

Supporting Information

In Situ Iron Coating on Nanocatalysts for Efficient and Durable Oxygen Evolution Reaction

Chunpeng Yang,^{1a} Mingjin Cui,^{1a} Na Li,^{2a} Zhijuan Liu,² Sooyeon Hwang,² Hua Xie,¹ Xizheng Wang,¹ Yudi Kuang,¹ Miaolun Jiao,¹ Dong Su,^{2*} Liangbing Hu^{1*}

¹ Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

² Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

* Email: Liangbing Hu, binghu@umd.edu; Dong Su, dsu@bnl.gov.

^a These authors contributed equally.

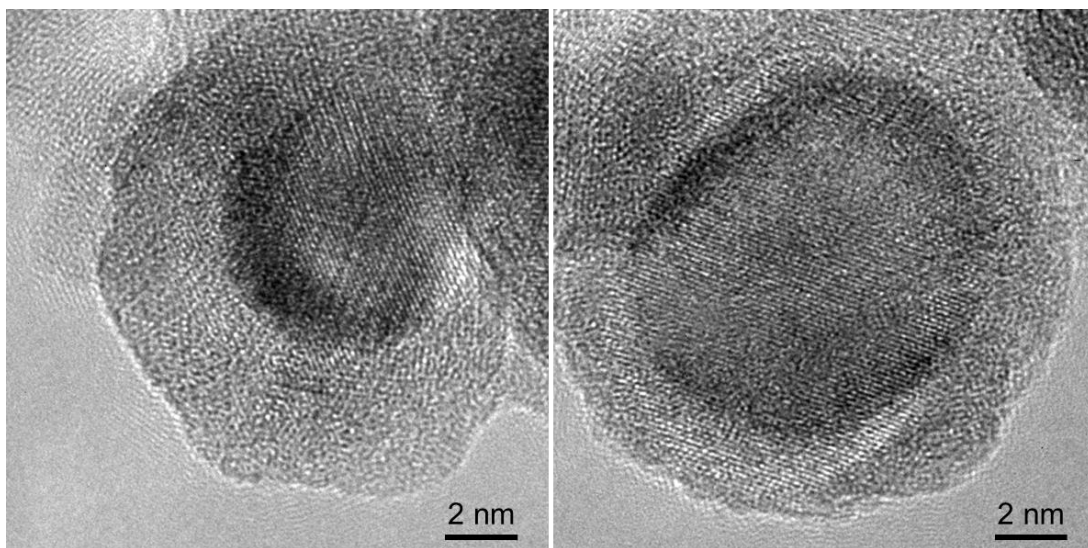


Figure S1. High-resolution TEM images of CoFeP_x nanoparticles on the c-wood substrate. The CoFeP_x core is crystalline while the Fe shell is mainly amorphous, with some small crystalline regions.

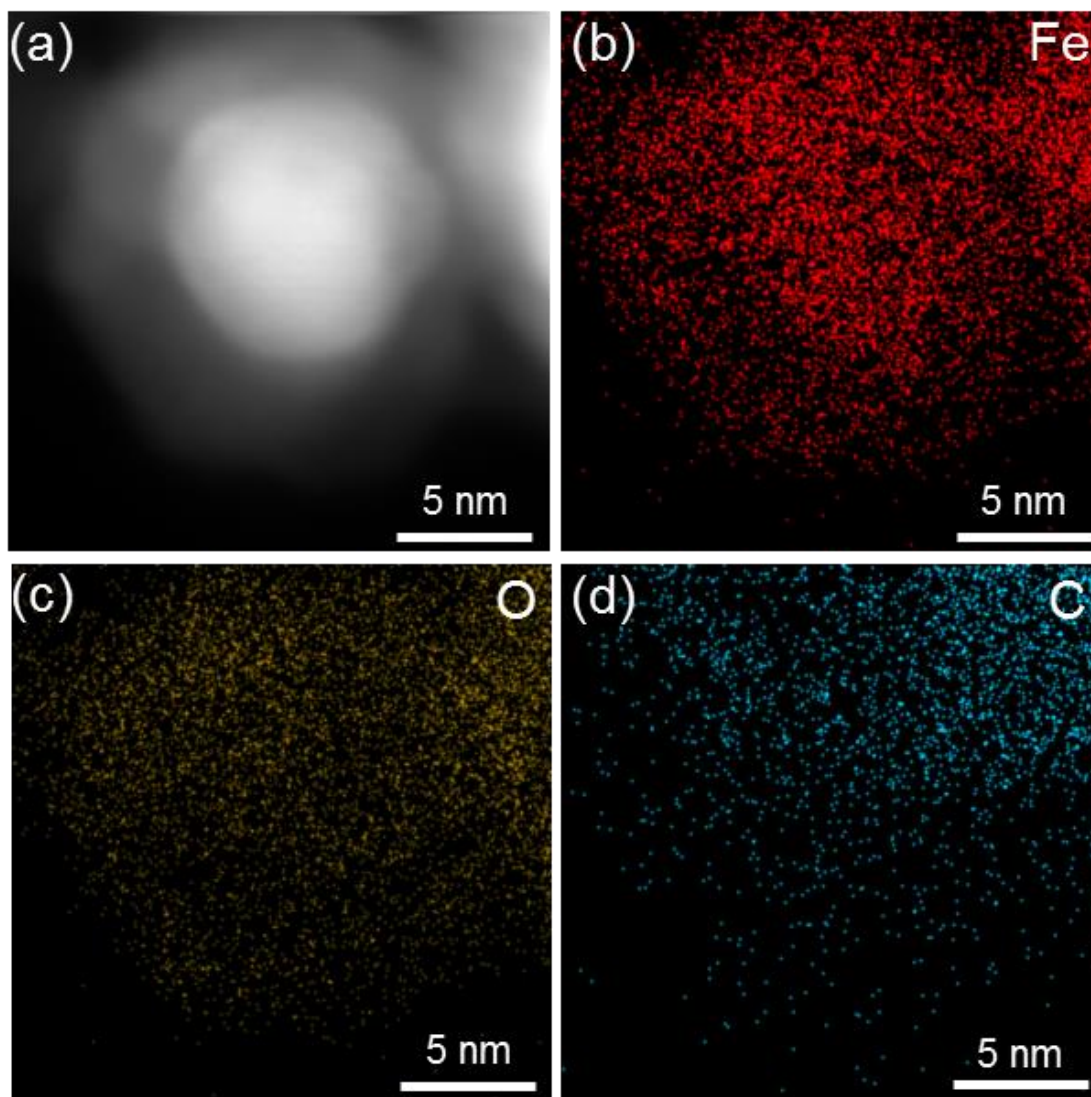


Figure S2. (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of a CoFeP_x nanoparticle and the corresponding elemental mapping: (b) Fe, (c) O, and (d) C.

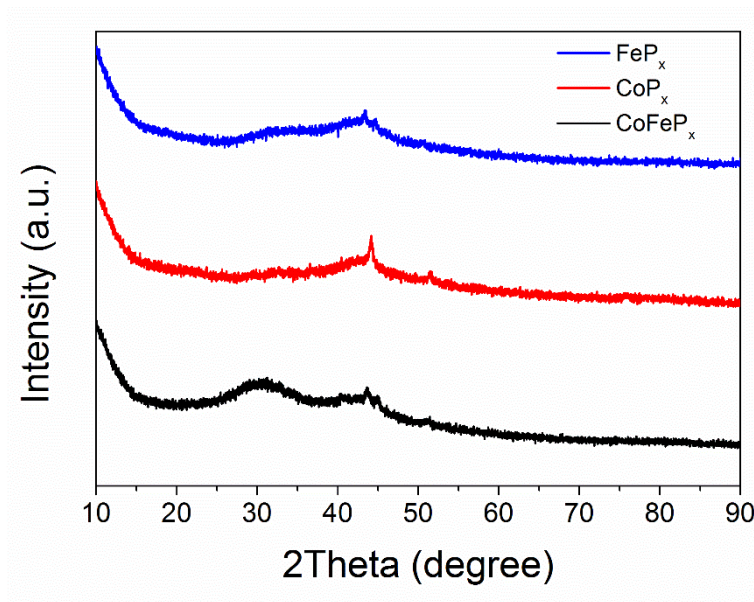


Figure S3. XRD profiles of FeP_x , CoP_x , and CoFeP_x on the carbonized wood substrate. The grain sizes derived from XRD according to Scherrer equation are listed in Table S1. The grain sizes show the same trend as the particle sizes measured by TEM. That is, CoP_x tends to form smaller nanoparticles than FeP_x .

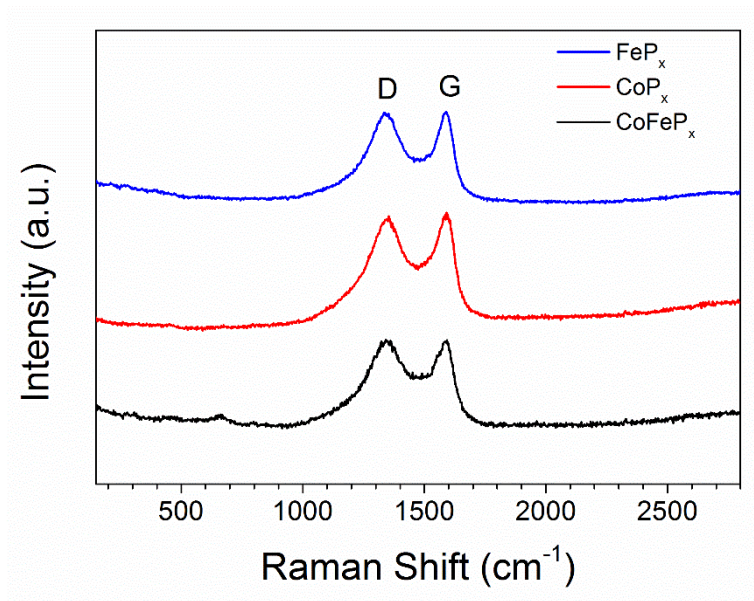


Figure S4. Raman spectra of FeP_x , CoP_x , and CoFeP_x on the carbonized wood substrates. The carbon substrates showed no significant differences with the three metal phosphide nanoparticles.

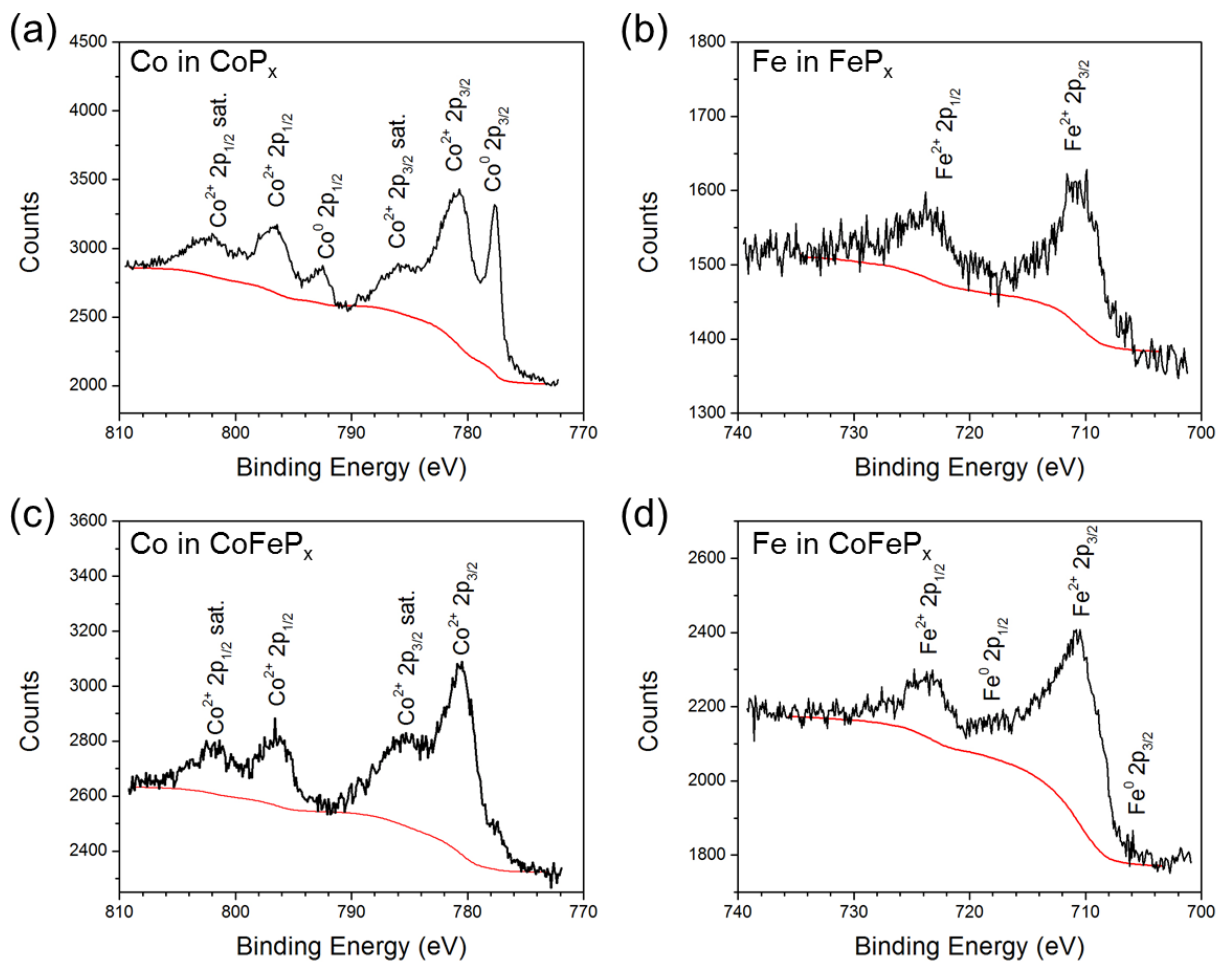


Figure S5. XPS of (a) Co 2p in CoP_x , (b) Fe 2p in FeP_x , (c) Co 2p in CoFeP_x , and (d) Fe 2p in CoFeP_x (sat.: satellite peak). The Co in CoP_x has a mixed chemical state of Co^{2+} and Co^0 (elemental Co), whereas in CoFeP_x , Co exists mainly as Co^{2+} . Compared with FeP_x , the Fe in CoFeP_x shows more elemental Fe.

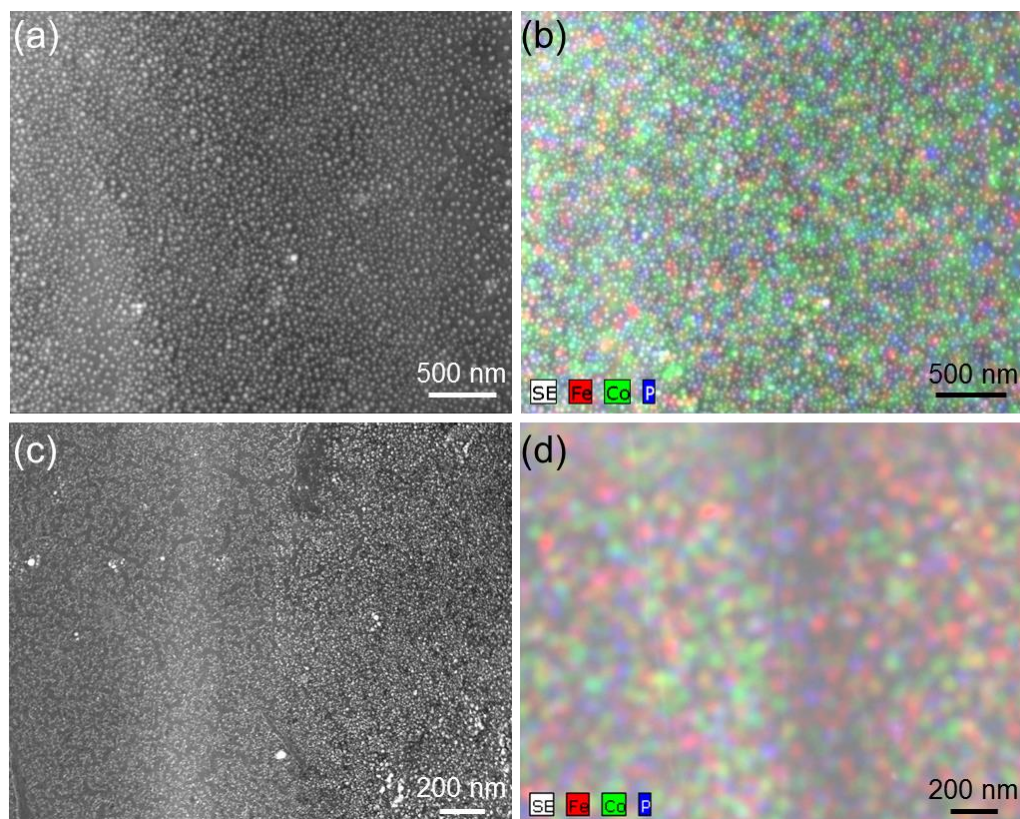


Figure S6. SEM image and corresponding EDS mapping elemental mapping of the CoFeP_x nanoparticles on c-wood: (a) and (b) before OER, (c) and (d) after OER stability test. The morphology and composition of the CoFeP_x nanoparticles on c-wood had little change after the 50 h chronopotentiometry experiment.

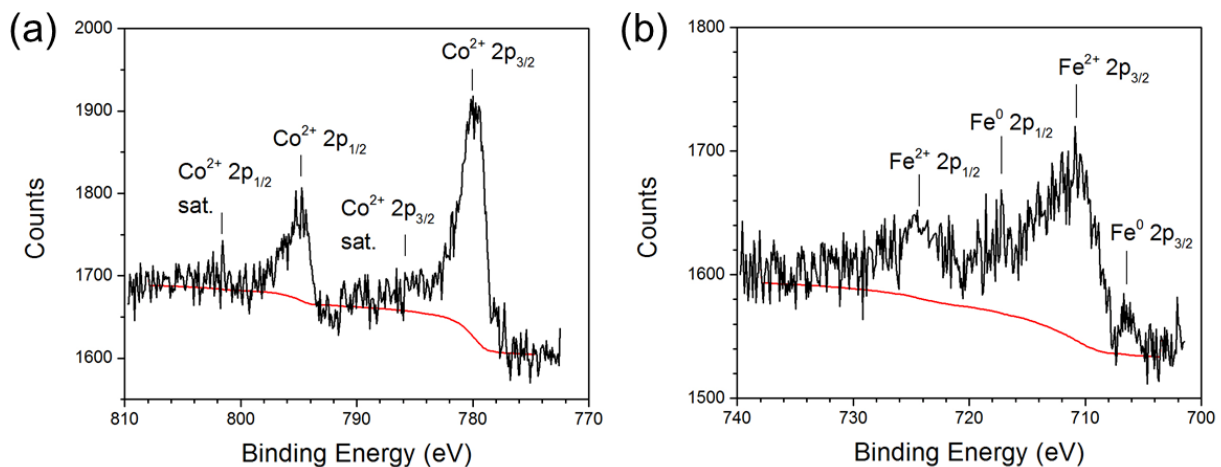


Figure S7. XPS of the CoFeP_x nanoparticles after the long-term OER stability test: (a) Co 2p (sat.: satellite peak) and (b) Fe 2p in FeP_x. No binding energy shift (valence change) of Co and Fe was observed compared to the ones before OER (Figure S5, c and d), indicating the stability of the CoFeP_x during OER.

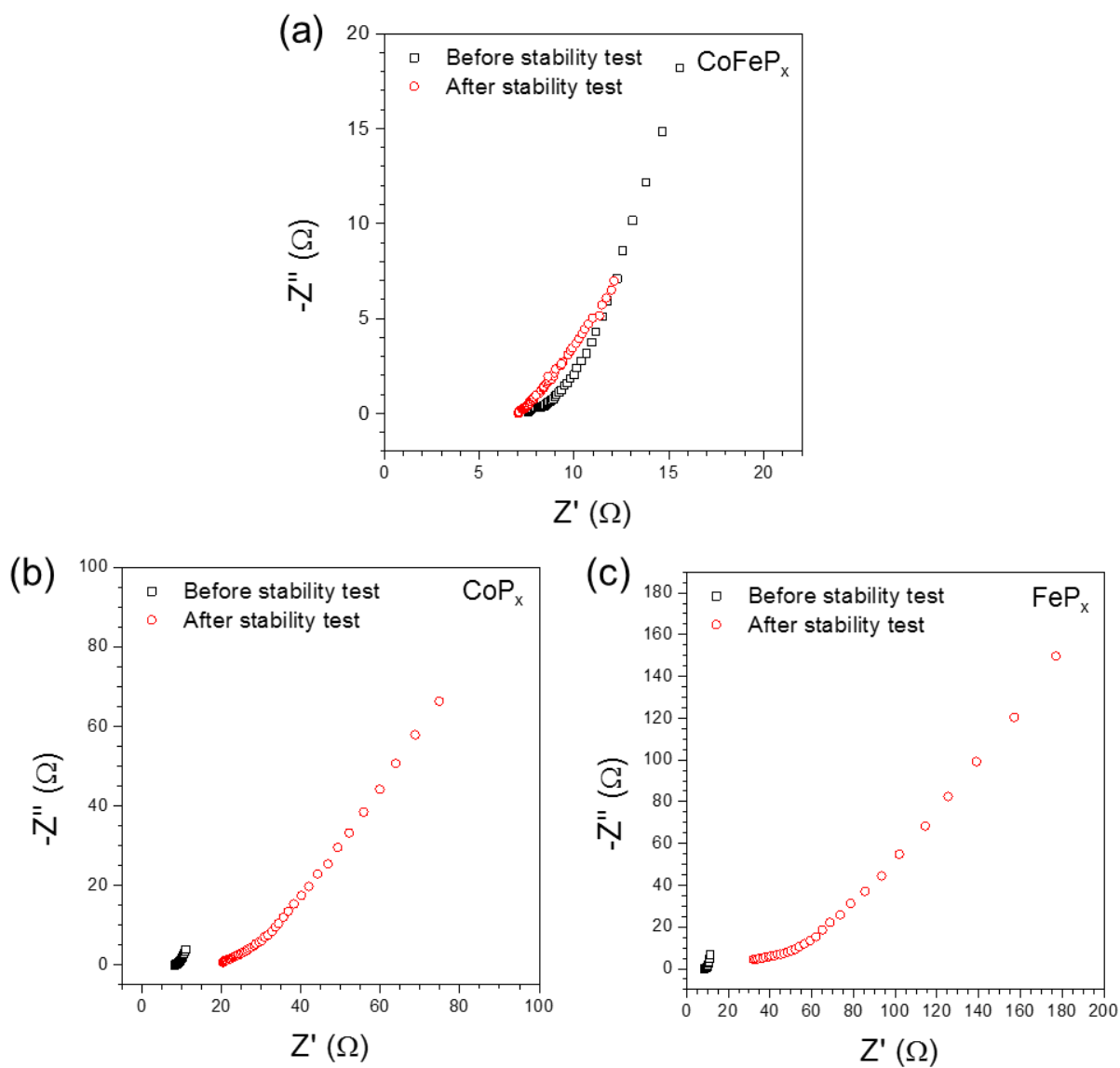


Figure S8. EIS Nyquist plots of the nanocatalysts before and after the OER-stability test: (a) CoFeP_x, (b) CoP_x, and (c) FeP_x.

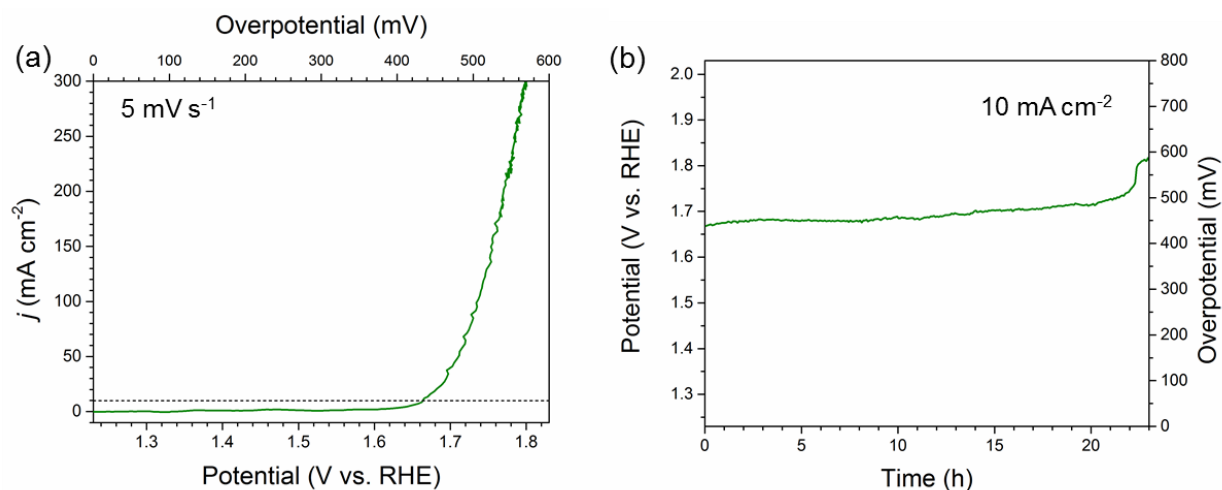


Figure S9. (a) Polarization curve of Fe nanoparticles in the carbonized wood in 1 M KOH with a scan rate of 5 mV s^{-1} . (b) Chronopotentiometric curve of the Fe nanoparticles in carbonized wood recorded at 10 mA cm^{-2} in 1 M KOH. Pure Fe nanoparticles without the CoFeP_x in core only show a relatively low activity toward OER.

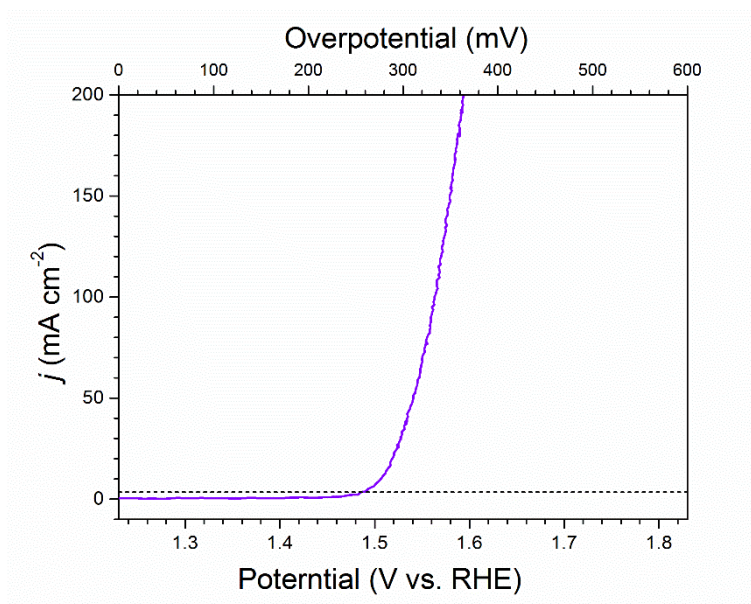


Figure S10. Polarization curve of IrO_x nanoparticles in c-wood (synthesized by the high-temperature shock method) in 1 M KOH with a scan rate of 5 mV s^{-1} .

Table S1. The grain size of FeP_x, CoP_x, and CoFeP_x nanoparticles derived from XRD, in comparison with the particle size measured by TEM.

	Grain size (nm) by XRD	Particle size (nm) by TEM
CoFeP _x	16.1	18.0
CoP _x	11.9	8.0
FeP _x	18.3	19.3

Table S2. OER performances of different metal phosphide nanocatalysts.

Catalyst	Solution	Substrate	Overpotential (at 10 mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	Stability testing (Current density at 10 mA cm ⁻²)	Reference
Fe-coated CoFeP _x	1 M KOH	Carbonized wood	310 mV	58	50 h	This work
NiFe LDH@NiCoP	1 M KOH	Ni foam	220 mV	48.6	100 h (without obvious degradation)	[1]
FeCoNiP	1 M KOH	Glassy carbon	200 mV	70	24 h (stabilized)	[2]
FeP/C	1 M KOH	graphitic carbon	278 mV	87	20 h (negligible degradation)	[3]
NiCoP/C nanoboxes	1 M KOH	Glassy carbon	330 mV	115	10 h (3.5% current loss)	[4]
Ni ₁₂ P ₅ /Ni ₃ (PO ₄) ₂	1 M KOH	Glassy carbon	318 mV	51.7	24 h (stable)	[5]
Fe- and O-doped Co ₂ P	1 M KOH	Ni foam	274.5 mV	51.7	100 h (74% retention of the initial current density)	[6]
CoP/rGO-400	1 M KOH	Glassy carbon	340 mV	66	22 h	[7]
Ni ₂ P nanoparticles	1 M KOH	Glassy carbon	290 mV	59	10 h	[8]

Supplementary References

- [1] H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin, S. Azimi, S.L. Schweizer, A.W. Maijenburg, R.B. Wehrspohn, *Adv. Funct. Mater.* 28 (2018) 1706847.
- [2] J.Y. Xu, J.J. Li, D.H. Xiong, B.S. Zhang, Y.F. Liu, K.H. Wu, I. Amorim, W. Li, L.F. Liu, *Chem. Sci.* 9 (2018) 3470-3476.
- [3] Y.D. Yao, N. Mahmood, L. Pan, G.Q. Shen, R.R. Zhang, R.J. Gao, F.E. Aleem, X.Y. Yuan, X.W. Zhang, J.J. Zou, *Nanoscale* 10 (2018) 21327-21334.
- [4] P. He, X.Y. Yu, X.W. Lou, *Angew. Chem. Int. Ed.* 56 (2017) 3897-3900.
- [5] J.F. Chang, Q. Lv, G.Q. Li, J.J. Ge, C.P. Liu, W. Xing, *Applied Catalysis B-Environmental* 204 (2017) 486-496.
- [6] J.J. Duan, S. Chen, A. Vasileff, S.Z. Qiao, *ACS Nano* 10 (2016) 8738-8745.
- [7] L. Jiao, Y.X. Zhou, H.L. Jiang, *Chem. Sci.* 7 (2016) 1690-1695.
- [8] L.-A. Stern, L. Feng, F. Song, X. Hu, *Energy Environ. Sci.* 8 (2015) 2347-2351.