

## **Preparation of Hierarchical Trimetallic Coordination Polymer Film as Efficient Electrocatalyst for Oxygen Evolution Reaction†**

Xiao-Jue Bai,<sup>‡a</sup> Yu-Nong Li,<sup>‡a</sup> Xi-Man Yang,<sup>a</sup> Ming-Yu Zhang,<sup>a</sup> Lei Shao,<sup>a</sup>  
Bing Zhang,<sup>a</sup> Tie-Qiang Wang,<sup>a</sup> Xue-Min Zhang,<sup>a</sup> Li-Ying Zhang,<sup>a</sup> Yu Fu<sup>\*a</sup>  
and Wei Qi<sup>\*b</sup>

a. Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, P. R. China

b. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, P. R. China

\*E-mail: fuyu@mail.neu.edu.cn (Y. F.).

\*E-mail: wqi@imr.ac.cn (W. Q.).

## Experimental section

### *Materials*

Cobalt acetate tetrahydrate ( $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ), nickel acetate tetrahydrate ( $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2$ ), terephthalic acid ( $\text{H}_2\text{BDC}$ ) and potassium hydroxide (KOH) were purchased from Energy Chemical (Shanghai). Nafion,  $\text{RuO}_2$ , *N,N*-Dimethylformamide (DMF) and acetonitrile ( $\text{CH}_3\text{CN}$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in this work was deionized water. All chemicals used in this study were of analytical grade and used without further purification.

### *Preparation of hierarchical trimetallic coordination polymer film onto Ni foam*

$\text{H}_2\text{BDC}$  (33.2 mg, 0.2 mmol) was dissolved in 7.5 mL of mixture of DMF and  $\text{CH}_3\text{CN}$  (V:V=2:1) in a vial. Then the transparent solution was added into a glass petri dish covered with solid substrates. After that,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (5 mg),  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3 mg) and  $\text{FeCl}_2$  (1 mg) were dissolved in 1.5 mL of mixture of DMF and  $\text{CH}_3\text{CN}$  (V:V=1:2), and the metal solution was uniformly sprayed into the glass petri dish on the top of the BDC solution with the flow rate of 5  $\mu\text{L}/\text{sec}$ . The synthetic process was maintained in static conditions, and the brown thin films floated at the liquid surface as free-standing films. Subsequently, the reaction solution was carefully removed from the glass petri dish, and the resulting hierarchical trimetallic coordination polymer film was deposited onto Ni foam substrate.

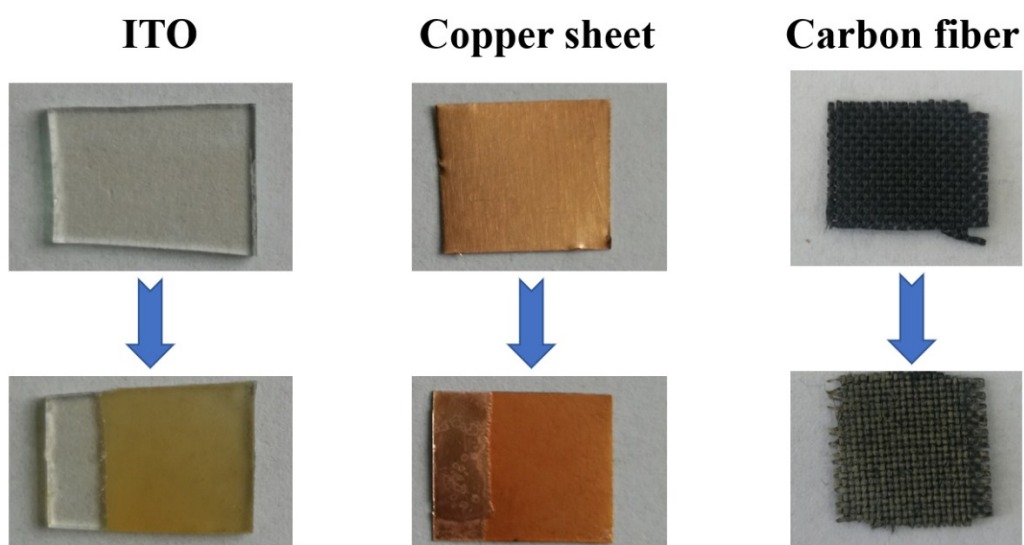
### *Characterization*

Morphologies of samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi SU8010). The elemental mapping was done by energy-dispersive X-ray (EDX, Oxford Instruments). The crystallographic information was analyzed by X-ray diffraction (XRD, PANalytical Empyrean) equipped with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The organic groups in the hierarchical trimetallic coordination polymer film was characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70). The composition of the materials was analyzed through quantitative X-ray photoelectron spectroscopy (XPS) which gave

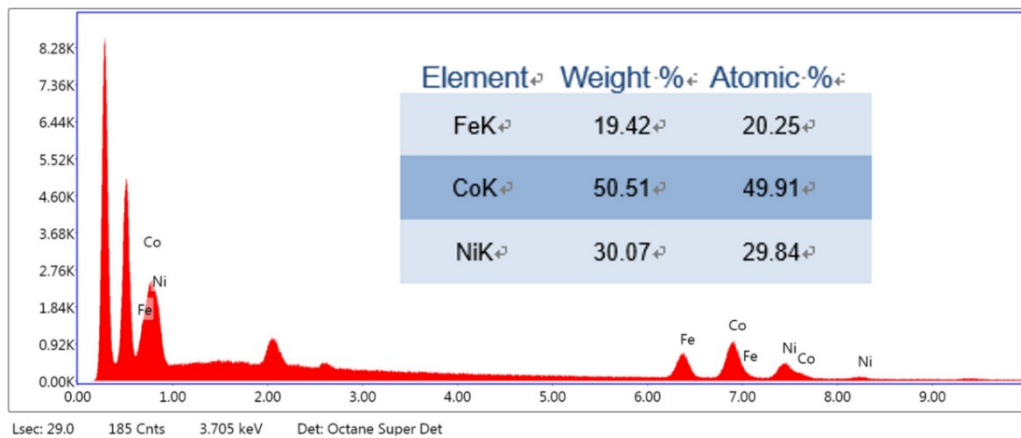
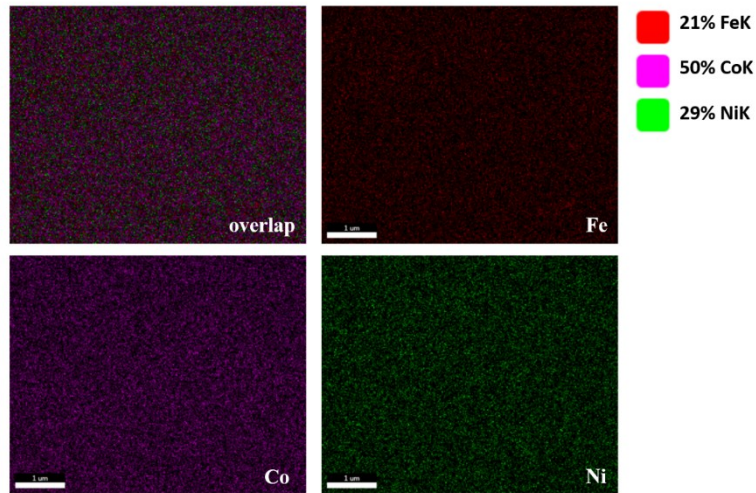
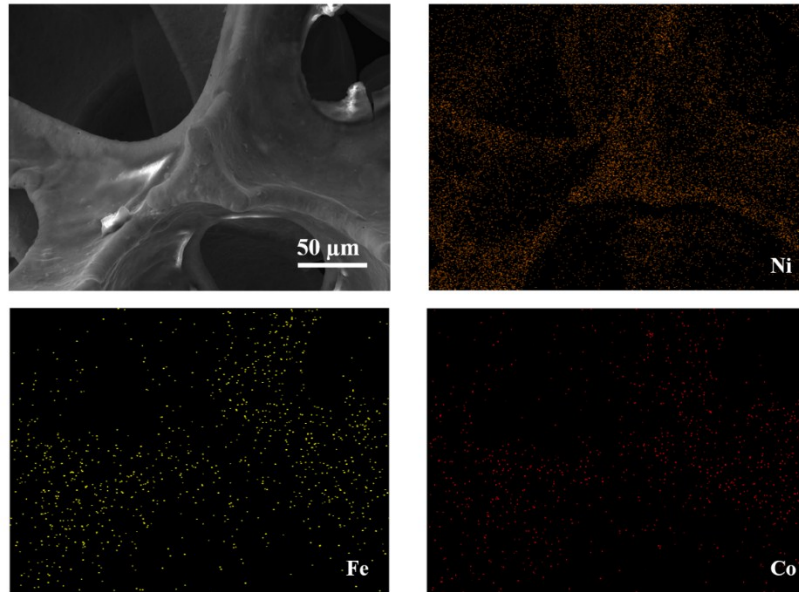
information about the surface electronic states of the elements (THERMO VG ESCALAB250). Thermogravimetric analysis (TGA) was carried out with a thermobalance (TGA-2050, TA Instruments) under N<sub>2</sub> from room temperature to 700 °C with a temperature ramp of 10 °C/min. Specific surface areas of the samples were determined by using nitrogen adsorption-desorption isotherms at 77 K (Micromeritics ASAP 2020 system). The ultrasonic spray nozzle & system was manufactured by Siansonic Technology Co., Ltd. The ultrasonic generator was DP30 and the nozzle is ZPQ-S-95.

#### *Electrochemical Tests*

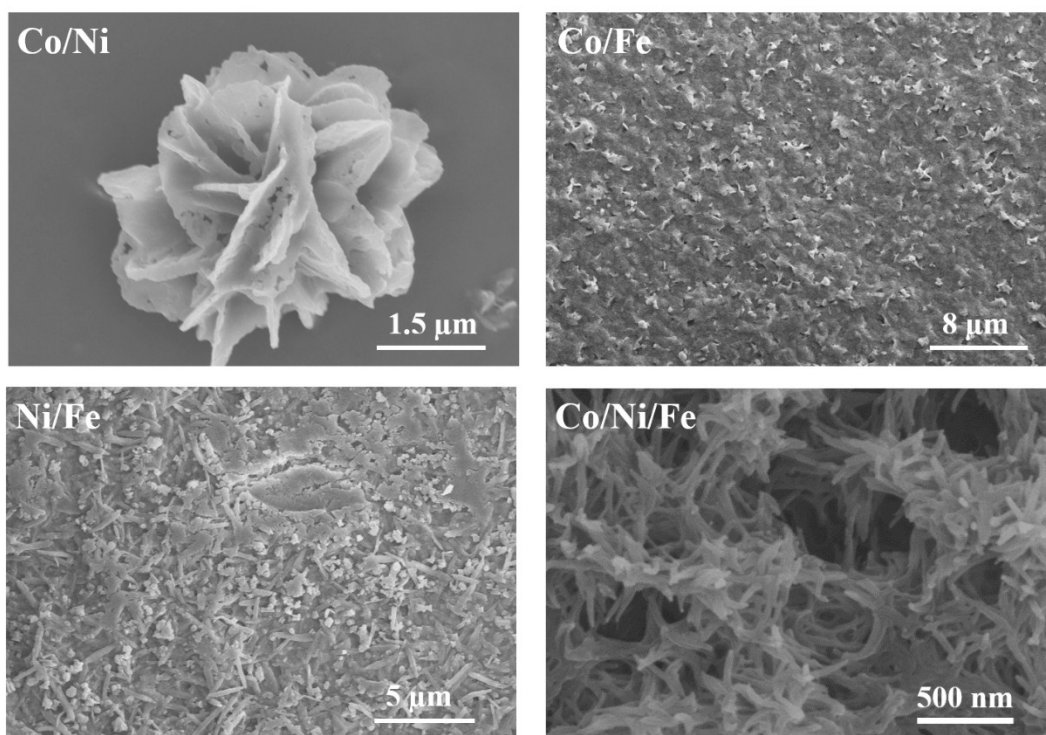
The electrochemical test for OER was performed on a CHI 660E electrochemical workstation in a standard three-electrode system using Co<sub>0.5</sub>Ni<sub>0.3</sub>Fe<sub>0.2</sub>BDC-HCP/Ni foam as working electrode, a Platinum as counter electrode, and an Ag/AgCl as reference electrode. RuO<sub>2</sub> ink was prepared by ultrasonication of the mixture of 3 mg of RuO<sub>2</sub>, 1 mL of ethanol and 50 μL of 5 wt % Nafion. Then, the RuO<sub>2</sub> ink was loaded on Ni foam to achieve a mass loading of 0.6 mg cm<sup>-2</sup>. Linear sweep voltammetry (LSV) curves of the samples were recorded in 1 M KOH at a scan rate of 5 mV s<sup>-1</sup>, and the potentials reported here were calibrated with respect to the reversible hydrogen electrode (RHE):  $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \times \text{pH} + 0.197$ . Polarization curves were expressed as the potential ( $\eta$ ) vs log current ( $\log |j|$ ) to obtain the Tafel plots. By fitting the linear portion of the Tafel plots to the Tafel equation [ $\eta = b \log(j) + a$ ], the Tafel slope ( $b$ ) was obtained. Electrochemical impedance spectra (EIS) were recorded in the frequency range from 0.1 to 10<sup>5</sup> Hz with an AC amplitude of 5 mV at an applied potential of 1.53 V (vs the RHE). The effective surface area of catalysts material was tested by estimating its electrochemical double layer capacitances ( $C_{dl}$ ) with CV. CV curves were performed at a potential range of 0.2-0.3 V vs RHE where no obvious electrochemical features corresponding to the Faradaic current were observed. The capacitive currents at 0.25 V were plotted against the scan rate (0.02 mV/s-0.2m V/s). Durability of the Co<sub>0.5</sub>Ni<sub>0.3</sub>Fe<sub>0.2</sub>BDC-HCP/Ni foam for OER catalysis was evaluated by chronoamperometry at a potential of 1.47 V (vs the RHE).



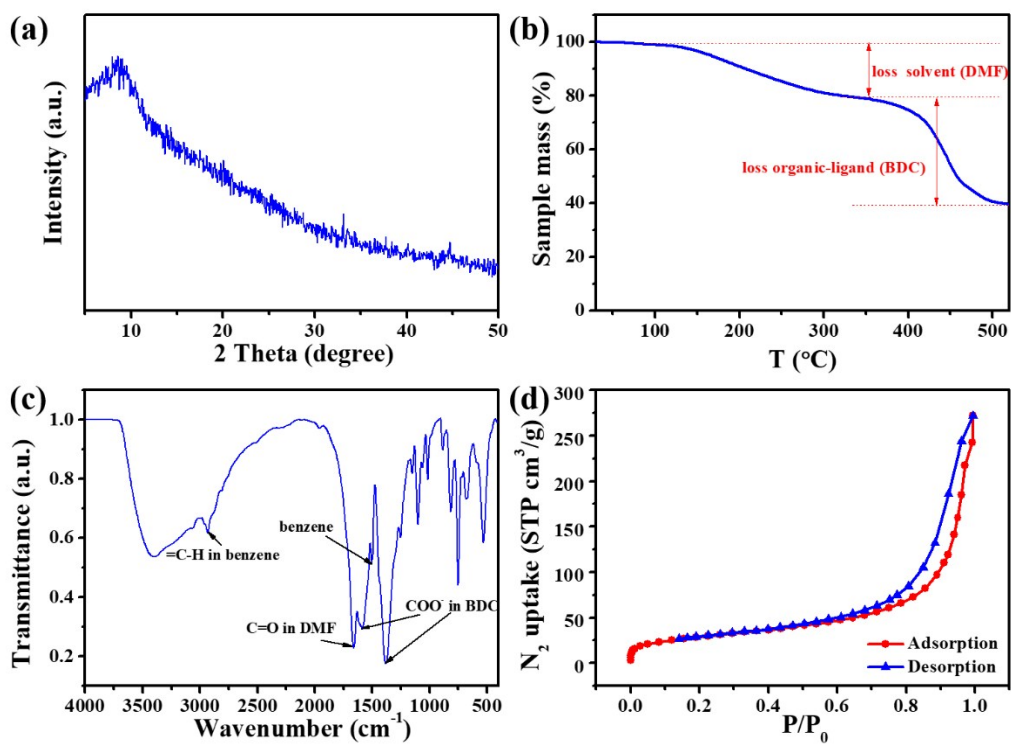
**Fig. S1** The optical images of  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF}$  on ITO, copper sheet and carbon fiber (from left to right).



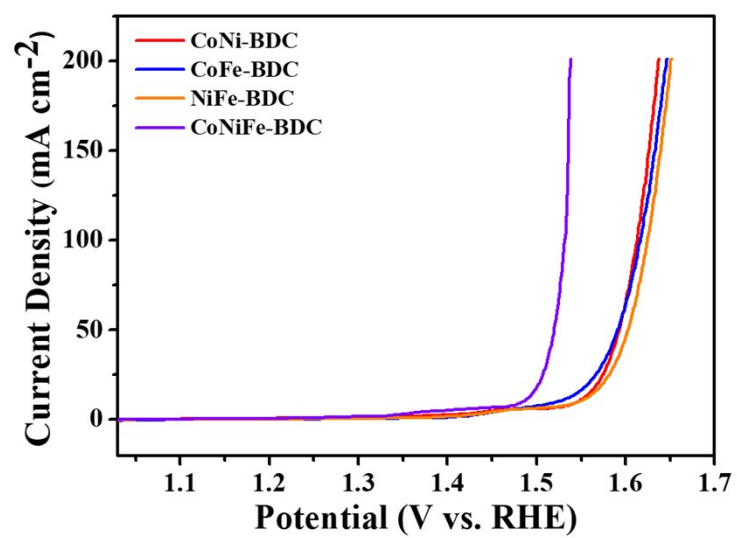
**Fig. S2** Energy dispersive X-ray (EDX) elemental map images of  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF/Ni}$  foam



**Fig. S3** The SEM images CoNi-BDC (without Fe), CoFe-BDC (without Ni), NiFe-BDC (without Co) and CoNiFe-BDC. (from left to right)

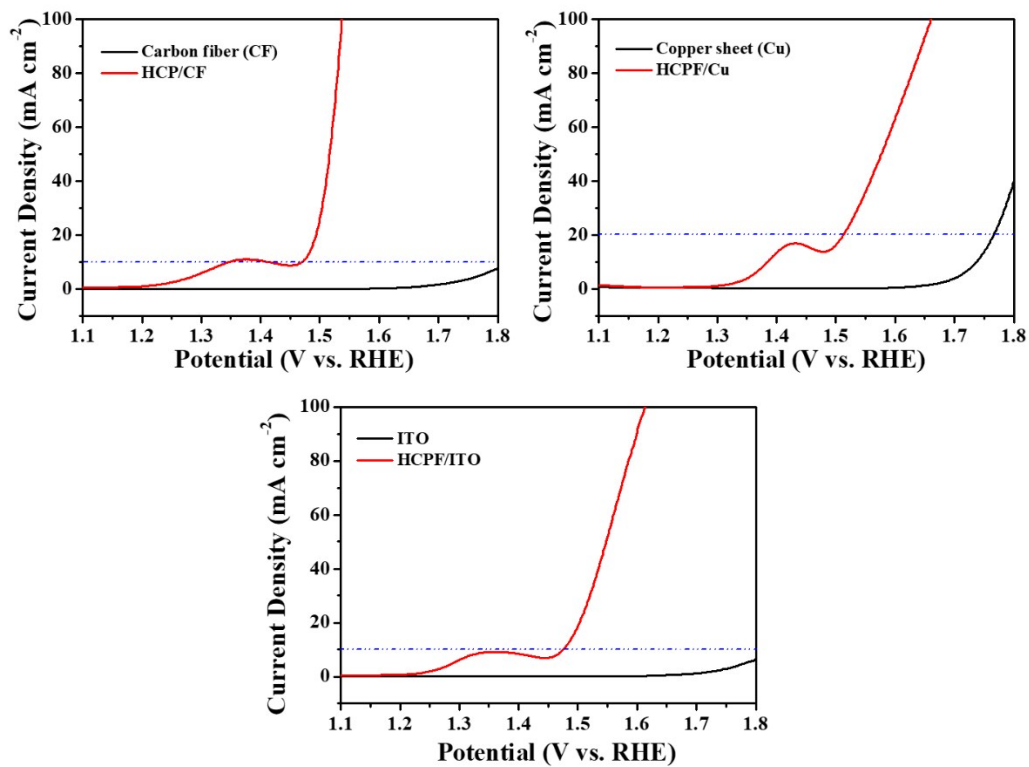


**Fig. S4** (a) XRD patterns, (b) thermogravimetric analysis, (c) FT-IR spectrum and (d)  $\text{N}_2$  adsorption/desorption isotherms of  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF}$ .

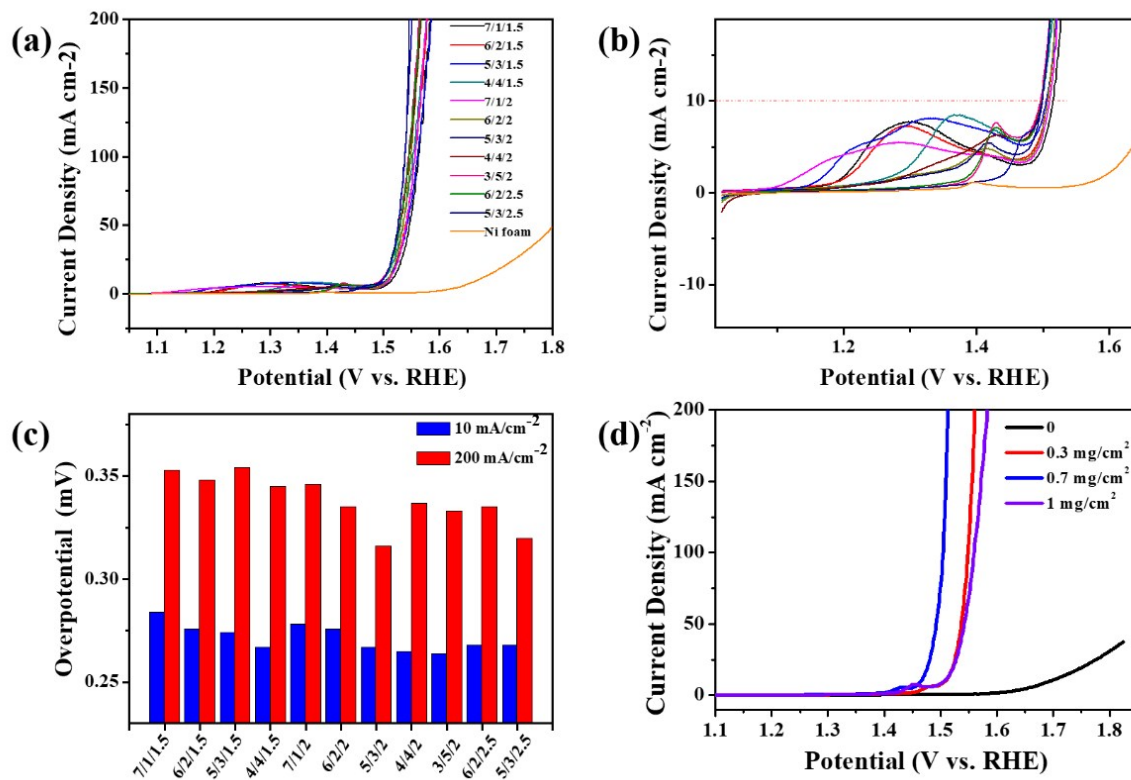


**Fig. S5** LSV curves of CoNi-BDC/Ni foam, CoFe-BDC/Ni foam, NiFe-BDC/Ni foam and CoNiFe-BDC/Ni foam for OER electrocatalysis in 1m KOH.

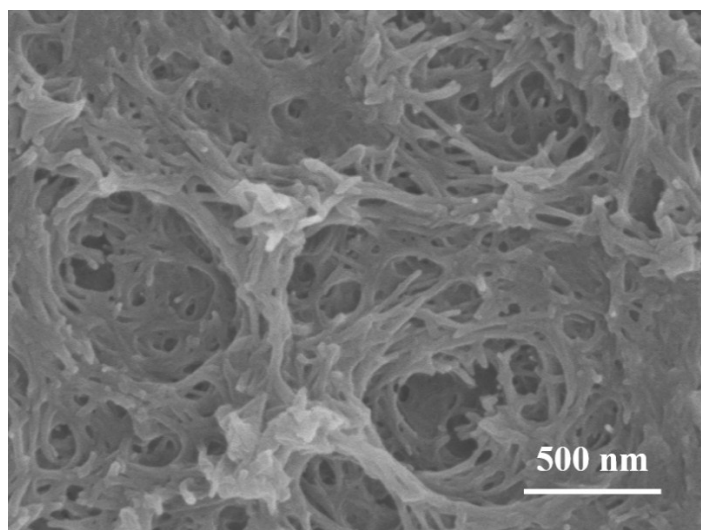




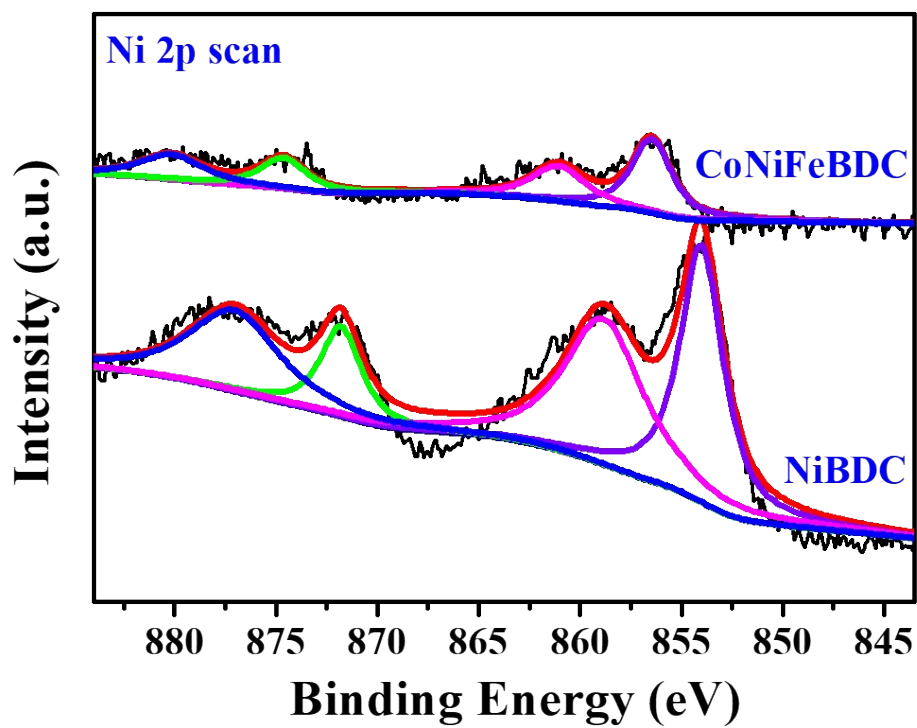
**Fig. S6** LSV curve of  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF}$  onto different substrates, i.e.,  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF}$ /carbon fiber,  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF}$ /copper sheet,  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC-HCPF}$ /ITO



**Fig. S7** The LSV curves of Co<sub>x</sub>Ni<sub>y</sub>Fe<sub>z</sub>-BDC film/Ni foam with different proportion (x y z) of three metals (Co Ni Fe) and Co<sub>0.5</sub>Ni<sub>0.3</sub>Fe<sub>0.2</sub>BDC-HCPF/Ni foam with different loading mass for OER.



**Fig. S8** The SEM image of the catalysts after OER.



**Fig. S9** High-resolution Ni 2p XPS spectra of NiBDC and  $\text{Co}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{BDC}$ .