

## Co<sub>2</sub>P Nanoparticle/Multi-Doped Porous Carbon nanosheet for Oxygen Evolution Reaction

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### Experimental

#### Reagents and materials

Cobaltous nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99% pure), potassium hydroxide (KOH, 90%) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd used without further purification. Analytical-grade iridium(IV) oxide (IrO<sub>2</sub>) and 5% Nafion were bought from Macklin and Alfa Aesar, respectively. 2-methylimidazole (Hmim, 99% pure), branched polyethylenimine (PEI, Mw = 10,000 g/mol), and phytic Acid (PA, 50% in water) were supplied by Sigma-Aldrich.

#### Sample preparation

Firstly, leaf-like ZIF-L was synthesized with a Hmim to cobalt ions molar ratio of 4 at room temperature as previous reported.<sup>1</sup> Typically, 1 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 4 mmol of Hmim were dissolved in 5 mL deionized water respectively, and then the aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub> was mixed with the Hmim solution under stirring. After stirring for 2 hours, 0.5 mL PEI with a concentration of 0.05 g/mL was added. ZIF-L/PEI can be obtained 5 minutes later by centrifugation and re-dispersed in ethanol. Finally, 0.1 mL PA solution was introduced into ZIF-L/PEI dispersion. The product ZIF-L/PEI/PA was collected by repeated centrifugation (at 6000 rpm for 20 min) and

washed with water for three times, and then dried in an oven at 70 °C overnight. The ZIF-L/PEI/PA hybrid was then heated in a tube furnace under Ar atmosphere from 50 °C to 700 °C with a heating rate of 2 °C min<sup>-1</sup>, and maintained at 800 °C for 2 h. The final products were grounded to fine powders, named as Co<sub>2</sub>P@CoNPC. As comparisons, the carbonization products of ZIF-L and ZIF-L/PEI are named Co@NC-Z and Co@NC-ZP. Moreover, ZIF-L/PEI/PA hybrids with different volumetric PA addition were also carbonized as catalysts. Catalysts obtained from different ZIF-L/PEI/PA hybrids were named as ZPP<sub>0.05</sub> and ZPP<sub>0.5</sub> based on volume of PA solution 0.05 and 0.5 mL.

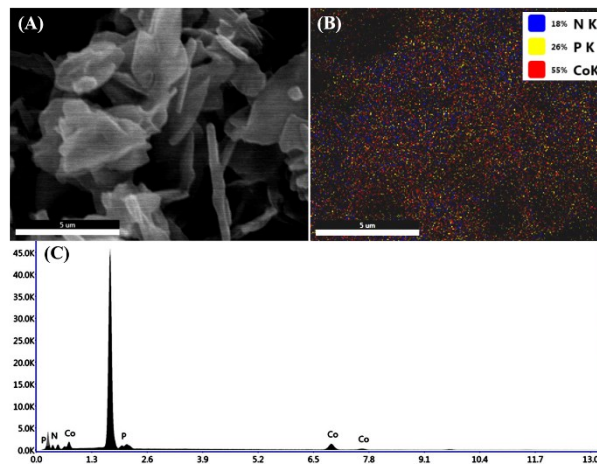
### **Materials characterization**

The morphology of the samples were observed by the scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopic (TEM, JEM-2100F). The crystalline phase was identified by X-ray diffraction (XRD, BRUKER D8 ADVANCE X-ray diffractometer, Cu-K $\alpha$  X-ray source). X-ray photoelectron spectroscopy (XPS) is recorded on an ESCALab220i-XL spectrometer with a 300W Al K $\alpha$  X-ray source.

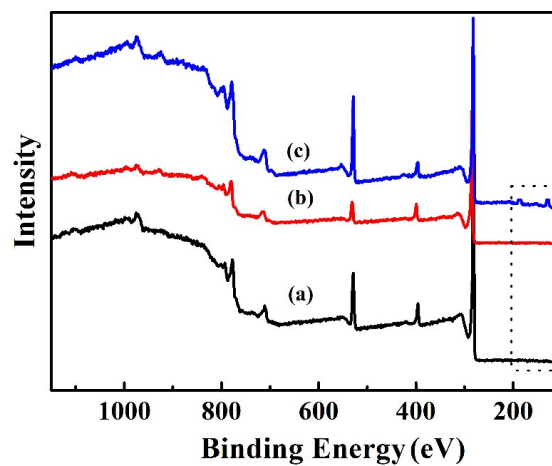
### **Electrochemical measurements**

The oxygen evolution reactions (OER) was performed on a CHI760E electrochemical workstation (Shanghai Chenhua, China). Electrodes were prepared by drop-casting ink containing catalyst powder on a glassy carbon electrode. 5 mg of the electrocatalyst sample was sonicated in a mixture of 1 mL deionized water and ethanol (v:v = 1:1) and 10  $\mu$ l Nafion for 60 min to form a homogeneous catalyst ink (5 mg·mL<sup>-1</sup>). The activities of catalysts were measured via a conventional three-electrode system, including graphite rod auxiliary electrode and Ag/AgCl reference electrode. The catalyst ink was then coated onto the glassy carbon electrode at a loading of 10  $\mu$ l and dried at room temperature. The loading of the catalysts for the activity evaluation is calculated to be 0.255 mg·cm<sup>-2</sup>. The OER activities of catalysts were measured in O<sub>2</sub>-saturated 1 M KOH aqueous solution at 1600 rpm rotation rates and a scan rate of 5 mV·s<sup>-1</sup>. All results reported in this work were converted to

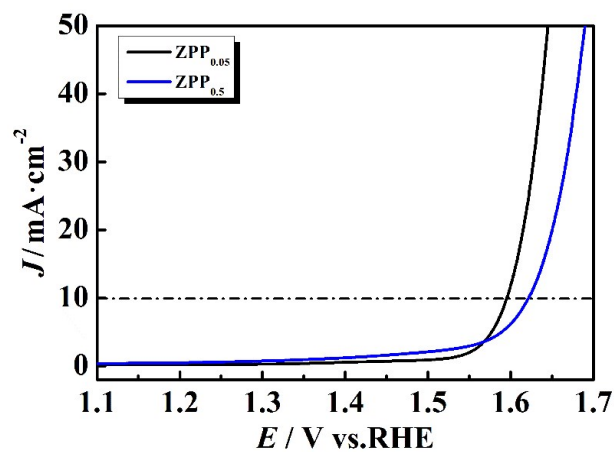
the RHE scale according to the Nernst equation ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197$ ).



**Fig. S1** (A) SEM image, (B) elemental mapping and (C) energy dispersive X-ray (EDX) spectrum of ZIF-L/PEI/PA.



**Fig. S2** Survey XPS spectra of (a) Co@NC-Z, (b) Co@NC-ZP and (c) Co<sub>2</sub>P@CoNPC.



**Fig. S3** Linear scan voltammetry (LSV) of various samples for OER: ZPP<sub>0.05</sub> (black) and ZPP<sub>0.5</sub> (blue).

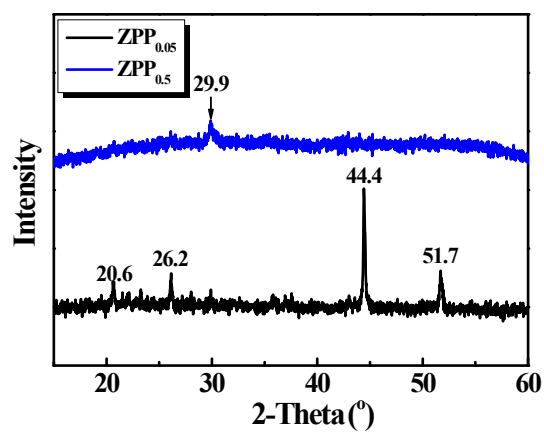


Fig. S4 XRD patterns of ZPP<sub>0.05</sub> (black) and ZPP<sub>0.5</sub> (blue).

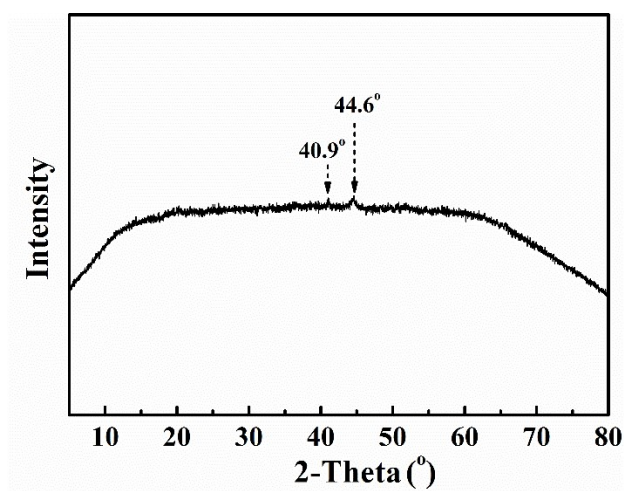


Fig. S5 XRD patterns of Co<sub>2</sub>P@CoNPC hybrids after stability test.

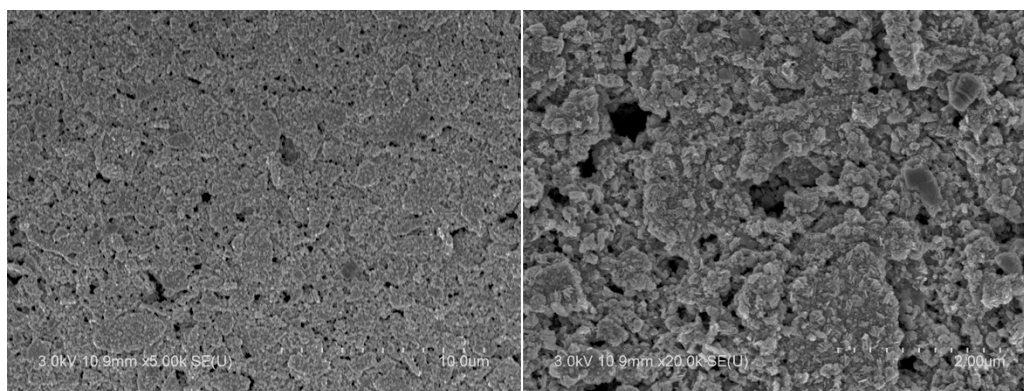
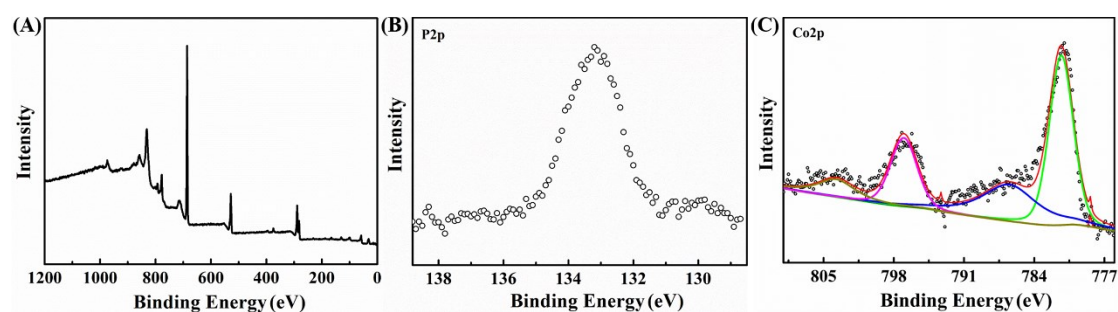


Fig. S6 SEM images of Co<sub>2</sub>P@CoNPC hybrids after stability test.



**Fig. S7** (A) XPS survey spectra and high-resolution P 2p (B), Co 2p (C) spectra of Co<sub>2</sub>P@CoNPC hybrids after stability test.

**Table S1** Summary of TMP-based electrocatalysts for OER in 1 M KOH.

Materials	Overpotential @J <sub>10</sub> /mV	Tafel slope (mV dec <sup>-1</sup> )	"P" sources	Reference
CoP <sub>3</sub> CPs	343	76	Red phosphorus	2
CoP/NCNHP	310	70	NaPO <sub>2</sub> H <sub>2</sub>	3
CoP/rGO-400	340	66	NaPO <sub>2</sub> H <sub>2</sub>	4
CoP hollow polyhedron	400	57	NaPO <sub>2</sub> H <sub>2</sub>	5
Co-P/NC	319	52	NaPO <sub>2</sub> H <sub>2</sub>	6
Fe <sub>1</sub> Co <sub>2</sub> -P/C	362	50.1	NaPO <sub>2</sub> H <sub>2</sub>	7
NiCoP/C	330	96	NaPO <sub>2</sub> H <sub>2</sub>	8
Co <sub>2</sub> P/CoNPC	328	78	Red phosphorus	9
C-CoP-1/12	333	71.1	NaPO <sub>2</sub> H <sub>2</sub>	10
Co <sub>2</sub> P@C	328	57	NaPO <sub>2</sub> H <sub>2</sub>	11
Co <sub>2</sub> P/CoNPC	311	78	Phytic acid	This work

## References

- [S1] J. Zhang, T. Zhang, D. Yu, K. Xiao and Y. Hong, *CrystEngComm*, 2015, **17**, 8212-8215.
- [S2] T. Wu, M. Pi and X. Wang, D. Zhang and S. Chen, *Phys. Chem. Chem. Phys.*, 2017, **19**, 2104-2110.
- [S3] 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 and Y. Li, *J. Am. Chem. Soc.*, 2018, **140**, 2610-2618.
- [S4] L. Jiao, Y. X. Zhou and H. L. Jiang, *Chem. Sci.*, 2016, **7**, 1690-1695.
- [S5] M. Liu and J. Li, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2158-2165.
- [S6] B. You, N. Jiang, M. Sheng, S. Gul, J. Yano and Y. Sun, *Chem. Mater.*, 2015, **27**, 7636-7642.
- [S7] W. Hong, M. Kitta and Q. Xu, *Small Methods*, 2018, **2**, 1800214.
- [S8] P. He, X. Y. Yu and X. W. Lou, *Angew. Chem. Int. Ed.*, 2017, **56**, 3897-3900.
- [S9] H. Liu, J. Guan, S. Yang, Y. Yu, R. Shao, Z. Zhang, M. Dou, F. Wang and Q. Xu, *Adv. Mater.*, 2020, 2003649
- [S10] W. Li, G. Cheng, M. Sun, Z. Wu, G. Liu, D. Su, B. Lan, S. Mai, L. Chen and L. Yu, *Nanoscale*, 2019, **11**, 17084-17092.

[S11] M. Yang, W. Zhu, R. Zhao, H. Wang, T. Ye, Y. Liu and D. Yan, *J. Solid State Chem.*, 2020, **288**, 121456.