

## Supporting Information

### Cobalt Iron phosphide Nanoparticles Embedded within Carbon Matrix as Highly Efficient and Durable Electrocatalyst for Oxygen Evolution Reaction

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## Experimental Section

*Synthesis of Co<sub>3</sub>Fe layered double hydroxides.* Co<sub>3</sub>Fe LDHs were synthesized through our previously reported topochemical oxidation method<sup>24</sup>. Briefly, 2.5 mmol of CoCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O with the Co:Fe ratio at 3:1, anthraquinone-2-sulfonic acid sodium salt monohydrate (AQS2, 5/3 mmol) and hexamethylenetetramine (HMT, 20 mmol) were dissolved in 300 mL of deionized water. The solution was refluxed under continuous magnetic stirring and nitrogen gas protection for 6 h.

*Synthesis of Co<sub>3</sub>Ni hydroxides.* Layered CoNi hydroxides were synthesized through the same method as the above except replacing a quarter of FeCl<sub>2</sub>·4H<sub>2</sub>O with NiCl<sub>2</sub>·6H<sub>2</sub>O. Briefly, 2.5 mmol of CoCl<sub>2</sub>·6H<sub>2</sub>O and NiCl<sub>2</sub>·6H<sub>2</sub>O with the ratio of Co and Ni ratio at 3:1, anthraquinone-2-sulfonic acid sodium salt monohydrate (AQS2, 5/3 mmol) and hexamethylenetetramine (HMT, 20 mmol) were dissolved in 300

mL of deionized water. The solution was refluxed under continuous magnetic stirring and nitrogen gas protection for 6 h.

*Synthesis of layered Co hydroxides.* Layered Co hydroxides were synthesized through the same method as the above except replacing a quarter of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .

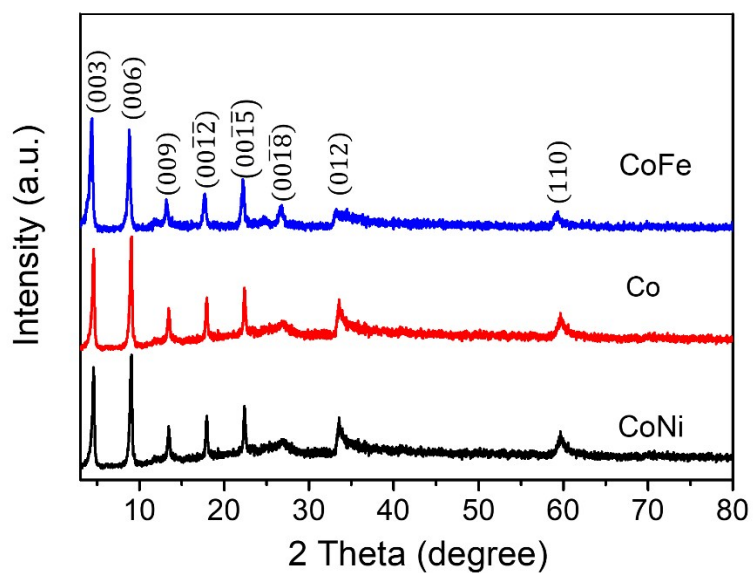
*Synthesis of layered CoFe hydroxides without intercalating AQS.* The sample was synthesized via the same method as the fabricating intercalated  $\text{Co}_3\text{Fe}$  layered double hydroxides except not adding AQS2.

*Synthesis of  $\text{Co}_3\text{Fe}$  phosphide,  $\text{Co}_3\text{Ni}$  phosphide, Co phosphide and  $\text{Co}_3\text{Fe}$  phosphide without carbon matrix.* To prepare cobalt iron phosphide, the obtained  $\text{Co}_3\text{Fe}$  LDH powder was placed into two separate positions in a quartz tube with a corundum boat loading of 0.6 g of  $\text{NaH}_2\text{PO}_2$  at the upstream side of the furnace. The mass ratio of LDH and  $\text{NaH}_2\text{PO}_2$  is 1:8. Subsequently, the samples were heated at 360 °C for 120 min in a static Ar atmosphere, and then naturally cooled to ambient temperature under Ar. The methods of fabricating  $\text{Co}_3\text{Ni}$  phosphide, Co phosphide and  $\text{Co}_3\text{Fe}$  phosphide without carbon matrix are similar with the above mentioned.

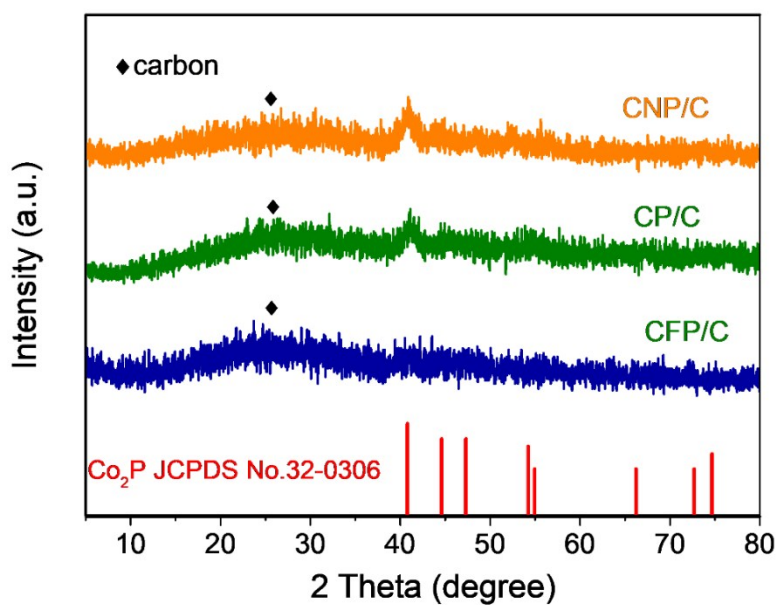
*Characterizations.* The morphology of as-obtained products was investigated by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, FEI Tecnai F20). SEAD, EELS, STEM, TEM and HRTEM images were all recorded on a FEI Tecnai F20. The crystal structures of the products were characterized using powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer,  $\text{Cu K}\alpha 1$ ). The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB250Xi X-ray photoelectron spectrometer using Mg as the excitation source. The element content was tested by ICP-AES (Optima 5300).

*Electrochemical Measurements.*

To prepare the working electrode, a 5 mg portion of catalyst powder was dispersed in a mixed water and ethanol (1:1, v/v) solution (1 mL), and then 5  $\mu\text{L}$  of Nafion solution (5 wt %) was added. The suspension was treated in an ultrasonic bath for 30 min and stirred for 8 h to prepare a homogeneous ink. The working electrode was prepared by dripping the catalyst ink onto a glassy carbon electrode with a diameter of 3 mm (catalyst loading  $0.27 \text{ mg cm}^{-2}$ ), and subsequent drying at  $80 \text{ }^\circ\text{C}$  for 6 h. Electrochemical characterizations were performed on a CHI760E (CH Instrument, Shanghai, China) electrochemical workstation using 1 M KOH as an electrolyte. A platinum wire was used as the counter electrode, while a saturated calomel electrode (SCE) acted as the reference electrode. The catalyst film coated rotating disk electrode (RDE, diameter: 3 mm) were used as the working electrode. During the measurements, the working electrode was constantly rotated at 1600 rpm to remove generated  $\text{O}_2$ . To evaluate the stability of CFP/C-2 electrode during OER process, galvanostatic measurements were performed at a current density of  $10 \text{ mA cm}^{-2}$ .



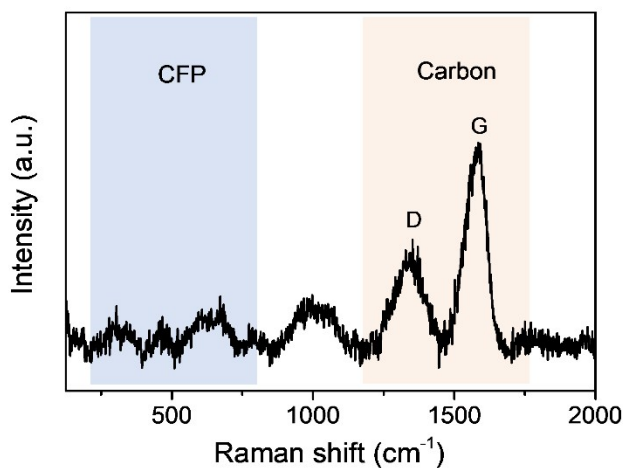
**Figure S1.** The XRD pattern of AQS2-intercalated  $\text{Co}_3\text{FeLDHs}$ ,  $\text{Co}_3\text{Ni LDHs}$  and  $\text{Co LDHs}$ .



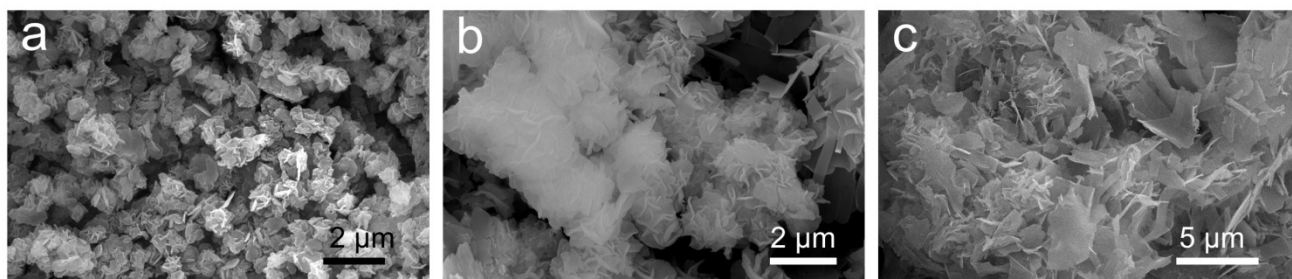
**Figure S2.** XRD patterns of as-prepared CFP/C, CNP/C and CP/C nanocomposites.

$\text{Co}_3\text{FeP}_x/\text{C}$  (the samples are labelled as CFP/C) nanocomposites are obtained via a one-step phosphorization of AQS2-intercalated  $\text{Co}_3\text{Fe LDHs}$  using sodium hypophosphite monohydrate as the

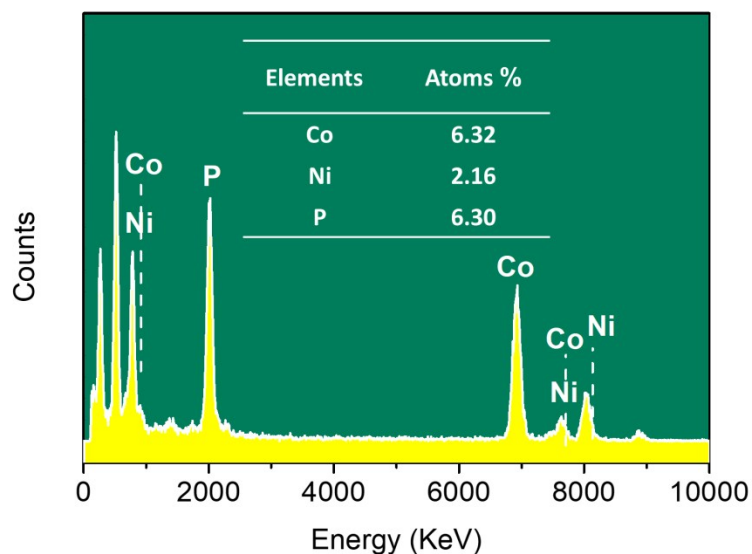
phosphorus source. The  $\text{Co}_3\text{Fe}$  LDH transformed into  $\text{Co}_3\text{FeP}_x$  nanoparticles embedded in carbon was derived via phosphorization at  $360\text{ }^\circ\text{C}$ . The process contributes to the carbonization of intercalated AQS2.  $\text{Co}_3\text{NiP}_x/\text{C}$  are labelled as CNP/C.



**Figure S3.** Raman spectra of as-prepared CFP/C nanocomposites.

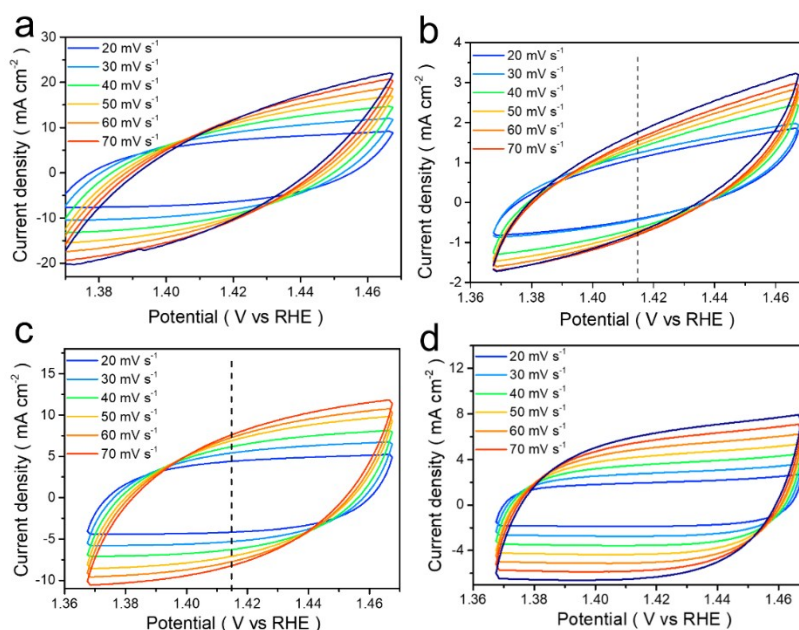


**Figure S4.** The SEM of the hierarchical structured (a)  $\text{Co}_3\text{Fe}$  LDHs, (b)  $\text{Co}_3\text{Ni}$  LDHs and (c) CoLDHsmicroflowers assembled from nanoplates.

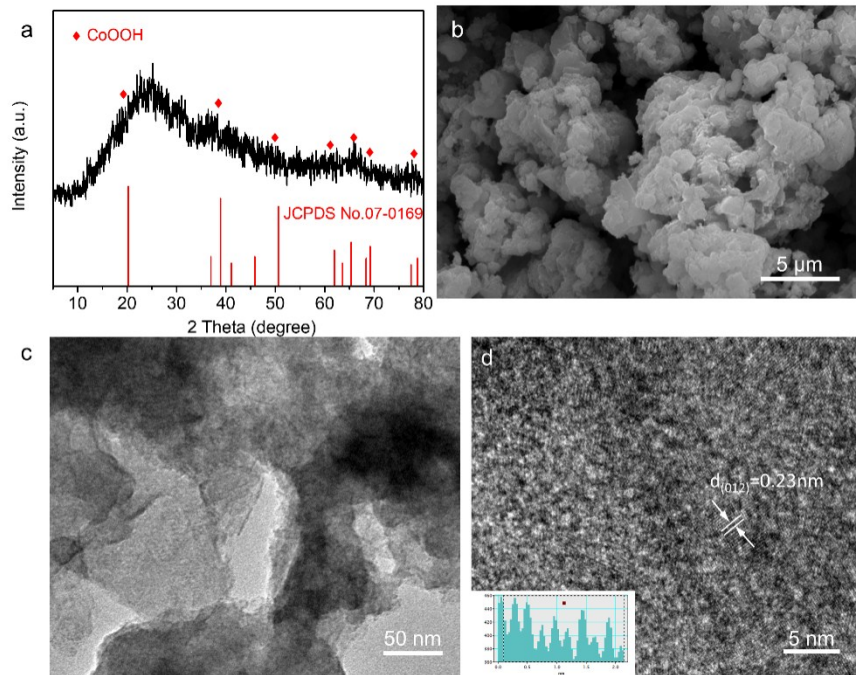


**Figure S5.** The XPS spectra of survey scan of as-prepared CNP/C.

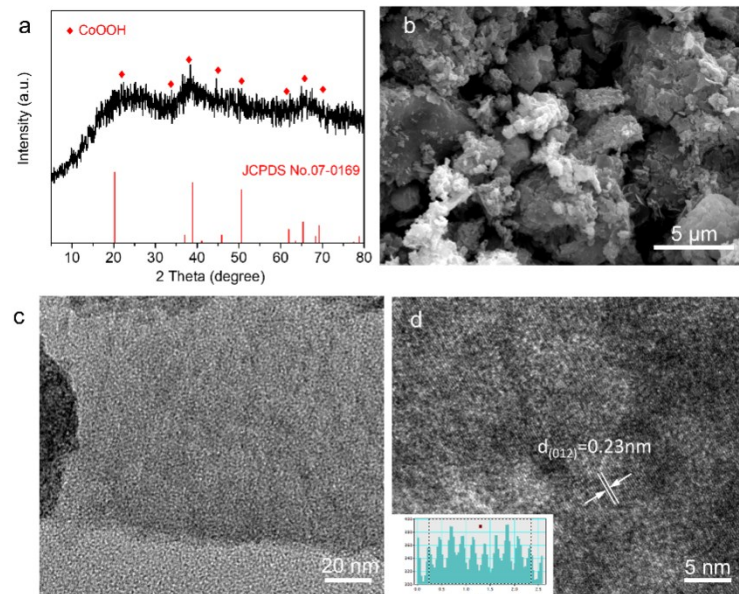
On the basis of the results of energy dispersive spectroscopy (EDS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Table S1, ESI†), the chemical composition of the asprepared Fe incorporated Co<sub>2</sub>P/C is (anal. calcd: the mole ratio of Co: Fe = 3:1). The EDS image of CNP/C in Fig. S5 (ESI†) shows a mole ratio of Co:Ni = 3:1.



**Figure S6.** The cyclic voltammogram (CV) curves of (a) Co<sub>3</sub>Fe LDHs, (b) CFP/C, (c) CNP/C and (d) CP/C.

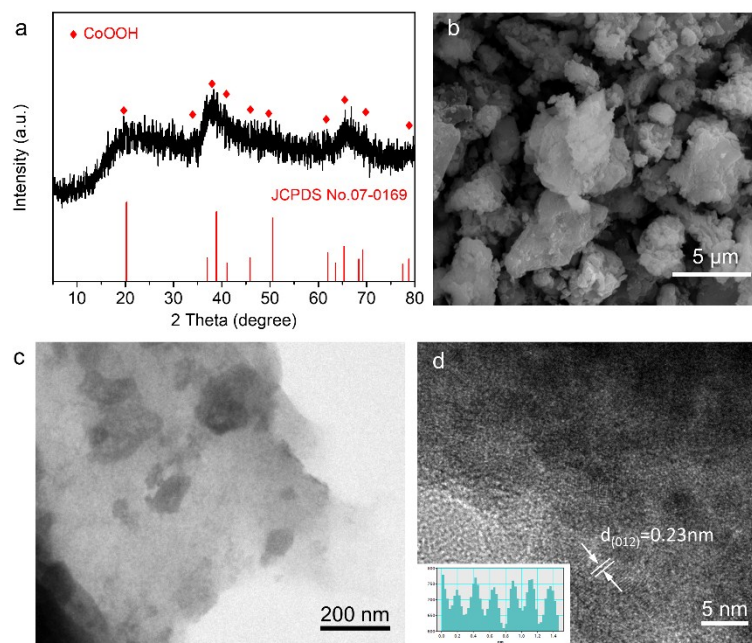


**Figure S7.** The XRD (a), SEM (b), TEM (c) and HRTEM (d) of CFP/C after OER.

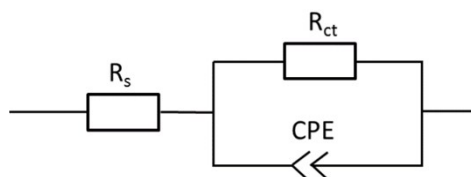


**Figure S8.** The XRD (a), SEM (b), TEM (c) and HRTEM (d) of CNP/C after OER.





**Figure S9.** The XRD (a), SEM (b), TEM (c) and HRTEM (d) of CP/C after OER.



**Figure S10.** Equivalent circuit model used in impedance analysis of as-prepared CFP/C.



**Table S1.** Mental element content based on ICP-AES

Samples	Co (wt%)	Fe (wt%)
CFP/C	26.57%	9.32%

**Table S2.** Comparison of phosphide catalysts for oxygen evolution reaction recently reported.

Catalysts	Electrolyte	Substrate	Current density (mA cm <sup>-2</sup> )	Overpotential (mV) at the corresponding current density	Reference
CFP/C	1 M KOH	Glassy carbon	10	260	This work
NiCoP/C nanoboxes	1 M KOH	Glassy carbon	10	330	Ref. S <sup>1</sup>
CoP	1 M KOH	Glassy carbon	10	320	Ref. S <sup>2</sup>
Ni <sub>2</sub> P	1 M KOH	Glassy carbon	10	320	Ref. S <sup>3</sup>
Co/Co <sub>2</sub> P	1 M KOH	Nickel foam	10	390	Ref. S <sup>4</sup>
CoP	1 M KOH	arbon cloth	10	281	Ref. S <sup>5</sup>
Ni-P	1 M KOH	arbon cloth	10	300	Ref. S <sup>6</sup>
CoP	1 M KOH	Glassy carbon	10	345	Ref. S <sup>7</sup>

**Table S3.** Optimum fitting parameters for the impedance spectra shown in Figure 5d ( $R_s$  and  $R_{ct}$  represents solution resistance and material intrinsic resistance, respectively).

Catalyst	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
CFP/C	12.09	30.61
Co <sub>3</sub> FeLDHs	12.16	106.70
CNP/C	16.27	33.07
CP/C	12.96	97.10

## Reference

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