

**Self-templating method of metal-organic frameworks to  
construct multi-shelled bimetallic phosphides hollow  
microsphere as highly efficient electrocatalysts for hydrogen  
evolution reaction**

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**Fig. S1** XRD pattern of the NiP microspheres.

**Fig. S2** (a, b) SEM images of the NiP microspheres.

**Fig. S3** XRD pattern of CoP.

**Fig. S4.** (a, b) SEM images of CoP.

**Fig. S5** EDX image of the as-synthesized CoNiP-0.25 microspheres.

**Fig. S6**  $N_2$  adsorption-desorption isotherm (inset: corresponding NLDFT pore diameter distribution) of (a) CoNiP-0.12; (b) CoNiP-0.17; (c) CoNiP-0.25; (d) CoNiP-0.47.

**Fig. S7** XPS patterns of CoNiP-0.25 hollow microspheres after HER reaction in alkaline electrolyte solution: (a) Co 2p post-HER; (b) Ni 2p post-HER; (c) P 2p post-HER.

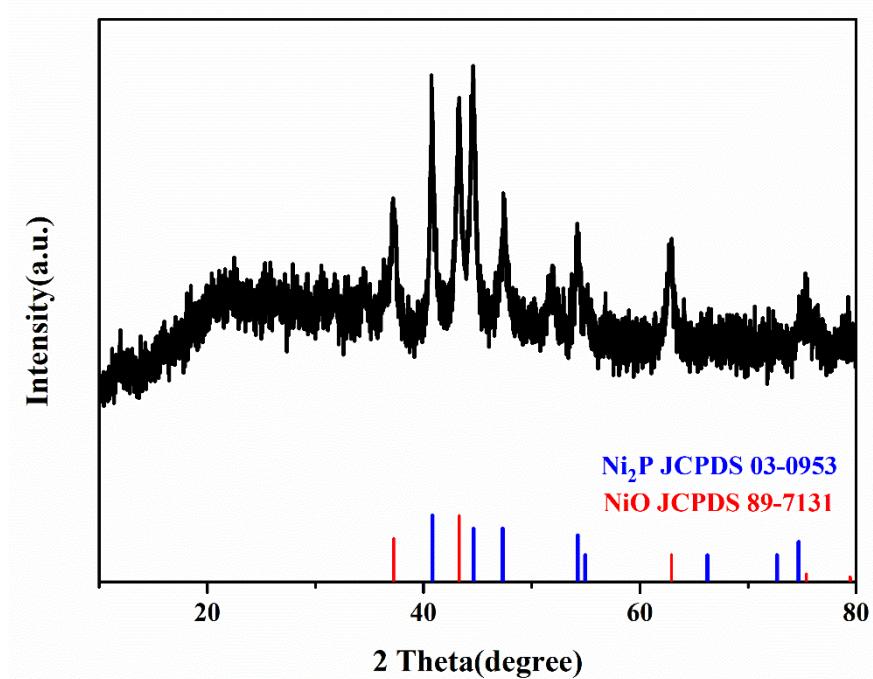
**Fig. S8** (a) Nyquist plots of the as-synthesized CoNiP-0.25 microspheres in 1.0 M KOH. (b) Tafel slop of the as-synthesized CoNiP-0.25 microspheres fitted from EIS data.

**Fig. S9** (a) HER polarization curves of Pt/C, CoNiP-n ( $n=0.12, 0.17, 0.25, 0.47$ ) microspheres obtained by two-step phosphatization, (b) Nyquist plots at a potential of -150 mV vs. RHE, (c) HER polarization curves of CoNiP-0.12 microspheres obtained by two-step phosphatization (solid line) and one-step phosphorization (dash dot line), (d) HER polarization curves of CoNiP-0.17 microspheres obtained by two-step phosphatization (solid line) and one-step phosphorization (dash dot line), (e) HER polarization curves of CoNiP-0.25 microspheres obtained by two-step phosphatization (solid line) and one-step phosphorization (dash dot line), (f) HER polarization curves

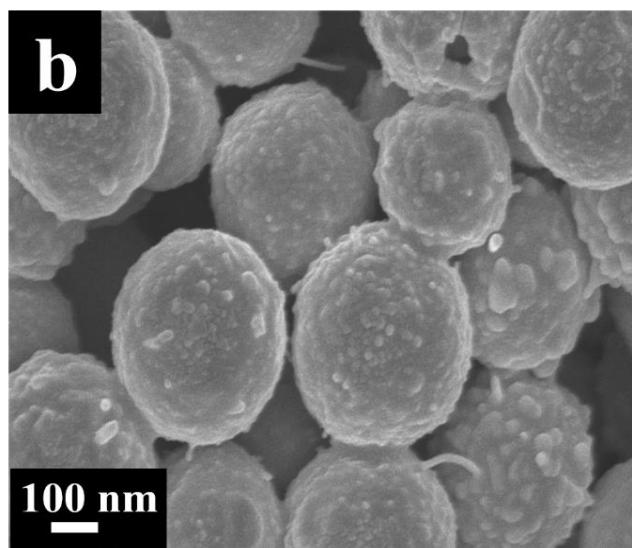
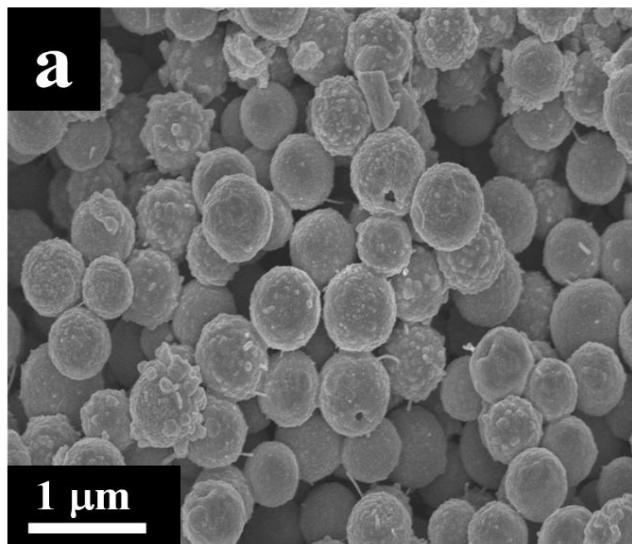
of CoNiP-0.47 microspheres obtained by two-step phosphatization (solid line) and one-step phosphorization (dash dot line). For all the measurements, iR-compensation was performed. The scan rate was  $5 \text{ mV s}^{-1}$  and electrolyte solution was 1.0 M KOH.

**Table S1** Summery of ICP results of CoNiP-n

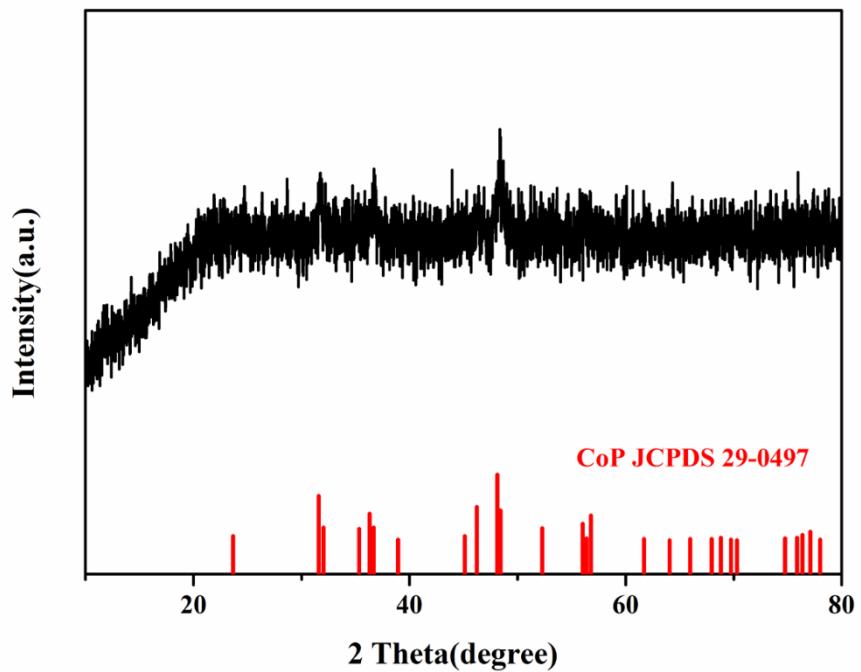
**Table S2** Summary of various catalytic electrodes for HER.



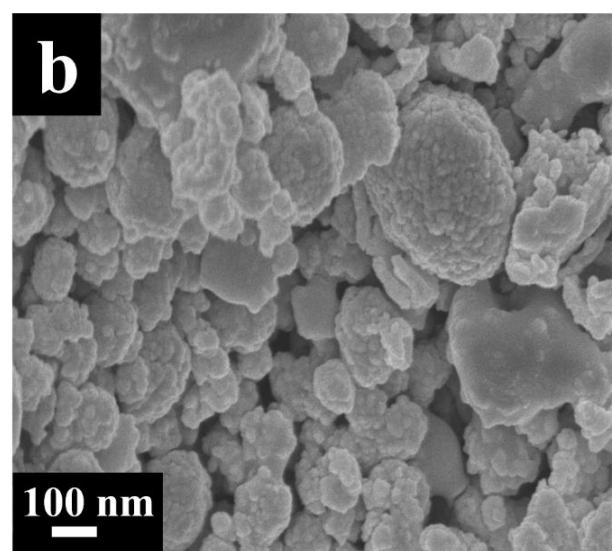
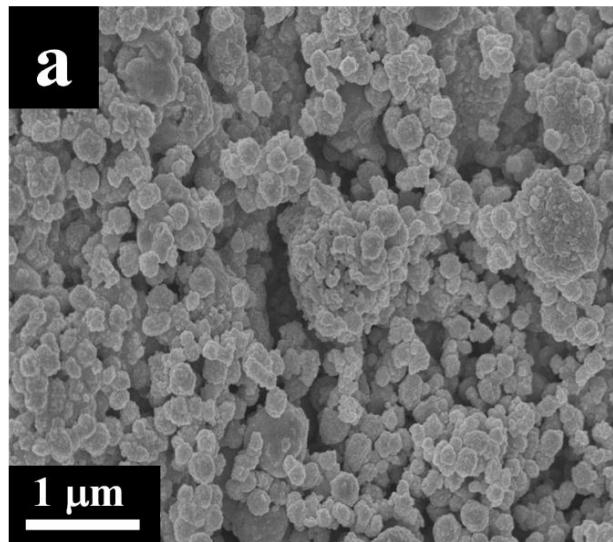
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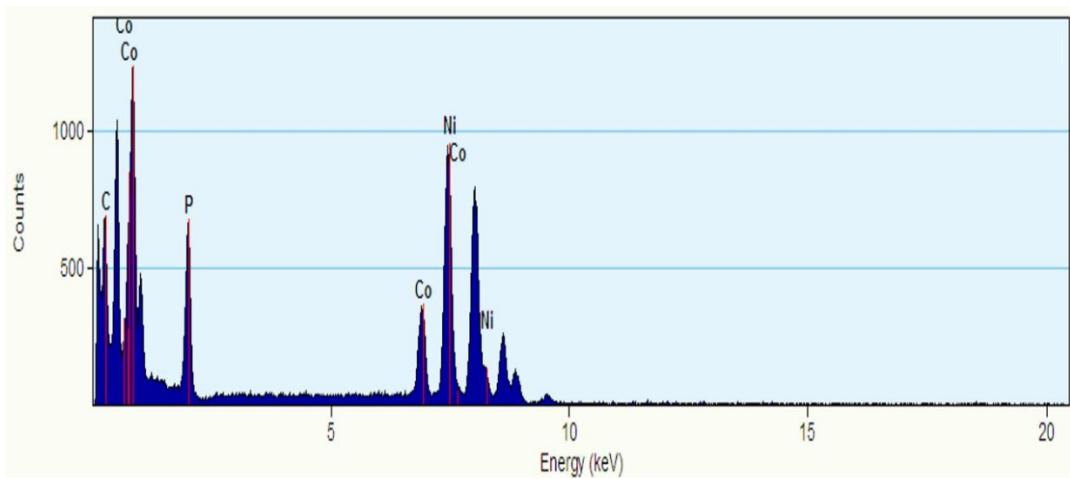
**Fig. S2** (a, b) SEM images of the NiP microspheres.



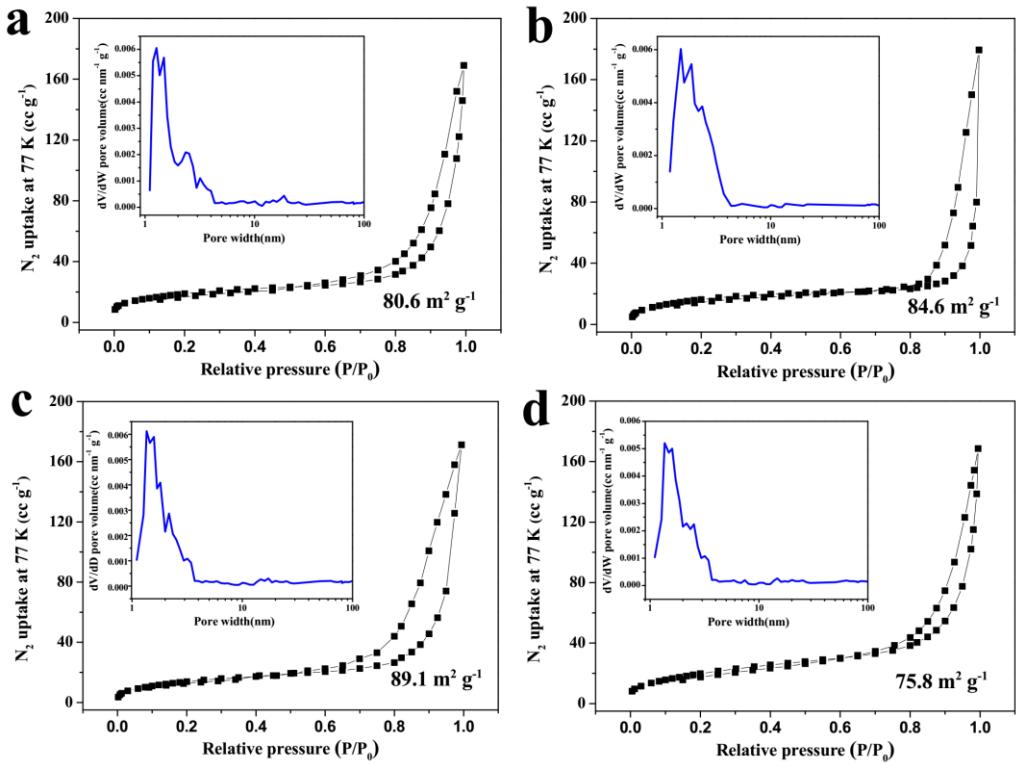
**Fig. S3** XRD pattern of CoP.



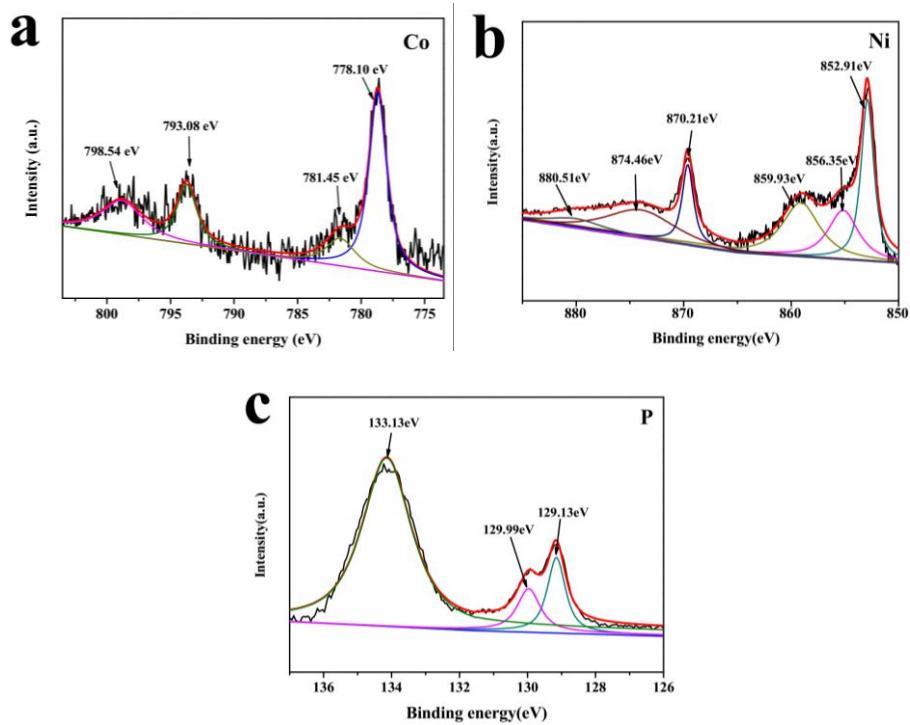
**Fig. S4.** (a, b) SEM images of CoP.



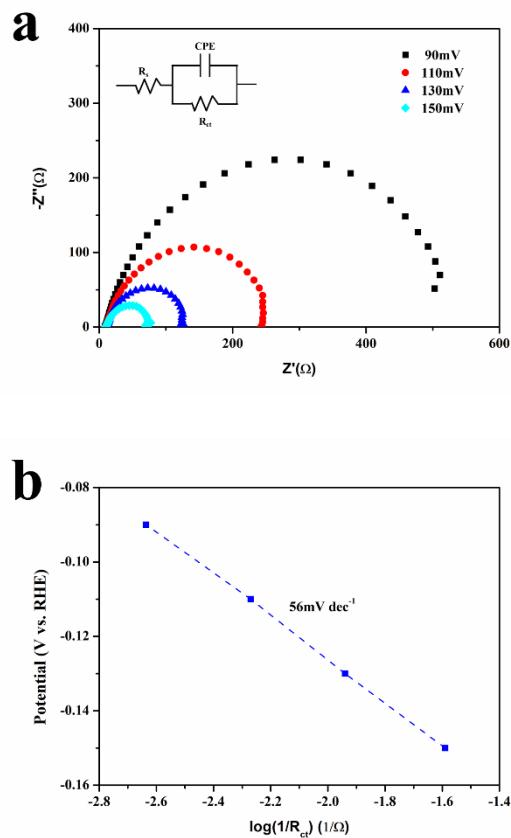
**Fig. S5** EDX image of the as-synthesized CoNiP-0.25 microspheres.



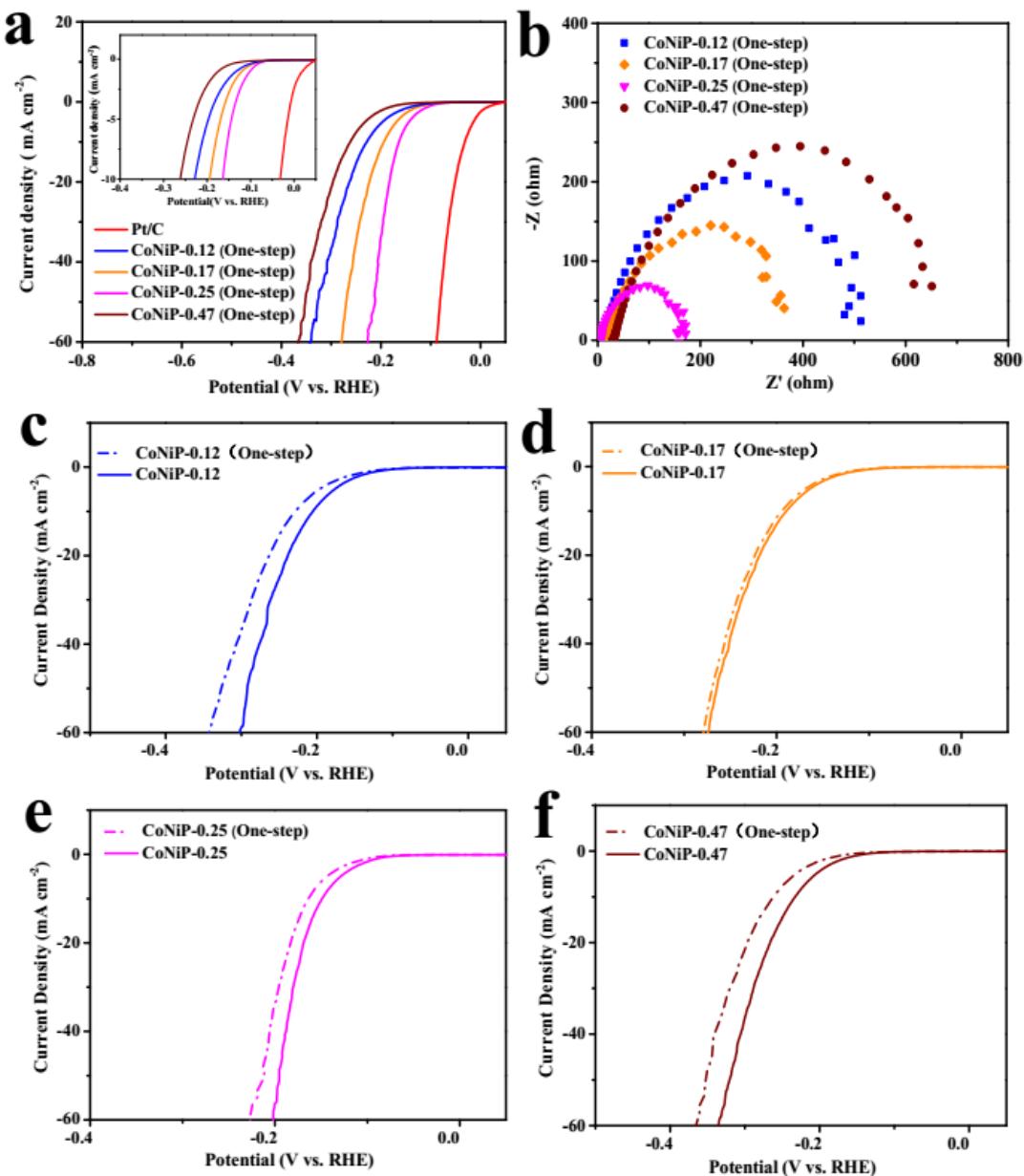
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**Table S1** Summery of ICP results of CoNiP-n

<b>Phosphides</b>	CoNiP-0.12	CoNiP-0.17	CoNiP-0.25	CoNiP-0.47
<b>ICP Co/Ni/P ratio in phosphides</b>	1:8.12:3.25	1:5.81:2.41	1:3.98:1.64	1:2.13:0.98
<b>Co/Ni ratio in reactants</b>	1:8	1:6	1:4	1:2

**Table S2** Summary of various catalytic electrodes for HER.

Catalysts	Voltages $j_{10}(\text{mV})$	Tafel slop (mV dec $^{-1}$ )	Reference
CoNiP microspheres	145.8	52	This work
CoP@NPMG	151	75	1
NiCo <sub>2</sub> O <sub>4</sub> /NF	164	88	2
Co phosphide /phosphate	380	53	3
Ni <sub>5</sub> P <sub>4</sub>	150	53	4
Co-P/NC	154	51	5

## Supplementary References

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