Supporting Information

Iron-doped Cobalt Phosphide Nano-Electrocatalyst Derived from Metal-Organic Framework for Efficient Water Splitting

Can Lin[a], Pengyan Wang[a], Huihui Jin[a], Jiahuan Zhao[a], Ding Chen[a], Suli Liu[b,*], Chengtian Zhang[a], Shichun Mu[a,*]

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

[b]*Key Laboratory of Advanced Functional Materials of Nanjing, Nanjing Xiaozhuang University, Nanjing 211171, China*

**Corresponding author: E-mail: msc@whut.edu.cn, niuniu_410@126.com*

Materials: Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Aladdin), Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Aladdin), 2-methylimidazole ($C_4H_6N_2$, Aladdin), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$, Aladdin), ethanol (Aladdin), Nafion (Sigma-Aldrich), IrO_2 (Sigma-Aldrich). All reagents are purchased from commercial companies without further treatment. Deionized water acts as solvent in the experiment.

Electrochemical Measurements: OER and HER tests were carried out at room temperature with an electrochemical workstation (CHI660E, Shanghai, China) with a standard three-electrode system. Comprising a graphite rod as the counter electrode, a saturated Hg/HgO as the reference electrode, and Ni foam coated with catalyst as working electrode. To prepare the working electrode, the as-prepared electrocatalyst (5 mg) and Nafion (20 μL, 5 wt%) were scattered in 980 μL isopropanol-water solution (volume ratio of isopropanol to water is 9:1) and then mixture was ultrasonicated for 1 h to form homogeneous ink. The well-mixed ink was used to coat and cover Ni foam surface to achieve a mass loading of 3 mg cm^{-2}. For comparison, IrO_2 ink was prepared by the same method. Ni foam substrate was thoroughly cleaned with 0.5 M H_2SO_4 (15 min), absolute ethanol (20 min) and finally rinsed with deionized water (20 min) in an ultrasound bath. Polarization curves were obtained at room temperature with a scan rate of 5 mV s^{-1} in 1.0 M KOH. All potentials were transformed to the reversible hydrogen electrode (RHE) by following the equation: E (RHE) = E (Hg/HgO) + 0.059 pH + 0.098 V. The overpotential (η) of OER was calculated by the formula (η (V) = E (RHE) - 1.23 V) and the overpotential (η) of HER was calculated by the following formula (η (V) = - E (RHE)). The obtained polarization curves were iR-compensated. Tafel plots were fitted according to the formula (η = blog j + a), where η is the overpotential, j represents the current density, a and b represent constant and Tafel slope, respectively. Electrochemical impedance spectroscopy (EIS) was performed at open circuit potential with the frequency range of 10^{-1} Hz to 10^{5} Hz. The double layer capacitance (C_{dl}) was determined by cyclic voltammetry curves measured by scan rates of 80, 100, 120, 140 and 160 mV s^{-1}.

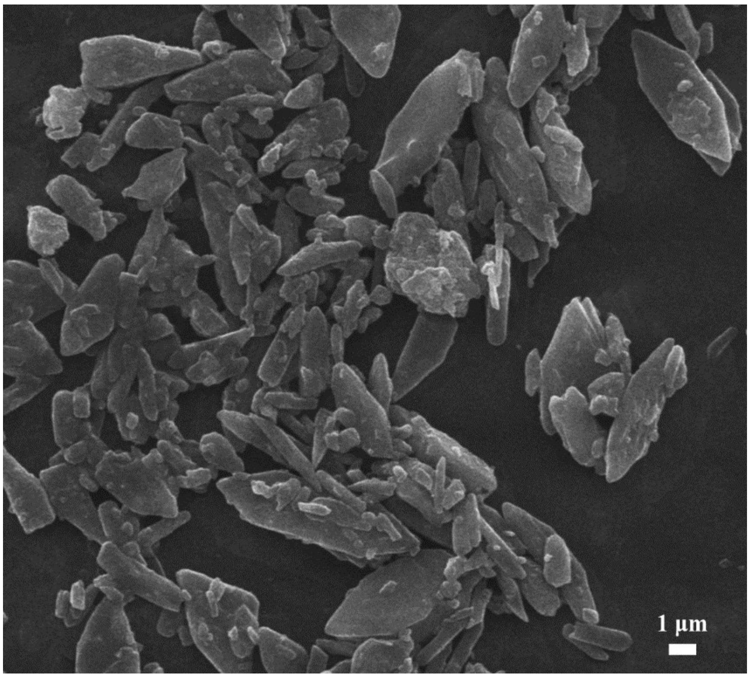

Figure S1. SEM image of $Fe_{0.27}Co_{0.73}$ precursor

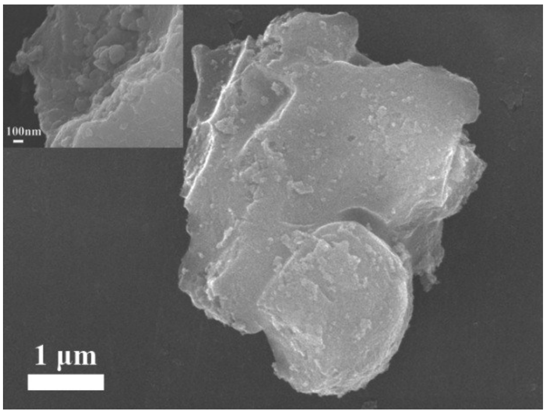

Figure S2. SEM images of $Fe_{0.27}Co_{0.73}$ precursor that was calcined in nitrogen without adding phosphorus source.

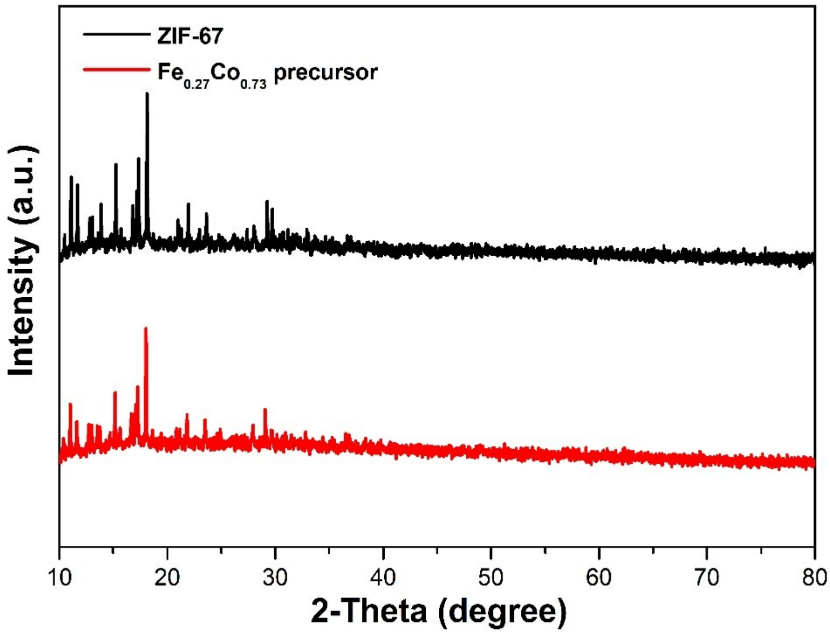

Figure S3. XRD patterns of ZIF-67 and $Fe_{0.27}Co_{0.73}$ precursor

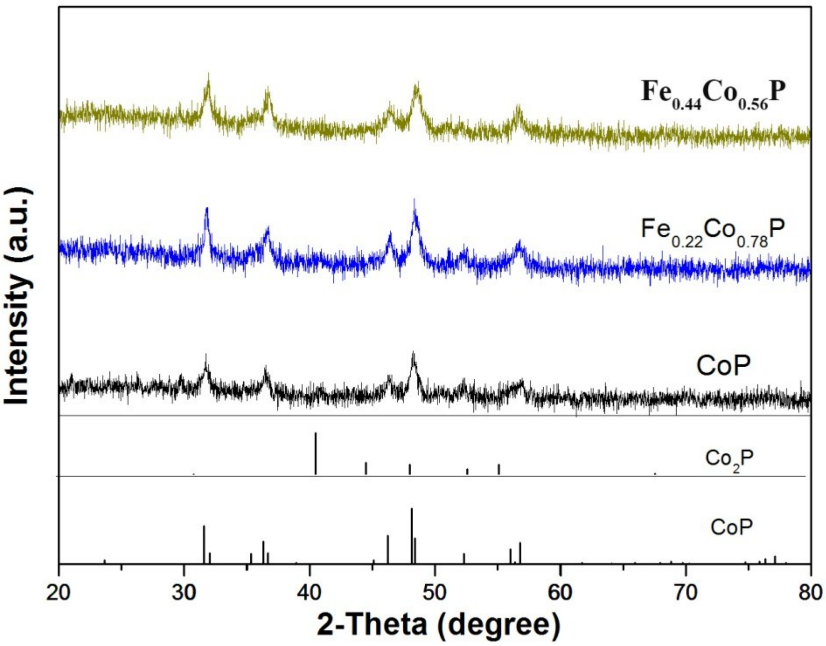

Figure S4. XRD patterns of $Fe_{0.22}Co_{0.78}P$, $Fe_{0.44}Co_{0.56}P$, CoP.

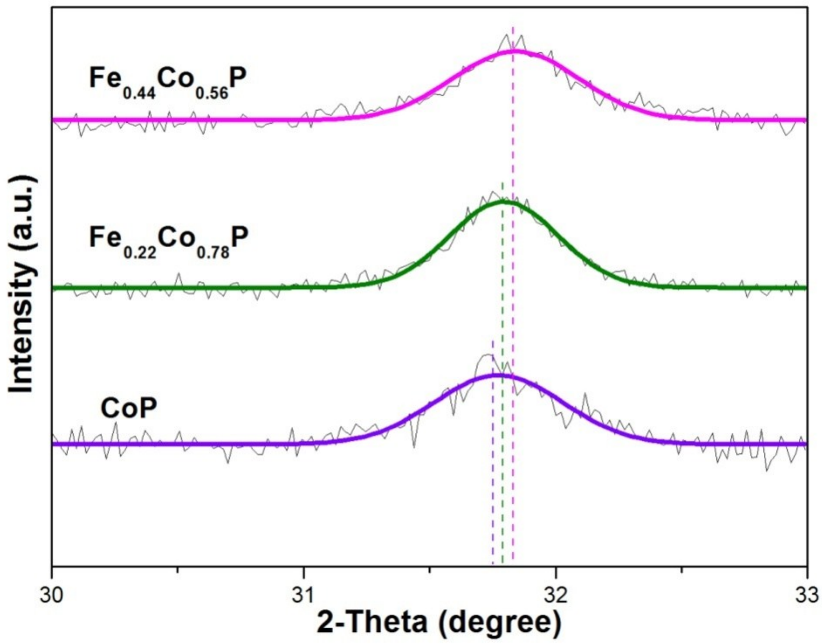

Figure S5. XRD patterns for a slow scan of 1 degree per minute for a specific diffraction angle including CoP, $Fe_{0.22}Co_{0.78}P$ and $Fe_{0.44}Co_{0.56}P$.

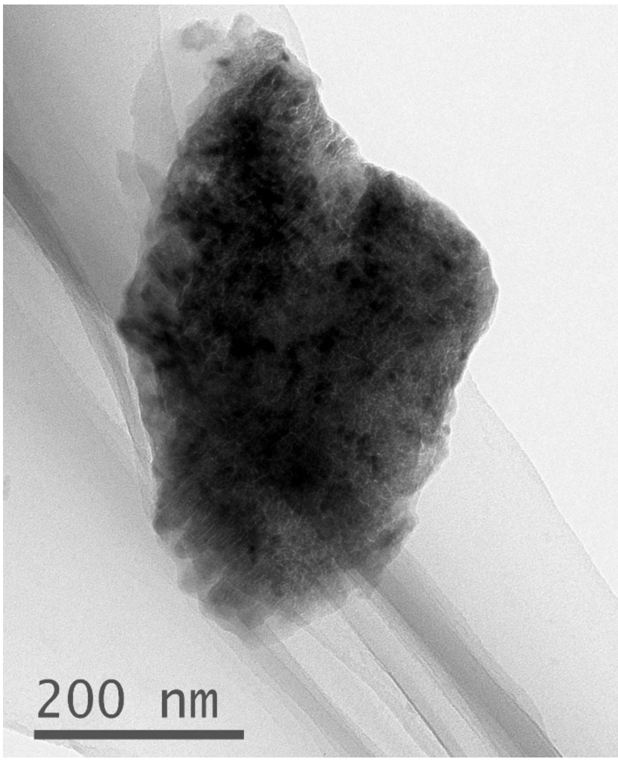

Figure S6. Low-resolution TEM image of $Fe_{0.27}Co_{0.73}P$

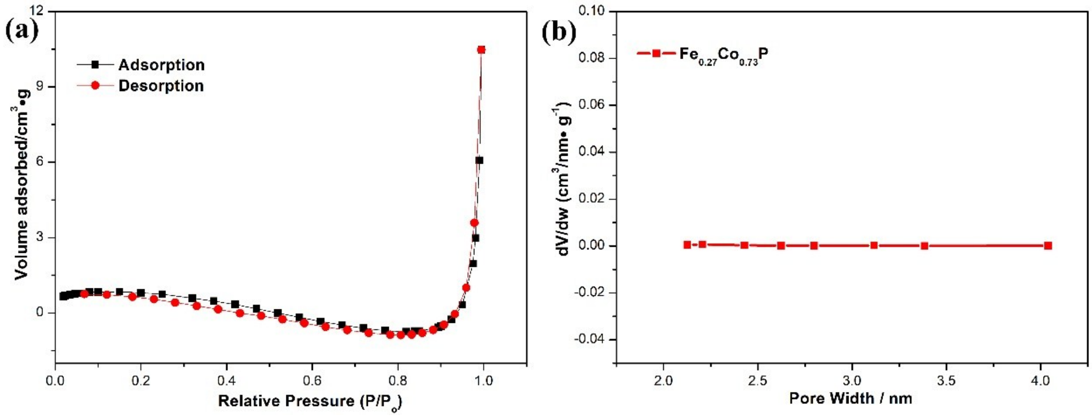

Figure S7. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of $Fe_{0.27}Co_{0.73}P$.

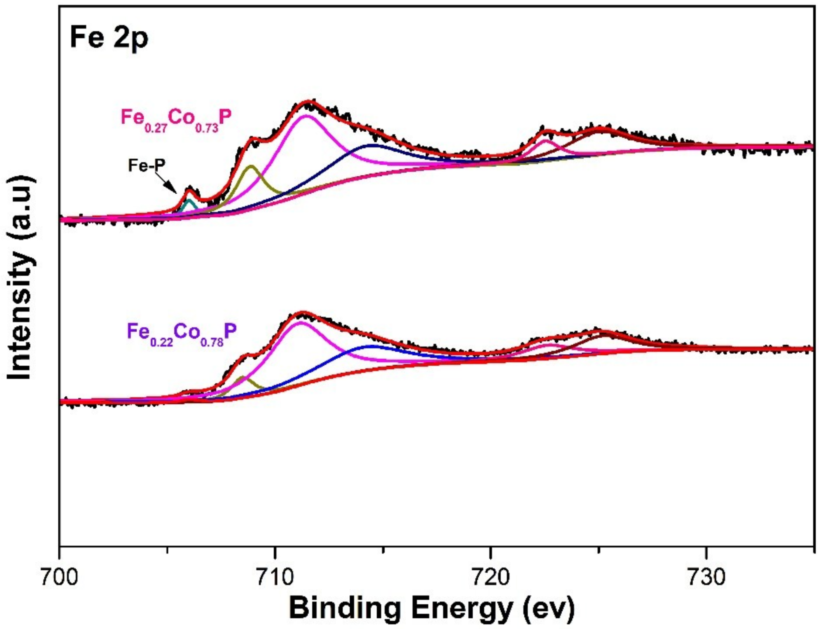

Figure S8. XPS spectrum of $Fe_{0.27}Co_{0.73}P$ and $Fe_{0.22}Co_{0.78}P$ in Fe 2p region.

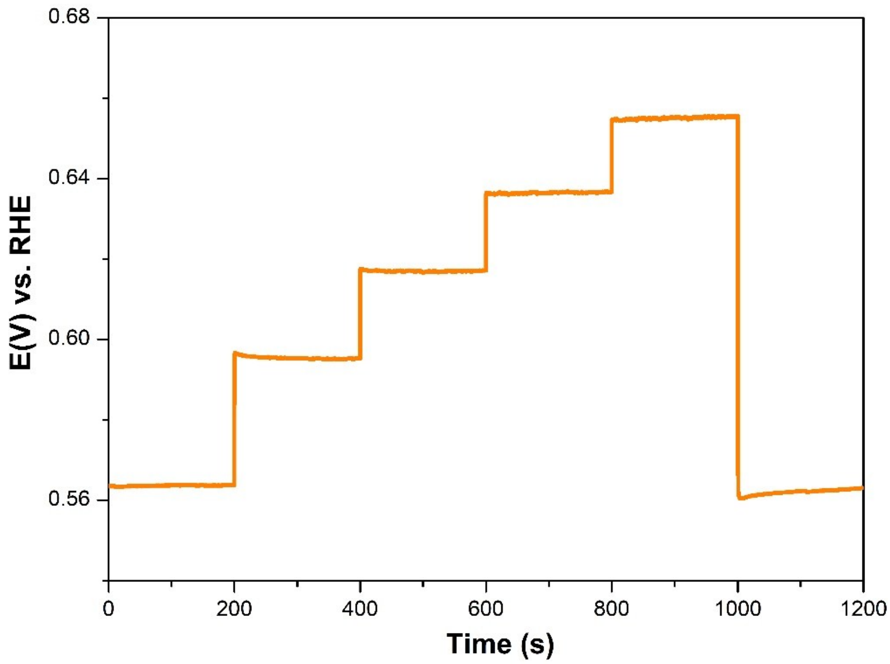

Figure S9. Multi-step current curve for $Fe_{0.27}Co_{0.73}P$/NF without iR correction.

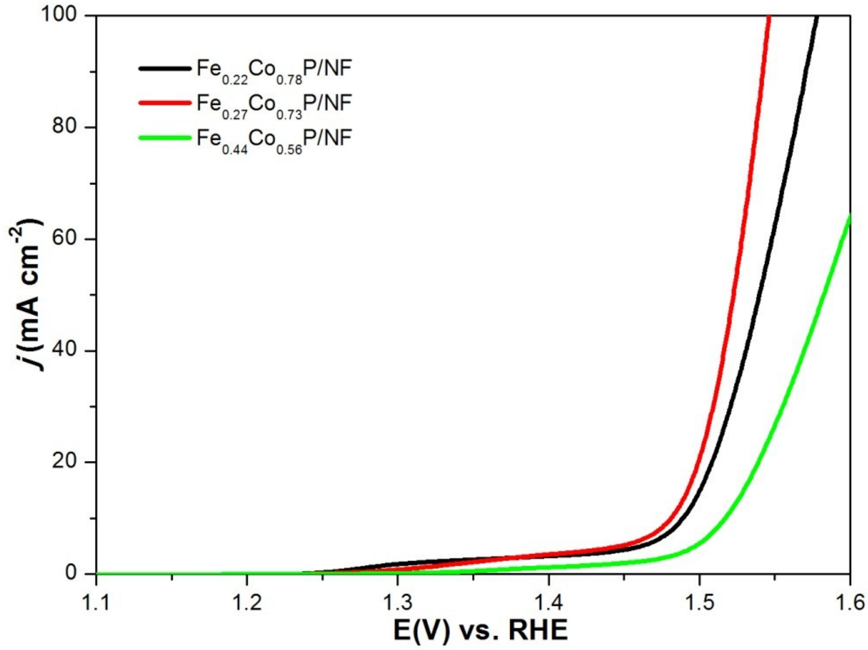

Figure S10. Polarization curves of $Fe_{0.27}Co_{0.73}P$/NF, $Fe_{0.22}Co_{0.78}P$/NF and $Fe_{0.44}Co_{0.56}P$/NF.

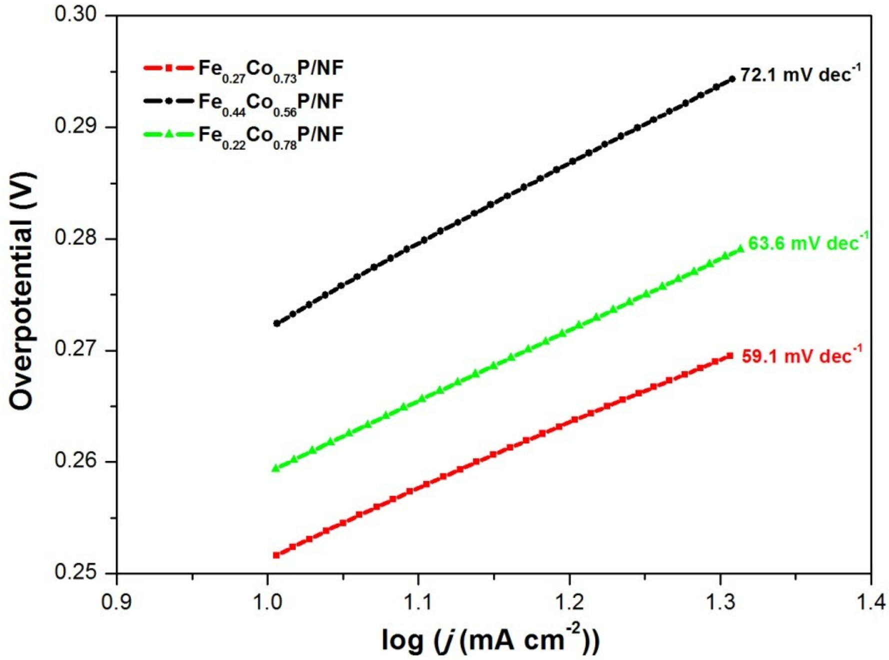

Figure S11. Tafel slopes of $Fe_{0.27}Co_{0.73}P$/NF, $Fe_{0.22}Co_{0.78}P$/NF and $Fe_{0.44}Co_{0.56}P$/NF.

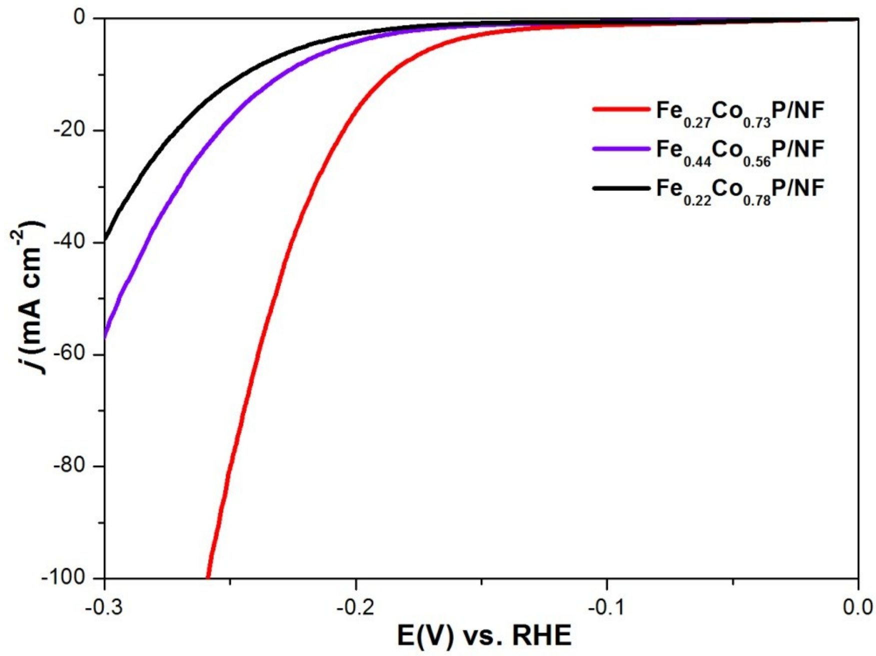

Figure S12. Polarization curves of $Fe_{0.27}Co_{0.73}P$/NF, $Fe_{0.22}Co_{0.78}P$/NF and $Fe_{0.44}Co_{0.56}P$/NF.

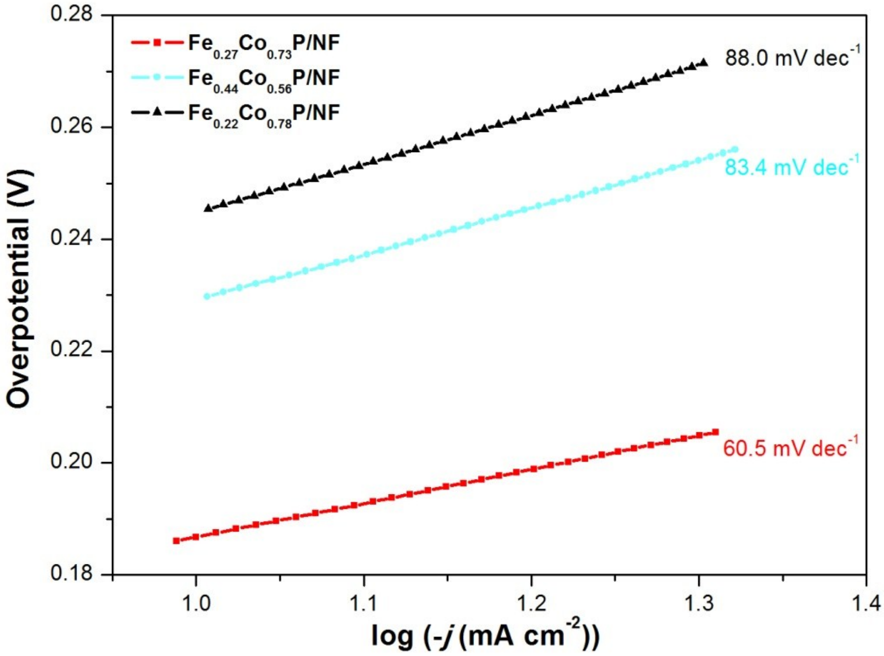

Figure S13. Tafel slopes of $Fe_{0.27}Co_{0.73}P$/NF, $Fe_{0.22}Co_{0.78}P$/NF and $Fe_{0.44}Co_{0.56}P$/NF.

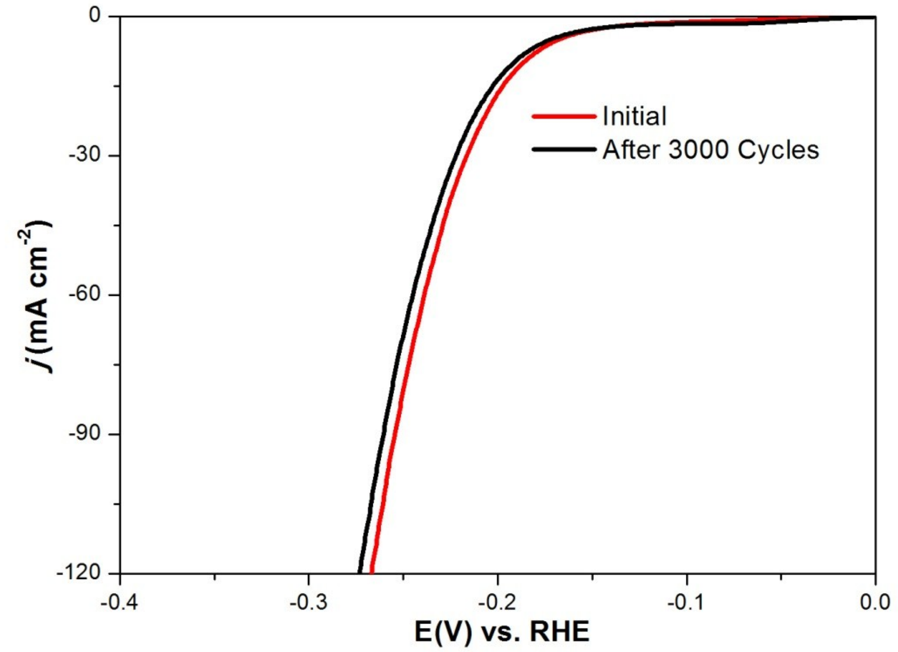

Figure S14. Polarization curves for $Fe_{0.27}Co_{0.73}P$/NF initial and after 3000 CV cycles.

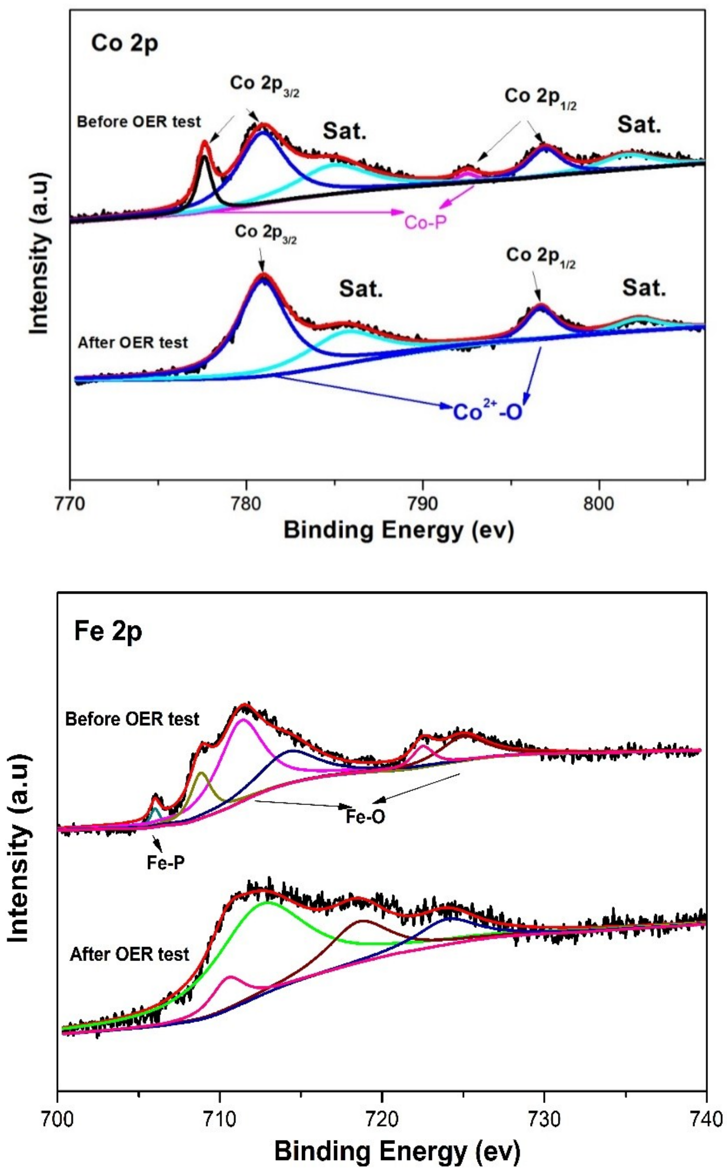

Figure S15. XPS spectrum of $Fe_{0.27}Co_{0.73}P$ before and after OER test in Co 2p region and Fe 2p region.

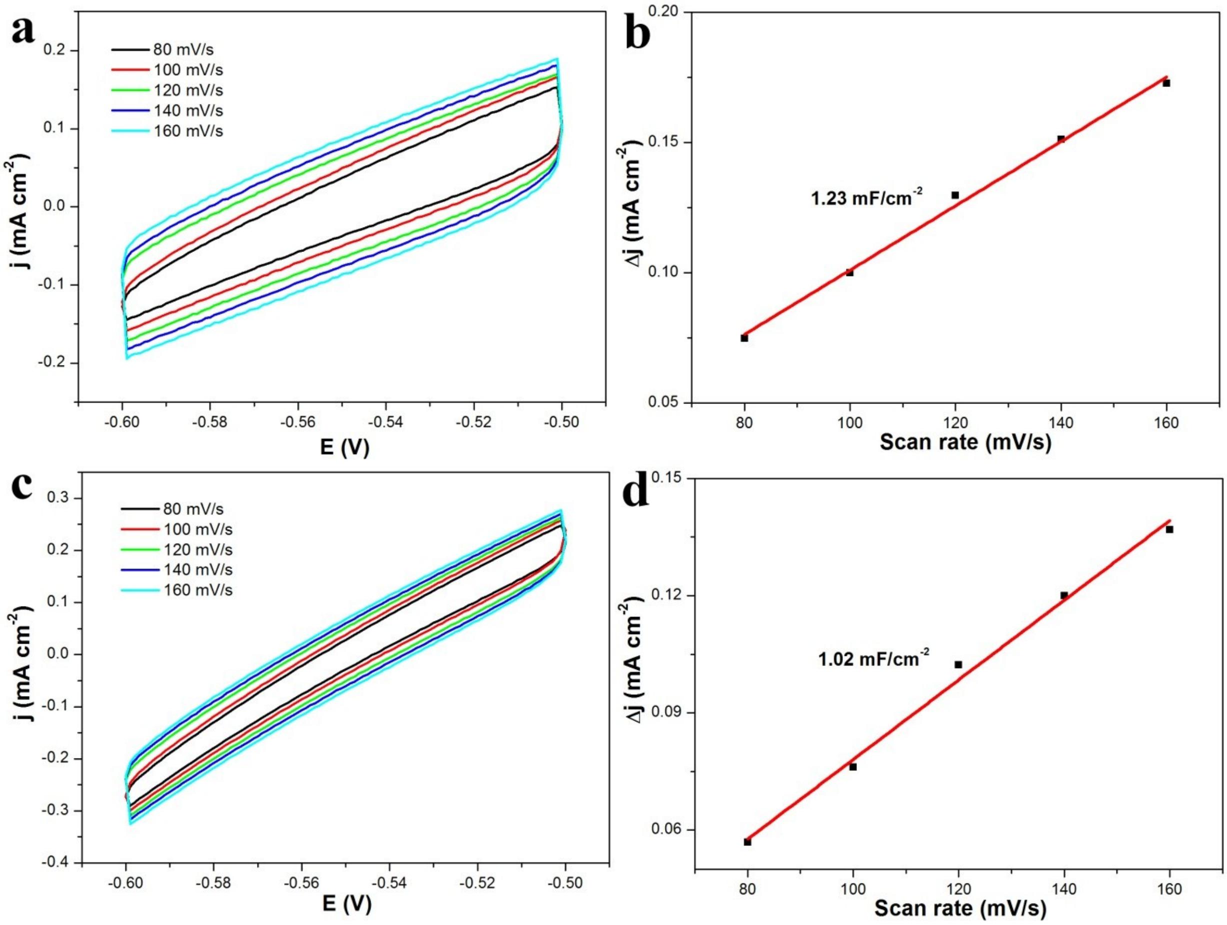

Figure S16. CVs of (a) CoP/NF and (c) $Fe_{0.27}Co_{0.73}P$/NF and corresponding current densities of (b) CoP/NF and (d) $Fe_{0.27}Co_{0.73}P$/NF plotted as a function of scan rate.

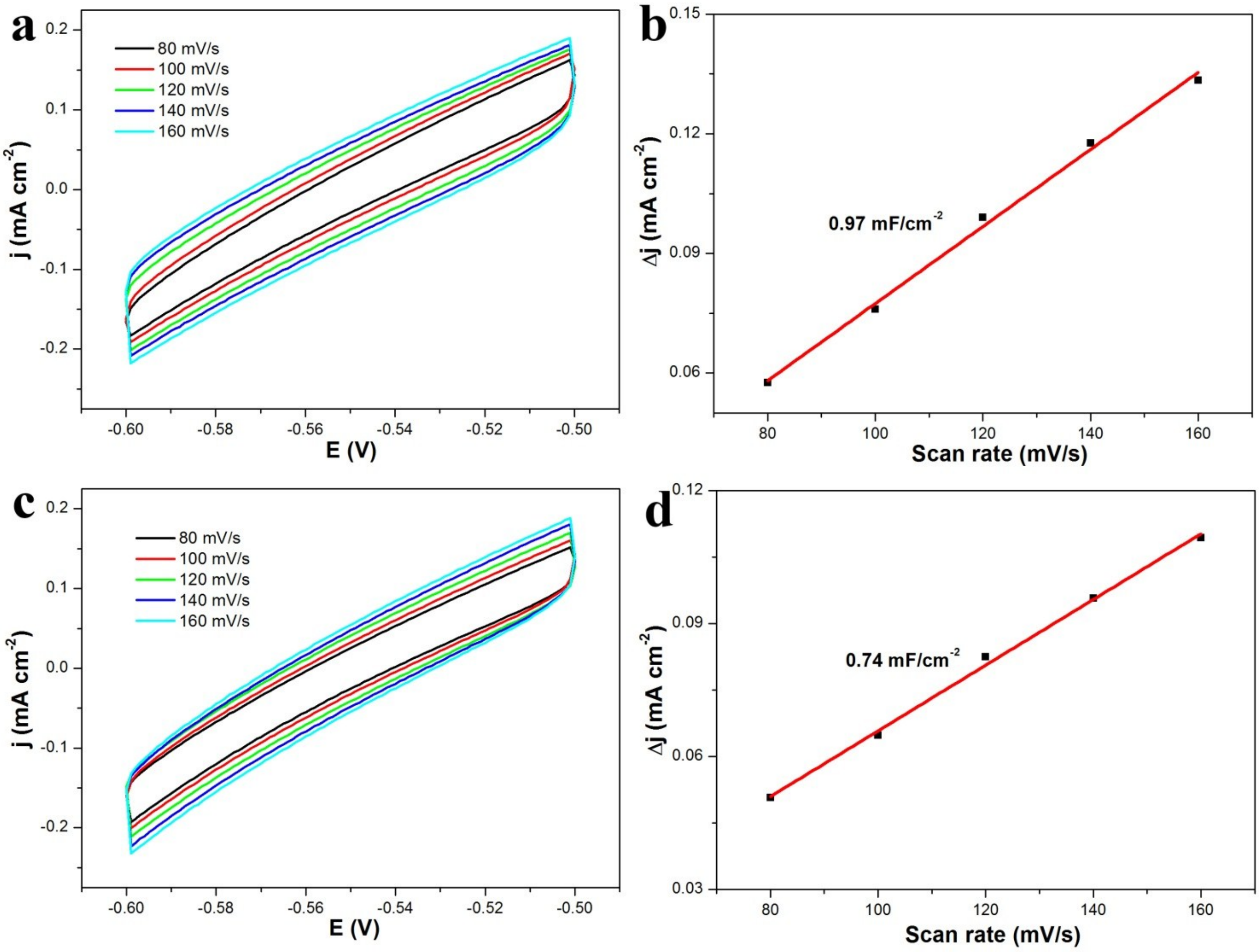

Figure S17. CVs of (a) $Fe_{0.22}Co_{0.78}P$/NF and (c) $Fe_{0.44}Co_{0.56}P$/NF and corresponding current densities of (b) $Fe_{0.22}Co_{0.78}P$/NF and (d) $Fe_{0.44}Co_{0.56}P$/NF plotted as a function of scan rate.

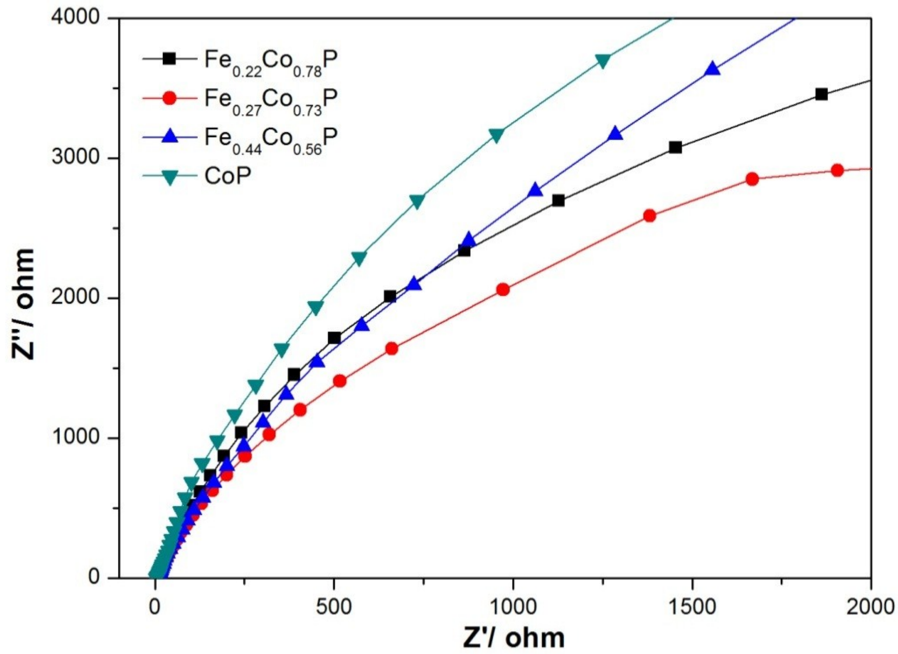

Figure S18. EIS spectra of $Fe_{0.27}Co_{0.73}P$/NF, $Fe_{0.22}Co_{0.78}P$/NF, CoP/NF and $Fe_{0.44}Co_{0.56}P$/NF.

Table S1. Comparison of OER performance in 1.0 M KOH for $Fe_{0.27}Co_{0.73}P$ /NF with other recently reported representative OER electrocatalysts in alkaline solution.

Electrocatalysts	**Current density (mA cm^{-2})**	**Overpotential (mV)**	**Reference**
$Fe_{0.27}Co_{0.73}P$/NF	10	251	This work
CeOx/CoS	10	259	Angew. Chem. Int. Ed. 2019, 58, 139.
NiCo LDH	20	393	Nano Lett. 2015, 15, 1421.
ZIF-67/LDH	10	340	J. Am. Chem. Soc. 2015, 137, 5590.
ZIF-8/ZIF-67 core/shell structure	10	450	Adv. Mater. 2017, 29, 1700874.
$Ni_{1.85}Fe_{0.15}P$ NSAs/NF	20	270	ACS Appl. Mater. Interfaces 2017, 9, 26001.
Ni_3N/NF	20	399	J. Mater. Chem. 2015, 3, 8171.

Video S1. Video of $Fe_{0.27}Co_{0.73}P$/NF electrodes electrolyze water in electrolyzed water reaction tank containing 1.0 M KOH alkaline solution.

Video S2. Video demonstration uses a drainage method to collect hydrogen and oxygen for characterizing the $Fe_{0.27}Co_{0.73}P$ Faradaic efficiency.