Fe-Co-P multi-heterostructure arrays for efficient electrocatalytic water splitting

Hanwen Xu[a, b], *Jiawei Zhu*[a], *Pengyan Wang*[a], *Ding Chen*[a], *Chengtian Zhang*[a], *Manjie Xiao*[a], *QianLi Ma*[a], *Huawei Bai*[a], *Rui Qin*[a], *Jingjing Ma*[a], *Shichun Mu*[a, b *]

[a] Address here. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing,Wuhan University of Technology, Wuhan 430070, China

[b] Foshan Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, Xianhu Hydrogen Valley, Foshan 528200, China.

*E-mail: msc@whut.edu.cn.

1. Experimental Details

1.1 Materials and Reagents

Cobaltous Nitrate Hexahydrate ($Co(NO_3)_2.6H_2O$), Ammonium fluoride (NH_4F), Urea ($CO(NH_2)_2$), Sodium hypophosphite ($NaH_2PO_2.H_2O$), Potassium hydroxide (KOH), Potassium ferricyanide (III) ($K_3Fe(CN)_6$), Potassium hexacyanoferrate (II) (($K_4Fe(CN)_6$) and Ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) were purchased from Sinopharm Group Chemical Reagent. Ruthenium (IV) oxide (RuO_2) was from Wokai Reagents Ltd. Commercial Pt/C catalyst (20 %) were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. All regents were analytical reagents and used without further purification.

1.2 Preparation of Co-P / NF

Co-P / NF was obtained by using CoCH / NF as the precursor and phosphated under the same conditions as Fe-Co-P / NF.

1.3 Preparation of Fe-P / NF

2 mmol $Fe(NO_3)_3.9H_2O$, 4 mmol NH_4F and10 mmol urea was dissolved in 40 mL DI water and stirred for 10 min. A piece of treated NF and the clear solution was poured into a Teflon-lined stainless-steel autoclave (50 mL) and kept 100 °C for 6 h. The NF was carefully washing with DI water afterwards. Next, 0.15g $K_4Fe(CN)_6$ was dissolved in 20 mL DI water, and the obtained Fe precursor was put into the solution aged for 24 h. Finally, Fe-P / NF was obtained by phosphating the Fe precursor under the same conditions as Fe-Co-P / NF.

1.4 Electrochemical Measurements.

Typical three-electrode system connected to CHI660E electrochemical workstation (CHI Instruments, Shanghai, China) was used to measure the electrocatalytic performance of catalysts, with a graphite rod and Hg/HgO were used as the counter electrode and the reference electrode. The as-prepared electrocatalysts with a geometric area of 0.25 cm^2 were directly served as the working electrodes. As for powdery catalysts (RuO_2 and Pt/C), the working electrodes were prepared by dropping electrocatalyst ink onto NF. The 1M KOH aqueous solution was used as the electrolytes, and the scan rate of the polarization curves of HER and water splitting was 1 mV s^{-1}, but OER was 0.5 mV s^{-1} in order to reduce the effect of nickel oxidation peak. In HER and OER characterizations, the polarization curves were 100% iR-corrected using the equation: $E_{iR\text{-corrected}} = E - iR$ Furthermore, the HER and OER potentials were converted to RHE scale according to the equation: E (vs. RHE) = E (vs. Hg/HgO) + 0.059*pH + 0.098 V. The electrochemical double layer capacitance (C_{dl}) was determined with typical cyclic voltammetry (CV) measurements at various scan rates (80,70,60,50,40 mV s^{-1}) in 0 ~ 0.1 V versus Hg/HgO. The electrochemical impedance spectroscopy (EIS) was conducted at the corresponding potentials of 20 mA cm^{-2} (for HER) and 30 mA cm^{-2} (for OER) from LSV curves, with the frequency range of 0.01 to 100 000 Hz. The electrocatalyst Fe-Co-P

/ NF was used as both cathode and anode in a two-electrode configuration for full water splitting. Notably, the generated H_2 and O_2 gases during overall water splitting were quantitatively collected by the water drainage method.

1.5 Density Functional Theory (DFT) calculations.

All the density functional theory (DFT) calculations were carried out by the CASTEP module of Materials Studio. The cutoff energy and Monkhorst-Pack grid k-points were set as 300 eV and 1×1×1, respectively. The self-consistence field (SCF) tolerance was set as 1.0×10^{-5} eV/atom. The FeP (001), Co_2P (100) and CoP (101) crystal planes were utilized in DFT calculations. The three interface models were built by regulating the arrangement between single surfaces.

The Gibbs free energies of H adsorption were calculated as follow:

$$\Delta G_{H*} = \Delta E_{H*} + \Delta ZPE - T\Delta S = E(H^*) - E(^*) - E(H_2)/2 + \Delta ZPE - T\Delta S$$

Where ΔZPE is the zero-point energy and TΔS stands for the entropy corrections. According to previous report by Norskov et al., we used the 0.24 eV for the ΔZPE - TΔS of hydrogen adsorption in this work.[1]

For the OER in alkaline environment, the following four elementary steps were considered:

$$OH^- + {}^* \rightarrow OH^* + e^- \qquad (1)$$

$$OH^* + OH^- \rightarrow O^* + H_2O + e^- \qquad (2)$$

$$O^* + OH^- \rightarrow OOH^* + e^- \qquad (3)$$

$$OOH^* + OH^- \rightarrow O_2 + H_2O + e^- \qquad (4)$$

1 Supplementary Figures and Tables

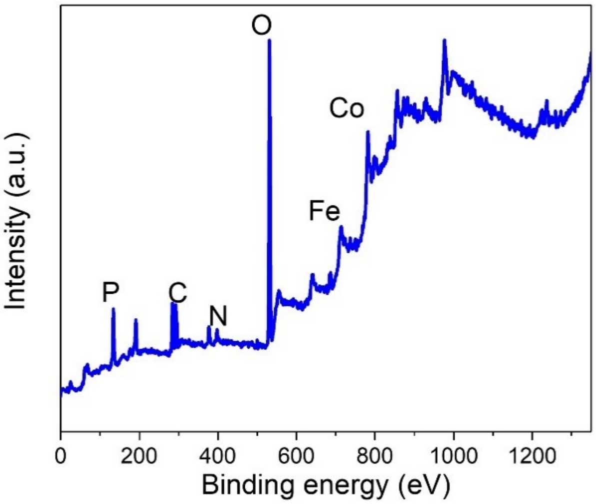


Figure S1 XPS survey pattern of Fe-Co-P / NF.

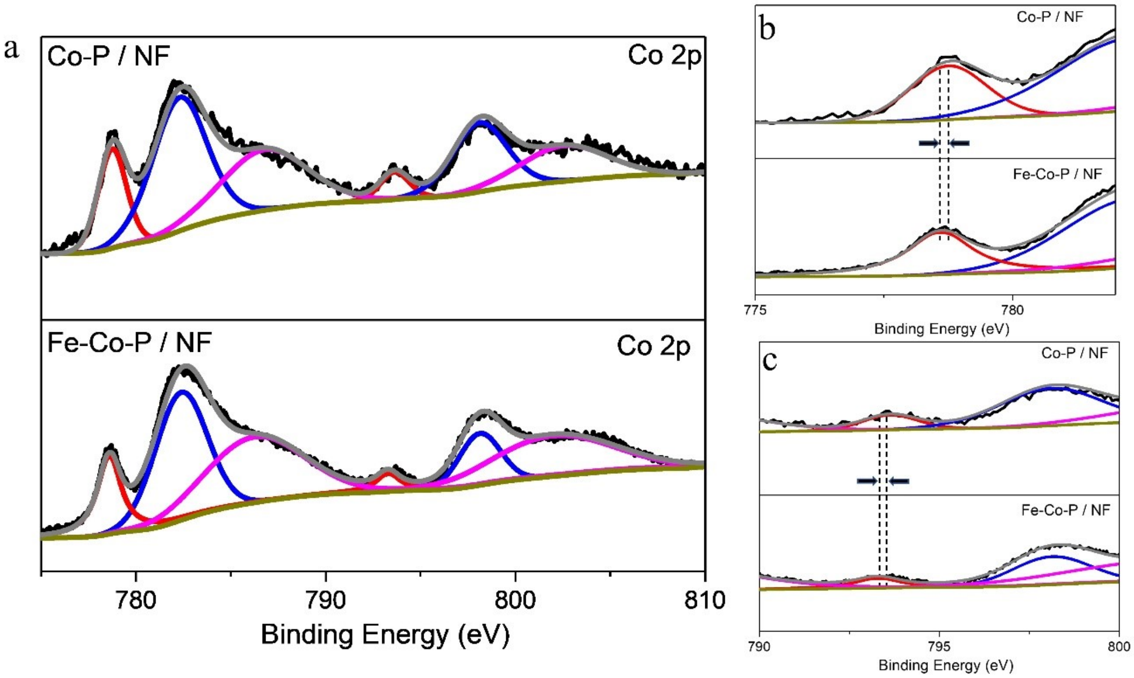


Figure S2 Co 2p spectrum comparison of Co-P / NF and Fe-Co-P / NF with the partial enlargement pictures.

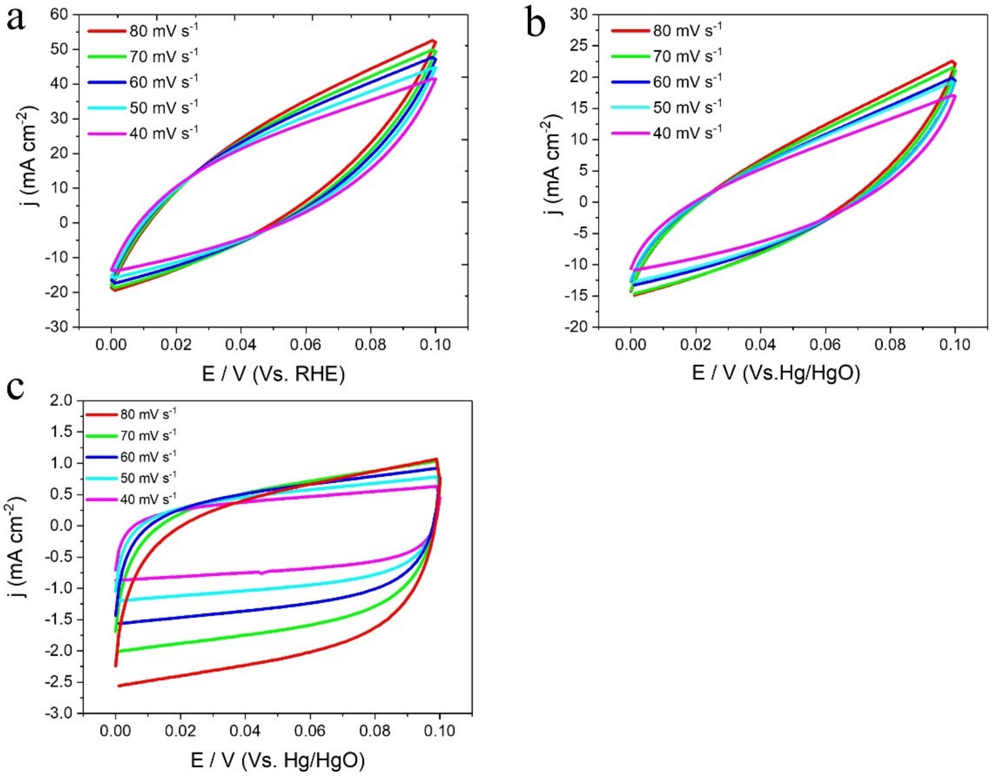


Figure S3 Cyclic voltammograms of (a) Fe-Co-P/NF (b) Co-P/NF (c) Fe-P/NF.

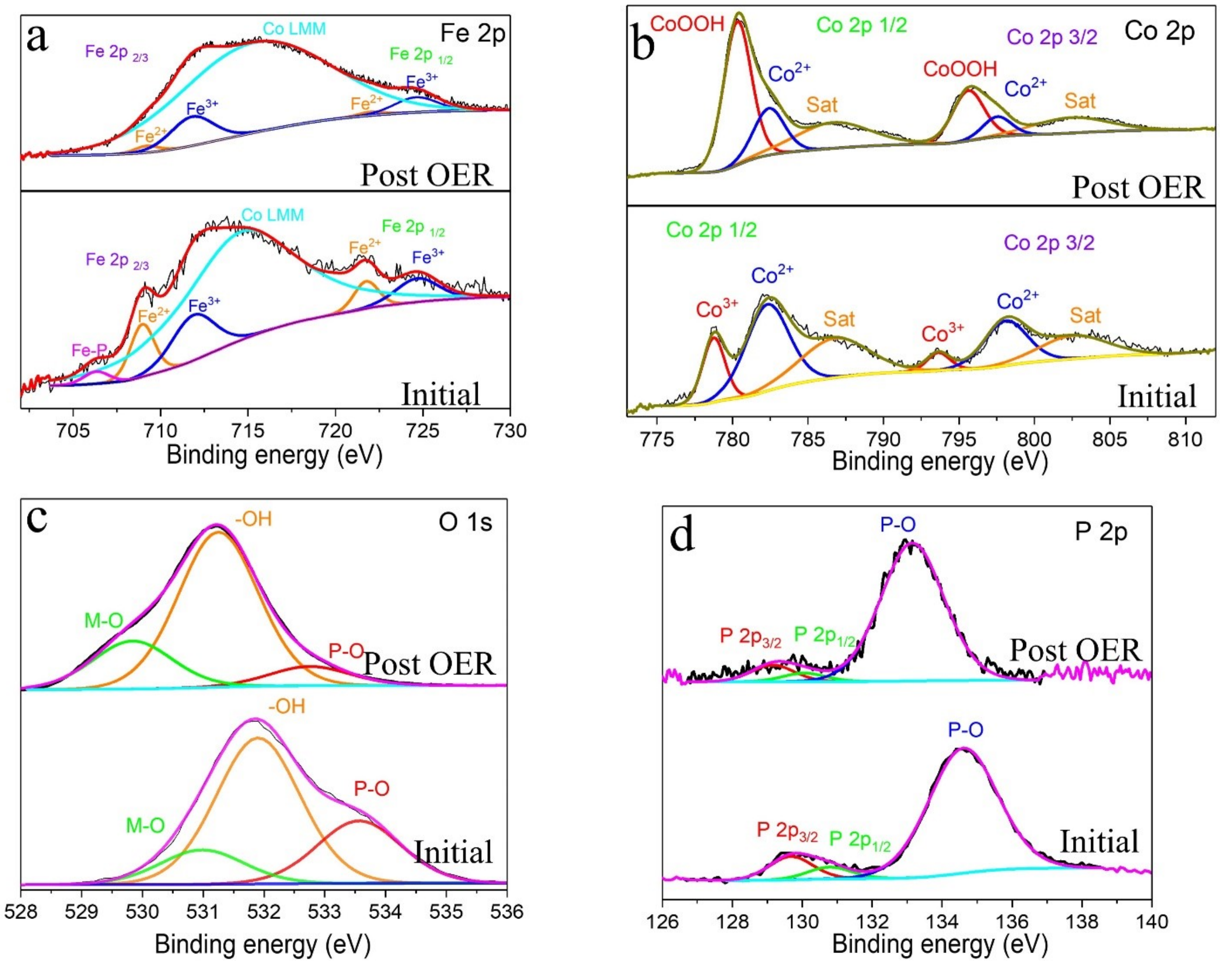


Figure S4 (a) Fe 2p, (b) Co 2p, (c) O 1s, (d) P 2p of Fe-Co-P / NF spectrums before and after OER test.

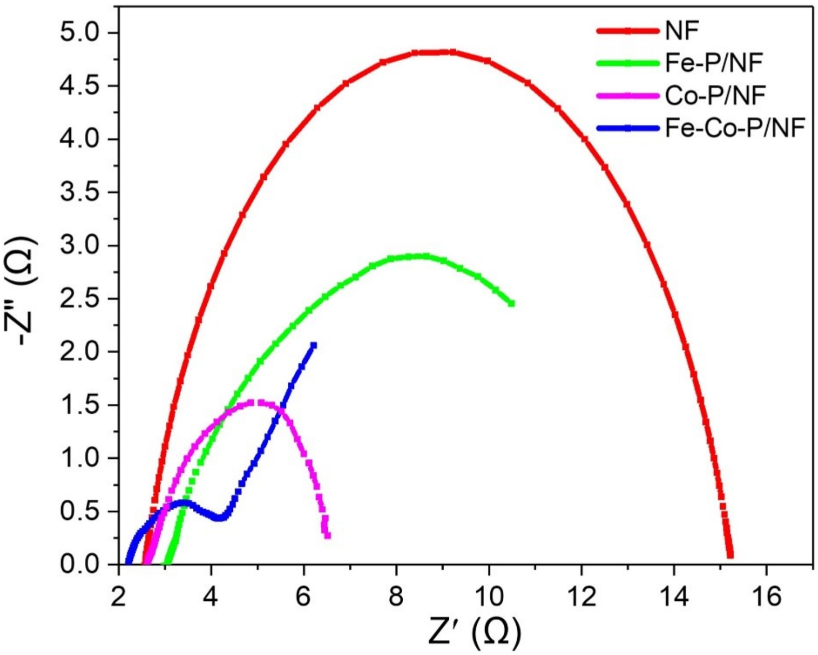


Figure S5 Electrochemical impedance spectroscopy for bare NF, Fe-Co-P / NF, Co-P / NF, Fe-P / N of HER.

`

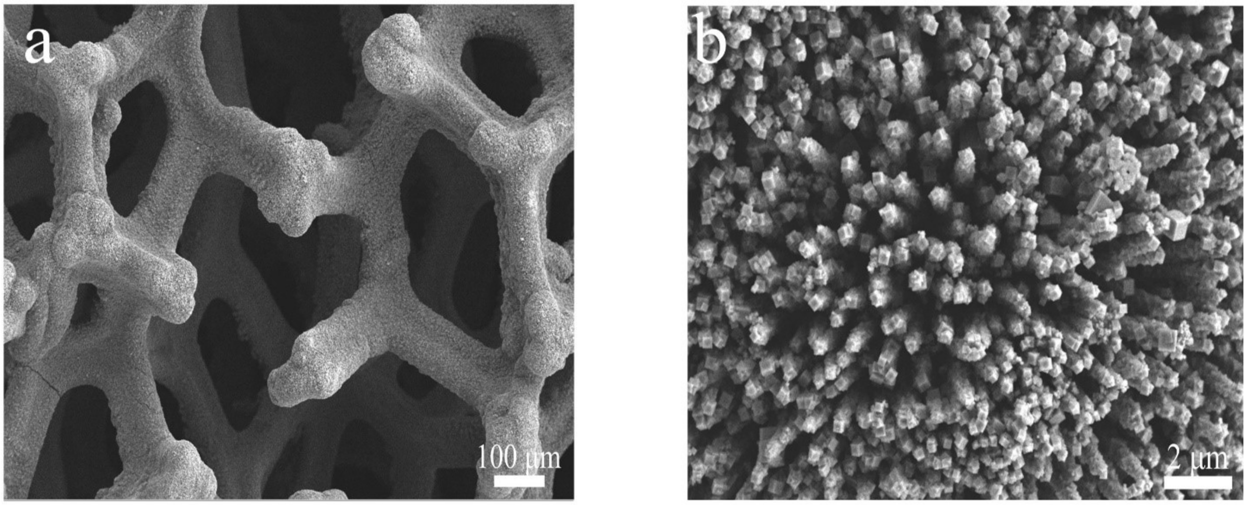


Figure S6 (a)-(b) SEM imagines of CoCH @ Fe-Co-PBA / NF.

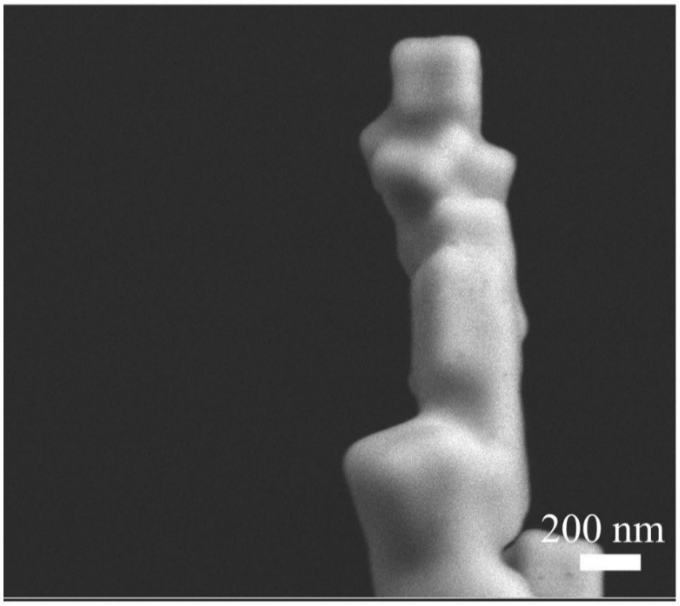


Figure S7 SEM imagines of Fe-Co-P / NF.

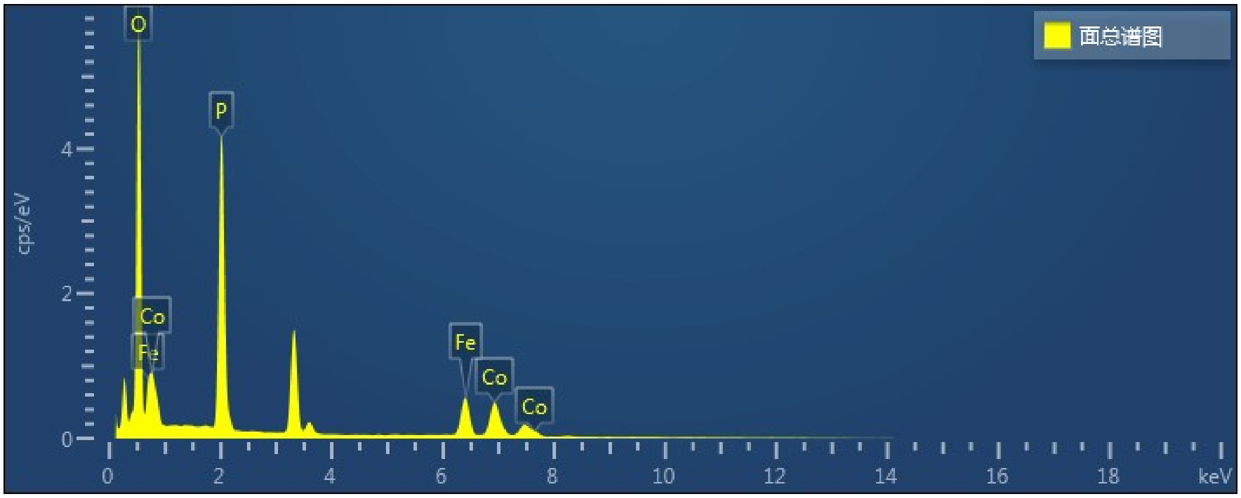


Figure S8 EDS spectrum of Fe-Co-P / NF.

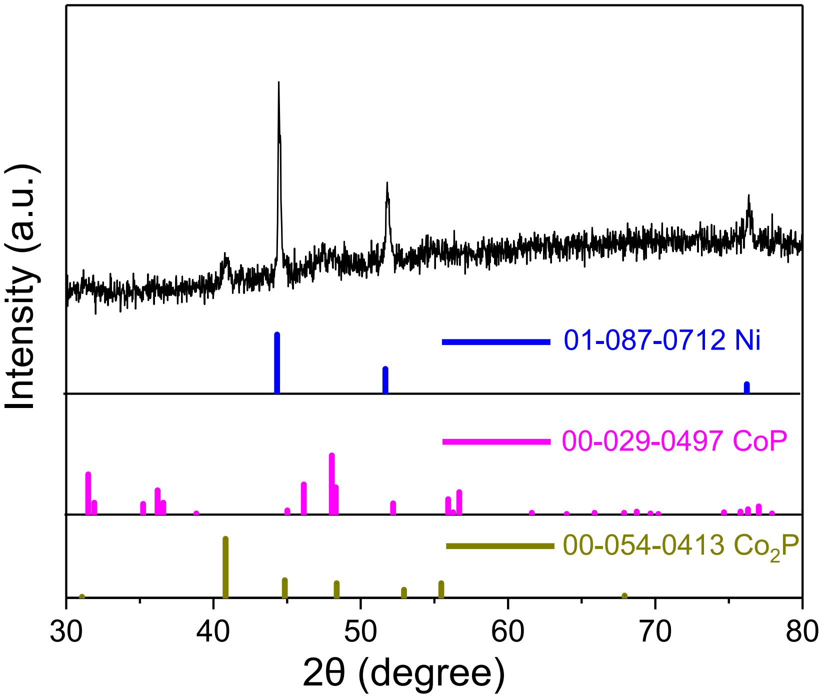


Figure S9 XRD spectrum of Co-P / NF.

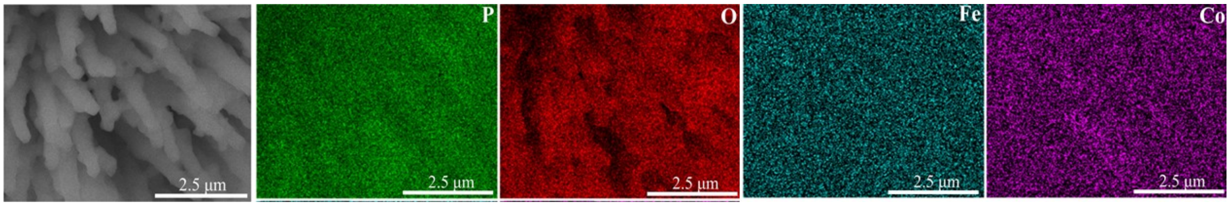


Figure S10 SEM mapping of Fe-Co-P / NF at a larger range.

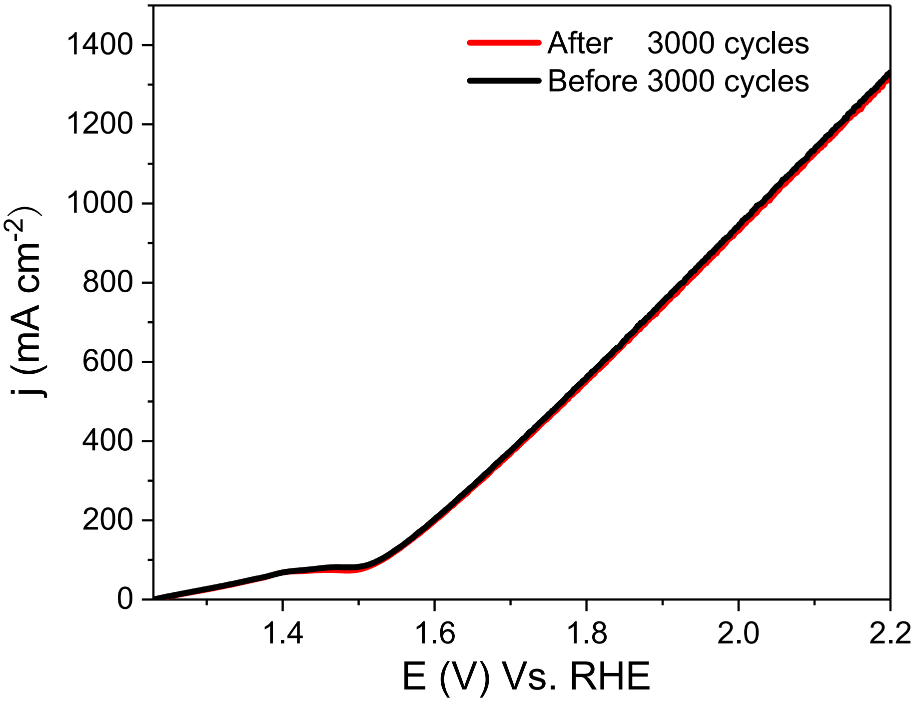


Figure S11 LSV cruves for Fe-Co-P/NF at high current.

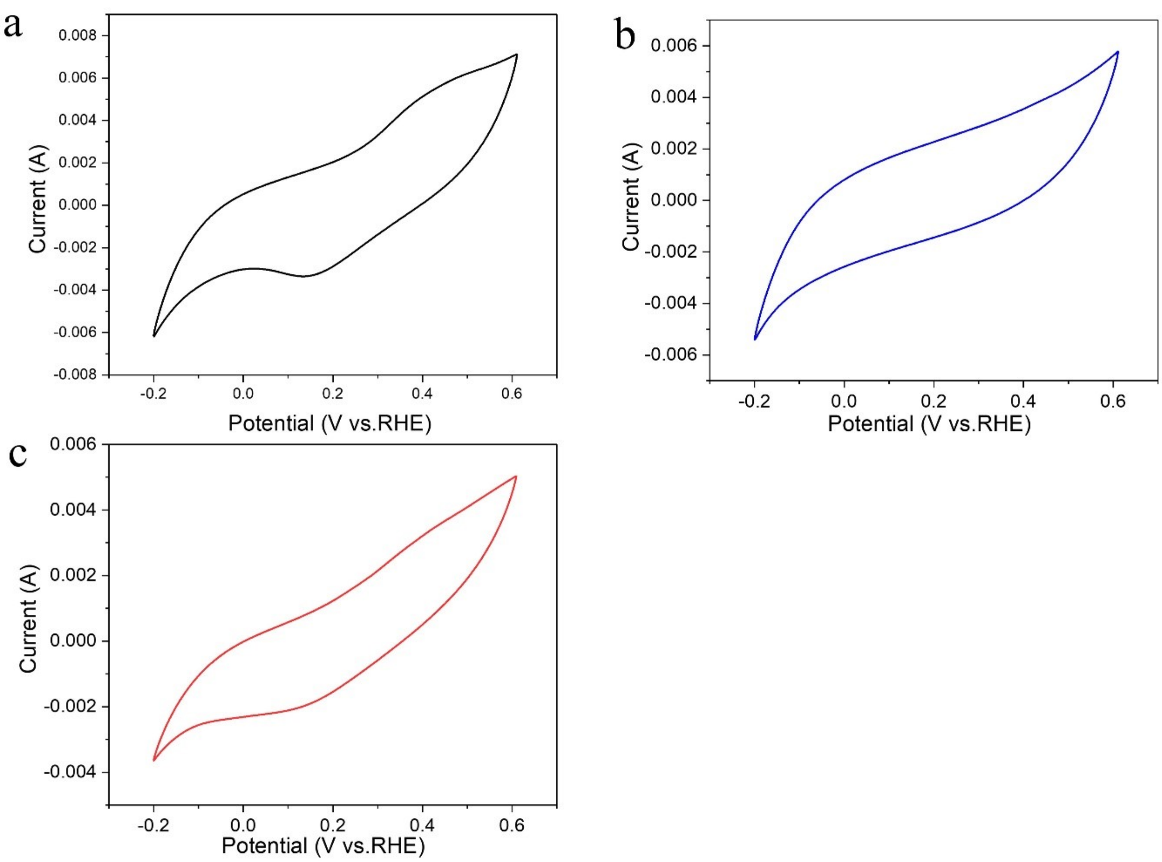


Figure S12 Cyclic voltammogram (CV) curves of (a) Fe-Co-P/NF (b) Co-P/NF and (c) Fe-P/NF electrocatalysts measured in 1 M PBS (pH = 7) electrolyte at a scan rate of 50 mV s^{-1}. Based on the formula of n = IV/2Fv, the number of active sites was determined to be 3.23221e-7 mol, 2.55062e-7 mol and 1.82949e-7 mol for Fe-Co-P/NF, Co-P/NF and Fe-P/NF, respectively.

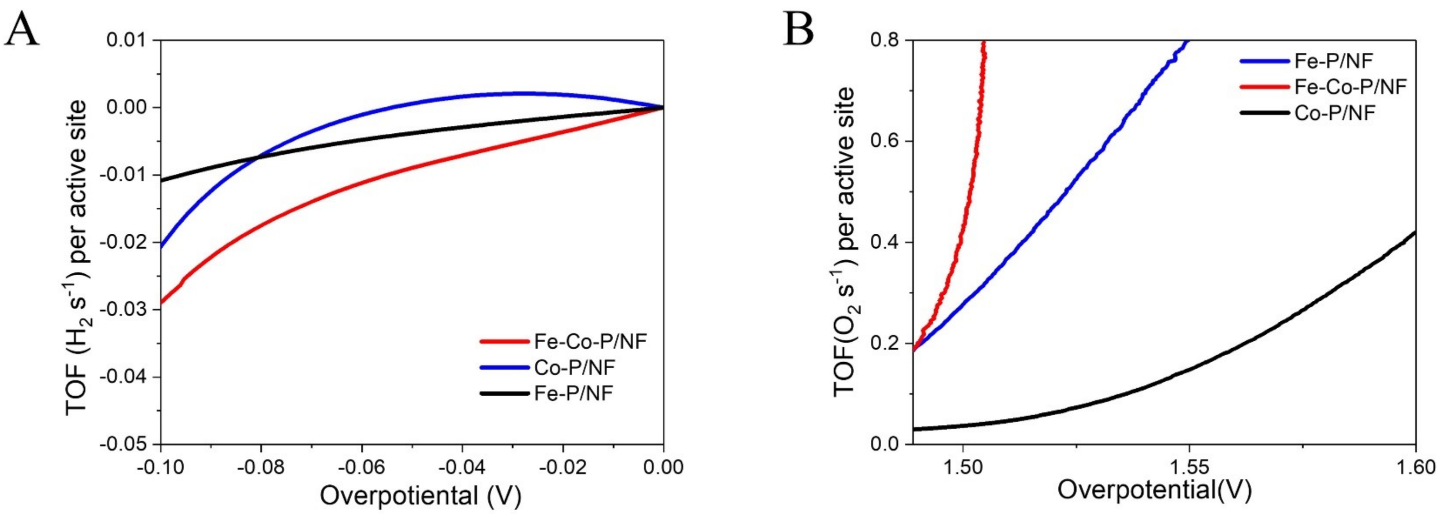
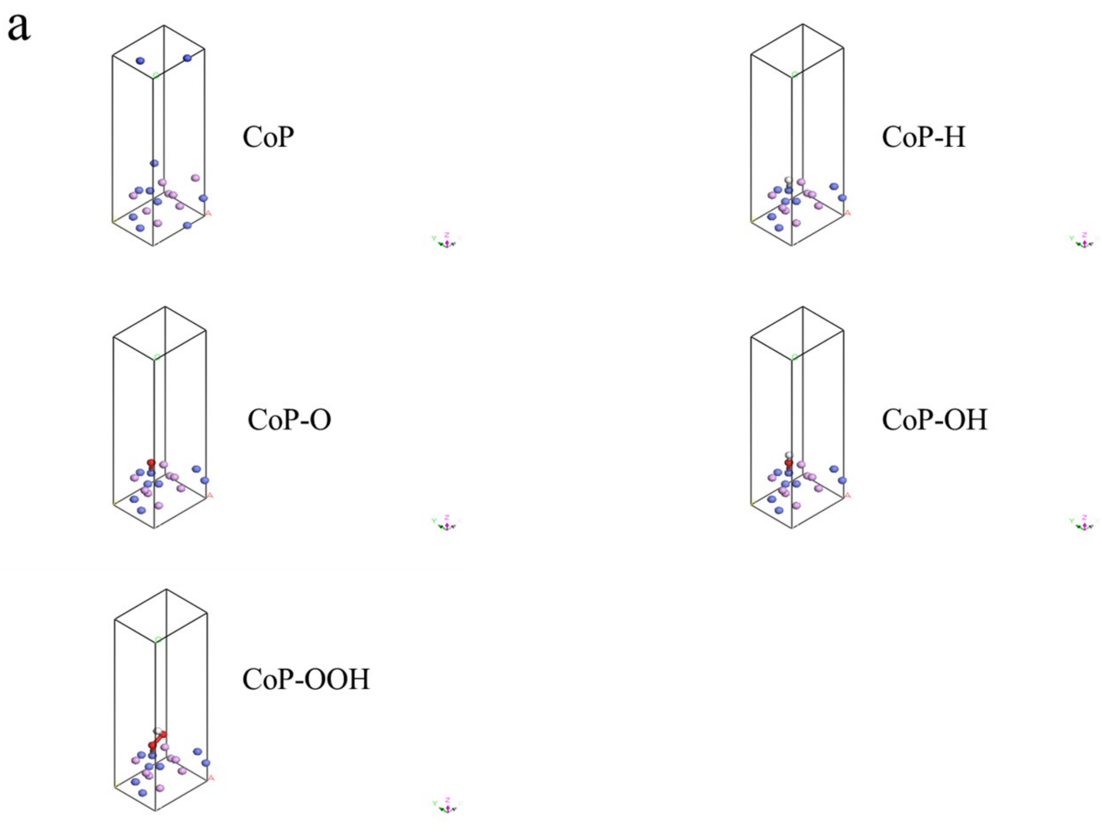
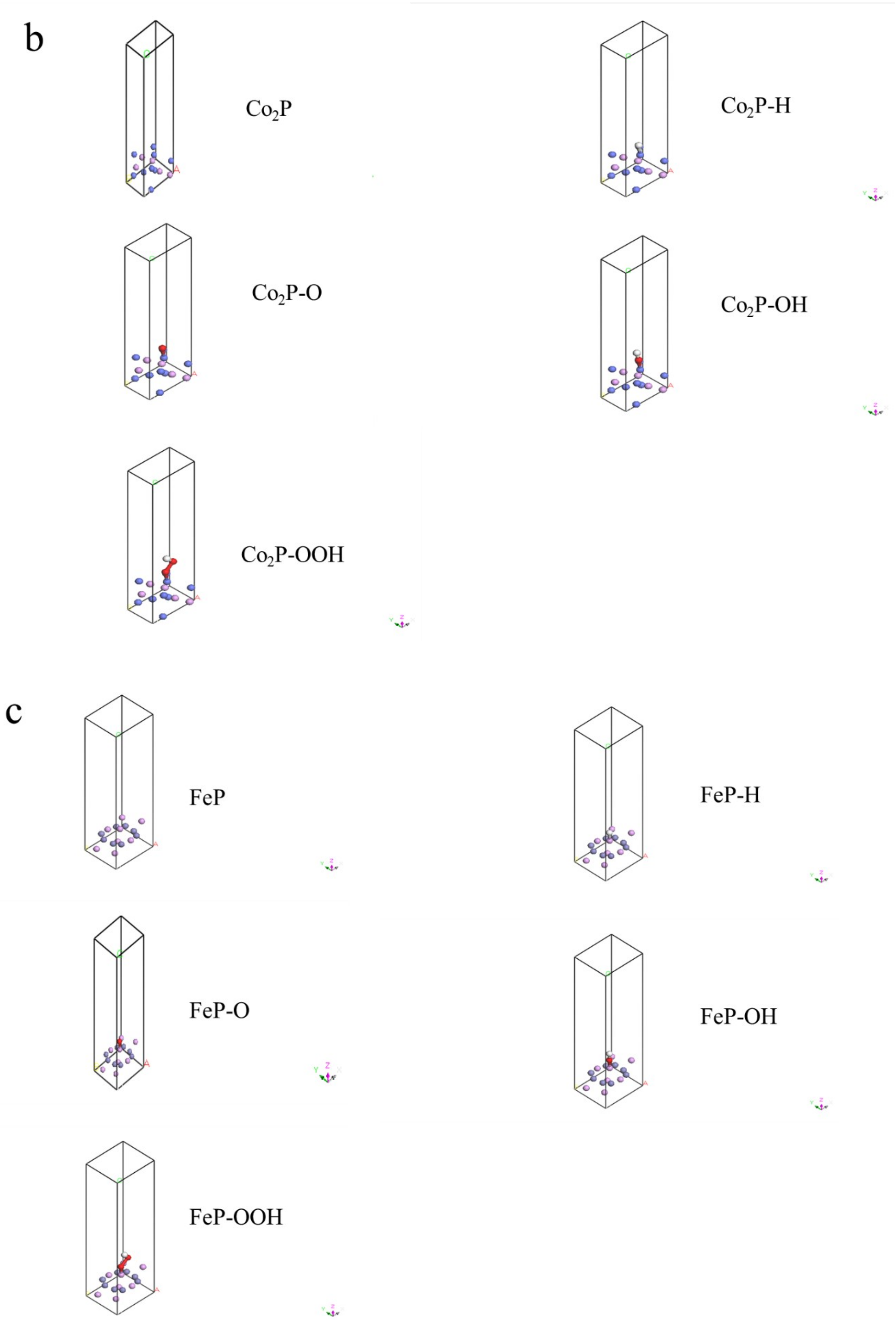
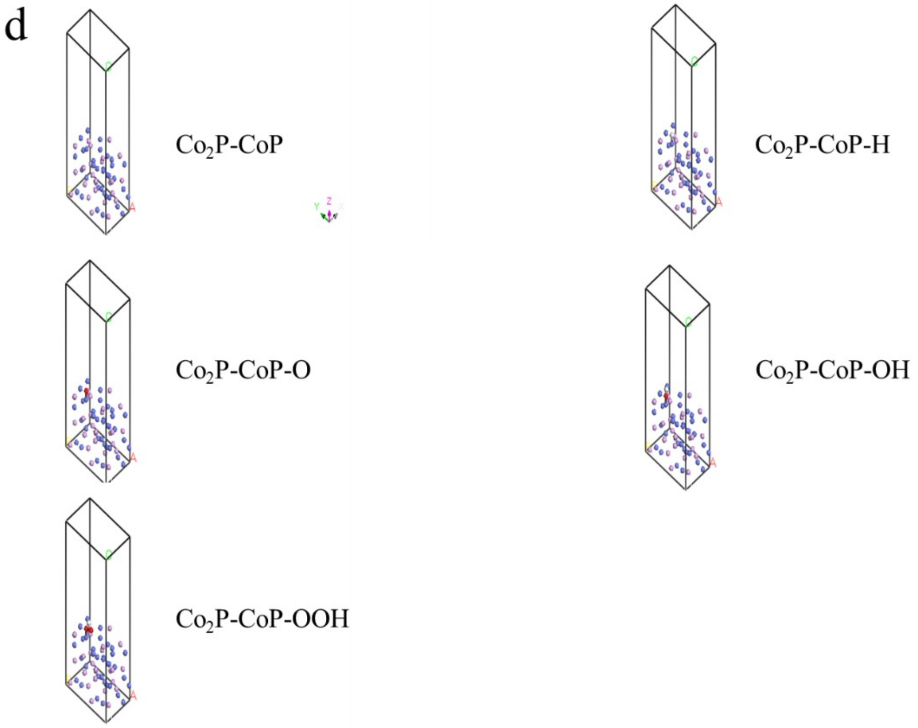
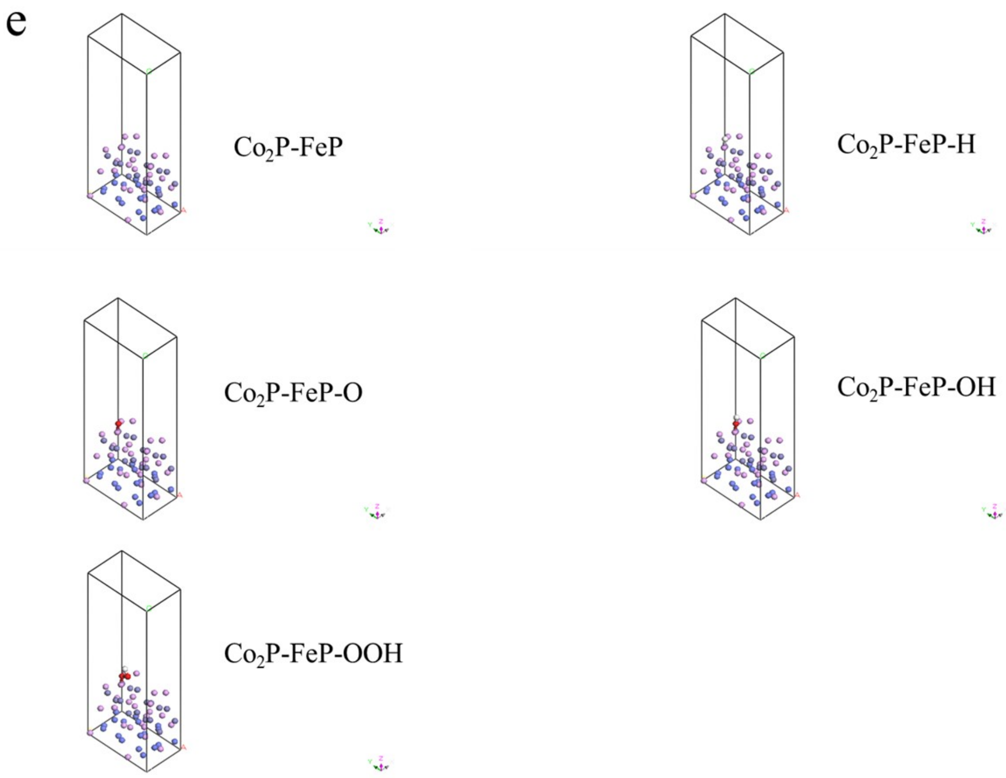


Figure S13 (a) Calculated H_2 TOF values for Fe-Co-P/NF, Co-P/NF and Fe-P/NF. (b) Calculated O_2 TOF values for Fe-Co-P/NF, Co-P/NF and Fe-P/NF.




b
Co$_2$P
Co$_2$P-H
Co$_2$P-O
Co$_2$P-OH
Co$_2$P-OOH
c
FeP
FeP-H
FeP-O
FeP-OH
FeP-OOH


d
Co_2P-CoP
Co_2P-CoP-H
Co_2P-CoP-O
Co_2P-CoP-OH
Co_2P-CoP-OOH


e
Co_2P-FeP
Co_2P-FeP-H
Co_2P-FeP-O
Co_2P-FeP-OH
Co_2P-FeP-OOH

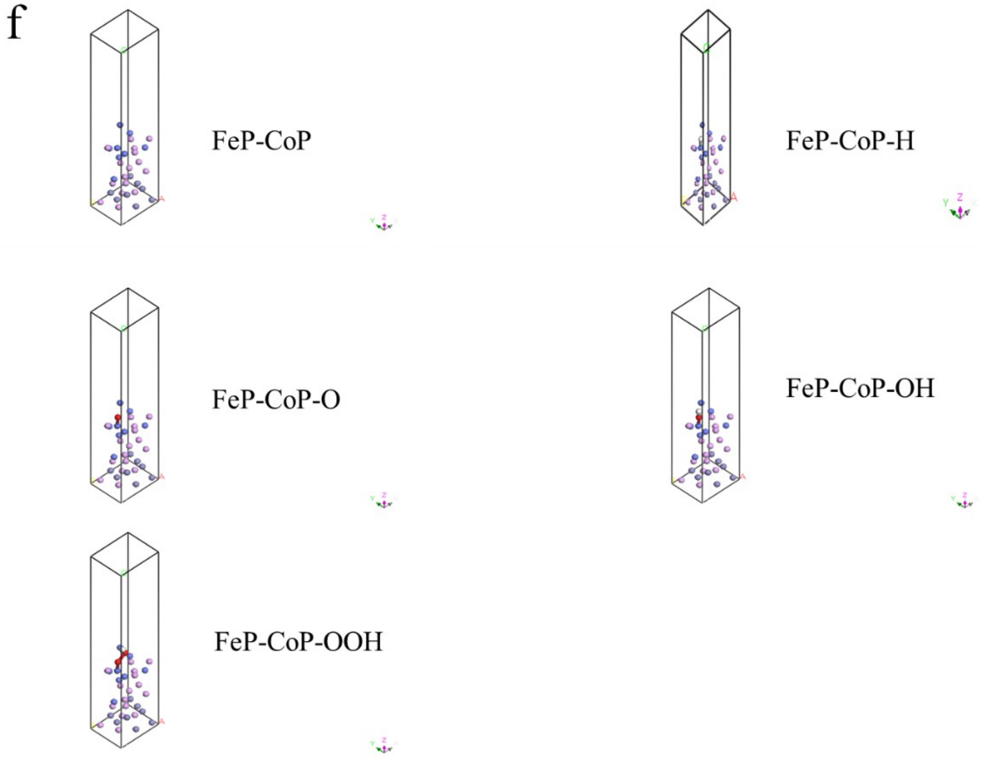


Figure S14 The theoretical models of DFT.

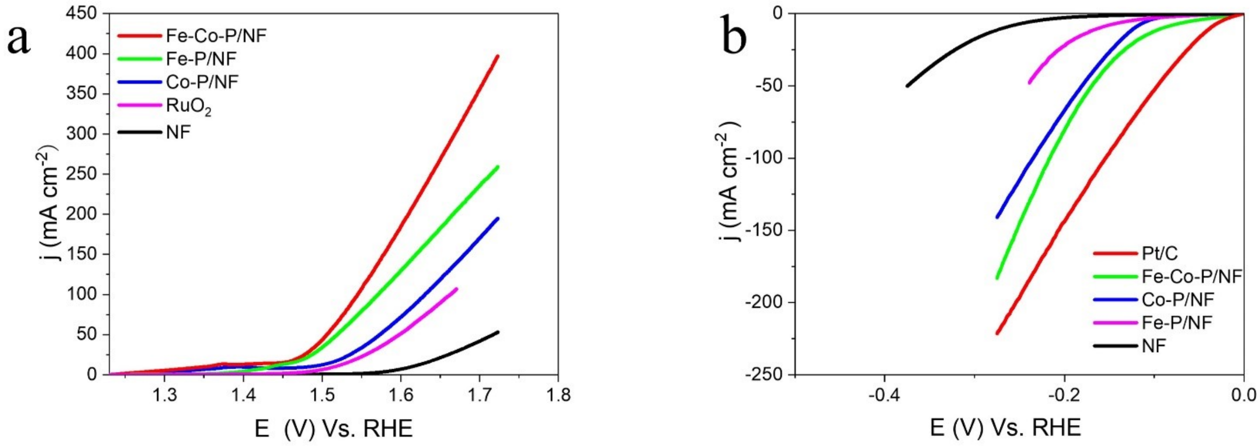


Figure S15 The pristine polarization curves without iR correction of the catalysts of (a) HER (b) OER.

Table S1. Comparison of catalytic performance of Fe-Co-P / NF with other reported self-supported highly active OER electrocatalysts in 1 M KOH.

Catalyst	**Support**	**Overpotential for OER @j (mV @ mA cm^{-2})**	**Overpotential for HER @j (mV @ mA cm^{-2})**	**Cell voltage (at 10 mA cm^{-2})**	**Reference**
Fe-Co-P	NF	227@20	87@10	1.55 V	This work
Co-Fe-P	NF	244@10	_______	_______	2
NiCoP	CC	242@10	62@10	1.52 V	3
NiCoP	NF	268@10	71@10	1.57 V	4
FeCo/C	NF	219@10	_______	_______	5
FeCoP/C NS	NF	_______	107@10	1.55 V	5
$Co_{0.63}Fe_{0.21}P_{0.16}$	NF	217@10	_______	_______	6
$Co(OH)_2$/Ag/FeP	Ti foil	236@10	118@10	1.56 V	7
Co-P film	Cu foil	345@10	94@10	1.64 V	8
FeCoP UNSAs	NF	260@20	188@100	1.60 V	9

1. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152,** J23.
2. T. Zhang, J. Du, P. Xi and C. Xu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 362-370.
3. C. Du, L. Yang, F. Yang, G. Cheng and W. Luo, *ACS Catalysis*, 2017, **7**, 4131-4137.
4. J. G. Wang, W. Hua, M. Li, H. Liu, M. Shao and B. Wei, *ACS Appl. Mater. Interfaces*, 2018, **10**, 41237-41245.
5. R. Xiang, Y. Duan, C. Tong, L. Peng, J. Wang, S. S. A. Shah, T. Najam, X. Huang and Z. Wei, *Electrochim. Acta*, 2019, **302**, 45-55.
6. T. Wang, C. Wang, Y. Jin, A. Sviripa, J. Liang, J. Han, Y. Huang, Q. Li and G. Wu, *J. Mater. Chem. A*, 2017, **5**, 25378-25384.
7. X. Ding, Y. Xia, Q. Li, S. Dong, X. Jiao and D. Chen, *ACS Appl. Mater. Interfaces*, 2019, **11**, 7936-7945.

8. N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed. Engl.*, 2015, **54**, 6251-6254.

9. L. Zhou, M. Shao, J. Li, S. Jiang, M. Wei and X. Duan, *Nano Energy*, 2017, **41**, 583-590.