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Supporting Information

In situ growth of bimetal organic framework-derived phosphide on conductive substrate materials as bifunctional electrocatalysts for overall water splitting

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Experimental Section

(1) Synthesis of ZIF-67/NF

The electrodeposition process was done by three-electrode system, with Ni foam as the working electrode, Hg/HgO as the reference electrode, and Pt as the counter electrode. 1.427 g of $CoCl_2 \cdot 6H_2O$ was dissolved in 60 mL of deionized water as the electrolyte for the electrodeposition process. Electrodeposition was performed at -1.2 V against the reference electrode, and the deposition process lasted 10 min. Then, the electrodeposited Ni foam and 2 g of 2-methylimidazole were put into 20 mL of deionized water. The solution of electrodeposited Ni foam was transferred to a Teflon-lined autoclave, heated at 120 ^oC and held for 24 h. The obtained ZIF-67/NF was washed several times with water and ethanol, and finally dried for use.

(2) Synthesis of ZIF-67-Fe/NF, ZIF-67-Fe/NF-1 and ZIF-67-Fe/NF-2

1.427 g (0.006 mol) of $CoCl_2 \cdot 6H_2O$ and 1.621 g (0.006 mol) of $FeCl_3 \cdot 6H_2O$ were dissolved in 60 mL of deionized water as electrolytes for the electrodeposition process. Electrodeposition was performed at -1.2 V against the reference electrode, and the deposition process lasted 10 min. Then, the electrodeposited Ni foam and 2 g of 2-methylimidazole were put into 20 mL of deionized water. The solution of electrodeposited nickel foam was transferred to a Teflon-lined autoclave, heated at 120 ^oC and held for 24 h. The obtained ZIF-67-Fe/NF was washed several times with water and ethanol, and finally dried for use. In order to find the best element content ratio, ZIF-67-Fe/NF-1 and ZIF-67-Fe/NF-2 were synthesized. 1.427 g (0.006 mol) of $CoCl_2 \cdot 6H_2O$ and 0.54 g (0.002 mol) of $FeCl_3 \cdot 6H_2O$ were dissolved in 60 mL of deionized water as electrolytes for the electrodeposition process. The following steps are the same as the previous synthesis steps. The synthetic substance is named ZIF-67-Fe/NF-1. 1.427 g (0.006 mol) of $CoCl_2 \cdot 6H_2O$ and 3.242 g (0.012 mol) of $FeCl_3 \cdot 6H_2O$ were dissolved in 60 mL of deionized water as electrolytes for the electrodeposition process. The following steps are the same as the previous synthesis steps. The synthetic substance is named ZIF-67-Fe/NF-2.

(3) Synthesis of CoP/NF, CoFeP/NF, CoFeP/NF-1 and CoFeP/NF-2

ZIF-67/NF, ZIF-67-Fe/NF, ZIF-67-Fe/NF-1 and ZIF-67-Fe/NF-2 were placed in

the center of the tube furnace, respectively, and 0.5 g $NaH_2PO_2 \cdot H_2O$ was placed on the upstream side of the tube furnace. The reaction was heated at 350 ^oC for 120 min under nitrogen protection at a heating rate of 5 $^oC\ min^{-1}$.

Characterization of materials

Scanning electron microscopy (SEM) images were obtained using a MIRA3 TESCAN microscope. Transmission electron microscopy (TEM) images were obtained using a Hitachi H600 microscope. Powder X-ray diffraction (XRD) data were acquired by a Bruker D8 advance diffractometer at 40 KV and 40 mA using Cu Ka radiation (λ = 0.15405 nm), with a 2θ step size of 0.02°. Before the measurement, the sample was degassed at 120 ^oC for 6 h in the vacuum line. X-ray photoelectron spectroscopy (XPS) was performed using an Escalab 250 Xi from Thermo Fisher Scientific. Inductively coupled plasma-optical emission spectrometer (ICP) was performed by PerkinElmer Avio500.

Electrochemical performance test

All electrochemical measurements were performed in a typical three-electrode system on an electrochemical workstation (Wuhan Corrtest Instruments Corp., Ltd.), The 1.0 M KOH were used as electrolytes. The FeP-x/NF and Fe_2O_3-x/NF were directly utilized as working electrode, graphite electrode and Hg/HgO as counter electrode and reference electrode, respectively. All potentials measured were converted to the reversible hydrogen electrode (RHE) scale:

E(RHE) = E(Hg/HgO) + 0.098 + 0.059 * pH

Linear sweep voltammetry (LSV) polarization curves were performed at a scan rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was determined in frequency from 100000–0.1 Hz with an AC voltage of 5 mV.

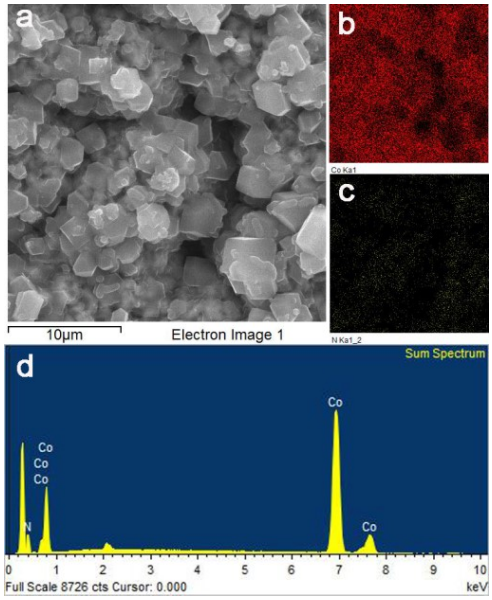

Fig. S1 (a) SEM image, corresponding elemental mapping images of (b) Co, (c) N and (d) EDX curve of ZIF-67/NF.

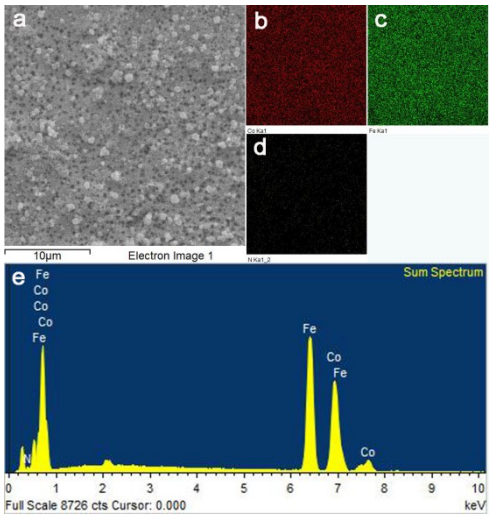

Fig. S2 (a) SEM image, corresponding elemental mapping images of (b) Co, (c) Fe，(d) N and (e) EDX curve of ZIF-67-Fe/NF.

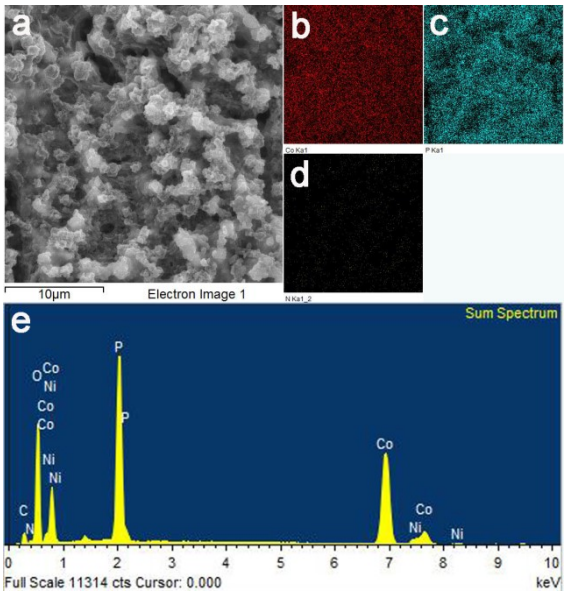

Fig. S3 (a) SEM image, corresponding elemental mapping images of (b) Co, (c) P, (d) N and (e) EDX curve of CoP/NF

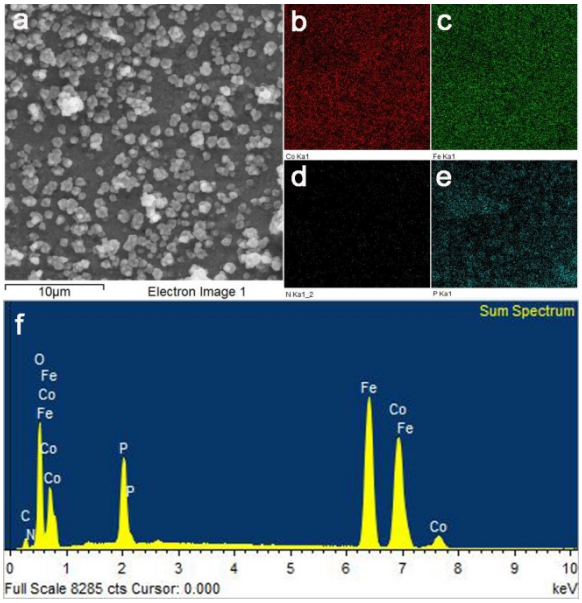

Fig. S4 (a) SEM image, corresponding elemental mapping images of (b) Co, (c) P, (d) N, (e) P and (f) EDX curve of CoFeP/NF.

Table S1 Elemental concentration of CoFeP/NF, CoFeP/NF-1 and CoFeP/NF-2.

materials	Co(mg/L)	Fe(mg/L)	Co/Fe (Atomic ratio)
CoFeP/NF-1	36.58	33.02	1:0.95
CoFeP/NF	17.86	25.6	1:1.51
CoFeP/NF-2	25.6	56.57	1:2.33

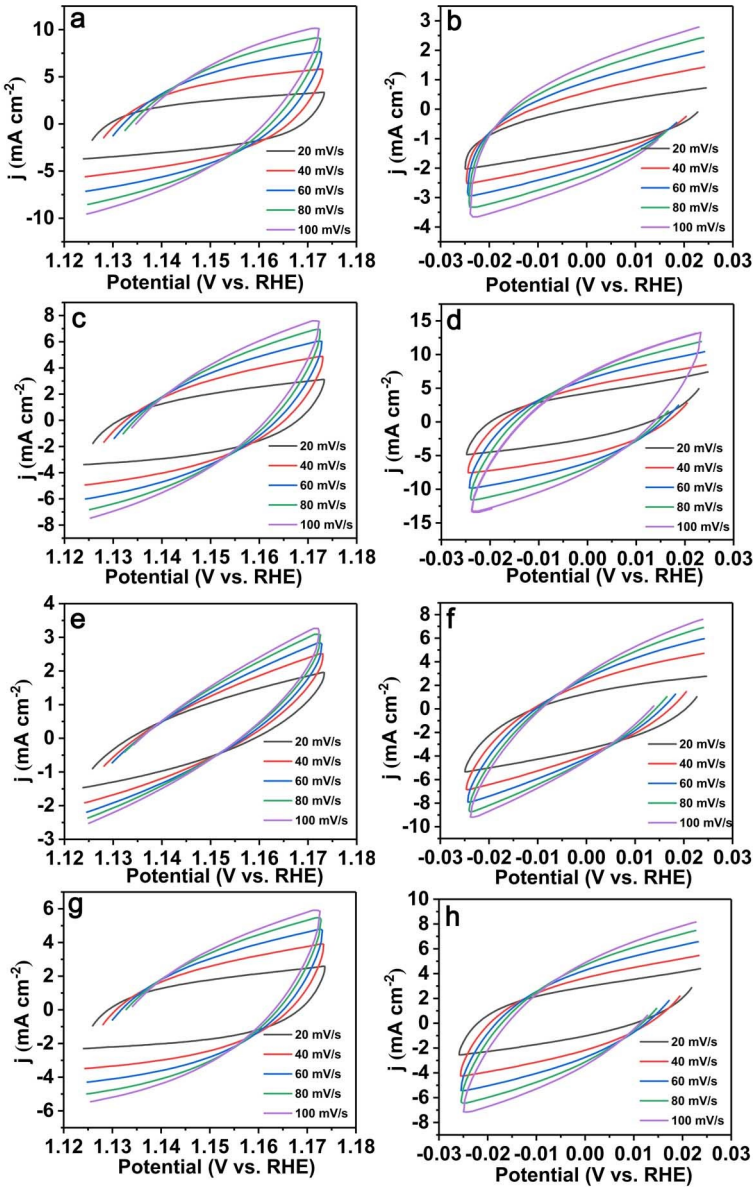

Fig. S5 CV curves for OER: (a) CoP/NF, (c) CoFeP/NF, (e) CoFeP/NF-1, (g) CoFeP/NF-2; CV curves for HER: (b) CoP/NF, (d) CoFeP/NF, (f) CoFeP/NF-1, (h) CoFeP/NF-2 at different scan rates.

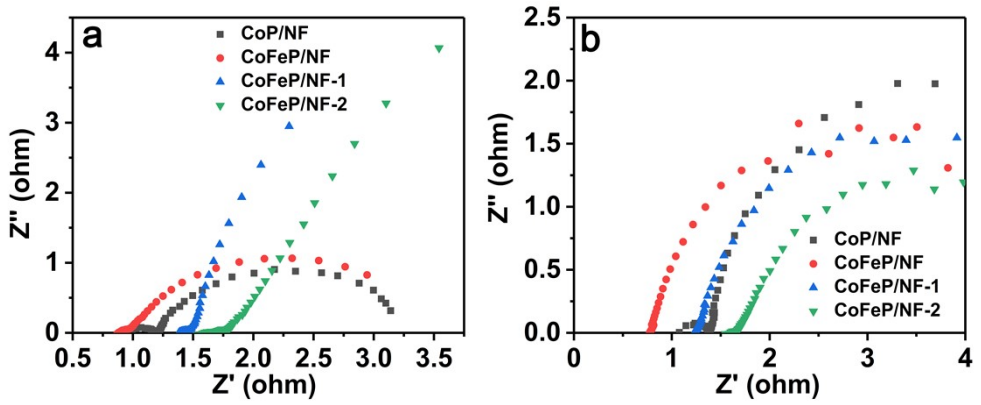

Fig. S6 Nyquist plots for (a) OER and (b) HER.

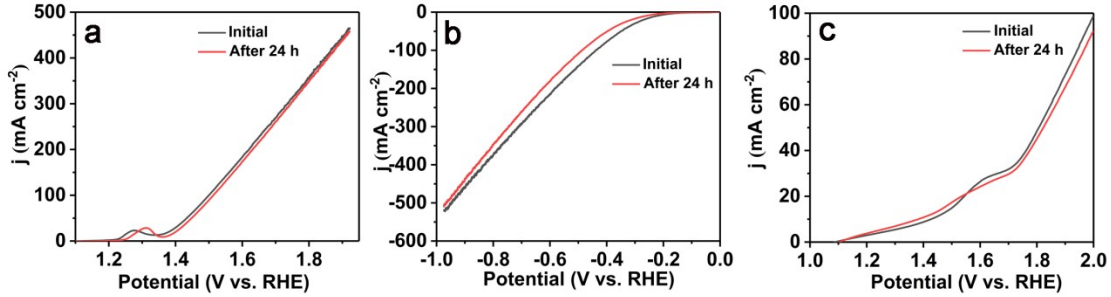

Fig. S7 Electrochemical OER measurements (a) and HER measurements (b) of electrocatalysts LSV curves for CoFeP/NF before and after stability testing, (c) LSV curves of overall water splitting for CoFeP/NF before and after stability testing.

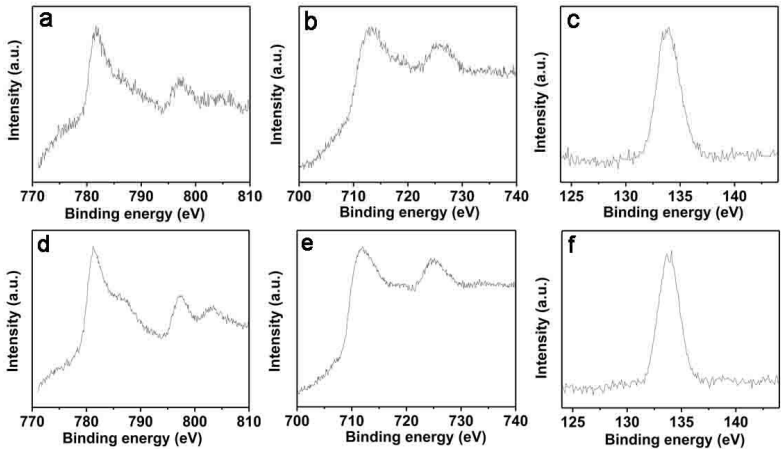

Fig. S8 XPS profile of CoFeP/NF: (a) Co, (b) Fe and (c) P after OER stability testing; XPS profile of CoFeP/NF: (d) Co, (e) Fe and (f) P after HER stability testing.

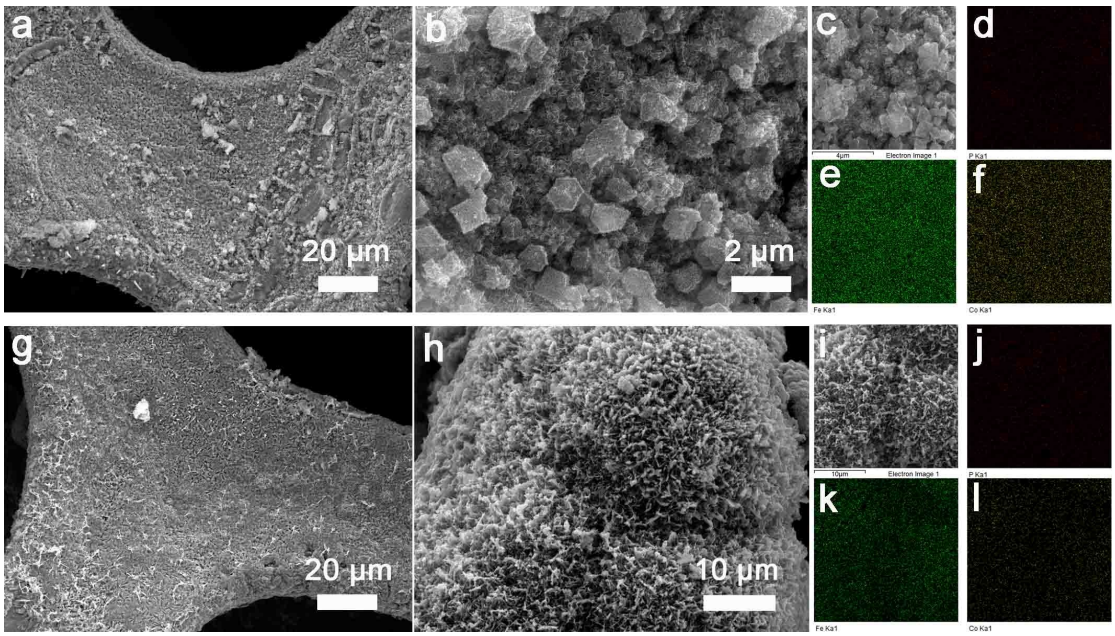

Fig. S9 (a-c) SEM images, corresponding elemental mapping images of (d) P, (e) Fe and (f) Co of CoFeP/NF after OER stability testing; (g-i) SEM images, corresponding elemental mapping images of (j) P, (k) Fe and (l) Co of CoFeP/NF after HER stability testing.

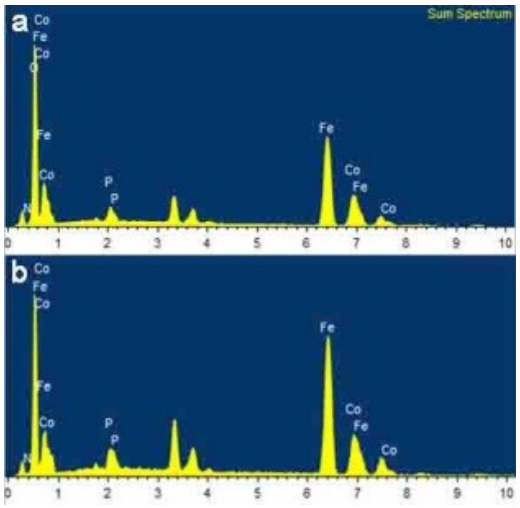

Fig. S10 EDX curve of CoFeP/NF after OER (a) and HER (b) stability testing.

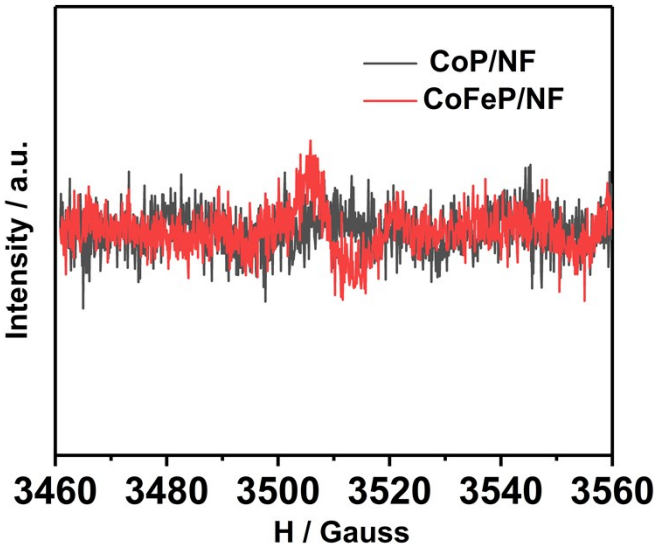

Fig. S11 Electron paramagnetic resonance (EPR) spectra of CoP/NF and CoFeP/NF.