Supporting Information for

## FeO<sub>x</sub>/FeP Hybrid Nanorods Neutral Hydrogen Evolution Electrocatalysis: Insight into Interface

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## **Experimental Section**

**FeOOH NRs/CC synthesis**: The FeOOH NRs/CC was prepared by a simple hydrothermal method. 1 mmol FeCl<sub>3</sub> and 1 mmol Na<sub>2</sub>SO<sub>4</sub> were dissolved in 30 ml deionized water. After sonication for 10 min, the yellow solution was transferred into a 50 mL Teflon-lined stainless autoclave. Then a piece of treated carbon cloth (1 cm  $\times$  4 cm) was immersed into the solution. The autoclave was sealed and maintained at 120 °C for 5 h in an electric oven. When the reaction was over, the sample was taken out and washed with water and ethanol for several times followed by drying in air.

**Fe-O-P NRs/CC synthesis**: The low-temperature phosphorizing was conducted with FeOOH NRs/CC and NaH<sub>2</sub>PO<sub>2</sub> (about 0.8 g) as precursors. The boat with NaH<sub>2</sub>PO<sub>2</sub> was put at the upstream side of the furnace. Then the sample was annealed at 300 °C for about 40 min in Ar/H<sub>2</sub> atmosphere. After the temperature cooled down, the Fe-O-P NRs/CC was obtained. When the Fe-O-P NRs/CC sample was treated by 1 M HCl solution for several minutes, the Fe-O-P-A NRs/CC was obtained.

**Characterizations:** The morphology was characterized by scanning electron microscopy (SEM) measurements (HITACHI SU8010). Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai G2 F20 microscope at 200 kV. The crystal structure was analyzed by D/MAX-2000 PC powder X-Ray diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda$ =1.54056 Å). X-Ray photoelectron spectroscopy (XPS) analyses were performed on a Japan Kratos Axis Ultra HAS spectrometer with a monochromatic Al K $\alpha$  source.

**Electrochemical measurement:** The electrochemical measurements were performed in a typical three-electrode system with Ag/AgCl electrode as the reference electrode and graphite rod as the counter electrode by using CHI 604E electrochemical analyzer (CH Instruments, Inc., Shanghai). All measurements were performed directly under room temperature with N<sub>2</sub> saturated solutions (1 M PBS, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1 M KOH). The exposed active area for measurement was 0.5 cm  $\times$  0.5 cm. The linear scanning voltammetry (LSV) was conducted at a scan rate of 5 mV s<sup>-1</sup>. Before LSV test, 20 cyclic voltammetry (CV) cycles were carried out at a scan rate of 100 mV s<sup>-1</sup> to achieve a stable current. The double layer capacitance (C<sub>dl</sub>) was estimated by measuring the CV under different scan rates in non-faradic region of 0.1-0.2 V. The C<sub>dl</sub> value is equal to half of the linear slope. All potentials used in this work are marked with or without iR correction, which are given versus reversible hydrogen electrode (RHE) according to the following equation:  $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH(V)$ .

**Theoretical calculations:** Using spin-polarized density functional theory (DFT) with generalized gradient approximation (GGA) for exchange-correlation potential, we have calculated the total energies and atomic structure of the chosen system.<sup>1,2</sup> All calculations were performed by using Perdew-Burke-Ernzerhof (PBE) form of the GGA functional embedded in the Vienna Ab Initio Simulation Package (VASP).<sup>3</sup> The cutoff energy of the plane-wave basis set was set at 500 eV. In order to avoid interaction between periodic surface layers, a vacuum space of 10 Å along the *z*-direction was applied. The Brillouin zone integrations were performed by using Monkhorst-Pack  $7 \times 7 \times 7$  and  $3 \times 3 \times 1$  for geometric optimization of the bulk FeP and the other slab

surfaces, respectively. The convergence thresholds for structural optimization and transition state (TS) search were set at 0.01 and 0.05 eV/Å in force, respectively.<sup>4</sup> The convergence criterion for energy is  $10^{-5}$  eV. The van der Waals (vdW) dispersion by employing the D3 method of Grimme was considered for all the calculation.<sup>5</sup> The climbing image nudged elastic band (CI-NEB) method was used to search the TSs and five images inserted between two stable states.<sup>6</sup> The total hydrogen evolution reaction can be written in Eq. (1).

$$e^- + H^+ \rightarrow \frac{1}{2}H_2 \tag{1}$$

For each step, the reaction Gibbs free energy  $\Delta G$  is defined by Eq. (2).

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{2}$$

where  $\Delta E$  is the electronic energy difference,  $\Delta ZPE$  is the change in zero-point energies, T is the temperature (T = 298.15 K), and  $\Delta S$  is the entropy change. The zero-point energy of adsorbed atomic hydrogen was computed from the vibrational frequencies, in which only the adsorbated species were calculated, while the catalysts were all fixed.<sup>7</sup> The entropy of adsorption of  $1/2H_2$  is  $\Delta S_H \approx -\frac{1/2S_{H_2}^0}{2}$ , where  $S_{H_2}^0$  is the entropy of H<sub>2</sub> in the gas phase at standard conditions.



Figure S1. XRD pattern of FeOOH NRs/CC. Inset is the corresponding SEM image.



Figure S2. The HRTEM images of FeOOH NRs (a) and Fe-O-P NRs (b). Inset in (a) shows the magnified crystal lattice. Insets in (b) show the FFT patterns of corresponding crystalline or amorphous areas.



Figure S3. Structure comparison. The SEM (a) and TEM (c) images of Fe-O-P NRs. The SEM (b) and TEM (d) images of Fe-O-P-A NRs. Insets: the low magnification images.



Figure S4. The HRTEM images of Fe-O-P-A NRs.



Figure S5. HRTEM and STEM line scan analyses of Fe-O-P interface. (a) The STEM-HAADF image. (b) Corresponding HRTEM image from marked area in a. (c) Line scan elemental analyses.



Figure S6. The EDX elemental analyses of Fe-O-P NRs and Fe-O-P-A NRs



Figure S7. XPS survey of Fe-O-P-A NRs/CC. (a) XPS survey for elements. (b) Fe 2p, (c) P 2p and (d) O 1s spectra of Fe-O-P-A NRs/CC. A clear Fe  $2p_{3/2}$  shift is observed from 707.2 to 707.4 eV after acid treatment.



Figure S8. The Nyquist plots of Fe-O-P NRs and Fe-O-P-A NRs.



Figure S9. The double-layer capacitance measurements for determining the electrochemical active surface area. CV curves for (a) FeOOH NRs/CC, (b) Fe-O-P NRs/CC and (c) Fe-O-P-A NRs/CC measured at different scan rates in 1 M PBS, respetively.



Figure S10. The polarization curves of Fe-O-P NRs/CC during 60 h electrolysis.



Figure S11. Comparison of XRD patterns before and after electrolysis.



Figure S12. The SEM image of Fe-O-P NRs/CC after electrolysis.



Figure S13. The *I-t* measurement of Fe-O-P-A NRs/CC electrode for 6 h electrolysis.



Figure S14. The SEM images of Fe-O-P-A NRs/CC after 6 h electrolysis. Inset: corresponding low magnification image.

Catalyst	Tafel slope (mV dec <sup>-1</sup> )	η <sub>10</sub> (mV)	Stability	Reference
Fe-O-P NRs	47	96	60 h	This work
Fe-O-P-A NRs	72	93	6 h	This work
N-Ni	106	64	18 h	J. Am. Chem. Soc., <b>2017</b> , 139, 12283–12290
CoP foam/Hb	106	121	100 h	Nano Res. <b>2017</b> , 10, 1010–1020
Ni-C-N NSs	38	92.1	70 h	J. Am. Chem. Soc. <b>2016</b> , 138, 14546–14549
SiO <sub>2</sub> /PPy NTs-CFs	100.2	187	30 h	Angew. Chem. Int. Ed. 2017, 56, 8120–8124
PtSA-NT-NF	30	24	24 h	Angew. Chem. Int. Ed. 2017, 56, 13694–13698
Ni <sub>3</sub> S <sub>2</sub> /NF	-	170	200 h	J. Am. Chem. Soc. 2015, 137, 14023–14026
FeP/Ti foil	-	102	16 h	ACS Nano. <b>2014</b> , 8, 11101–11107
FeP NP/CC	70	115	22 h	ACS Appl. Mater. Interfaces <b>2014</b> , 6, 20579–20584
Zn <sub>0.30</sub> Co <sub>2.70</sub> S <sub>4</sub>	-	90	210 min	J. Am. Chem. Soc. <b>2016</b> , 138, 1359–1365
NiCo <sub>2</sub> P <sub>x</sub>	63.3	63	30 h	Adv. Mater. <b>2017</b> , 29, 1605502
MoP NA/CC	94	187	46 h	<i>Applied Catal. B</i> Environ. <b>2016</b> , 196, 193–198
Co-S/FTO	93	160	40 h	J. Am. Chem. Soc. <b>2013</b> , 135, 17699–17702
CoMoS <sub>4</sub> NTA/CC	77	104	32 h	<i>Chem. Eur. J.</i> <b>2017</b> , 23,12718–12723
Mo <sub>2</sub> C@NC	-	156	-	Angew. Chem. Int. Ed. 2015, 54, 10752–10757
FeP NAs	71	202	-	<i>ACS Catal.</i> <b>2014</b> , 4, 4065–4069

**Table S1.** The activity comparison of Fe-O-P NRs/CC with recently reported HER electrocatalysts in neutral media.

**Video S1.** Electrolytic hydrogen evolution in neutral media with the Fe-O-P NRs/CC electrode.

## **Note S1.** Calculation for the exchange current density $(j_0)$

Tafel relationship illustrates the catalytic activity of electrode material for hydrogen evolution reaction:

$$\eta = b \log(\frac{j}{j_0}) \tag{1}$$

where  $\eta$  is the overpotential, *b* is the Tafel slope related to the catalytic mechanism of the electrode reaction, *j* is the current density.  $j_0$  is the exchange current density, calculated when  $\eta = 0$ , which describes the intrinsic catalytic activity of electrode material under the equilibrium conditions.<sup>8,9</sup> The calculated Tafel slope of Fe-O-P NRs is 47 mV dec<sup>-1</sup> in 1 M PBS. The  $j_0$  of Fe-O-P NRs is computed when j = 10 mA cm<sup>-2</sup> and the corresponding  $\eta = 96$  mV. Then  $j_0$  can be obtained according to:

$$j_0 = \frac{j}{10^{\eta/b}} = \frac{10}{10^{96/47}} = 0.091 \, mA \, cm^{-2}$$
(2)

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