Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary data

Exploring CoP core-shell nanosheets by Fe and Zn dual cation doping as efficient electrocatalyst for overall water splitting

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1. Experimental Section

Fabrication of ZnCo MOF: The commercial carbon cloth was treated with concentrated HNO_3, ethanol and deionized water several times, according to previous research.[1] Firstly, 1.33 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 0.67 mmol $Zn(NO_3)_2 \cdot 6H_2O$ are dissolved in 40 mL deionized water to form a homogeneous solution, followed by adding a deionized water of 1.312 g 2-methylimidazole (40 mL). Then, a piece of clean carbon cloth (2×5 cm^2) was immersed in the prepared solution for 4h. After that, the obtained sample was washed by deionized water and ethanol for several time, and dried at 60 ^oC overnight.

Fabrication of Fe/Zn-Co_3O_4: First, 80 mg $FeSO_4 \cdot 7H_2O$ is dissolved in 10 ml H_2O to get a homogeneous solution, while adding 10 ml ethanol. Subsequently, a piece of ZnCo MOF is immersed in above solution and aged for 15 min at room temperature. Then, the obtained Fe-ZnCo precursor is washed by deionized water and ethanol, and dried at 60 ^oC overnight. Finally, the Fe/Zn-Co_3O_4 is obtained by annealing in air at 450 ^oC for 2h. Different amounts of $FeSO_4 \cdot 7H_2O$ (20, 50, 80 and 110 mg) are set to obtain various Fe/Zn-Co_3O_4, shortly named as Fe/Zn-Co_3O_4-20~110. In addition, the Zn-Co_3O_4 is prepared by directly annealing ZnCo-MOF via similar process.

Fabrication of Fe/Zn-CoP: The 0.3 g NaH_2PO_2 powers are placed on a glass plate placed at upstream, and Fe/Zn-Co_3O_4 are placed at the downstream of the tube furnace. The furnace is heated to 300 ^oC at Ar atmosphere with a heating rate of 5 ^oC min^{-1}, and maintained at 300 ^oC for 2h. Various Fe/Zn-CoP samples are obtained by the same phosphating process, and shortly named as Fe/Zn-CoP-20~110. For comparison, Zn-CoP is obtained by the similar phosphating process.

2. Material characterization

The morphologies and chemical constituents of the samples are characterized by

SEM, TEM and EDX. The XRD is used to detect the crystal structure of samples. The chemical constituents of the as-prepared samples were detected by XPS an Raman. The binding energy of obtained samples is calibrated based on the C 1s peak at 284.4 eV. The Brunauer-Emmett-Teller (BET) method is used to evaluate the surface areas of the powders scraped from carbon cloth.

3. Electrochemical measurements

All electrochemical performances were measured in the electrochemical workstation (CHI 760E). The HER and OER properties were measured in a three-electrode system, and the obtained samples, Hg/HgO and graphite rod were used as working electrode, reference electrode and counter electrode, respectively. The polarization curves were measured at 2 mV s^{-1}, and then compensated with iR-correction. Before tests, all samples were cycled at 20 mV s^{-1} until the stability of cyclic voltammetry (CV), then the data were collected. The reference electrode of Pt/C (20 wt% Pt) and RuO_2 are also prepared on carbon cloth, and the prepared method was according to previously reported researches.[2,3] The polarization curves of HER and OER are normalized by C_{dl}, as following: $ECSA=(C_{dl\text{-}catal.}-C_{dl\text{-}CC})/C_s$, where C_s value of 0.040 mF cm^{-2} is adopted.[4,5]

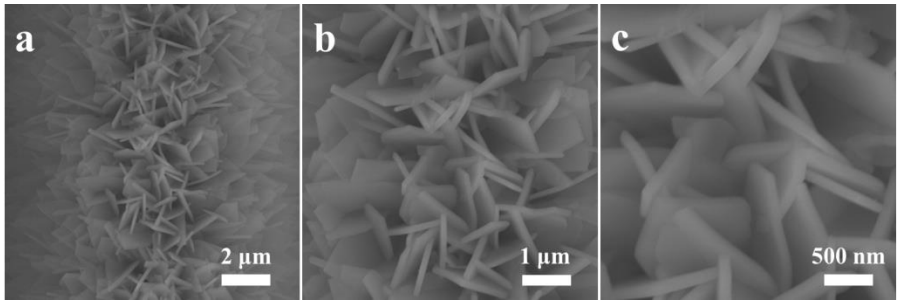

Fig. S1. SEM images of ZnCo MOF

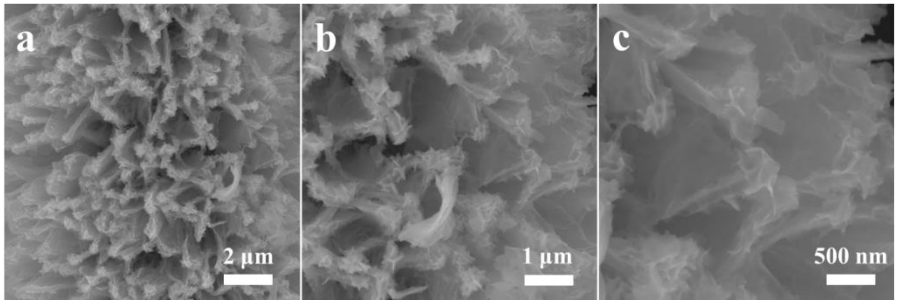

Fig. S2. SEM images of Fe/Zn-Co_3O_4 (The Fe content is 80 mg)

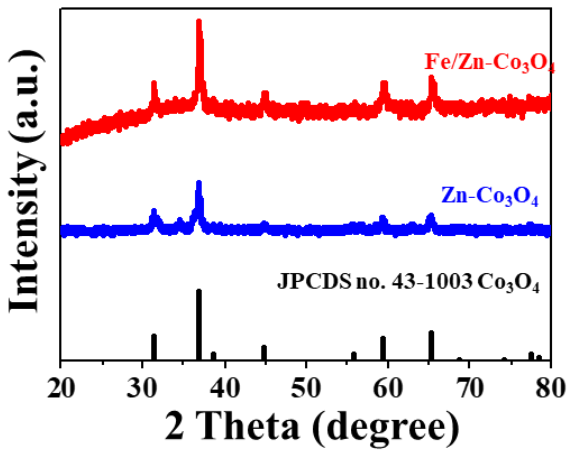

Fig. S3. XRD patterns of Fe/Zn-Co_3O_4 and Zn-Co_3O_4 (the XRD results were tested by the powder scraped from carbon cloth)

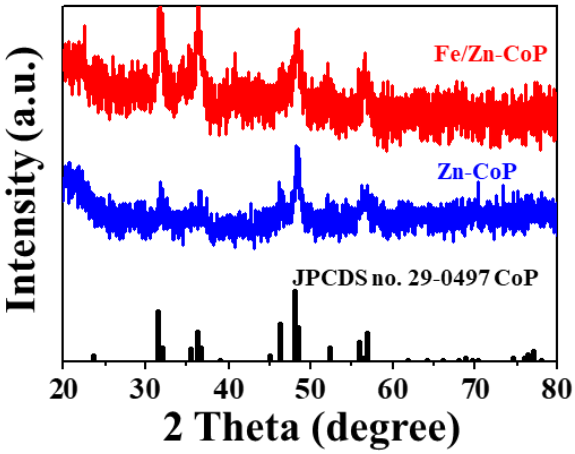

Fig. S4. XRD patterns of Fe/Zn-CoP and Zn-CoP (the XRD results were tested by the powder scraped from carbon cloth)

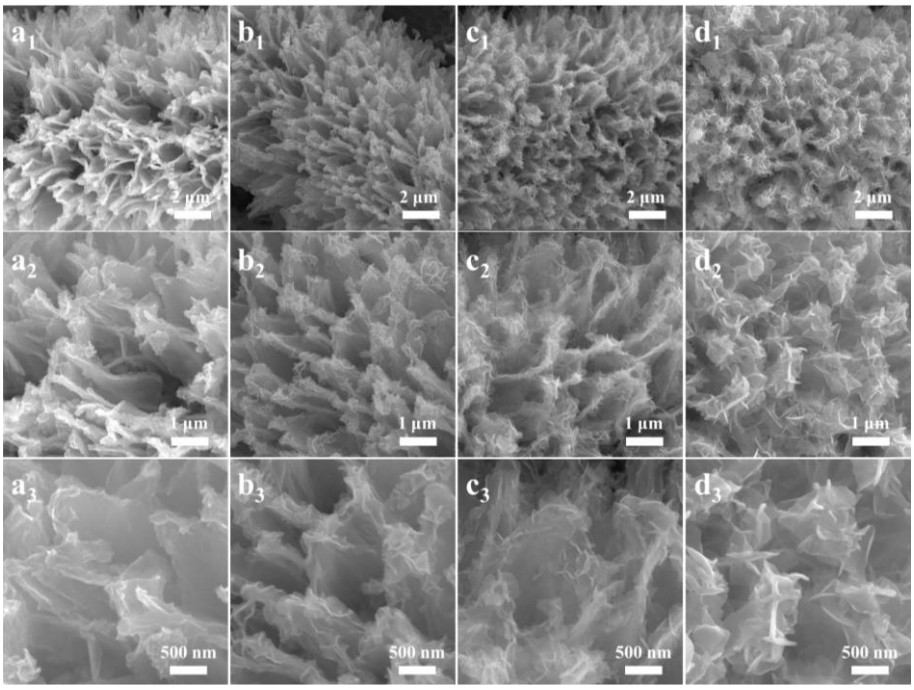

Fig. S5. SEM images of Fe/Zn-CoP-20 (a_1-a_3), Fe/Zn-CoP-50 (b_1-b_3), Fe/Zn-CoP-80 (c_1-c_3), and Fe/Zn-CoP-110 (d_1-d_3)

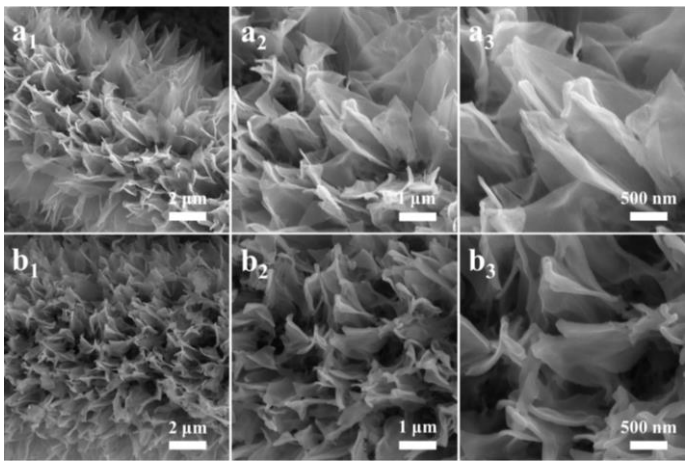

Fig. S6. SEM images of Zn-Co_3O_4 (a_1-a_3) and Zn-CoP (b_1-b_3)

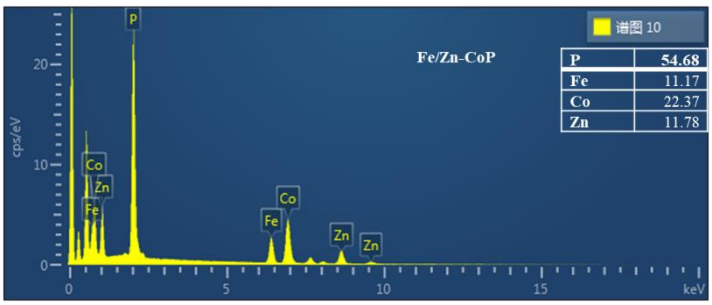

Fig. S7 EDX spectra of Fe/Zn-CoP

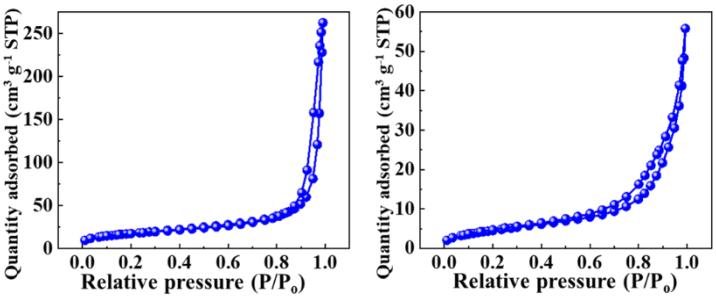

Fig. S8 BET surface areas of Fe/Zn-CoP and Zn-CoP

Table S1 EDX results of obtained samples

	Fe/Zn-CoP	After HER activation	After OER activation	After HER cycle	After OER cycle
P	54.68	33.79	1.42	37.42	2.57
Fe	11.17	23.15	35.94	25.91	23.15
Co	22.37	42.54	53.16	36.32	68.99
Zn	11.78	0.51	8.47	0.34	5.29

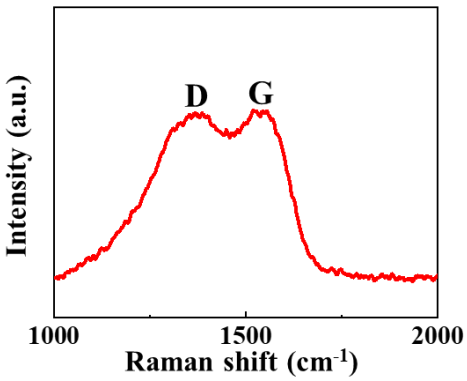

Fig. S9 Raman spectrum of Fe/Zn-CoP (the result show that the Fe/Zn-CoP is rich in carbon)

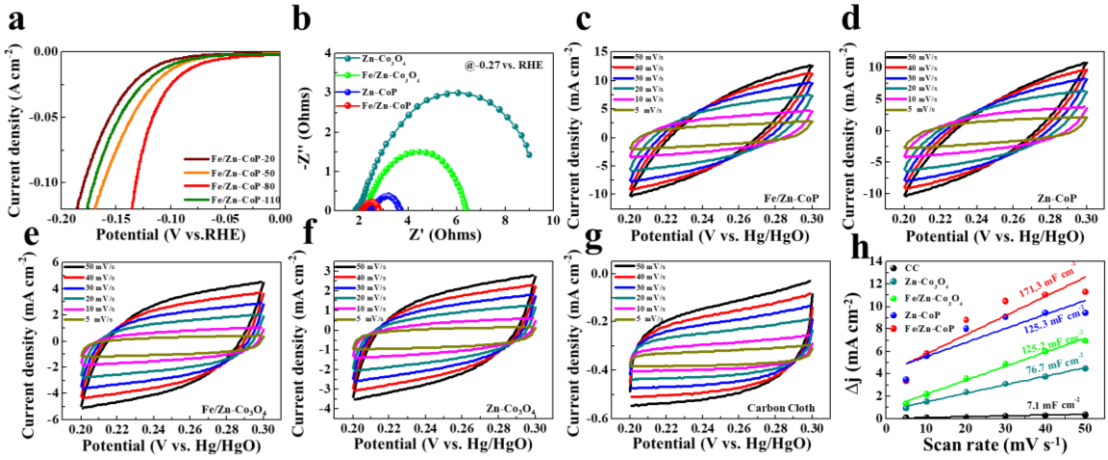

Fig. S10 (a) HER polarization curves for Fe/Zn-CoP with different conditions. (b) Nyquist plots of obtained samples. (c-g) The CV curves for estimating the ECSA in HER tests. (h) C_{dl} values of obtained samples.

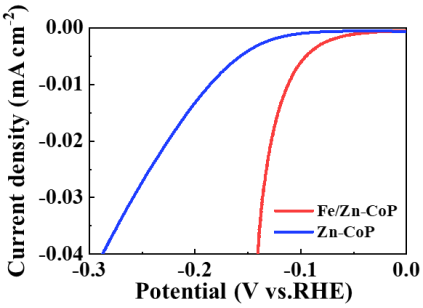

Fig. S11 HER polarization curves of Fe/Zn-CoP and Zn-CoP normalized by ECSA

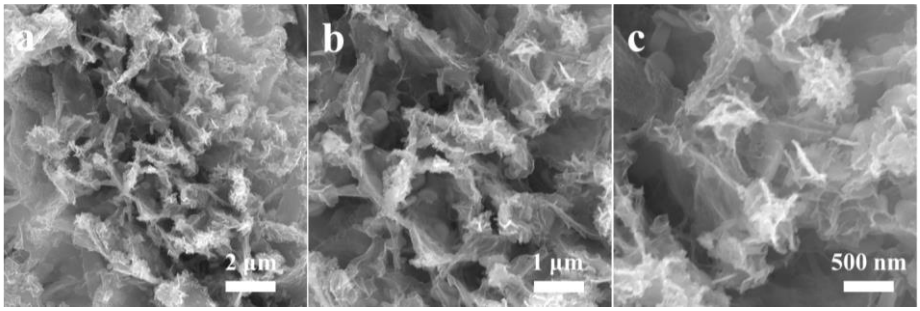

Fig. S12 SEM images of Fe/Zn-CoP after HER cycle.

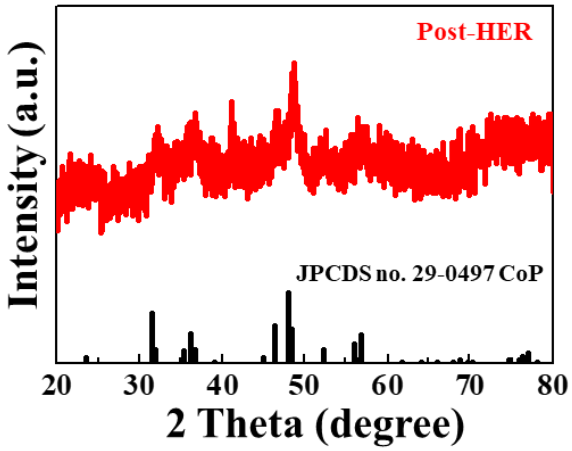

Fig. S13 XRD pattern of Fe/Zn-CoP after HER cycle.

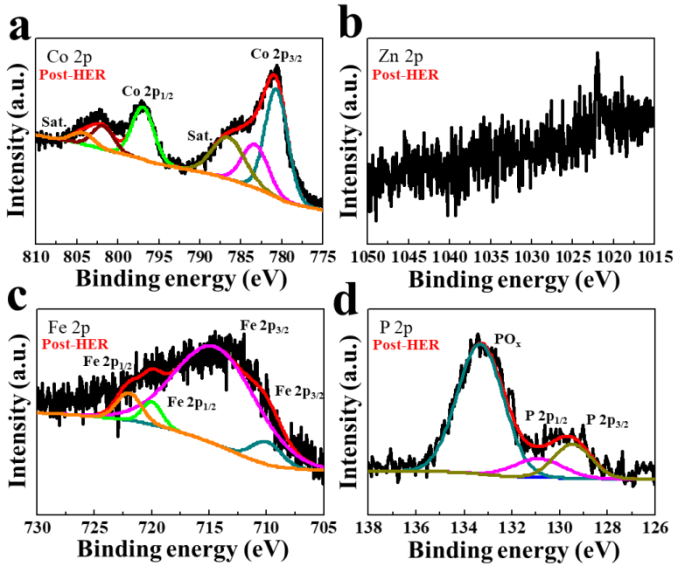

Fig. S14 XPS spectras of Fe/Zn-CoP after HER cycle.

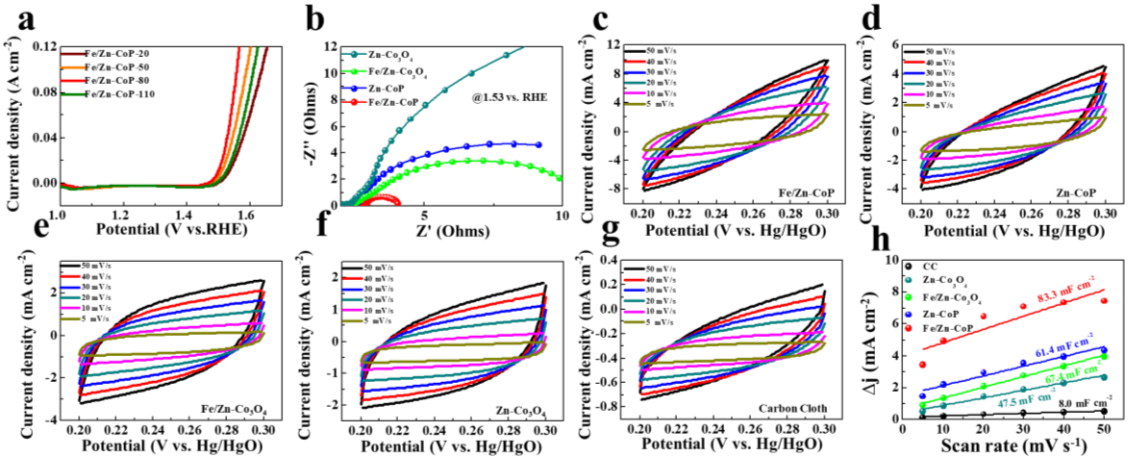

Fig. S15 (a) OER polarization curves for Fe/Zn-CoP with different conditions. (b) Nyquist plots of obtained samples. (c-g) The CV curves for estimating the ECSA in OER tests. (h) C_{dl} values of obtained samples.

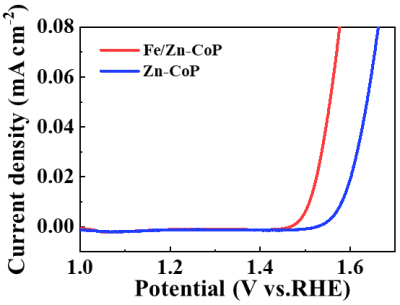

Fig. S16 OER polarization curves of Fe/Zn-CoP and Zn-CoP normalized by ECSA.

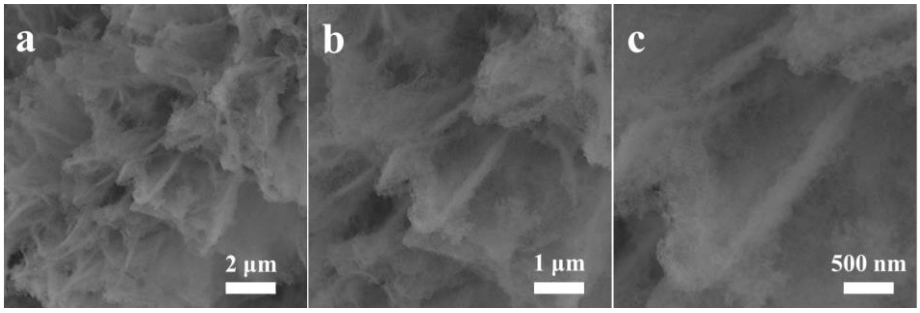

Fig. S17 SEM images of Fe/Zn-CoP after OER cycle.

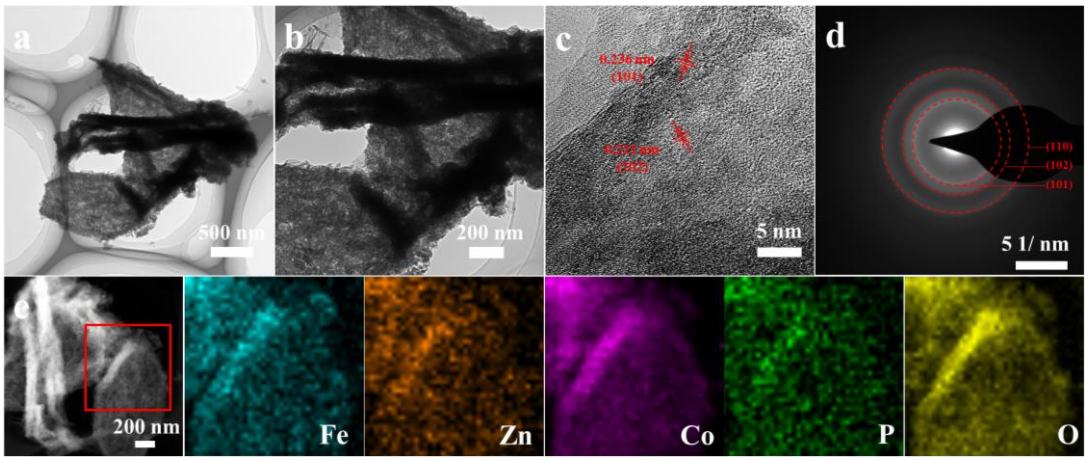

Fig. S18 (a, b) TEM, (c) HRTEM, (d) corresponding SAED pattern, and (e) elemental mapping images of Fe/Zn-CoP after OER cycle.

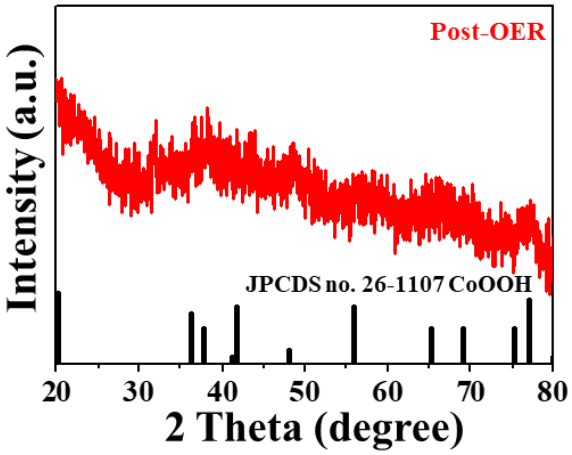

Fig. S19 XRD pattern of Fe/Zn-CoP after OER cycle.

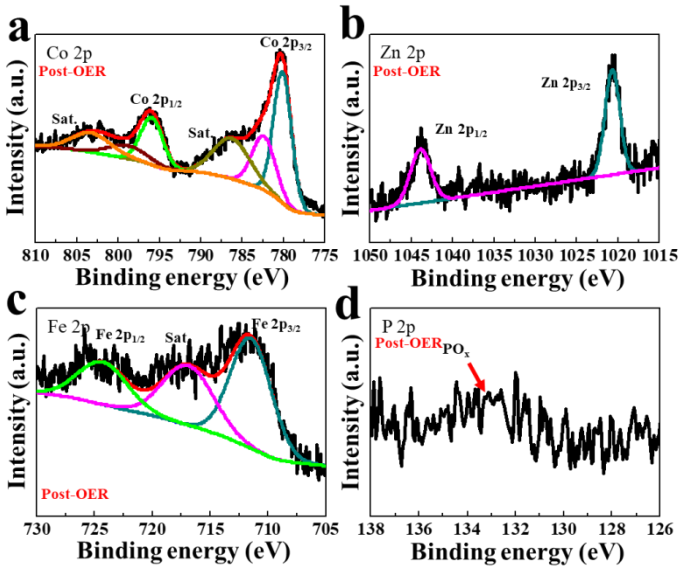

Fig. S20 XPS spectras of Fe/Zn-CoP after OER cycle.

Table S2 Comparison of HER performances for Fe/Zn-CoP core-shell nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
Fe/Zn-CoP	Carbon cloth	75, 116, 132 at 10, 50, 100 mA cm^{-2}	57.9	**This work**
$Co_5Mo_{1.0}P$ nanosheets	Ni foam	173, 300 at 10, 100 mA cm^{-2}	190.1	*Nano Energy* 2018, **45**, 448
Ni_2P nanosheets	Glassy carbon electrode	168 at 10 mA cm^{-2}	63	*J. Mater. Chem. A* 2018, **6**, 18720-18727
Al-Ni_2P	Ti mesh	129 at 10 mA cm^{-2}	129	*Chem. Commun.* 2018, **54**, 2894-2897.
CoP nanowire by oxygen plasma engraving	Carbon cloth	180 at 100 mA cm^{-2}	42.8	*Adv. Mater.* 2018, **30**, 1703322.
Co/CoP	Glassy carbon rotating disk electrode	340 at 10 mA cm^{-2}	79.5	*Adv. Energy Mater.* 2017, **7**, 1602355
Ni-Co-P HNBs	-	107 at 10 mA cm^{-2}	76	*Energy Environ. Sci.* 2018, **11**, 872-880
CoP/NCNHP	Glassy carbon electrode	115 at 10 mA cm^{-2}	53	*J. Am. Chem. Soc.* 2018, **140**, 2610-2618
CoP_3 HSs	Carbon cloth	116 at 10 mA cm^{-2}	82	*Appl. Surf. Sci.* 2018, **427**, 800-806
Multishelled Ni_2P	Rotation disk electrode	98 at 10 mA cm^{-2}	86.4	*Chem. Mater.* 2017, **29**, 8539-8547
CeO_2-Cu_3P	Ni foam	148 at 20 mA cm^{-2}	132	*Nanoscale* 2018, **10**, 2213-2217
MoP/CNT	Glass carbon disk	114 at 10 mA cm^{-2}	51.6	*ACS Sustainable Chem. Eng.* 2018, **6**, 11414-11423
$Cu_{0.3}Co_{2.7}P$/NC	Glassy carbon electrode	220 at 10 mA cm^{-2}	122	*Adv. Energy Mater.* 2017, **7**, 1601555

1.If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.

Table S3 Comparison of OER performances for Fe/Zn-CoP core-shell nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
Fe/Zn-CoP	Carbon cloth	267, 302, 327 at 10, 50, 100 mA cm^{-2}	52.8	**This work**
Fe_1Co_1-P/C	Glassy carbon electrode	360 at 10 mA cm^{-2}	-	*Small Methods* 2018, **2**, 1800214
CoP/NCNHP	Glassy carbon electrode	305 at 10 mA cm^{-2}	70	*J. Am. Chem. Soc.* 2018, **140**, 2610-2618
Mo-CoP	Carbon cloth	310, 370 at 10, 100 mA cm^{-2}	56	*Nano Energy* 2018, **48**, 73–80
H-CoP@NC	Glassy carbon electrode	320 at 10 mA cm^{-2}	73	*Inorg. Chem.* 2019, **58**, 14652-14659
Co/CoP	Glassy carbon rotating disk electrode	340 at 10 mA cm^{-2}	79.5	*Adv. Energy Mater.* 2017, **7**, 1602355
FeP-FeP_xP_y	Glassy carbon electrode	280 at 10 mA cm^{-2}	48	*ACS Appl. Nano Mater.* 2018, **1**, 617-624
Multishelled Ni_2P	Rotation disk electrode	270 at 10 mA cm^{-2}	40.4	*Chem. Mater.* 2017, **29**, 8539-8547
Ni_2P nanosheets	Glassy carbon electrode	320 at 10 mA cm^{-2}	105	*J. Mater. Chem. A* 2018, **6**, 18720-18727
Co3O4/NiCo2O4 DSNCs	Ni foam	340 at 10 mA cm^{-2}	88	*J. Am. Chem. Soc.* 2015, **137**, 5590
CoP-Fe_2O_3	ITO substrate	302 at 10 mA cm^{-2}	-	*J. Mater. Chem. A* 2018, **6**, 4783-4792
CoP/rGO-400	Glass carbon electrode	340 at 10 mA cm^{-2}	66	*Chem. Sci.* 2016, **7**, 1690
Ni-Co-P	Glass carbon electrode	300 at 10 mA cm^{-2}	80	*Adv. Funct. Mater.* 2018, **28**, 1706008

1.If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.

Table S4 Comparison of all water-splitting performances for Fe/Zn-CoP core-shell nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Voltage	Ref.
Fe/Zn-CoP	Carbon cloth	1.59, 1.62, 1.65 at 10, 20, 50 mA cm^{-2}	**This work**
CoP/NCNHP	Glassy carbon electrode	1.64 at 10 mA cm^{-2}	*J. Am. Chem. Soc.* 2018, **140**, 2610-2618
Ni-Co-P HNBs	-	1.62 V at 10 mA cm^{-2}	*Energy Environ. Sci.* 2018, **11**, 872-880
$Cu_{0.3}Co_{2.7}P$/NC	Glassy carbon electrode	1.74 at 70 mA cm^{-2}	*Adv. Energy Mater.* 2017, **7**, 1601555
H-$Co_{0.85}$Se|P	exfoliated graphene	1.64 V at 10 mA cm^{-2}	*Adv. Mater.* 2017, **29**, 1701589
Fe-CoP	Ti foam	1.60 V at 10 mA cm^{-2}	*Adv. Mater.* 2017, **29**, 1602441
CoP-Fe_2O_3	ITO substrate	1.67 V at 100 mA cm^{-2}	*J. Mater. Chem. A* 2018, **6**, 4783-4792
CoOx-CoSe film	Ni foam	1.66 V at 10 mA cm^{-2}	*J. Mater. Chem. A* 2016, **4**, 10933
H-CoP@NC	Glassy carbon electrode	1.72 V at 10 mA cm^{-2}	*Inorg. Chem.* 2019, **58**, 14652-14659

1.If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.

Reference

[1] T. Liu, W. Wang, M. Yi, Q. Chen, C. Xu, D. Cai, H. Zhan, Chem. Eng. J. 354 (2018) 454-462.

[2] Z. Peng, D. Jia, A. M. Al-Enizi, A. A. Elzatahry, G. Zheng, Adv. Energy Mater. 5 (2015) 1402031.

[3] C. C. Mccrory, S. Jung, J. C. Peters and T. F. Jaramillo, J. Am. Chem. Soc. 135 (2013) 16977-16987.

[4] D. Voiry, M. Chhowalla, Y. Gogotsi, N. Kotov, Y. Li, R. Penner, R. Schaak, P. Weiss, ACS Nano 12 (2018) 9635-9638.

[5] T. Liu, P. Li, N. Yao, G. Cheng, S. Chen, W. Luo, Y. Yin, Angew. Chem. Int. Ed. 58 (2019) 4679-4684.