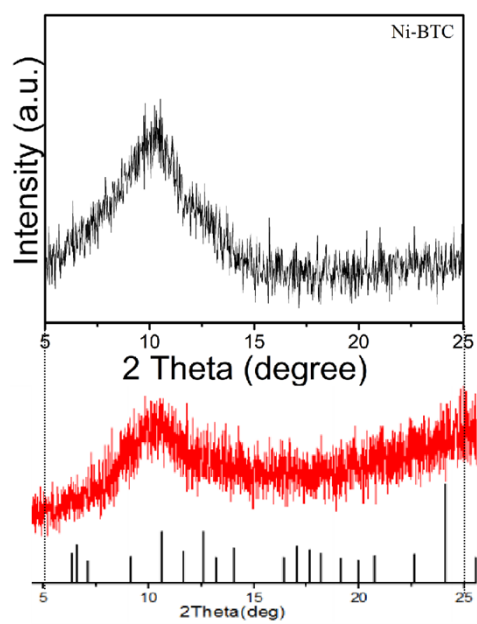


**Fig. S1** the atomic space structure of F-NixCoy-BTC samples (M = Ni and Co).



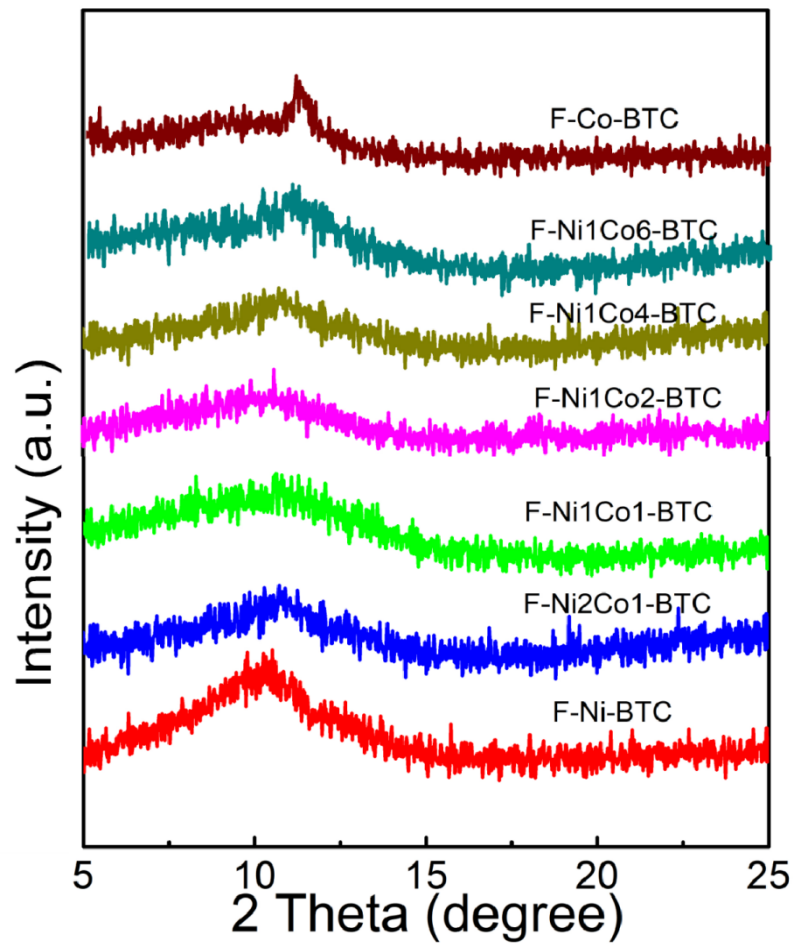
RSC Adv., 2019, 9, 15642-15647

**Fig. S2** PXRD patterns of the F-Co-BTC.



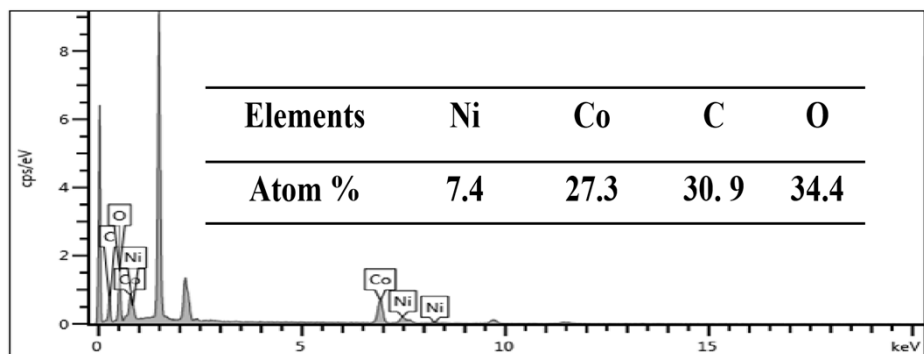
Chem. Commun., 2014, 50, 9485-9488

**Fig. S3** PXRd patterns of the F-Ni-BTC.

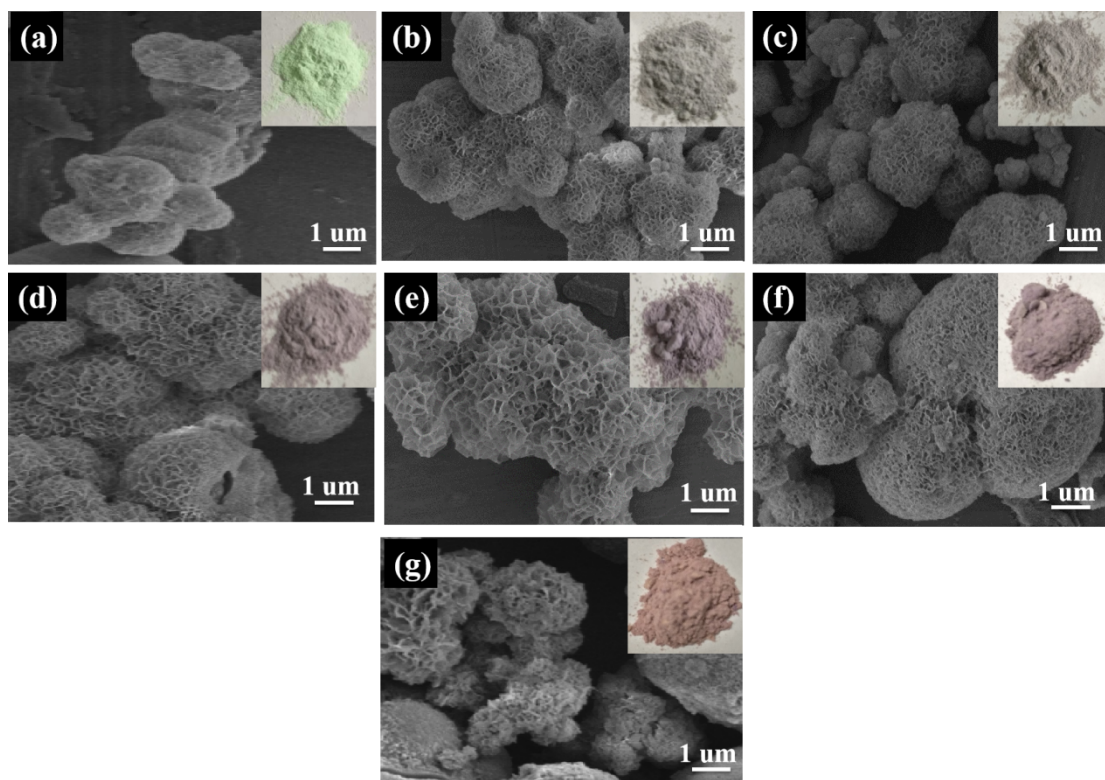


**Fig. S4** PXRD patterns with 5~25° of F-NixCoy-BTC.

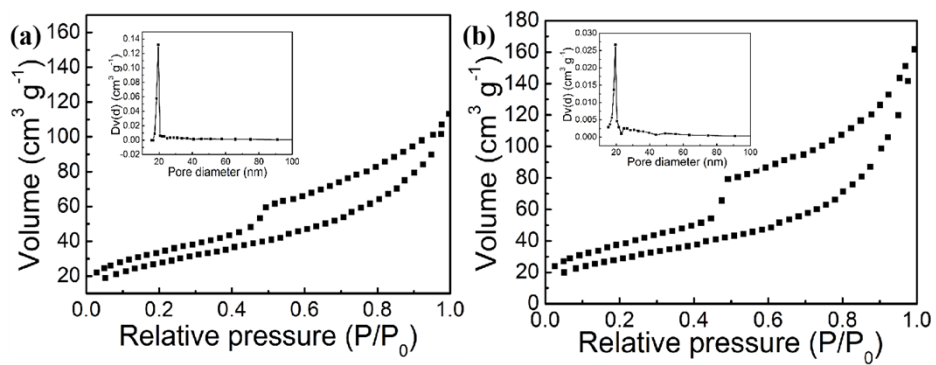




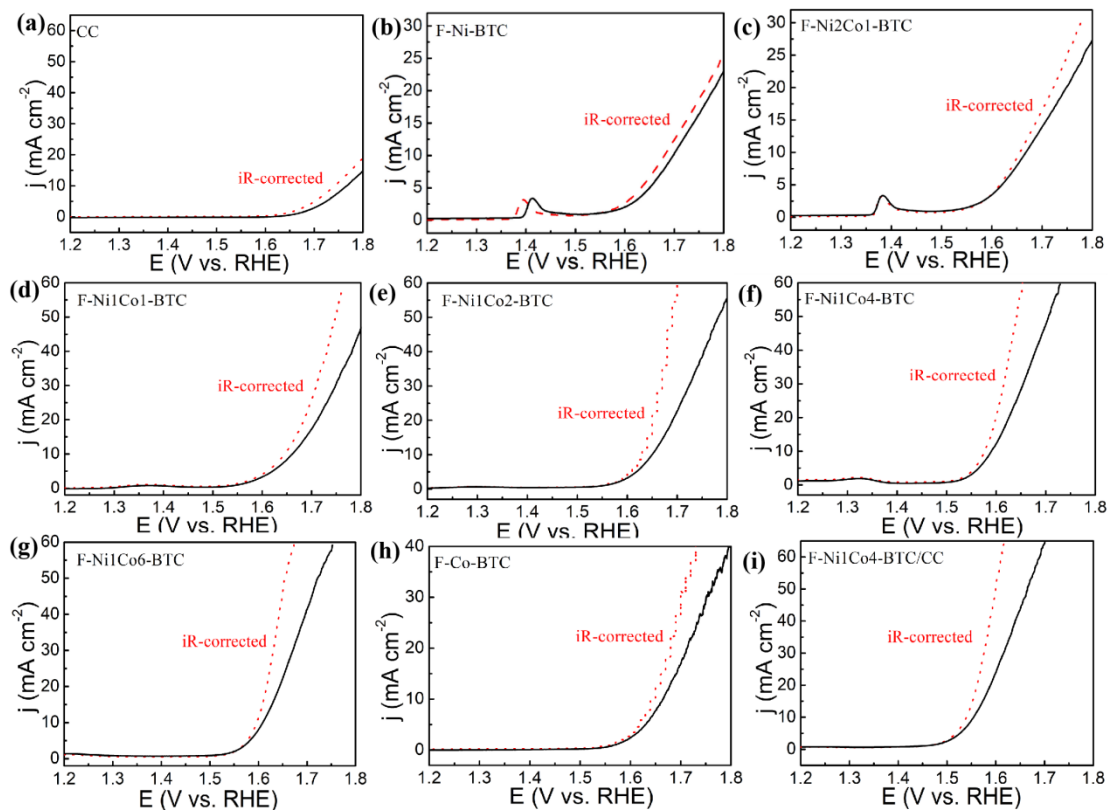
**Fig. S5** EDS spectra of the F-Ni<sub>1</sub>Co<sub>4</sub>-BTC.



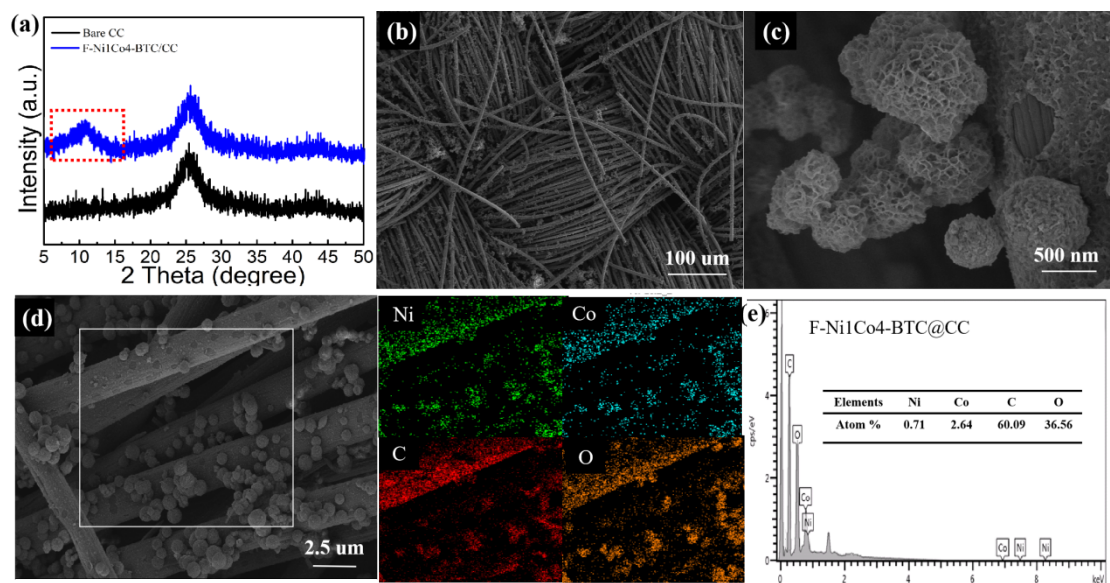
**Fig. S6** SEM images of different F-NixCoy-BTC MOFs and their corresponding optical photograph. (a) Ni-BTC, (b) Ni<sub>2</sub>Co<sub>1</sub>-BTC, (c) Ni<sub>1</sub>Co<sub>1</sub>-BTC, (d) Ni<sub>1</sub>Co<sub>2</sub>-BTC, (e) Ni<sub>1</sub>Co<sub>4</sub>-BTC, (f) Ni<sub>1</sub>Co<sub>6</sub>-BTC and (g) Co-BTC.



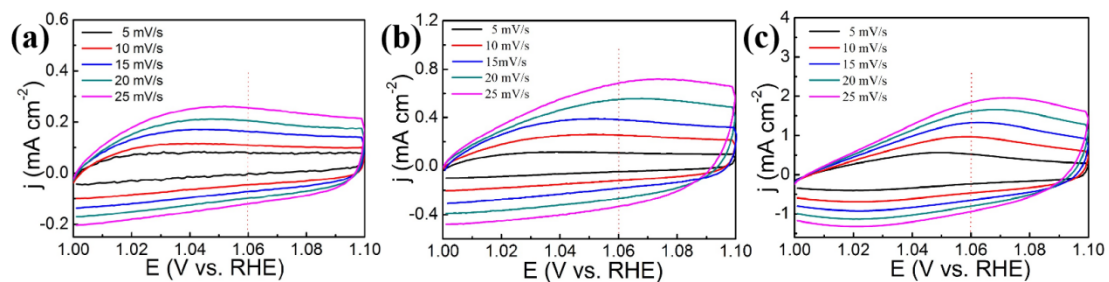
**Fig. S7** N<sub>2</sub> adsorption-desorption isotherms and pore size distributions of (a) F-Ni-BTC and (b) F-Co-BTC.



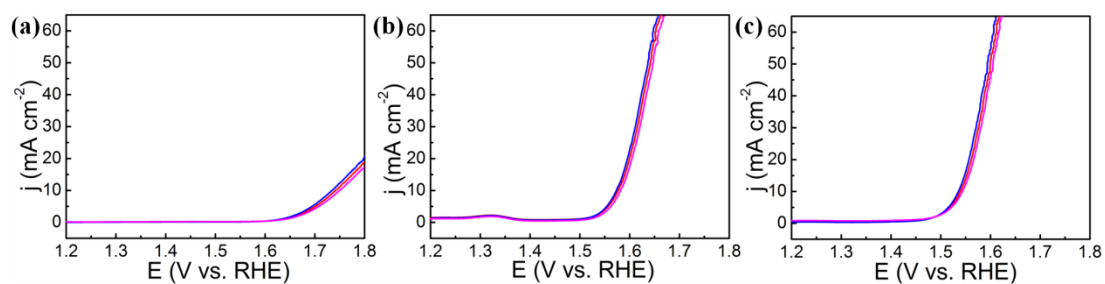
**Fig. S8** Polarization curves of various samples with and without iR compensation on GCE and F-Ni1Co4-BTC grown on carbon cloth in 1.0 M KOH. The solution series resistances ( $R$ ) were determined by the EIS, all of the catalysts show the similar  $R$  ( $\sim 8.3 \Omega$ ).



**Fig. S9** (a) PXRD patterns, (b, c) SEM images and (d, e) EDS spectrum and elemental content of F-Ni<sub>1</sub>Co<sub>4</sub>-BTC grown on the carbon cloth (F-Ni<sub>1</sub>Co<sub>4</sub>-BTC/CC).



**Fig. S10** Cyclic voltammograms at different scan rate for (a) CC, (b) F-Ni1Co4-BTC and (c) F-Ni1Co4-BTC/CC in 1.0 M KOH electrolyte solution.



**Fig. S11** Reproducibility of the OER properties by various catalysts. (a) CC, (b) F-Ni1Co4-BTC and (c) F-Ni1Co4-BTC/CC. Three electrodes were obtained from the same ink by drop casting.

**Table S2.** Comparison of OER activity data for Ni1Co4-BTC with various MOFs and their derivatives.

Catalysts	$\eta$ (mV) at (x) mA cm <sup>-1</sup>	Tafel slope (mV dec <sup>-1</sup> )	Reference
F-Ni1Co4-BTC	343 (10)	61	This work
F-Ni1Co4-BTC/CC	298 (10)	48	This work
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -CoBDC	410 (10)	48	ACS Nano 2017,11,5800
NiCoFe-MOF	320 (10)	49	Adv. Funct. Mater., 2018, 28, 1802129
Ni-MOF/NF	320 (100)	123	Inorg. Chem. Front., 2018,5, 1570
MOF(Fe <sub>1</sub> -Co <sub>3</sub> ) <sub>550N</sub>	390 (10)	73	Nanoscale 2016, 8, 1033
Co-MoF/NF	340 (50)	77	Inorg. Chem. Front. 2018, 5, 344
CNTs@NiCoP/C	297 (10)	57	Nanoscale 10 (2018) 13555
NiCoP/C	330 (10)	96	Angew. Chem. Int. Ed. Engl., 2018, 56, 3897
Co@Co <sub>3</sub> O <sub>4</sub> @NMCC/rGO	340 (10)	71	Dalton Trans., 2016, 45, 5575
Co-B/C	320 (10)	75	Electrochem. Commun., 2018, 86, 140
NiCoS-3	320 (10)	59	Int. J. Hydrogen Energy 2018, 43, 8815
$\alpha$ -Co(OH) <sub>2</sub>	340 (10)	44.6	Electrochim. Acta 2018, 273, 327