

## Supplementary Information

### **Engineering Co/Co<sub>2</sub>P Mott-Schottky heterostructure encased in hollow N-doped carbon polyhedron as an advanced nanoreactor towards high-efficiency electrocatalytic oxygen evolution**

Jing Li,<sup>a</sup> Xiaoxuan Feng,<sup>a</sup> Weida Zhong,<sup>a</sup> Mingjun Zhou,<sup>a</sup> Min Qian,<sup>a</sup> Jianping Xu,<sup>c</sup> Huang Pang,<sup>d</sup> Lin Xu,<sup>\*a</sup> Jun Yang<sup>\*b</sup> and Yawen Tang<sup>\*a</sup>

<sup>a</sup>Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, P. R. China.

<sup>b</sup>State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, P. R. China.

<sup>c</sup>Evercos Battery Co., LTD, Suichang, Zhejiang, 323300, P. R. China

<sup>d</sup>School of Chemistry and Chemical Engineering, Institute for Innovative Materials and Energy, Yangzhou University, Yangzhou, 225009, P. R. China.

## Experimental section

### Chemicals

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and methanol were supplied by Sinopharm Chemical Reagent Co., Ltd. Cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and potassium hydroxide (KOH) were purchased from Aladdin Biochemical Technology Co., Ltd. 2-Methylimidazole (2-MeIm) and Triphenylphosphine ( $\text{PPh}_3$ ) were purchased from Shanghai Macklin Biochemical Co., Ltd.  $\text{RuO}_2$  was provided by Shanghai D&B Biological Science and Technology Co., Ltd. All the reagents were of analytical grade and used as received without any further purification.

### Synthesis of core-shell-structured ZIF-8@ZIF-67

Typically, for the synthesis of core-shell-structured ZIF-8@ZIF-67, we used the synthetic method reported.<sup>1</sup> Briefly,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (5.82 g) and 2-MeIm (6.61 g) were dissolved in 150 ml MeOH, respectively. Then two solutions were added in turn to 100 ml ZIF-8 methanol solution (5mg/mL). Finally, the solution was stirred at room temperature for 24 h, and the obtained bright purple solution was centrifuged, rinsed with MeOH and dried at 60°C.

### Synthesis of Co/Co<sub>2</sub>P@N-C

The core-shell-structured ZIF-8@ZIF-67 and  $\text{PPh}_3$  were mixed uniformly with the mass ratio of 1:20. Subsequently, the solid mixture was annealed at 950 °C for 1.5 h under an Ar atmosphere with a ramping rate of 2 °C/min. After cooling down to room temperature, the black product of Co/Co<sub>2</sub>P@N-CHRDs were obtained. For comparison, the Co@N-CHRDs were prepared without the involvement of  $\text{PPh}_3$ , and Co<sub>2</sub>P@N-CHRDs were prepared with the involvement of tenfold  $\text{PPh}_3$  using the same procedure as the Co/Co<sub>2</sub>P@N-CHRDs. Similarly, the electrocatalyst derived from ZIF-67 (denote as Co/Co<sub>2</sub>P-1@N-CHRDs) were also synthesized under the same condition.

### Materials characterization

XRD was used to carried out the crystallinity and phase of obtained products using a Rigaku D/max-RC diffractometer with a Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). TEM, HRTEM and EDS tests were implemented on a JEOL JEM-2010F transmission electron microscope operated at an accelerating voltage of 200 kV. SEM and EDS measurements were performed on a Hitachi S5500 scanning

electron microscope. XPS analyses were operated on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K $\alpha$  light source. Raman spectra were conducted on a Raman spectrometer (Lab RAM HR800,  $\lambda = 514$  nm). Thermal analysis was obtained with a Perkin Elmer thermogravimetric analyzer under air atmosphere. The product's data of BET were obtained with a Micromeritics ASAP 2050 system at 77K.

### **Electrochemical measurement**

The electrochemical measurements were performed on a CHI 760E electrochemical workstation with a three-electrode system. The typical system consisted of a glassy carbon electrode (GCE), a saturated calomel electrode (SCE) and a graphite electrode. Three types of electrodes were used as the working electrode, reference electrode, and counter electrode, respectively. The catalyst ink was formed by dispersing 5 mg of catalysts into 1.0 mL of ethanol solution (the volume ratio of water to ethanol is 3:1) by ultrasonication. Then, 15  $\mu$ L of the catalyst ink was loaded on the surface of polished GCE and then dried at 40  $^{\circ}$ C. After that, 3  $\mu$ L of Nafion (5 wt.%, Sigma-Aldrich) was dropped on the catalysts-modified GCE surface and dried before electrochemical test. The OER measurements were performed by linear sweep voltammetry (LSV) in 1.0 M KOH solution saturated with O<sub>2</sub> at a scan rate of 5 mV s<sup>-1</sup>. The electrochemical double-layer capacitances ( $C_{dl}$ ) were conducted by a series of CV tests (scan rate: 20 ~ 100 mV s<sup>-1</sup>). The stability tests were implemented by continuous CV scanning 1000 cycles using a scan rate with 0.1 V s<sup>-1</sup>. All the potentials have been calculated with reversible hydrogen electrode (RHE) as standard in this work. The conversion equation from SCE to RHE was as follows:  $E_{RHE} = E_{SCE} + 0.0592\text{pH} + 0.242$ .

### **Zn-air battery Measurements**

A series of tests were carried out on the rechargeable Zn-air batteries (ZABs) by constructing portable electrochemical cells in the laboratory. The batteries used in the test were composed of a thickness of 0.3 mm polished zinc sheet as anode and hydrophilic carbon paper coated with 40 mg mL<sup>-1</sup> catalyst and nickel foam as air cathode. Thereinto, carbon paper loading density of 5 mg cm<sup>-2</sup> catalyst by drop-casting faced the liquid layer and without coating the catalyst faced the gas diffusion layer in order to O<sub>2</sub> could easily diffuse from the atmosphere to the catalyst. The electrolyte consisted of 6 M KOH + 0.2 M ZnCl<sub>2</sub> mixed aqueous solution. The catalyst should firstly be naturally dried before assembling the ZABs,

then the ZABs accessories be assembled in turn and left for 1h, ultimately the test be carried out. The previously assembled ZABs were tested by setting the current density and cycle of each charge and discharge to  $10 \text{ mA cm}^{-2}$  and 20 min respectively in the Land CT2001A system. Meanwhile, the corresponding specific capacity ( $\text{mAh g}_{\text{Zn}}^{-1}$ ) and energy density ( $\text{Wh kg}_{\text{Zn}}^{-1}$ ) can be calculated according to the discharge curve when the constant current density is  $5 \text{ mA cm}^{-2}$ . The calculation formula is as follows:

Specific capacity = current  $\times$  service hours/weight of consumed Zn

Energy density = current  $\times$  service hours  $\times$  average discharge voltage/weight of consumed Zn

## Figures and Table

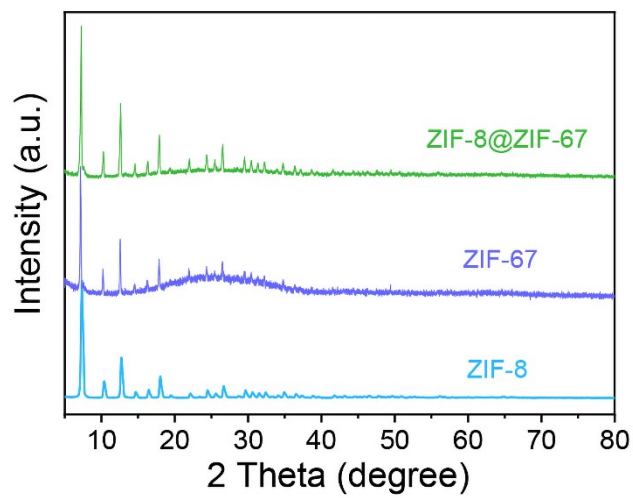


Figure S1. XRD patterns of ZIF-8@ZIF-67, ZIF-67, and ZIF-8.

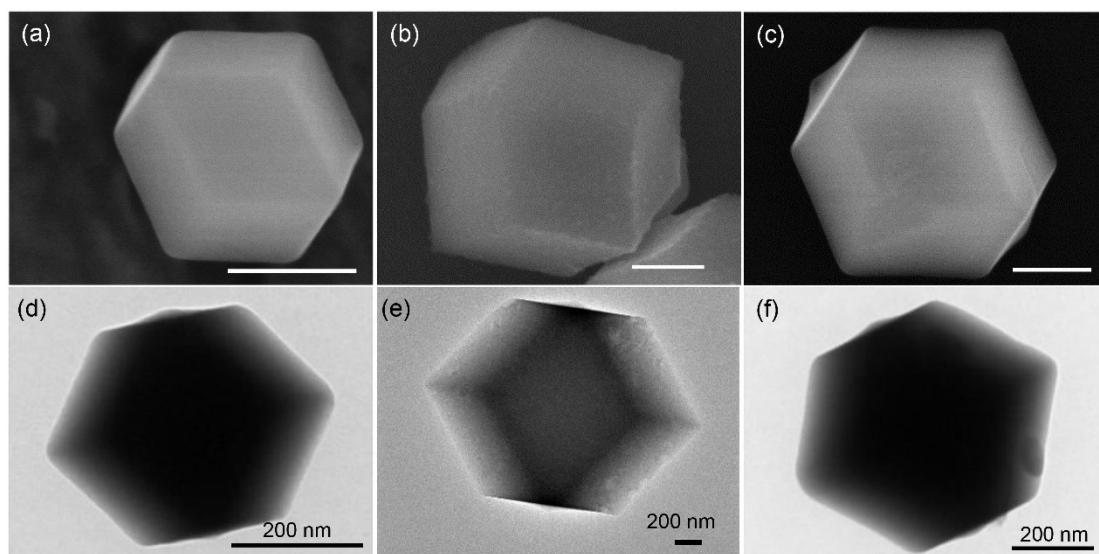
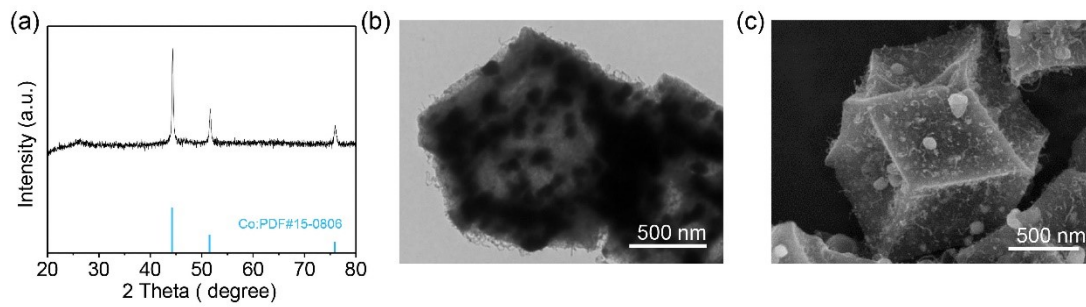
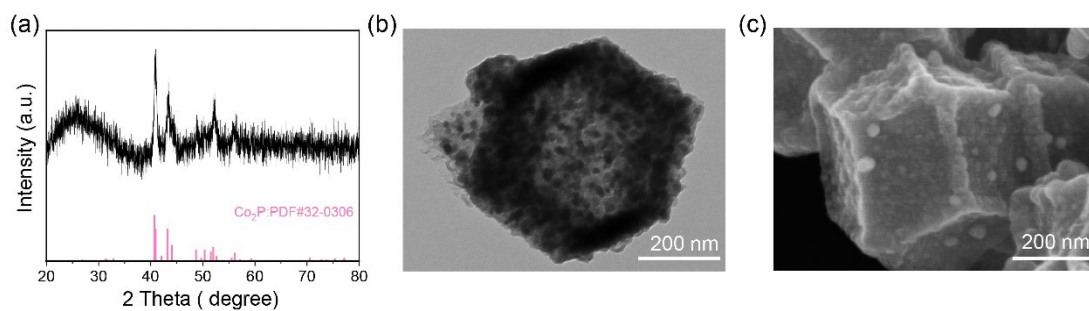


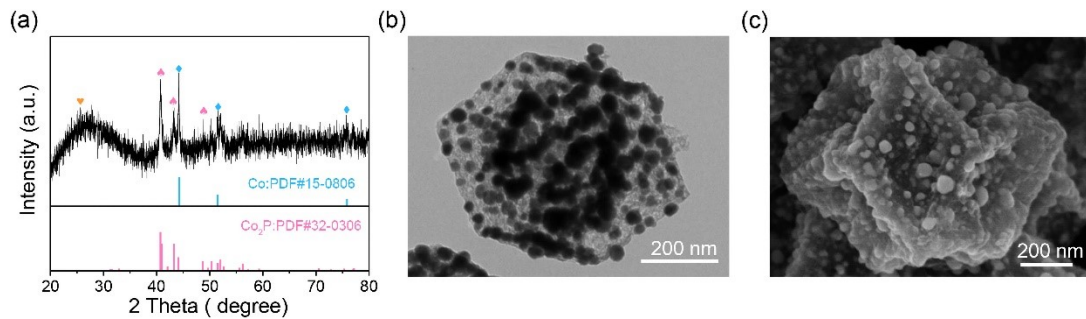
Figure S2. SEM images of (a) ZIF-8, (b) ZIF-67, and (c) ZIF-8@ZIF-67, TEM images of (d) ZIF-8, (e) ZIF-67, and (f) ZIF-8@ZIF-67.



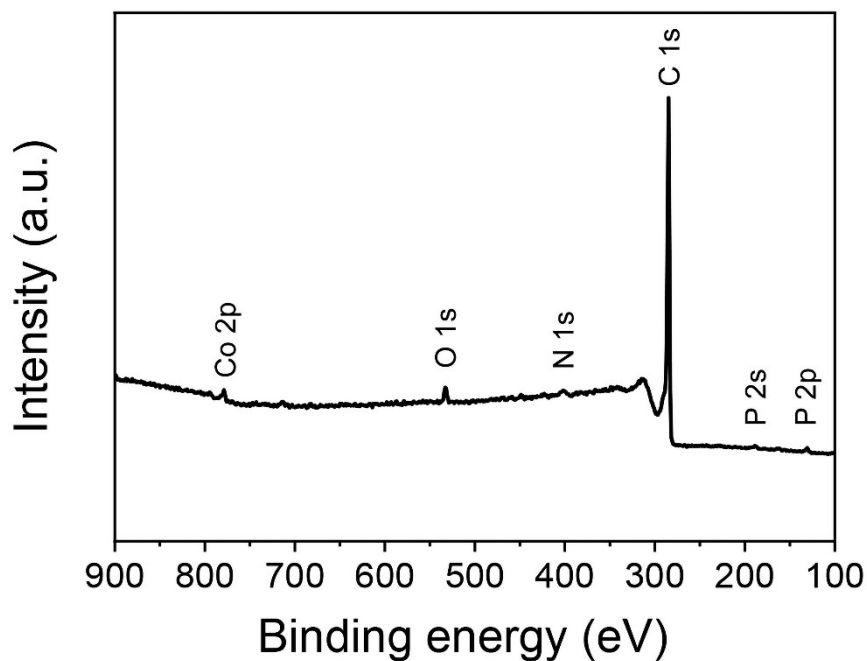
**Figure S3.** (a) XRD pattern, (b) TEM and (c) SEM image of the Co@N-CHRDs.



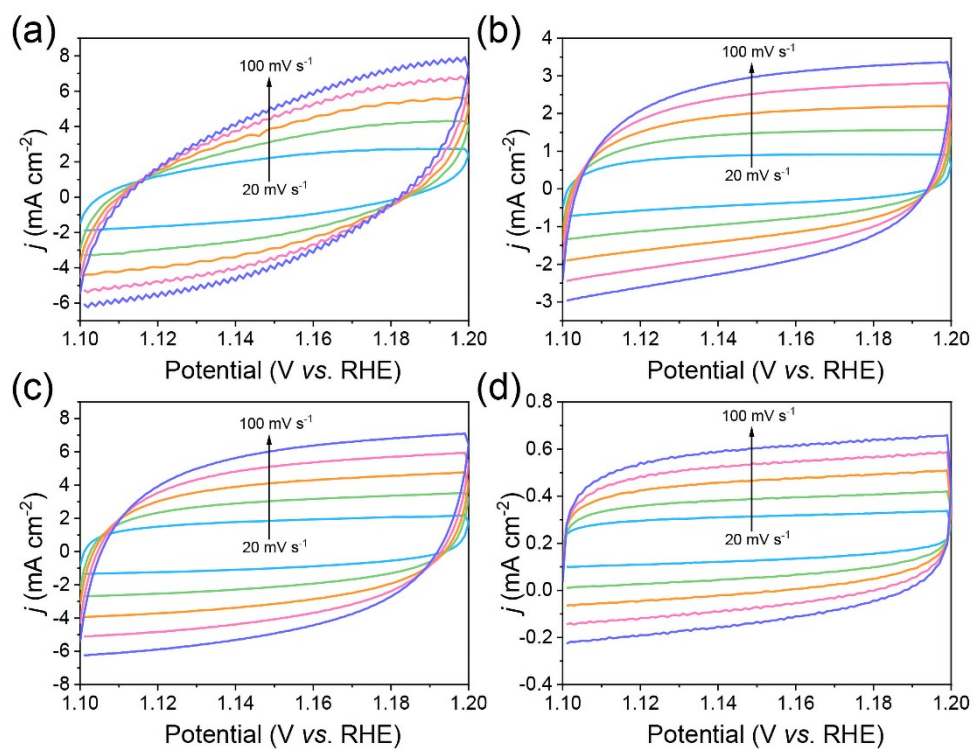
**Figure S4.** (a) XRD pattern, (b) TEM and (c) SEM image of the Co<sub>2</sub>P@N-CHRDs.



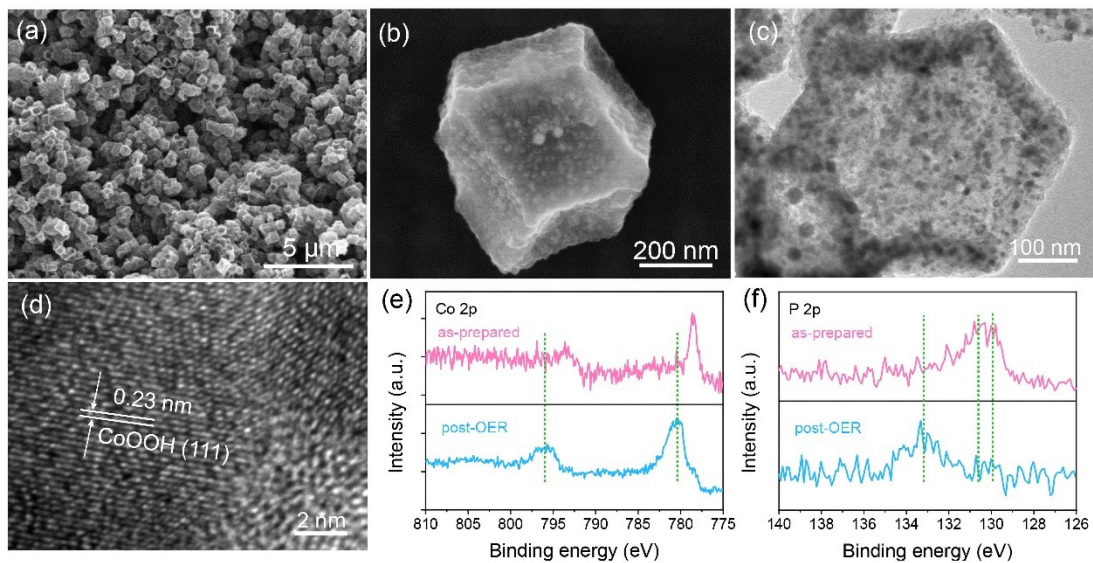
**Figure S5.** (a) XRD pattern, (b) TEM and (c) SEM image of the Co/Co<sub>2</sub>P-1@N-CHRDs.



**Figure S6.** XPS survey spectrum of the Co/Co<sub>2</sub>P@N-CHRDs.



**Figure S7.** CV curves of different catalysts in the non-Faradaic region (0.1 - 0.2 V) obtained at different scanning rates. (a) Co/Co<sub>2</sub>P@N-CHRDs, (b) Co/Co<sub>2</sub>P-1@N-CHRDs, (c) Co@N-CHRDs and (d) Co<sub>2</sub>P@N-CHRDs.



**Figure S8.** Morphology characterization and surface analysis of Co/Co<sub>2</sub>P@N-CHRDs after OER measurement. (a)-(b) SEM image, (c) TEM image, (d) HRTEM image, and (e)-(f) XPS spectra of Co 2p and P 2p.



**Table S1** Comparison of OER performance of Co/Co<sub>2</sub>P@N-CHRDs with some previously reported Co-based catalysts in 1.0 M KOH solution.

Catalyst	Overpotential / mV (10 mA cm <sup>-2</sup> )	Tafel slop (mV dec <sup>-1</sup> )	Reference
Co/Co <sub>2</sub> P@N-CHRDs	267	117.4	This work
CoS <sub>x</sub> @Cu <sub>2</sub> MoS <sub>4</sub> - MoS <sub>2</sub> /NSG	351.4	61.5	2
CoFe <sub>0.2</sub> S <sub>x</sub>	304	48.7	3
Co <sub>2</sub> P@NC-Fe <sub>2</sub> P-2	290	45	4
FeCo/Co <sub>2</sub> P@NPCF	330	61	5
Co/Co <sub>x</sub> M <sub>y</sub>	334	79.2	6
CoPS@NPS-C	326	98	7
rGO@CF:Pi	300	36	8
Co-N/GFs-700	313	84.1	9
Co <sub>2</sub> P NCs	280	60.4	10
Cl-doped Co(OH) <sub>2</sub>	330	98	11
CoCH/NF	332	126	12
Ce-MnCo <sub>2</sub> O <sub>4</sub> -3%	390	125	13
CoN <sub>x</sub> /NGA	295	82.3	14

## Reference

- 1 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, Core-Shell ZIF-8@ZIF-67-Derived CoP Nanoparticle-Embedded N-Doped Carbon Nanotube Hollow Polyhedron for Efficient Overall Water Splitting, *J. Am. Chem. Soc.*, 2018, **140**, 2610-2618.
- 2 D. C. Nguyen, D. T. Tran, T. L. L. Doan, D. H. Kim, N. H. Kim and J. H. Lee, Rational Design of Core@shell Structured  $\text{CoS}_x\text{@Cu}_2\text{MoS}_4$  Hybridized  $\text{MoS}_2/\text{N,S}$ -Codoped Graphene as Advanced Electrocatalyst for Water Splitting and Zn-Air Battery, *Adv. Energy Mater.*, 2020, **10**, 1903289.
- 3 M. Wang, C.-L. Dong, Y.-C. Huang and S. Shen, Operando Spectral and Electrochemical Investigation into the Heterophase Stimulated Active Species Transformation in Transition-Metal Sulfides for Efficient Electrocatalytic Oxygen Evolution, *ACS Catal.*, 2020, **10**, 1855-1864.
- 4 Y.-J. Tang, L. You and K. Zhou, Enhanced Oxygen Evolution Reaction Activity of a  $\text{Co}_2\text{P@NC-Fe}_2\text{P}$  Composite Boosted by Interfaces Between a N-Doped Carbon Matrix and  $\text{Fe}_2\text{P}$  Microspheres, *ACS Appl. Mater. Interfaces*, 2020, **12**, 25884-25894.
- 5 Q. Shi, Q. Liu, Y. Ma, Z. Fang, Z. Liang, G. Shao, B. Tang, W. Yang, L. Qin and X. Fang, High-Performance Trifunctional Electrocatalysts Based on  $\text{FeCo/Co}_2\text{P}$  Hybrid Nanoparticles for Zinc-Air Battery and Self-Powered Overall Water Splitting, *Adv. Energy Mater.*, 2020, **10**, 1903854.
- 6 J. Chen, C. Fan, X. Hu, C. Wang, Z. Huang, G. Fu, J.-M. Lee and Y. Tang, Hierarchically Porous  $\text{Co/Co}_x\text{M}_y$  ( $\text{M} = \text{P, N}$ ) as an Efficient Mott-Schottky Electrocatalyst for Oxygen Evolution in Rechargeable Zn-Air Batteries, *Small*, 2019, **15**, 1901518.
- 7 C. Lin, Z. Gao, J. Yang, B. Liu and J. Jin, Porous superstructures constructed from ultrafine  $\text{FeP}$  nanoparticles for highly active and exceptionally stable hydrogen evolution reaction, *J. Mater. Chem. A*, 2018, **6**, 6387-6392.
- 8 J. Li, Q. Zhou, C. Zhong, S. Li, Z. Shen, J. Pu, J. Liu, Y. Zhou, H. Zhang and H. Ma,  $(\text{Co/Fe})_4\text{O}_4$  Cubane-Containing Nanorings Fabricated by Phosphorylating Cobalt Ferrite for Highly Efficient Oxygen Evolution Reaction, *ACS Catal.*, 2019, **9**, 3878-3887.
- 9 Y. Tong, X. Yu, H. Wang, B. Yao, C. Li and G. Shi, Trace Level Co-N Doped Graphite Foams as High-Performance Self-Standing Electrocatalytic Electrodes for Hydrogen and Oxygen Evolution, *ACS Catal.*, 2018, **8**, 4637-4644.
- 10 H. Li, Q. Li, P. Wen, T. B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D. L. Carroll, G. L. Donati, P. M. Lundin, Y. Qiu and S. M. Geyer, Colloidal Cobalt Phosphide Nanocrystals as Trifunctional Electrocatalysts for Overall Water Splitting Powered by a Zinc-Air Battery, *Adv. Mater.*, 2018, **30**, 1705796.
- 11 Y. Kou, J. Liu, Y. Li, S. Qu, C. Ma, Z. Song, X. Han, Y. Deng, W. Hu and C. Zhong, Electrochemical Oxidation of Chlorine-Doped  $\text{Co(OH)}_2$  Nanosheet Arrays on Carbon Cloth as a Bifunctional Oxygen Electrode, *ACS Appl. Mater. Interfaces*, 2018, **10**, 796-805.
- 12 M. Xie, L. Yang, Y. Ji, Z. Wang, X. Ren, Z. Liu, A. M. Asiri, X. Xiong and X. Sun, An amorphous Co-carbonate-hydroxide nanowire array for efficient and durable oxygen evolution reaction in carbonate electrolytes, *Nanoscale*, 2017, **9**, 16612-16615.
- 13 X. Huang, H. Zheng, G. Lu, P. Wang, L. Xing, J. Wang and G. Wang, Enhanced Water Splitting

Electrocatalysis over  $\text{MnCo}_2\text{O}_4$  via Introduction of Suitable Ce Content, *ACS Sustain. Chem. Eng.*, 2019, **7**, 1169-1177.

- 14 H. Zou, G. Li, L. Duan, Z. Kou and J. Wang, In situ coupled amorphous cobalt nitride with nitrogen-doped graphene aerogel as a trifunctional electrocatalyst towards Zn-air battery derived full water splitting, *Appl. Catal. B*, 2019, **259**, 118100.