

*Supporting information*

# Cobalt-Iron-Phosphate hydrogen evolution reaction electrocatalyst for solar-driven alkaline seawater electrolyzer

Chiho Kim <sup>1</sup>, Seunghun Lee <sup>1</sup>, Seong Hyun Kim <sup>1</sup>, Jaehan Park <sup>1</sup>, Shinho Kim <sup>2</sup>, Se-Hun Kwon <sup>1</sup>, Jong-Seong Bae <sup>3</sup>, Yoo Sei Park <sup>1,4,\*</sup> and Yangdo Kim <sup>1,\*</sup>

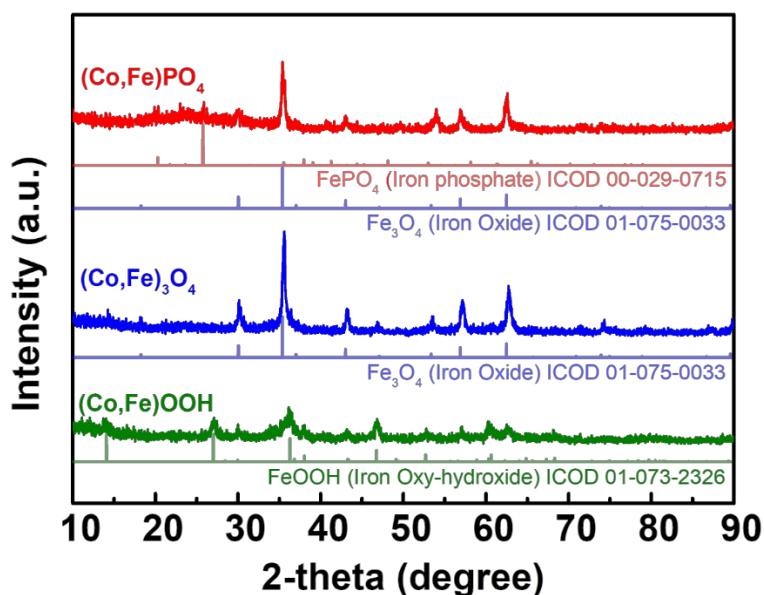
<sup>1</sup> Department of Materials Science and Engineering, Pusan National University, Busan 46241, Korea; chihokim@pusan.ac.kr (C.K.); basicroof@hanmail.net (S.L.); kshe1995@naver.com (S.H.K.); parkoo68@pusan.ac.kr (J.P.); sehun@pusan.ac.kr (S.-H.K.)

<sup>2</sup> BK21 four, Innovative Graduate Education Program for Global High-tech Materials & Parts, Pusan National University, Busan 46241, Republic of Korea; shinho@pusan.ac.kr (S.K.)

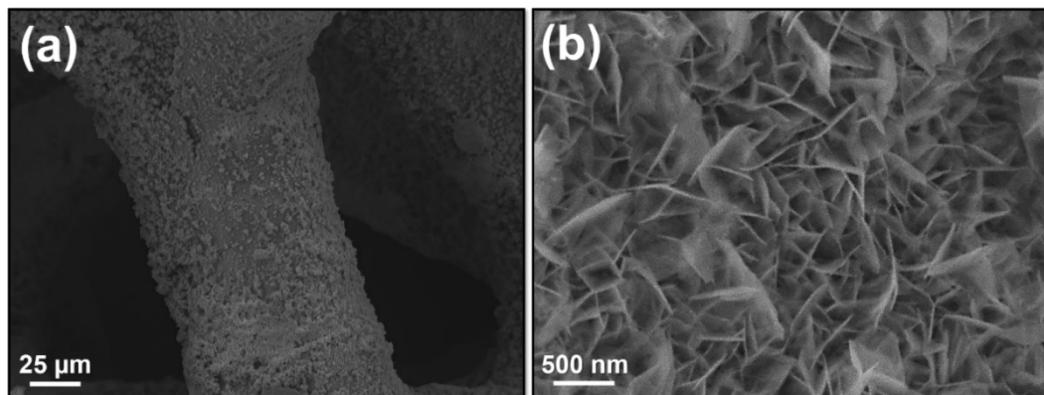
<sup>3</sup> Busan Center, Korea Basic Science Institute, Busan, Korea; jsbae@kbsi.re.kr (J.-S.B.)

<sup>4</sup> Department of Chemical Engineering, Kansas State University, 1701A Platt St Manhattan, KS, 66506, USA

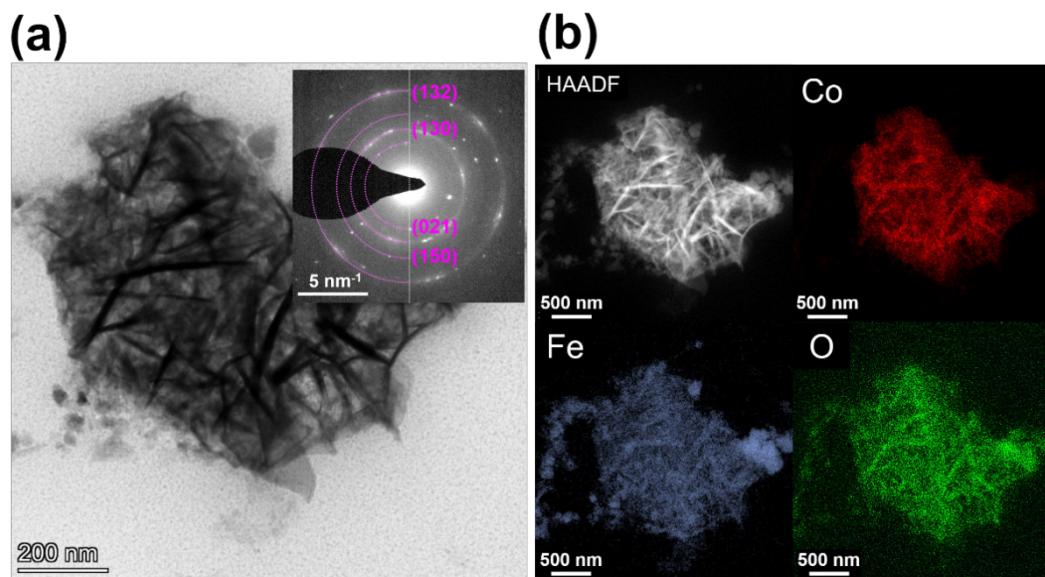
\* Correspondence: qkrdbtp@pusan.ac.kr (Y.S.P.); yangdo@pusan.ac.kr (Y.K.)



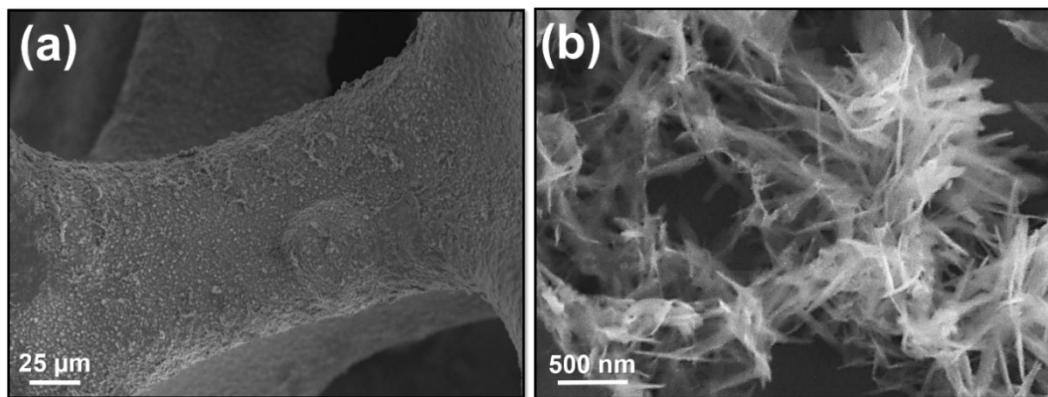
**Figure S1.** XRD patterns of  $(\text{Co},\text{Fe})\text{PO}_4$ ,  $(\text{Co},\text{Fe})_3\text{O}_4$ , and  $(\text{Co},\text{Fe})\text{OOH}$ .



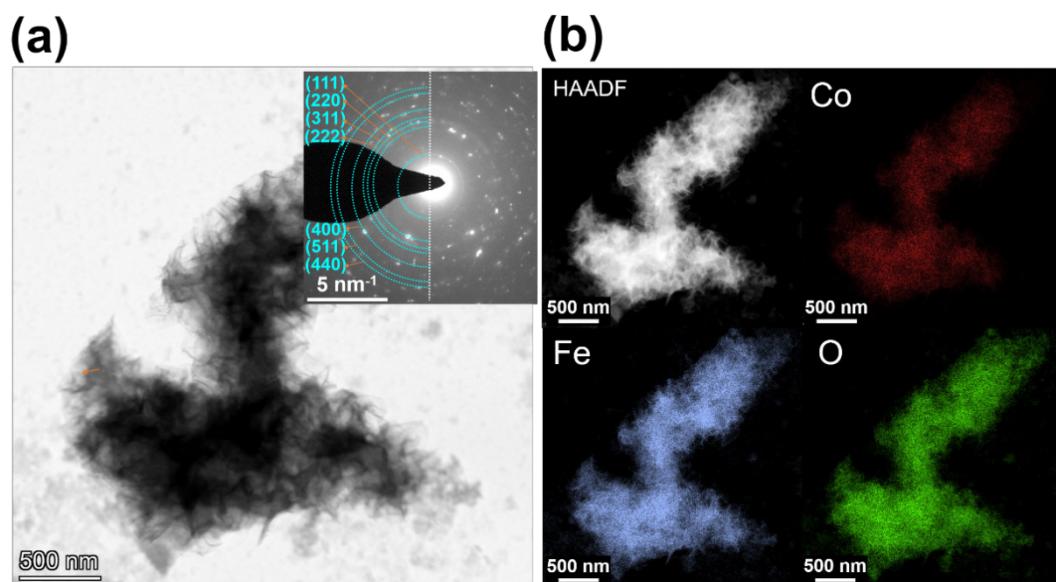
**Figure S2.** SEM images of (a)  $(\text{Co},\text{Fe})\text{OOH}$  and (b) iron foam.



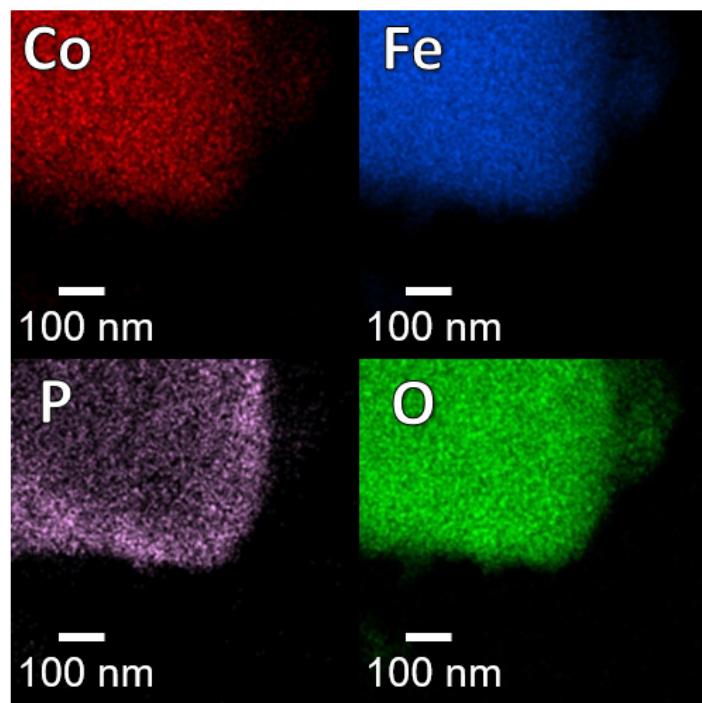
**Figure S3.** (a) TEM image of  $(\text{Co},\text{Fe})\text{OOH}$  with selected area electron diffraction (SAED) ring patterns (insert), and (b) TEM-EDS mapping images of  $(\text{Co},\text{Fe})\text{OOH}$ .



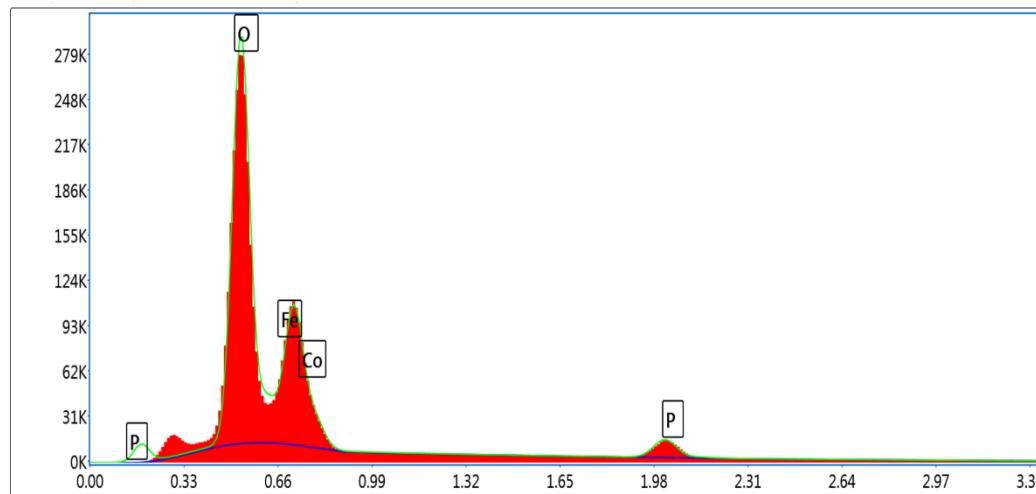
**Figure S4.** SEM images of (a)  $(\text{Co},\text{Fe})_3\text{O}_4$  and (b) iron foam.



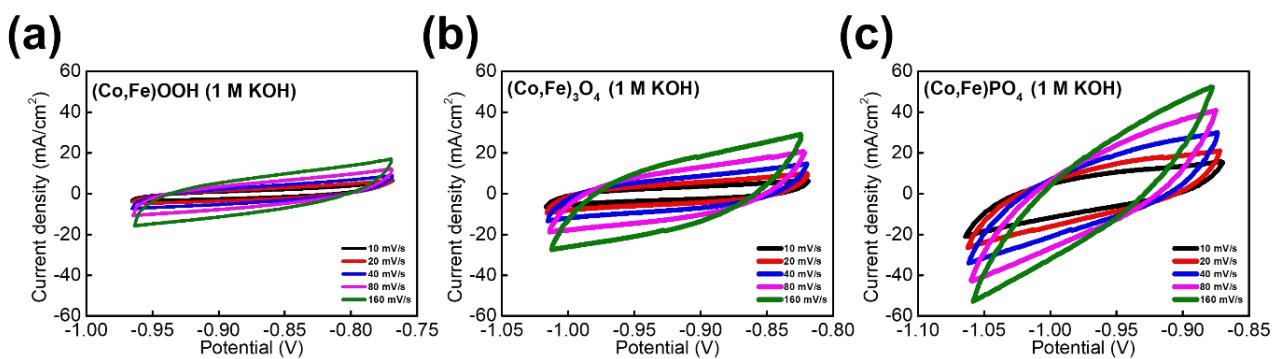
**Figure S5.** (a) TEM image of  $(\text{Co},\text{Fe})_3\text{O}_4$  with selected area electron diffraction (SAED) ring patterns (insert), and (b) TEM-EDS mapping images of  $(\text{Co},\text{Fe})_3\text{O}_4$ .



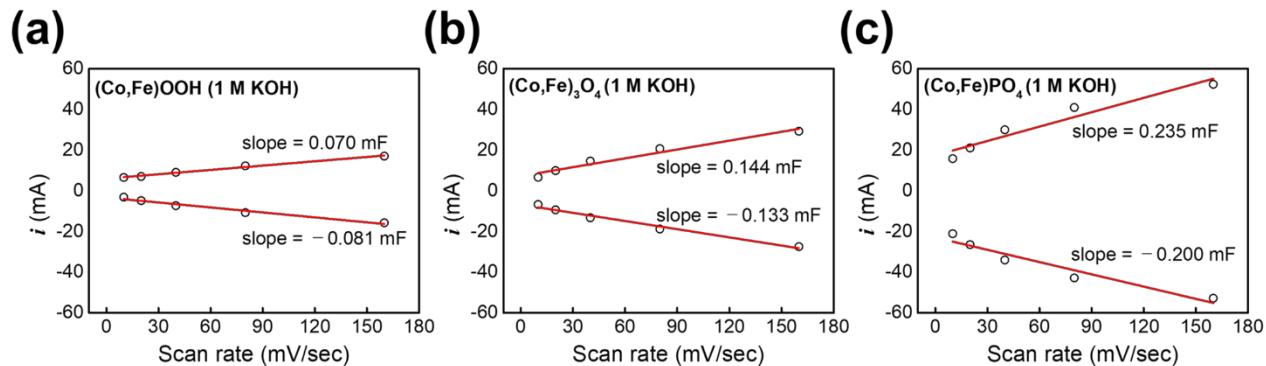
**Figure S6.** TEM-EDS mapping of  $(\text{Co},\text{Fe})\text{PO}_4$ .



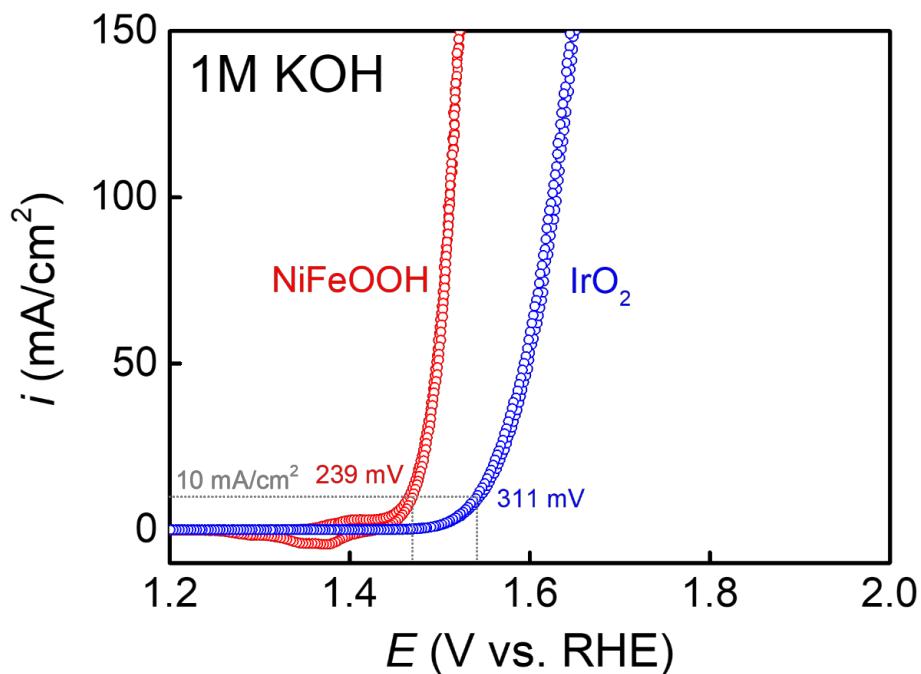
**Figure S7.** EDX spectrum of  $(\text{Co},\text{Fe})\text{PO}_4$



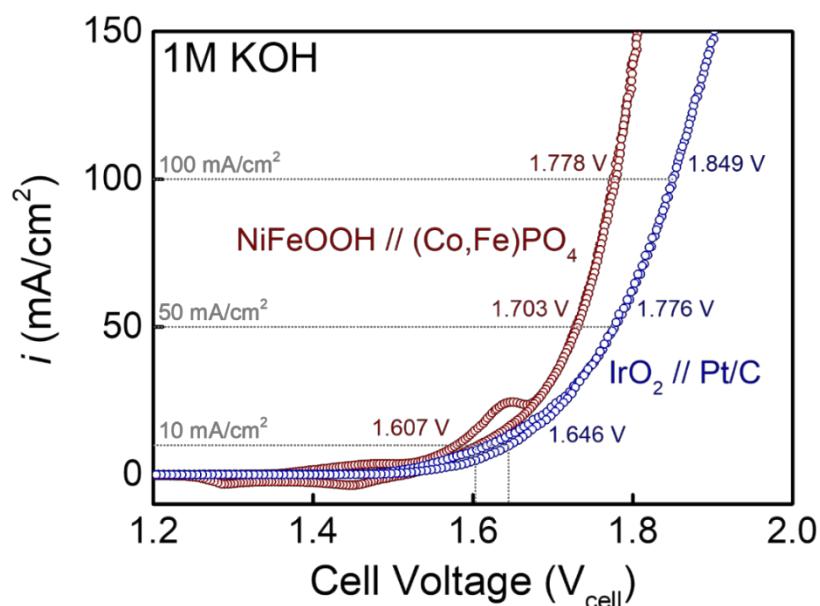
**Figure S8.** Cyclic voltammetry curves of (a)  $(\text{Co},\text{Fe})\text{OOH}$ , (b)  $(\text{Co},\text{Fe})_3\text{O}_4$ , and (c)  $(\text{Co},\text{Fe})\text{PO}_4$  in non-Faradaic region at different scan rates 10–160 mV/s.



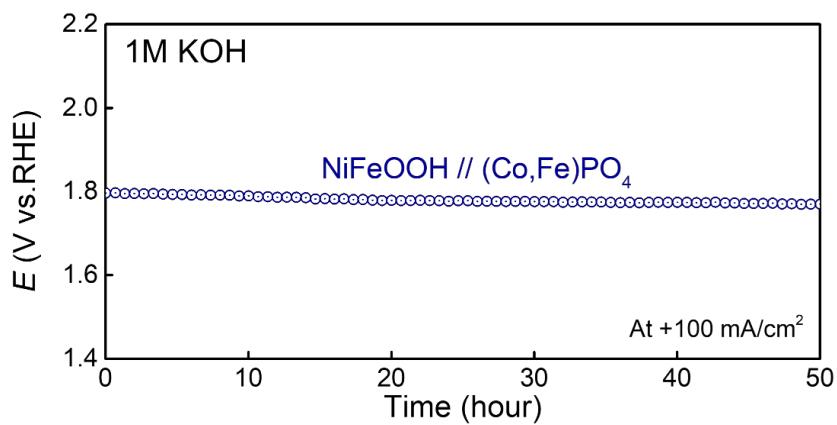
**Figure S9.** Double layer capacitance ( $C_{dl}$ ) of (a)  $(\text{Co},\text{Fe})\text{OOH}$ , (b)  $(\text{Co},\text{Fe})_3\text{O}_4$ , and (c)  $(\text{Co},\text{Fe})\text{PO}_4$ .



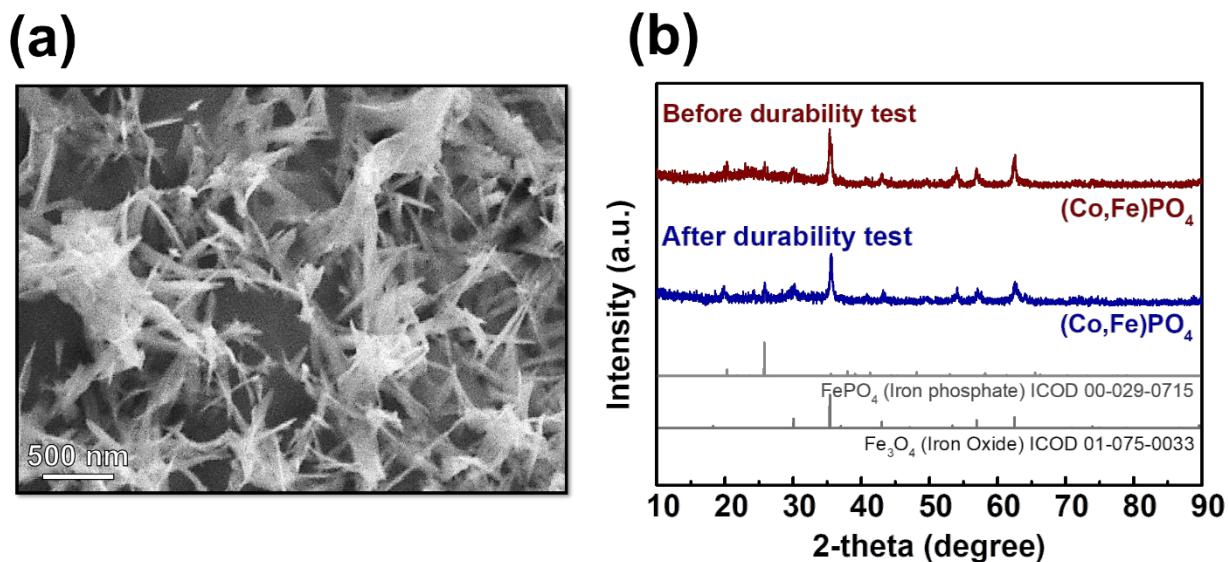
**Figure S10.** Polarization curves of NiFeOOH electrocatalysts for OER in 1 M KOH. To avoid interference with the oxidation current, a cell voltage of 10 mA/cm<sup>2</sup> was measured at the reverse-swept cyclic voltammetry.



**Figure S11.** Polarization curves of NiFeOOH // (Co,Fe)PO<sub>4</sub> electrolyzer for overall seawater splitting compared to IrO<sub>2</sub> // Pt/C noble metal electrolyzer in 1 M KOH electrolyte. To avoid interference with the oxidation current, a cell voltage of 10 mA/cm<sup>2</sup> was measured at the reverse-swept cyclic voltammetry.



**Figure S12.** Durability test of NiFeOOH // (Co,Fe)PO<sub>4</sub> electrolyzer conducted at constant current density of +100 mA/cm<sup>2</sup> for 50 h in 1 M KOH electrolyte.



**Figure S13.** (a) SEM image and (b) XRD results of (Co,Fe)PO<sub>4</sub> after durability test.

**Table S1.** Comparision of overall water splitting performance of the NiFeOOH // (Co,Fe)PO<sub>4</sub> with recently reported transition metal-based alkaline water electrolyzers in 1 M KOH.

| Catalyst  | Electrolyte        | $\eta_{10}$ for HER (mV) | $\eta_{10}$ for OER (mV) | Voltage( $\eta_{10}$ ) (V) | Reference |
|---|--------------------|--------------------------|--------------------------|----------------------------|-----------|
| NiFeOOH // (Co,Fe)PO <sub>4</sub>                     | 1 M KOH            | 122                      | 239                      | 1.607                      | This work |
| NiFeOOH // (Co,Fe)PO <sub>4</sub>                     | 1 M KOH + seawater | 136                      | -                        | 1.625                      | This work |
| FeCoP UNSAs/NF  | 1 M KOH            | 188 ( $\eta_{100}$ )     | 260 ( $\eta_{20}$ )      | 1.6                        | [1]       |
| Ni <sub>1.85</sub> Fe <sub>0.15</sub> P NSAs/NF       | 1 M KOH            | 106                      | 270 ( $\eta_{20}$ )      | 1.61                       | [2]       |
| Ni/NiP  | 1 M KOH            | 130                      | 270 ( $\eta_{30}$ )      | 1.61                       | [3]       |
| Ni-Fe <sub>x</sub> P                                  | 1 M KOH            | 119                      | 267 ( $\eta_{100}$ )     | 1.62                       | [4]       |
| hierarchical Ni-Co-P HNBs                             | 1 M KOH            | 107                      | 270                      | 1.62                       | [5]       |
| P-Co <sub>3</sub> O <sub>4</sub>                      | 1 M KOH            | 120                      | 290                      | 1.63                       | [6]       |
| Co <sub>0.9</sub> S <sub>0.58</sub> P <sub>0.42</sub> | 1 M KOH            | 141                      | 266                      | 1.637                      | [7]       |
| Co <sub>x</sub> Fe <sub>1-x</sub> -P film             | 1 M KOH            | 169                      | 290                      | 1.64                       | [8]       |
| CoP/NCNHP   | 1 M KOH            | 115                      | 310                      | 1.64                       | [9]       |
| Co-Ni-P   | 1 M KOH            | 103                      | 340                      | 1.65                       | [10]      |
| CoP-InNC@CNT  | 1 M KOH            | 159                      | 270                      | 1.659                      | [11]      |
| Co <sub>0.6</sub> Fe <sub>0.4</sub> P                 | 1 M KOH            | 133                      | 298                      | 1.661                      | [12]      |
| CoP <sub>2</sub> /rGO                                 | 1 M KOH            | 115                      | 370                      | 1.68                       | [13]      |
| CoP@FeCoP/NC YSMPs                                    | 1 M KOH            | 141                      | 238                      | 1.68                       | [14]      |
| CoP@3D Ti <sub>3</sub> C <sub>2</sub> -MXene          | 1 M KOH            | 168                      | 290                      | 1.688                      | [15]      |
| Co-Fe oxyphosphide                                    | 1 M KOH            | 180                      | 280                      | 1.69                       | [16]      |
| CoP film/Cu foil                                      | 1 M KOH            | 94                       | 345                      | 1.69                       | [17]      |
| FeP@Fe-P-O/CC   | 1 M KOH            | 120                      | 288                      | 1.69                       | [18]      |
| CoP/rGO   | 1 M KOH            | 150                      | 340                      | 1.70                       | [19]      |
| Co/CoP  | 1 M KOH            | 193                      | 283                      | 1.706                      | [20]      |
| S:Co <sub>2</sub> P NPs                               | 1 M KOH            | 184                      | 310                      | 1.724                      | [21]      |
| FeCo-FeCoNi   | 1 M KOH            | 211                      | 325                      | 1.766                      | [22]      |

## References

1. Zhou, L.; Shao, M.; Li, J.; Jiang, S.; Wei, M.; Duan, X. Two-dimensional ultrathin arrays of CoP: electronic modulation toward high performance overall water splitting. *Nano Energy* **2017**, *41*, 583–590.
2. Wang, P.; Pu, Z.; Li, Y.; Wu, L.; Tu, Z.; Jiang, M.; Kou, Z.; Amiinu, I.S.; Mu, S. Iron-doped nickel phosphide nanosheet arrays: an efficient bifunctional electrocatalyst for water splitting. *ACS applied materials & interfaces* **2017**, *9*, 26001–26007.
3. Chen, G.F.; Ma, T.Y.; Liu, Z.Q.; Li, N.; Su, Y.Z.; Davey, K.; Qiao, S.Z. Efficient and stable bifunctional electrocatalysts Ni/NixMy (M=P, S) for overall water splitting. *Advanced Functional Materials* **2016**, *26*, 3314–3323.
4. Zhang, C.; Xie, Y.; Deng, H.; Zhang, C.; Su, J.-W.; Dong, Y.; Lin, J. Ternary nickel iron phosphide supported on nickel foam as a high-efficiency electrocatalyst for overall water splitting. *International Journal of Hydrogen Energy* **2018**, *43*, 7299–7306.
5. Hu, E.; Feng, Y.; Nai, J.; Zhao, D.; Hu, Y.; Lou, X.W.D. Construction of hierarchical Ni–Co–P hollow nanobricks with oriented nanosheets for efficient overall water splitting. *Energy & Environmental Science* **2018**, *11*, 872–880.
6. Xiao, Z.; Wang, Y.; Huang, Y.-C.; Wei, Z.; Dong, C.-L.; Ma, J.; Shen, S.; Li, Y.; Wang, S. Filling the oxygen vacancies in Co<sub>3</sub>O<sub>4</sub> with phosphorus: an ultra-efficient electrocatalyst for overall water splitting. *Energy & Environmental Science* **2017**, *10*, 2563–2569.
7. Dai, Z.; Geng, H.; Wang, J.; Luo, Y.; Li, B.; Zong, Y.; Yang, J.; Guo, Y.; Zheng, Y.; Wang, X. Hexagonal-phase cobalt monophosphosulfide for highly efficient overall water splitting. *ACS nano* **2017**, *11*, 11031–11040.
8. Yoon, S.; Kim, J.; Lim, J.-H.; Yoo, B. Cobalt iron-phosphorus synthesized by electrodeposition as highly active and stable bifunctional catalyst for full water splitting. *Journal of The Electrochemical Society* **2018**, *165*, H271.
9. Pan, Y.; Sun, K.; Liu, S.; Cao, X.; Wu, K.; Cheong, W.-C.; Chen, Z.; Wang, Y.; Li, Y.; Liu, Y. Core–shell ZIF-8@ZIF-67-derived CoP nanoparticle-embedded N-doped carbon nanotube hollow polyhedron for efficient overall water splitting. *Journal of the American Chemical Society* **2018**, *140*, 2610–2618.
10. Pei, Y.; Yang, Y.; Zhang, F.; Dong, P.; Baines, R.; Ge, Y.; Chu, H.; Ajayan, P.M.; Shen, J.; Ye, M. Controlled electrodeposition synthesis of Co–Ni–P film as a flexible and inexpensive electrode for efficient overall water splitting. *ACS applied materials & interfaces* **2017**, *9*, 31887–31896.
11. Chai, L.; Hu, Z.; Wang, X.; Xu, Y.; Zhang, L.; Li, T.T.; Hu, Y.; Qian, J.; Huang, S. Stringing bimetallic metal – organic framework – derived cobalt phosphide composite for high – efficiency overall water splitting. *Advanced Science* **2020**, *7*, 1903195.
12. Lian, Y.; Sun, H.; Wang, X.; Qi, P.; Mu, Q.; Chen, Y.; Ye, J.; Zhao, X.; Deng, Z.; Peng, Y. Carved nanoframes of cobalt–iron bimetal phosphide as a bifunctional electrocatalyst for efficient overall water splitting. *Chemical science* **2019**, *10*, 464–474.
13. Wang, J.; Yang, W.; Liu, J. CoP 2 nanoparticles on reduced graphene oxide sheets as a super-efficient bifunctional electrocatalyst for full water splitting. *Journal of Materials Chemistry A* **2016**, *4*, 4686–4690.
14. Shi, J.; Qiu, F.; Yuan, W.; Guo, M.; Lu, Z.-H. Nitrogen-doped carbon-decorated yolk-shell CoP@ FeCoP micro-polyhedra derived from MOF for efficient overall water splitting. *Chemical Engineering Journal* **2021**, *403*, 126312.
15. Xiu, L.; Wang, Z.; Yu, M.; Wu, X.; Qiu, J. Aggregation-resistant 3D MXene-based architecture as efficient bifunctional electrocatalyst for overall water splitting. *ACS nano* **2018**, *12*, 8017–8028.
16. Zhang, P.; Lu, X.F.; Nai, J.; Zang, S.Q.; Lou, X.W. Construction of hierarchical Co–Fe oxyphosphide microtubes for electrocatalytic overall water splitting. *Advanced Science* **2019**, *6*, 1900576.
17. Anjum, M.A.R.; Okyay, M.S.; Kim, M.; Lee, M.H.; Park, N.; Lee, J.S. Bifunctional sulfur-doped cobalt phosphide electrocatalyst outperforms all-noble-metal electrocatalysts in alkaline electrolyzer for overall water splitting. *Nano Energy* **2018**, *53*, 286–295.
18. Yan, Y.; Xia, B.Y.; Ge, X.; Liu, Z.; Fisher, A.; Wang, X. A flexible electrode based on iron phosphide nanotubes for overall water splitting. *Chem.-Eur. J* **2015**, *21*, 18062–18067.
19. Jiao, L.; Zhou, Y.-X.; Jiang, H.-L. Metal–organic framework-based CoP/reduced graphene oxide: high-performance bifunctional electrocatalyst for overall water splitting. *Chemical Science* **2016**, *7*, 1690–1695.
20. Xue, Z.-H.; Su, H.; Yu, Q.-Y.; Zhang, B.; Wang, H.-H.; Li, X.-H.; Chen, J.-S. Janus Co/CoP Nanoparticles as Efficient Mott–Schottky Electrocatalysts for Overall Water Splitting in Wide pH Range. *Advanced Energy Materials* **2017**, *7*, 1602355, doi:<https://doi.org/10.1002/aenm.201602355>.
21. Anjum, M.A.R.; Bhatt, M.D.; Lee, M.H.; Lee, J.S. Sulfur-doped dicobalt phosphide outperforming precious metals as a bifunctional electrocatalyst for alkaline water electrolysis. *Chemistry of Materials* **2018**, *30*, 8861–8870.
22. Yang, Y.; Lin, Z.; Gao, S.; Su, J.; Lun, Z.; Xia, G.; Chen, J.; Zhang, R.; Chen, Q. Tuning electronic structures of nonprecious ternary alloys encapsulated in graphene layers for optimizing overall water splitting activity. *Acs Catalysis* **2017**, *7*, 469–479.