

## Supporting Information

# Bimetallic ZnCo Nanorods Array for Highly Reactive and Durable Hydrogen Evolution Reactions

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## Experimental Section

### Pretreatment of nickel foam

Nickel foam (NF 2\*3 cm<sup>2</sup>) was cleaned in 1 M HCl for 15 minutes beneath ultrasonication in order to eliminate the oxidation layer on the surface, Sonicate in ultrapure water and ethanol for 10 minutes, respectively. Finally, the treated nickel foam (NF) was once vacuum dried.

### Preparation of ZnCo<sub>2</sub>(OH)F on nickel foam

Typically, 2 mmol Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 4 mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 15 mmol (NH<sub>4</sub>F) and 10 mmol (CO(NH<sub>2</sub>)<sub>2</sub>) were dissolved in 30 mL ultrapure water, and the solution was fully stirred for 20 minutes to form a homogeneous solution, then the solution and as-prepared NF substrate were moved to a 50 mL Teflon-lined stainless steel vessel, which was then sealed, heated and maintained at 120 °C for 12 h. After cooling to room temperature naturally, the uniformly grown faint purple ZnCo<sub>2</sub>(OH)F/NF (zinc/cobalt was 1:2) was taken out from the solution and washed with ultrapure water and ethanol in sequence, then dried in a vacuum drying oven at 60 °C for 12 h. For comparison, different samples of ZnCo<sub>2</sub>(OH)F/NF-100 and ZnCo<sub>2</sub>(OH)F/NF-140 were obtained by adjusting the hydrothermal temperature to 100 °C and 140 °C. Similarly, when the hydrothermal temperature was 120 °C and the hydrothermal time was adjusted to 10 h and 14 h, respectively, the samples were named as ZnCo<sub>2</sub>(OH)F/NF-10 h and ZnCo<sub>2</sub>(OH)F/NF-14 h. By comparison, the molar ratios of zinc/cobalt were adjusted to 0:2, 0.11:1, and 1:1, and the samples were named Co<sub>2</sub>(OH)F/NF, Zn<sub>0.11</sub>Co(OH)F/NF, and ZnCo(OH)F/NF. Where, the load mass of Co<sub>2</sub>(OH)F/NF is 0.0313 g/cm<sup>2</sup>, the load

mass of  $\text{Zn}_{0.11}\text{Co}(\text{OH})\text{F}/\text{NF}$  is  $0.0405 \text{ g/cm}^2$ , the load mass of  $\text{ZnCo}_2(\text{OH})\text{F}/\text{NF}$  is  $0.0535 \text{ g/cm}^2$ , the load mass of  $\text{ZnCo}(\text{OH})\text{F}/\text{NF}$  is  $0.0221 \text{ g/cm}^2$ .

### Electrochemical measurements

Electrocatalytic residences had been measured in a three-electrode machine by using electrochemical station (CHI760E) in 1 M KOH at room temperature the use of the SCE as reference electrode. Graphite rods were used as auxiliary electrodes (auxiliary electrodes were also known as counter electrodes) and saturated glycury electrodes (SCE) or mercury/mercury oxide electrodes (Hg/HgO) as the reference electrode. All overpotentials are converted to reversible standard hydrogen electrodes (RHE):  $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{ V} + 0.059 \text{ PH}$  (used in 1 M KOH solution). Converting current to current density with the equation:

$$J = \text{在此处键入公式} \cdot = J = I \cdot 1000 / A$$

Where  $J$  is the current,  $I$  is the current density, and  $A$  is the cross-sectional area. Linear sweep (LSV) voltammetric curves were collected in 1 M KOH solution with a sweep frequency of  $5 \text{ mV} \cdot \text{s}^{-1}$ . The frequency was  $10^{-1}$ - $10^5 \text{ Hz}$  and the amplitude was 5 mV for electrochemical impedance testing. Using a previously reported electrochemical method, cyclic voltammograms (CVs) were performed in the non-Faraday region at a sweep rate of  $20 \text{ mV s}^{-1}$ - $100 \text{ mV} \cdot \text{s}^{-1}$  over a potential range of 0.05 V to 0.15 V. The electric double layer capacitance was calculated to recover the electrochemically active surface area of the electric double layer capacity, which was further modified to obtain the sample electrode was calculated. Cyclic voltammetry tests were performed for 1000 cycles at a scan rate of  $100 \text{ mV} \cdot \text{s}^{-1}$  to compare the change in voltammetry curves between the first and the 1000th linear scan. Long-term stability tests were performed using the constant current timing method. The pH value of the electrolyte did not change before and after the test. In order to eliminate the solution resistance, the voltage drop caused by the liquid connection resistance, the polarization curve is IR compensated.

### Materials Characterization

Scanning electron microscope (SEM, JSM-7610F, JEOL) and transmission electron microscope were used to observe the morphology and microstructure. (TEM Tecnai G2 F20). The Crystalline phase of the synthesized sample was tested by Y-2000 X-ray diffractometer, and the excitation source was Cu target  $K\alpha$  ray (XRD). The chemical configuration was determined by X-ray photoelectron spectroscopy (XPS) (AXIS-ULTRA DLD-600W). Hydrophilicity was measured using a contact angle measurement system. Contact angle test using contact angle tester (SHIOCA 25 France)

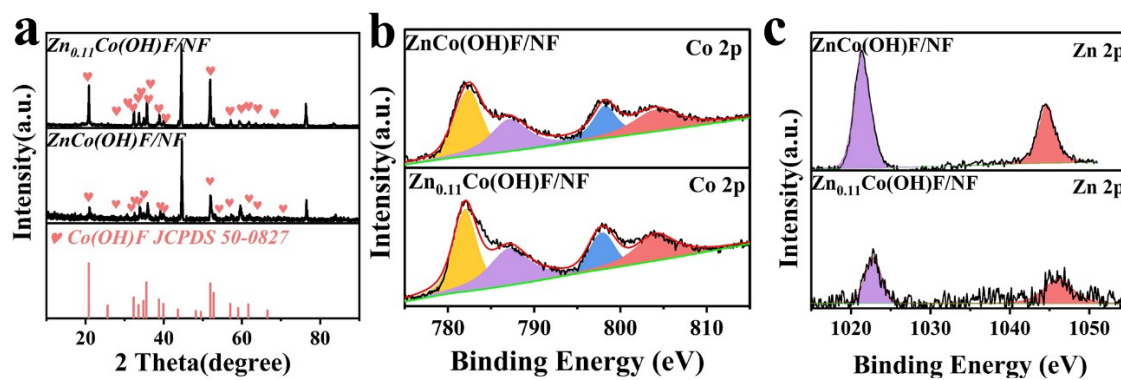


Fig. S1 (a) XRD pattern of  $Zn_{0.11}Co(OH)F/NF$  and  $ZnCo(OH)F/NF$ ; (b, c) XPS spectrum of Co 2p and Zn 2p of  $Zn_{0.11}Co(OH)F/NF$  and  $ZnCo(OH)F/NF$ .

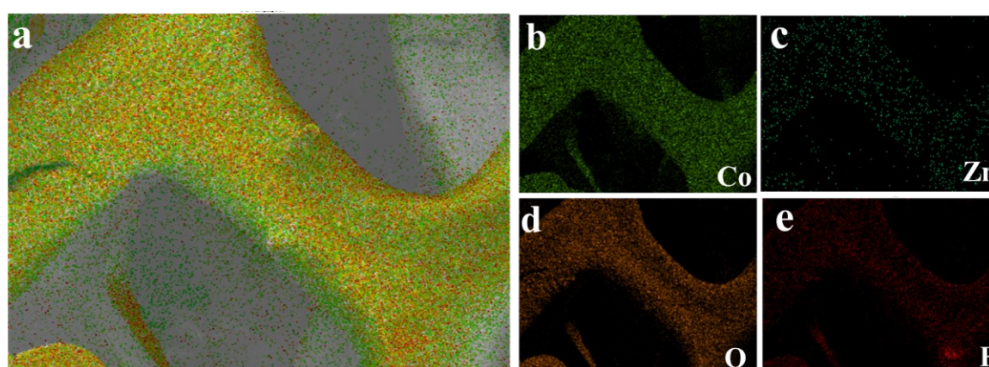


Fig. S2 EDS spectrum of  $Zn_{0.11}Co(OH)F/NF$  electrode after the test.

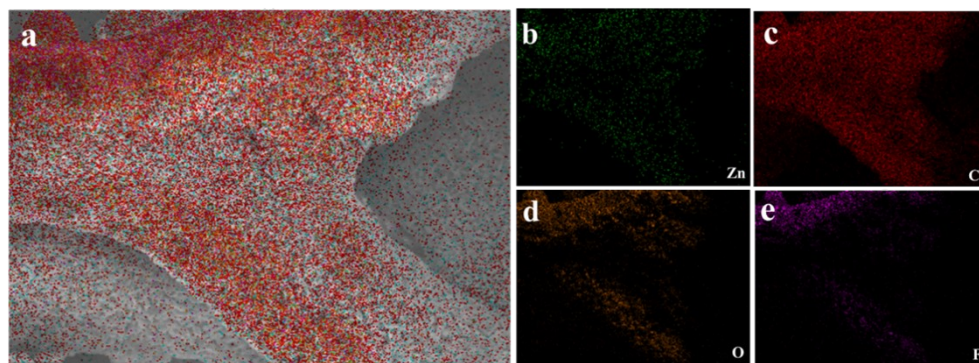


Fig. S3 EDS spectrum of  $ZnCo_2(OH)F/NF$  electrode after the test.

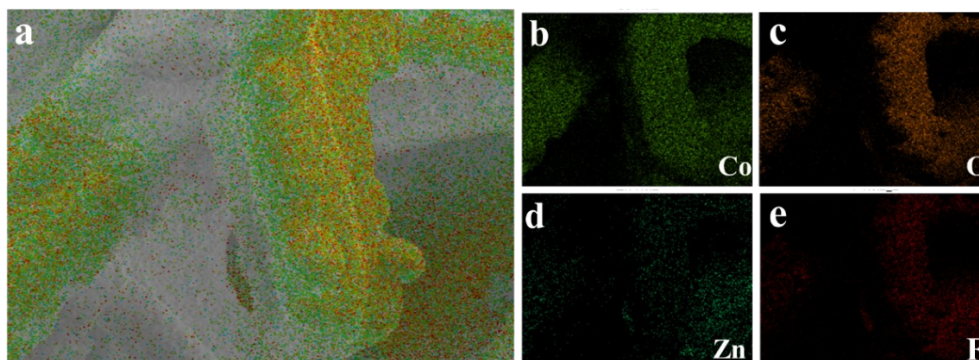


Fig. S4 EDS spectrum of  $ZnCo(OH)F/NF$  electrode after the test.

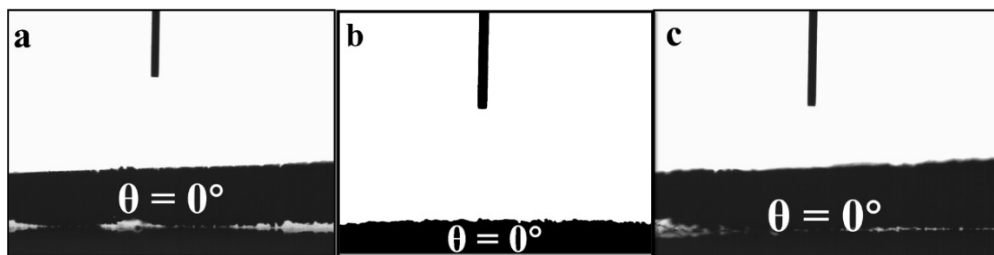


Fig. S5 The contact angle of water droplets of  $\text{Zn}_{0.11}\text{Co}(\text{OH})\text{F}/\text{NF}$ ,  $\text{ZnCo}_2(\text{OH})\text{F}/\text{NF}$ ,  $\text{ZnCo}(\text{OH})\text{F}/\text{NF}$  electrodes.

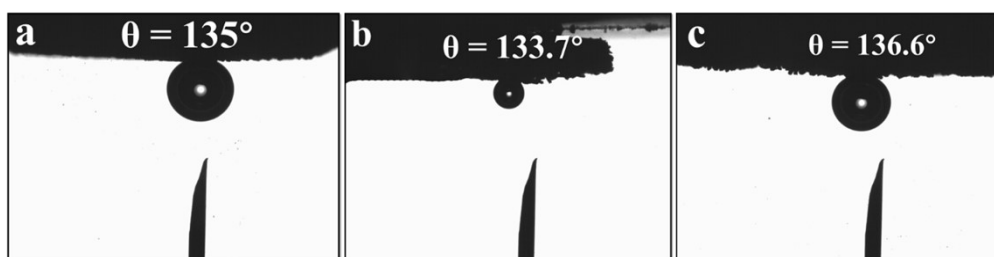


Fig. S6 Contact angle between bubbles of  $\text{Zn}_{0.11}\text{Co}(\text{OH})\text{F}/\text{NF}$ ,  $\text{ZnCo}_2(\text{OH})\text{F}/\text{NF}$ ,  $\text{ZnCo}(\text{OH})\text{F}/\text{NF}$  electrodes.

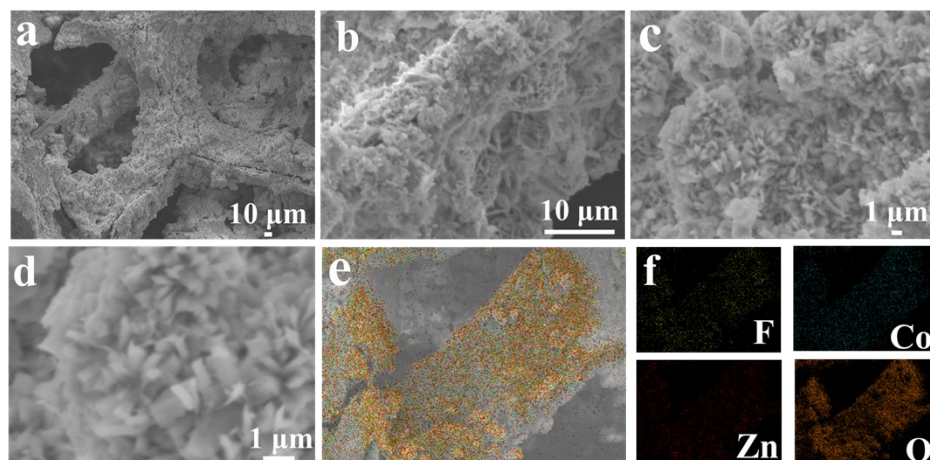


Fig. S7 (a-d) SEM images at different magnification rates after 24 h test. (e,f) EDS spectrum of  $\text{ZnCo}_2(\text{OH})\text{F}/\text{NF}$  electrode after the test.

Table S1 Comparison of the HER performances of non-noble metal electrocatalysts in 1M KOH.

Catalysts	Current density( $j$ , $\text{mA} \cdot \text{cm}^{-2}$ )	$\eta$ at the corresponding $j$	References
$\text{Co}(\text{OH})\text{F}$	10	238	1
$\text{Co-MoS}_2/\text{NF}$	10	179	2

Co <sub>3</sub> O <sub>4</sub> /NGF	10	181	3
CoFeP	10	177	4
Ni <sub>1</sub> Co <sub>1</sub> -P	10	169	5
Mo-ZnCoP	10	161.7	6
Zn <sub>0.975</sub> Co <sub>0.025</sub> S/CoS <sub>2</sub>	10	152	7
Zn-Co-S	10	157	8
ZnCo <sub>2</sub> (OH)F/NF	10	121	Our work

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