Electronic Supplementary Material (ESI) for CrystEngComm.

Ultrathin 2D Flower-Like CoP@C with Active (211) Facet for Efficient Electrocatalytic Water Splitting

Xiaowei Shi,[a] Ping Yang,[a] Yongyong Cao,[b] Chao Dai,[a] Weiqing Ye,[a] Lingxia Zheng,[a] Zhefei Zhao,[a] Jianguo Wang,*[b] and Huajun Zheng*[a]

[a]Department of Applied chemistry, Zhejiang University of Technology, Hangzhou 310032,P. R. China

E-mail: zhenghj@zjut.edu.cn

[b]Institute of Industrial Catalysis, College of Chemical Engineering, State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, Zhejiang University of Technology, Hangzhou 310032, P. R. China

E-mail: jgw@zjut.edu.cn

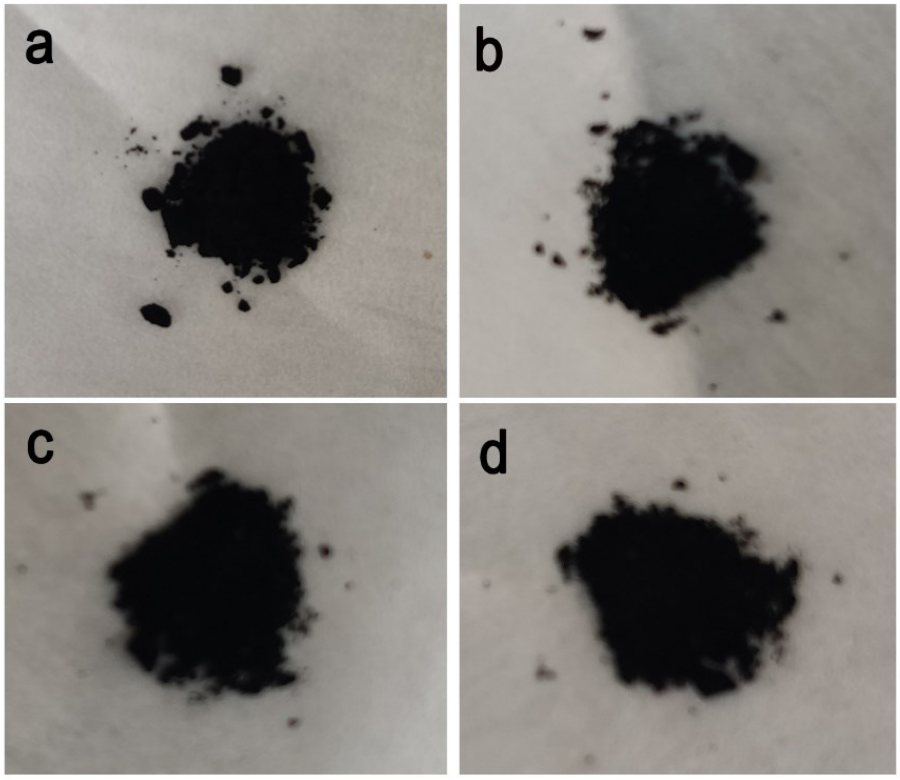

Fig. S1. The digital images of CoP@C-Y prepared in different proportion of Co^{2+} and 2-MeIM, CoP@C-1 (a), CoP@C-2 (b), CoP@C-3 (c) and CoP@C-4 (d).

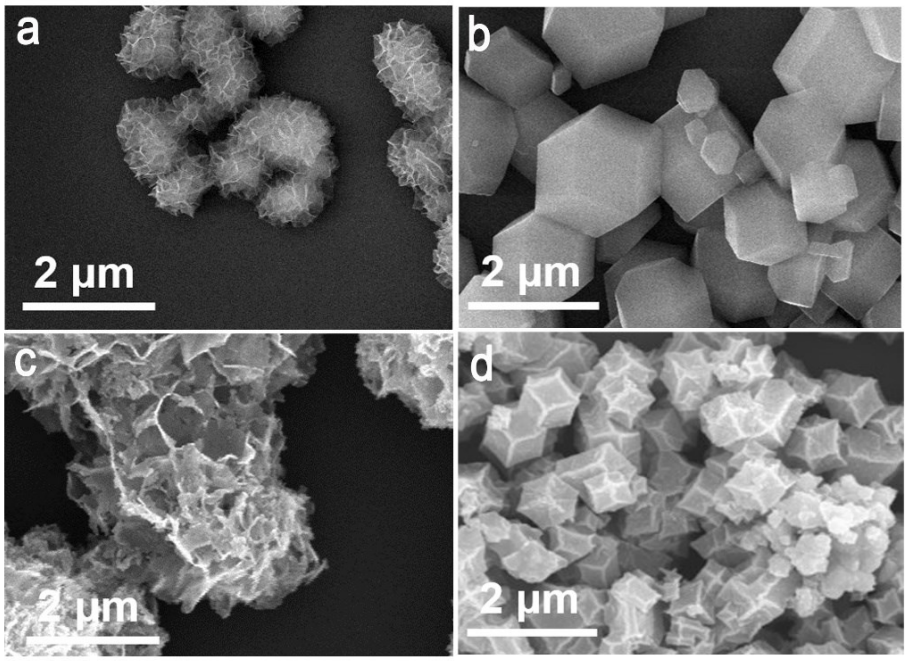

Fig. S2. SEM images of Co-MOF-1 (a), Co-MOF-3 (b), CoP@C-1 (c) and CoP@C-3 (d).

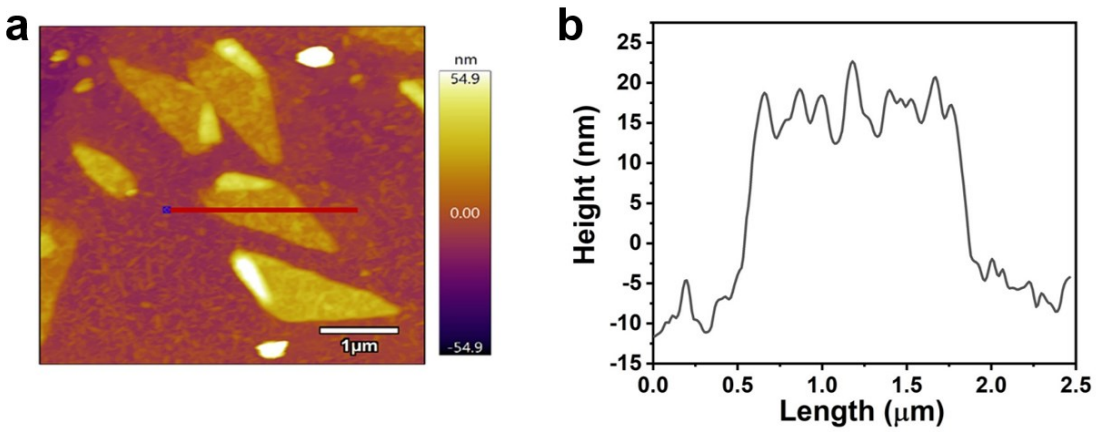

Fig.S3. AFM images and the corresponding height profiles of the CoP@C-2.

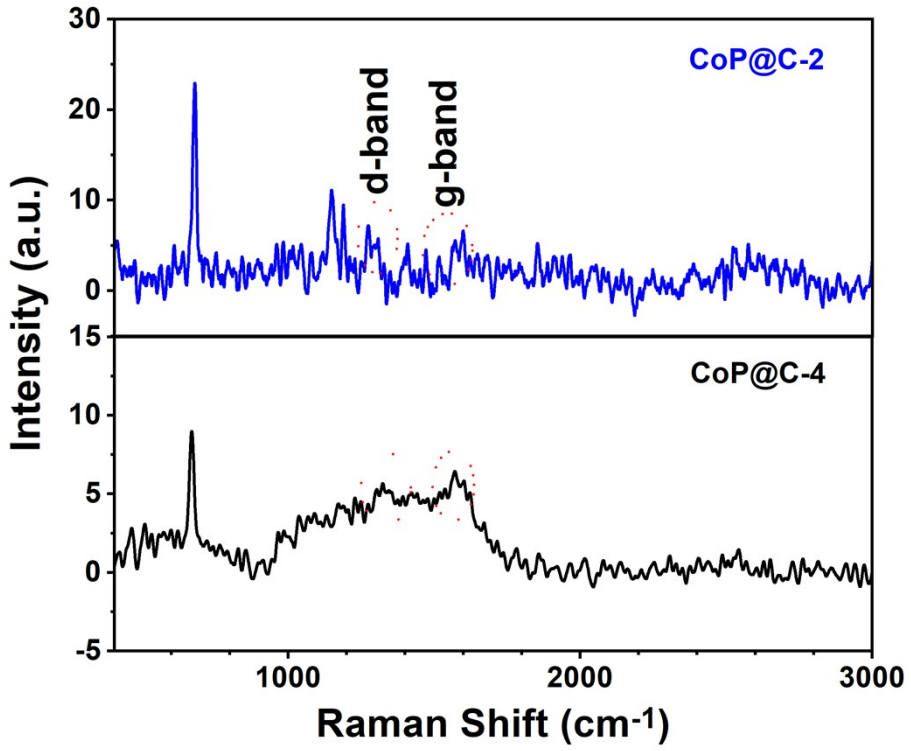

Fig. S4. Raman spectrum of the CoP@C-2 and CoP@C-4.

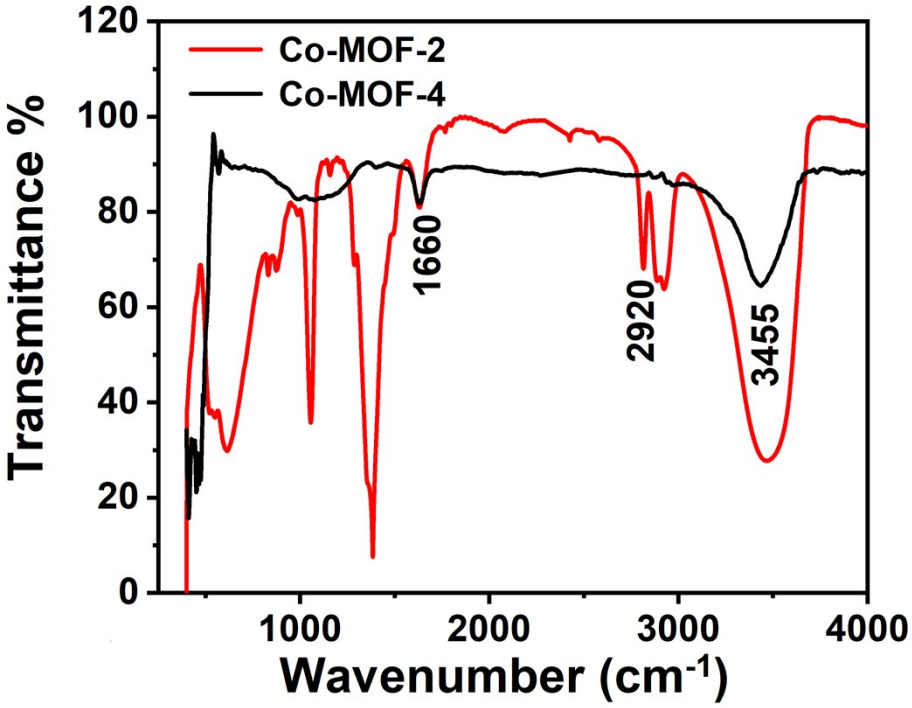

Fig. S5. FT-IR spectrums of Co-MOF-2 and Co-MOF-4.

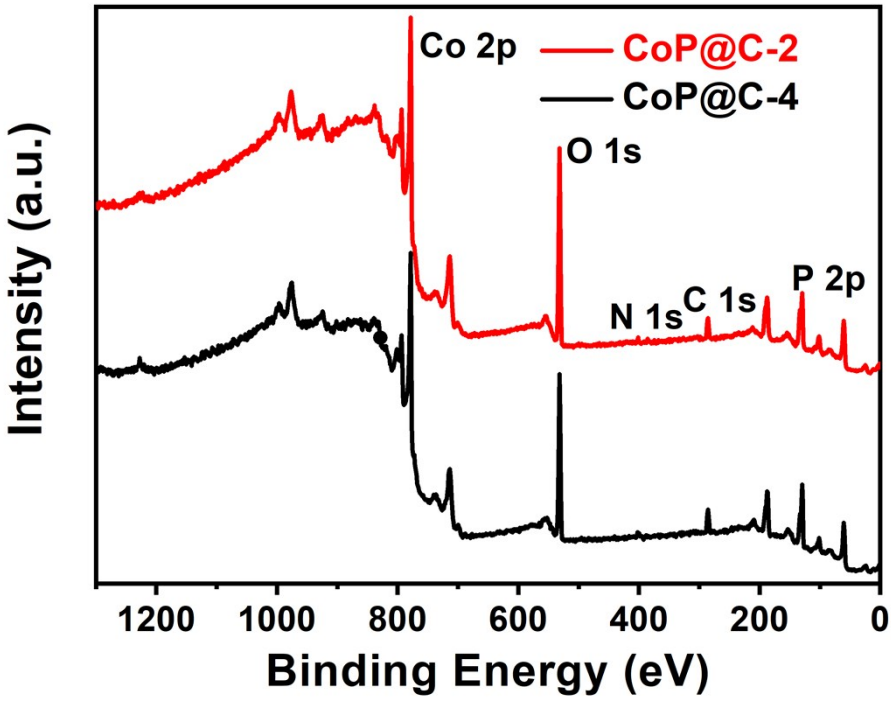

Fig. S6. XPS survey spectra of CoP@C-2 and CoP@C-4.

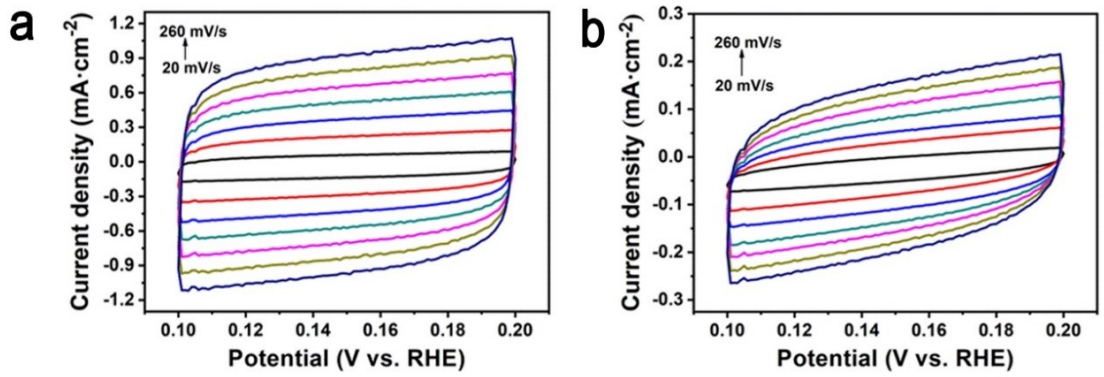

Fig. S7. The CV curves of the CoP@C at different sweep speeds in 1 M KOH, CoP@C-2 (a) and CoP@C-4 (b).

The Faradaic Efficiency calculations (FE):[1, 2]

The Faradaic Efficiency was tested by drainage method, CoP@C-2 on Ni foam (1×1 cm^2) at room temperature. H_2 was gathered use chronopotentiometry conducted at 10 $mA \cdot cm^{-2}$ in the self-regulating cell with gas collecting plant. The Faradaic Efficiency calculation formula is as follows:

$$FE = \frac{\alpha n F}{Q}$$

In which α is the numbers of transferred electrons, n is the number of moles of the obtained products, F is the faradaic constant (96485), Q is the total charge. The total charge Q is determined by the applied current and the operating time, Q = I × t, n can be obtained by the volume of H_2 (V), n = V / 24.5, (The molar volume of the gas is 24.5 $L \cdot mol^{-1}$ at 25 °C). So, the actual Faradaic Efficiency calculation formula is as follows:

$$FE = \frac{\alpha V F}{It \times 24.5}$$

The production rate of H_2 is expressed by the following equation：

$$r(H_2) = \frac{V}{24.5t}$$

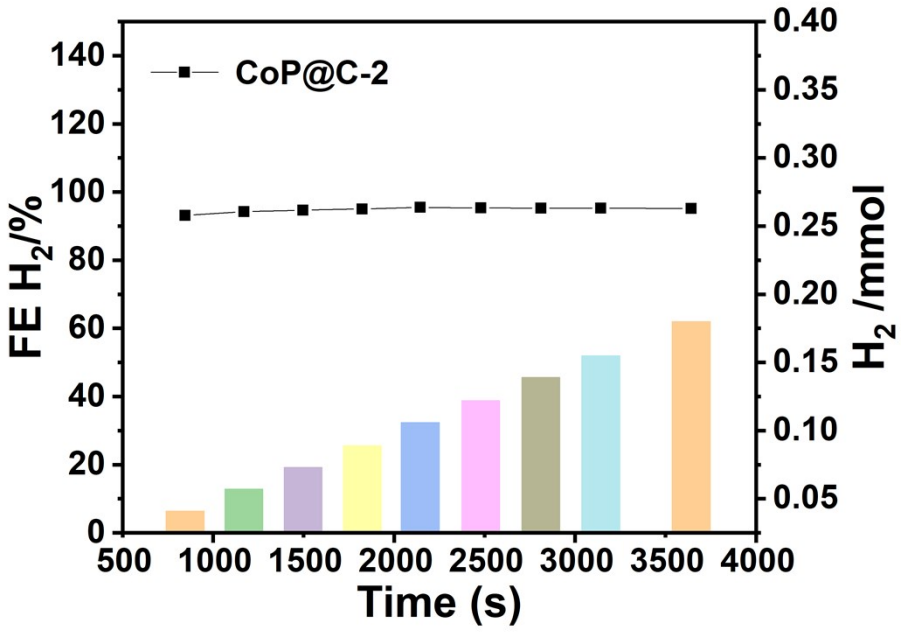

Fig. S8. Gas volume versus time and corresponding Faradaic efficiency.

Turnover frequency calculations (TOF):

The turnover frequency (TOF) was first calculated:[3]

$$TOF = \frac{j \cdot S}{2F \cdot n}$$

Where j is the current density (mA·cm^{-2}) at different overpotential, S represents the surface area of as prepared electrode (0.07 cm^{-2}), the number 2 means a two-electron hydrogen evolution reaction, F is the Faraday's constant (96485.3 C·mol^{-1}), and n represents the moles of metal atoms on the electrode.

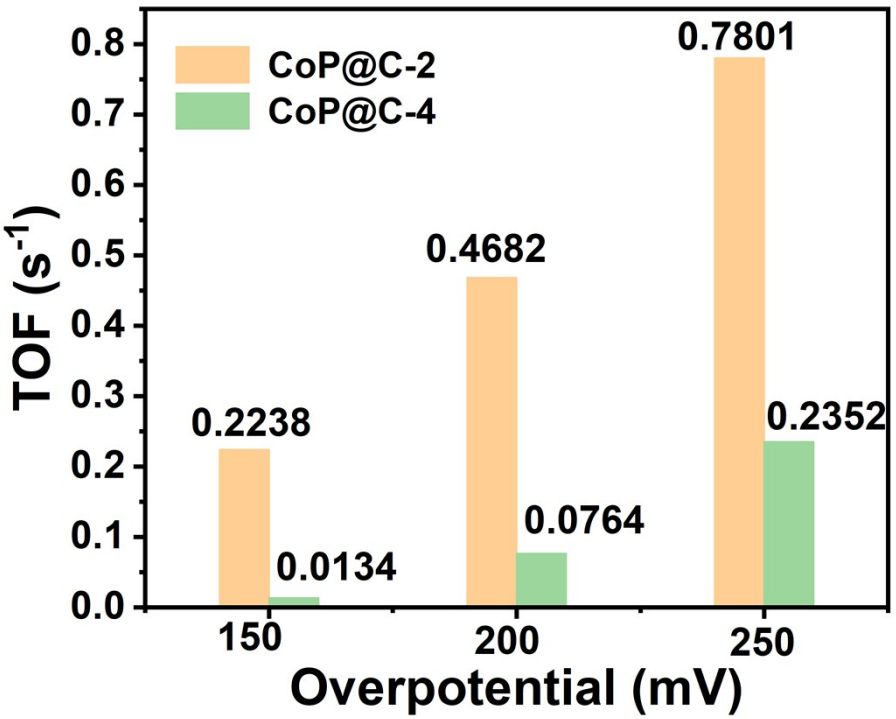

Fig. S9. The TOF values of different electrodes at 150, 200 and 250 mV (vs. RHE).

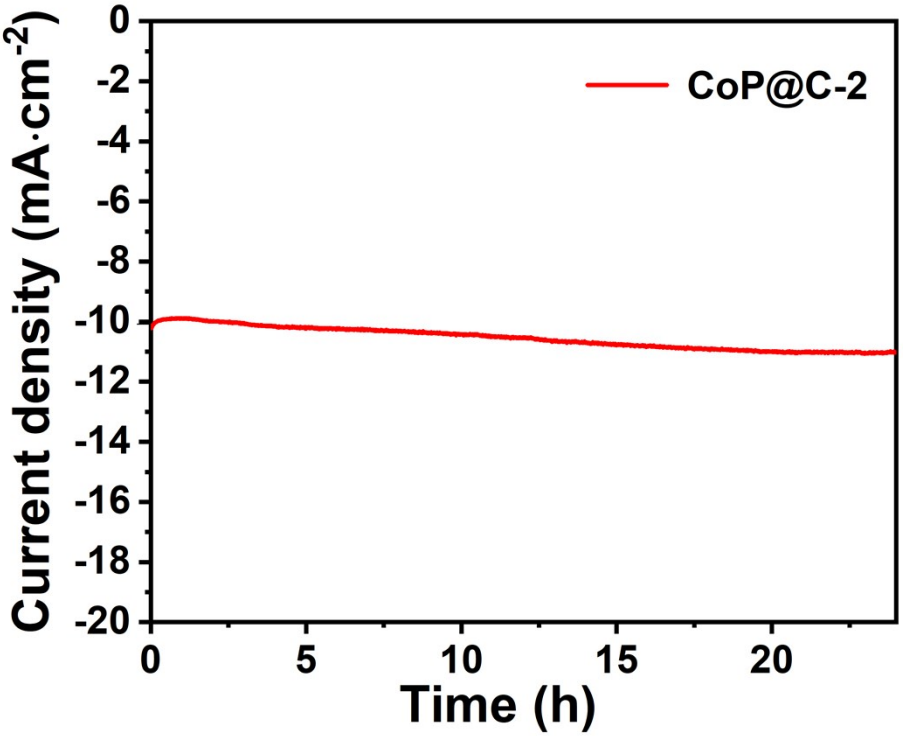

Fig. S10. Chronamperometric curves of the CoP@C-2 at 10 $mAcm^{-2}$.

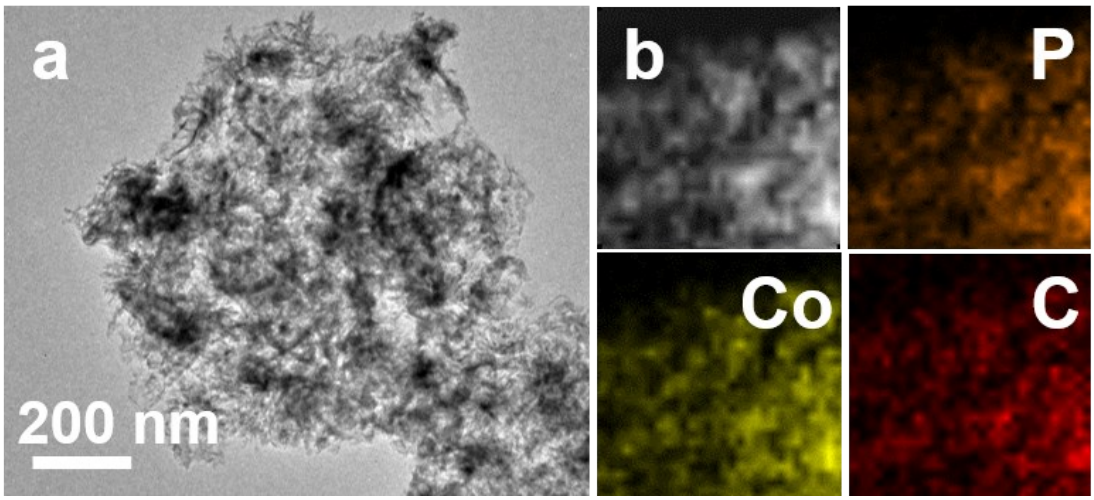

Fig. S11. TEM (a) and the elemental mapping (b) images of CoP@C-2 after stability testing.

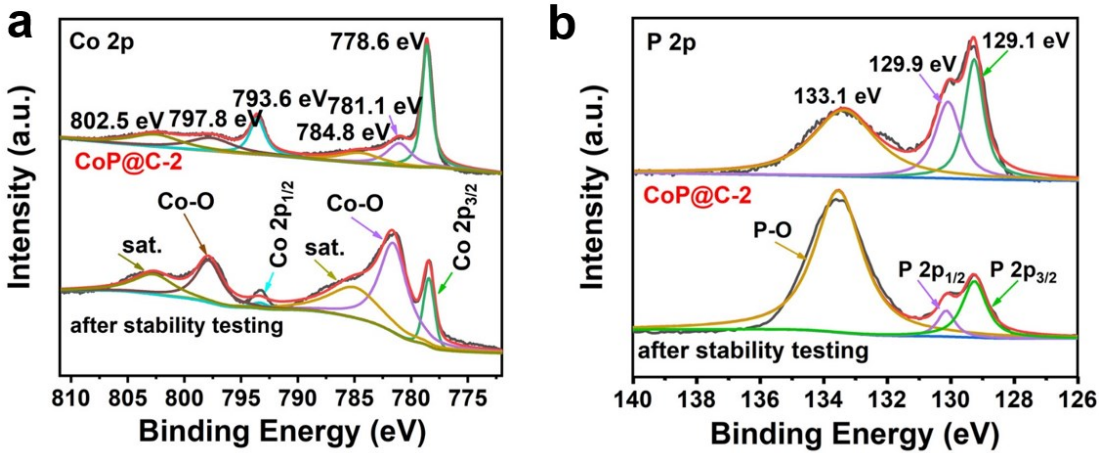

Fig. S12. The XPS of CoP@C-2 after the stability testing in 1.0 M KOH.

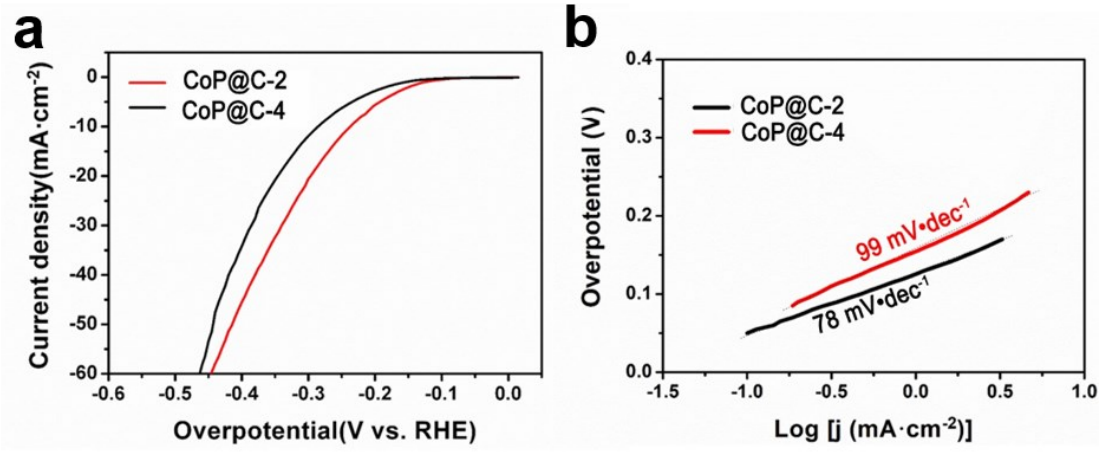

Fig. S13. (a) LSV curves, (b) Tafel slope of CoP@C-2 and CoP@C-4 in 0.5 M H_2SO_4.

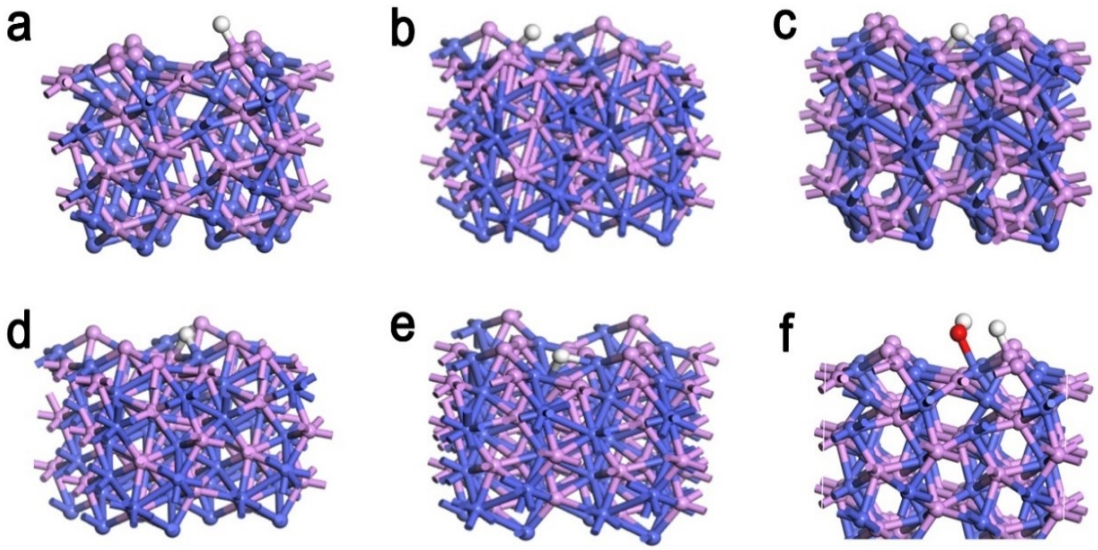

Fig. S14. The optimized structures of (a)-(e) hydrogen proton adsorption and (f) H_2O dissociation on CoP (011).

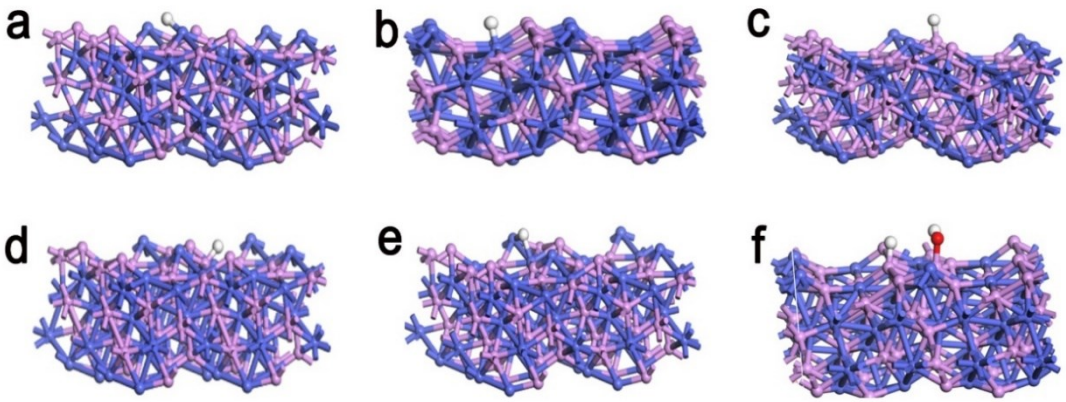

Fig. S15. The optimized structures of (a)-(e) hydrogen proton adsorption and (f) H_2O dissociation on CoP (221).

Table S1 the peak strength ration of the CoP@C crystal plane (011) and (211).

Molar Ratio	Crystal Plane (011)	Crystal Plane (211)	the Peak Intensity ratio
CoP@C-2	305	421	18:25
CoP@C-4	753	625	6:5

Table S2 the peak strength ration of the CoP@C crystal plane (112) and (011).

Molar Ratio	Crystal Plane (112)	Crystal Plane (011)	the Peak Intensity ratio
CoP@C-2	127	305	21:50
CoP@C-4	271	753	9:25

Table S3 Electrochemical Parameters of the catalysts for HER in 1 M KOH.

Catalyst	Substrate	Overpotential at 10mA·cm^{-2} (mV)	Tafel Slope (mV·dec^{-1})	Ref
CoP	Carbon cloth	209	129	[4]
Ni_2P	Ni foam	98	72	[5]
CoP@NC	GCE	129	58	[6]
CoP_3 NAs/CFP	Carbon fiber paper	65	46	[7]
CoP/CP	Carbon paper	128	62	[8]
CoP_2/RGO	RGO	88	50	[9]
Ni_2P/C	Ni foam	97	29	[10]
FeP/C		185	93	[11]
CoP NS/C		111	70.9	[12]
CoP/TF	Ti foil	118	50	[13]
CoP@C		127	78	This work

Table S4 Electrochemical Parameters of the catalysts for HER in 0.5 M H_2SO_4.

Catalyst	Substrate	Overpotential at 10mA·cm^{-2} (mV)	Tafel Slope (mV·dec^{-1})	Ref
CoP	Ti foil	77	50	[14]
g-CoP@NF VDNCs	Ni foam	71	46.7	[15]
CoP@PCM	Natural wood	155	58.8	[16]
CoP@CNT		122	54	[17]
CoP-CNTs		139	52	[18]
CoP/CC	Carbon cloth	95	119	[19]
CoP@NPMG		146	58	[20]
CoP/C		90	128	[21]
CoP-CNT		119	64	[22]
V,N-CoP/CC	Carbon cloth	81	59	[23]
CoP@C		236	78	This work

Table S5 The adsorption energy of hydrogen proton on different active sites of CoP (011) and CoP (211).

CoP(011) Active Sites	Adsorption Energy(eV)	CoP(211) Active Sites	Adsorption Energy(eV)
Top-1(P) site	-0.39	Top-1(Co) site	-0.17
Top-2(P) site	-0.30	Top-2(Co) site	0.02
Bridge-1(P-Co) site	0.25	Top-1(P) site	-0.27
Bridge-2(P-Co) site	0.08	Top-2(P) site	0.09
Bridge(Co-Co) site	0.66	Bridge(Co-Co) site	-0.11

Table S6 Summary of various catalytic electrodes for overall water splitting in 1 M KOH.

Catalyst	Cell Voltages η=10 mA·cm^{-2} (V)	Ref
Mo-CoP	1.56	[24]
CoP/NFs	1.7	[25]
CoP/NCNHP	1.64	[26]
FeCoP	1.60	[27]
CP/CNTs/Co-S	1.74	[28]
Co_2P	1.65	[29]
$Co_2P@Co_3O_4$	1.57	[30]
C-CoP-1/12	1.65	[31]
CoP-Co_2P@PC	1.56	[32]
Er-doped CoP	1.58	[33]
CoP@C	1.67	This work

References

1 Y. Men, P. Li, F. Yang, G. Cheng, S. Chen, W. Luo, *Appl. Catal. B: Environ.*, 2019, **253,** 21-27.
2 Z. Wang, H. Wang, S. Ji, X. Wang, P. Zhou, S. Huo, V. Linkov, R. Wang, *Chem. Eur. J.* 2020, **26,** 12067-12074.
3 P. Li, X. Duan, Y. Kuang, Y. Li, G.Zhang, W. Liu, X. Sun, *Adv. Energy Mater.,* 2018, 1703341.
4 Z. Pu, Q. Liu, A. M. Asiri, X. Sun, *ACS Appl. Mater. Interfaces,* 2014, **6**, 21874.
5 E. J. Popczun, C. W. Roske, C. G. Read, J. C. Crompton, J. M. McEnaney, J. F. Callejas, N. S. Lewis, R. E. Schaak, *J. Mater. Chem. A,* 2015, **3**, 5420.
6 F. Yang, Y. Chen, G. Cheng, S. Chen, W. Luo, *ACS Catal.,* 2017, **7**, 3824.
7 T. Wu, M. Pi, D. Zhang, S. Chen, *J. Mater. Chem. A,* 2016, **4**, 14539.
8 Y. Zeng, Y. Wang, G. Huang, C. Chen, L. Huang, R. Chen, S. Wang, *Chem. Commun.,* 2018, **54**, 1465.
9 J. Wang, W. Yang, J. Liu, *J. Mater. Chem. A,* 2016, **4**, 4686.
10 H. Qu, Y. Ma, Z. Gou, B. Li, Y. Liu, Z. Zhang, L. Wang, *J. Colloid Interf. Sci.,* 2020, **572**, 83.
11 F. Wang, X. Yang, B. Dong, X. Yu, H. Xue, L. Feng, *Electrochem. Commun.,* 2018, **92**, 33.
12 J. Chang, L. Liang, C. Li, M. Wang, J. Ge, C. Liu, W. Xing, *Green Chem.,* 2016, **18**, 2287.
13 X. Huang, X. Xu, C. Li, D. Wu, D. Cheng, D. Cao, *Adv. Energy Mater.,* 2019, **9**, 1803970.
14 J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney, R. E. Schaak, *Chem. Mater.,* 2015, **27**, 3769.
15 K. Ge, Y. Zeng, G. Dong, L. Zhao, Z. Wang, M. Huang, *Int. J. Hydrogen Energy,* 2019, **44**, 13490.
16 S. Min, W. Deng, Y. Li, F. Wang, Z. Zhang, *ChemCatChem,* 2020, **12**, 1.
17 Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri, X. Sun, *Angew. Chem. Int. Ed.,* 2014, **53**, 6710.
18 C. Wu, Y. Yang, D. Dong, Y. Zhang, J. Li, *Small,* 2017, **13**, 1602873.
19 P. Wang, F. Song, R. Amal, Y. H. Ng, X. Hu, *ChemSusChem,* 2016, **9**, 472.
20 Y. Liu, Y. Zhu, J. Shen, J. Huang, X. Yang, C. Li, *Nanoscale,* 2018, **10**, 2603.
21 W. Wang, J. Li, M. Bi, Y. Zhao, M. Chen, Z. Fang, *Electrochim. Acta,* 2018, **259**, 822.
22 J. K. Kim, S.-K. Park, Y. C. Kang, *J. Alloys Compd.,* 2018, **763**, 652.
23 W. Zhang, Y. Sun, Q. Liu, J. Guo, X. Zhang, *J. Alloys Compd.,* 2019, **791**, 1070.
24 C. Guan, W. Xiao, H. Wu, X. Liu, W. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J. Pennycook, J. Wang, *Nano Energy,* 2018, **48**, 73.
25 L. Ji, J. Wang, X. Teng, T. J. Meyer, Z. Chen, *ACS Catal.,* 2019, **10**, 412.
26 Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W. C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.,* 2018, **140**, 2610.
27 L. Zhou, M. Shao, J. Li, S. Jiang, M. Wei, X. Duan, *Nano Energy,* 2017, **41**, 583.
28 J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng, X. B. Zhang, *ACS Nano,* 2016, **10**, 2342.
29 M. Song, Y. He, M. Zhang, X. Zheng, Y. Wang, J. Zhang, X. Han, C. Zhong, W. Hu, Y. Deng, *J. Power Sources,* 2018, **402**, 345.
30 L. Yao, N. Zhang, Y. Wang, Y. Ni, D. Yan, C. Hu, *J. Power Sources,* 2018, **374**, 142.
31 W. Li, G. Cheng, M. Sun, Z. Wu, G. Liu, D. Su, B. Lan, S. Mai, L. Chen, L. Yu, *Nanoscale,* 2019, **11**, 17084.
32 J. Yang, D. Guo, S. Zhao, Y. Lin, R. Yang, D. Xu, N. Shi, X. Zhang, L. Lu, Y. Q. Lan, J. Bao, M. Han, *Small,* 2019, **15**, 1804546.
33 G. Zhang, B. Wang, J. Bi, D. Fang, S. Yang, *J. Mater. Chem. A,* 2019, **7**, 5769.