

## Supporting Information

### **CoP nanoparticles embedded in three-dimensional porous network-like structured N, O co-doped carbon nanofibers as effective bi-functional electrocatalyst for rechargeable zinc-air batteries**

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## 1. The detailed process of preparing CoP@PCNFs

**(1) Synthesis of ZIF-67:** Firstly, dissolve 5.747 g of 2-methylimidazole in a beaker containing 20 mL of anhydrous ethanol to form **Solution A**. Then, dissolve 0.291 g of cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in a beaker containing 20 mL of anhydrous ethanol to form **Solution B**. When 2-methylimidazole and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are completely dissolved in anhydrous ethanol, slowly pour **Solution A** into **Solution B**. The solution turns purple rapidly and is stirred on a magnetic stirrer for 20 minutes to obtain a uniformly mixed purple solution. The solution was allowed to stand for about 24 hours at room temperature, washed by the centrifugation with deionized water and anhydrous ethanol three times, and finally dried in a vacuum oven at  $80^\circ\text{C}$  for 12 hours to obtain the dried purple ZIF-67. It was ground into powder using an agate mortar and pestle.

**(2) Preparation of spinning solution:** Firstly, small amounts of ground ZIF-67 purple powder (where the mass ratio of ZIF-67 to PVP 1,300,000 powder was 1:20, 2:20, 3:20, 4:20, 5:20, 6:20, 7:20, 8:20) were added to beakers containing 9 g of distilled water, and a uniform suspension was formed in the beakers under the dual action of a sonicator and a magnetic stirrer. After that, 2 g of PVP powder was added to the beaker, and 15 g of 60 wt.% PTFE emulsion was slowly added to the beaker again after the powder was completely dissolved. And after stirring for 4 h, the obtained homogeneous solution was left to stand for 2 h at room temperature.

**(3) Preparation of virgin composite fibers:** The spinning solution, which has been left to stand at room temperature, is injected into the spinning die of a self-assembled electrostatic blowing spinning (EBS) device. When the device is turned on, the spinning solution is drawn by the dual interaction of high-speed air and electrostatic energy, accompanied by the evaporation of the solvent, and finally the primary composite fiber can be obtained on the receiving device. The EBS device has a gas pressure of 0.1 MPa, a voltage of 40 kV and a fiber reception distance of 80 cm.

**(4) Pretreatment of cobalt-doped porous carbon precursors:** The pre-treated composite nanofibers can be obtained by placing the primary composite fibers in an

oven and heating to 250°C at a heating rate of 2°C min<sup>-1</sup> in an environment of air, with a holding time of 1 h.

**(5) Preparation of cobalt-doped porous carbon nanofibers (Co@PCNFs):** The pre-treated porous carbon fibers with a three-dimensional network structure were mounted in an alumina crucible, placed in the holding layer of an open vacuum/atmosphere tube furnace, and heated to 800°C, 900°C or 1000°C in an N<sub>2</sub> atmosphere. The heating procedure was carried out at a heating rate of 3°C min<sup>-1</sup> to 600°C, then at a heating rate of 2°C min<sup>-1</sup> to the desired temperature, and after a holding time of 1 h and cooling to room temperature. Finally the cobalt-doped porous carbon nanofibers (Co@PCNFs) can be obtained. The final carbonized obtained nanofibers were labeled as Co@PCNFs-X (where  $X = \frac{m_{\text{ZIF-67}}}{m_{\text{PVP}}} * 100\% = 5\%, 15\%, 25\%$  and 35%). As a comparison, the spinning solution without ZIF-67 powder was spun, pretreated and carbonized at the same temperature to obtain pure porous carbon nanofibers (PCNFs).

**(6) Phosphorization:** The obtained Co@PCNFs materials were loaded again with ZIF-67 on porous carbon by in-situ growth method, and after 24 h of standing, they were washed with anhydrous ethanol and dried. The dried carbon nanofibers and sodium hypophosphite monohydrate were placed in a tube furnace in the ratio of 1:10, where the phosphorus source was placed in a graphite crucible at the upwind of the open vacuum/atmosphere tube furnace, and the porous carbon material was placed in an alumina crucible at the downwind of the open vacuum/atmosphere tube furnace. The prepared cobalt-doped porous carbon nanofibers were phosphorylated in an atmosphere of Ar, firstly heated to 300 °C at a 2 °C min<sup>-1</sup> ramp rate, and finally heated to 750 °C at a 3 °C min<sup>-1</sup> ramp rate with a holding time of 2 h. The final phosphorylated cobalt-doped porous carbon nanofibers (CoP@PCNFs) can be obtained. The final phosphorylated obtained carbon nanofibers were labeled as CoP@PCNFs-X (where,  $X = \frac{m_{\text{ZIF-67}}}{m_{\text{PVP}}} * 100\% = 5\%, 10\%, 15\%, 20\%, 25\%, 30\%, 35\%$  and 40%).

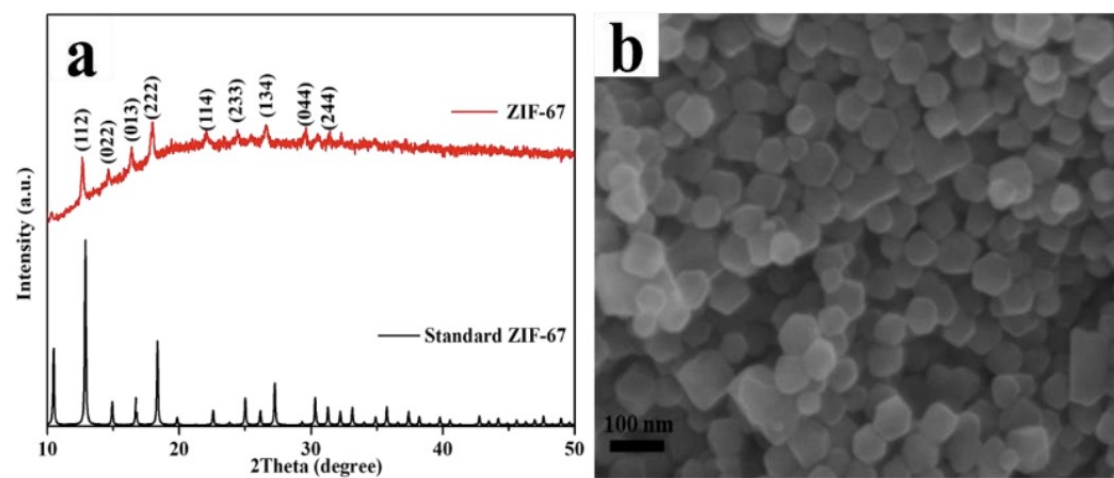
## 2. Preparation of working electrodes.

The electrochemical measurement system was performed on a CHI 760E

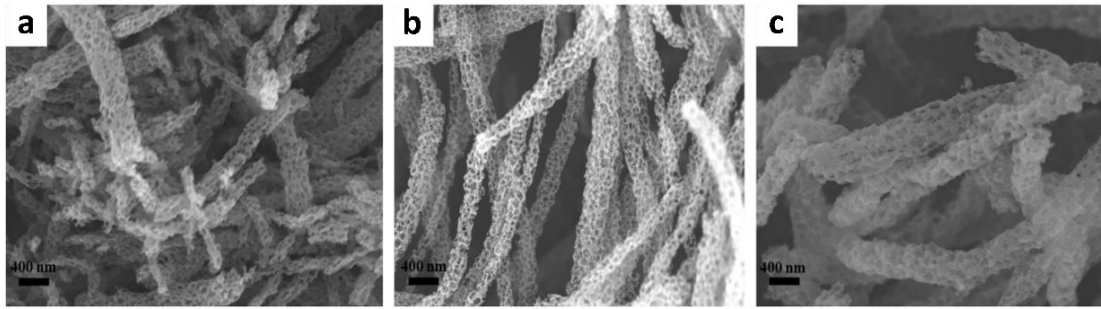
electrochemical workstation with a three-electrode configuration. The measurements were evaluated on a CHI 760E electrochemical workstation with a three-electrode configuration. Among them, the Hg/HgO (1 M KOH) electrode, the glassy carbon (GC) electrode (5 mm diameter) and graphite electrodes were used as reference, working and counter (or auxiliary) electrodes, respectively.

Before testing samples, the GC electrode was polished on a chamois with Al<sub>2</sub>O<sub>3</sub> polishing powder in an "8" pattern until the surface of the electrode was smooth as a mirror, and the cleaned with deionized water. And 4 mg of catalyst was dispersed in a mixture of 250 uL of distilled water, 250 uL of DMF and 50 uL of Nafion, and sonicated for 30 min using an ultrasonic cleaner to form a homogeneous catalyst dispersion. Next, 10 uL of catalyst dispersion was added to the GC electrode in two drops using a pipette gun and dried at room temperature. The preparation and coating process of commercial catalyst dispersions was similar to that described above.

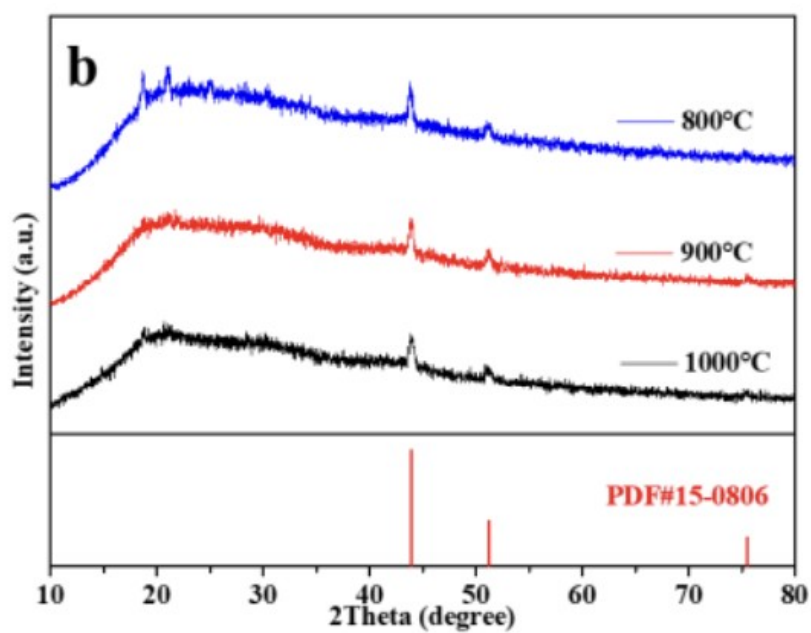
### 3. Supplementary Figures



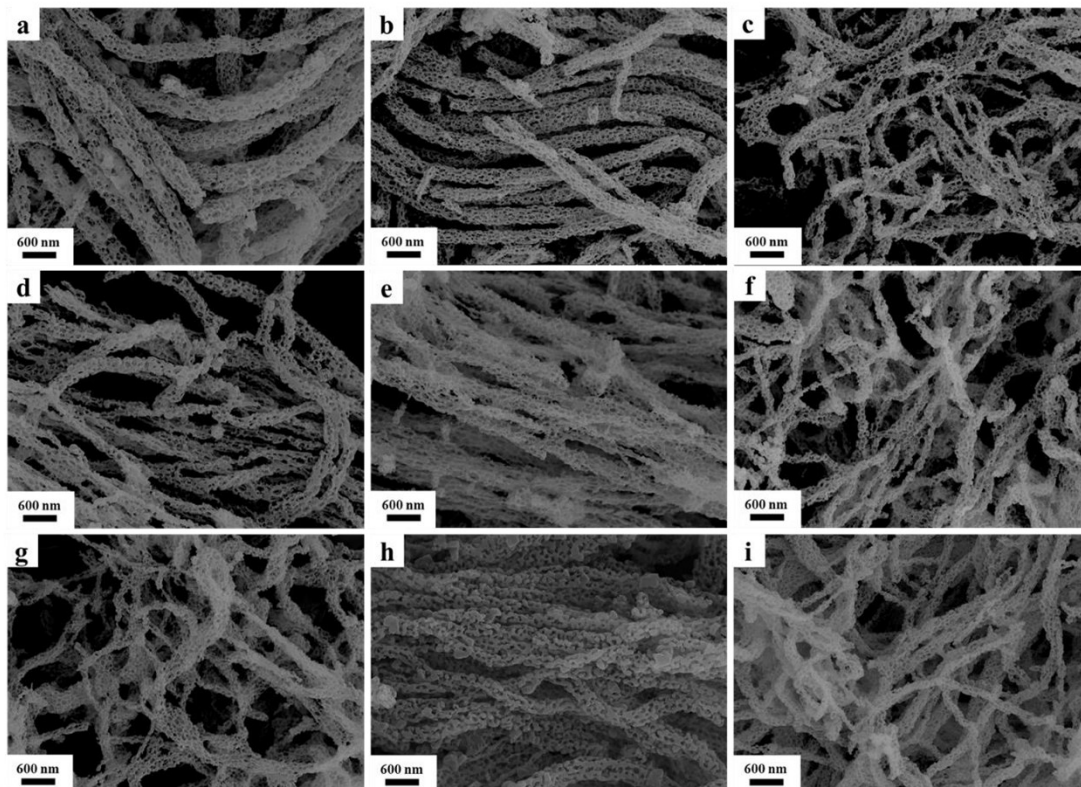
**Fig. S1 (a)** XRD of ZIF-67 synthesized in anhydrous ethanol; **(b)** SEM of ZIF-67 synthesized with anhydrous ethanol as solvent.



**Fig. S2 (a)** The SEM images of Co@PCNFs obtained by carbonization at 800°C; **(b)** The SEM images of Co@PCNFs obtained by carbonization at 900°C and **(c)** The SEM images of Co@PCNFs obtained by carbonization at 1000°C.

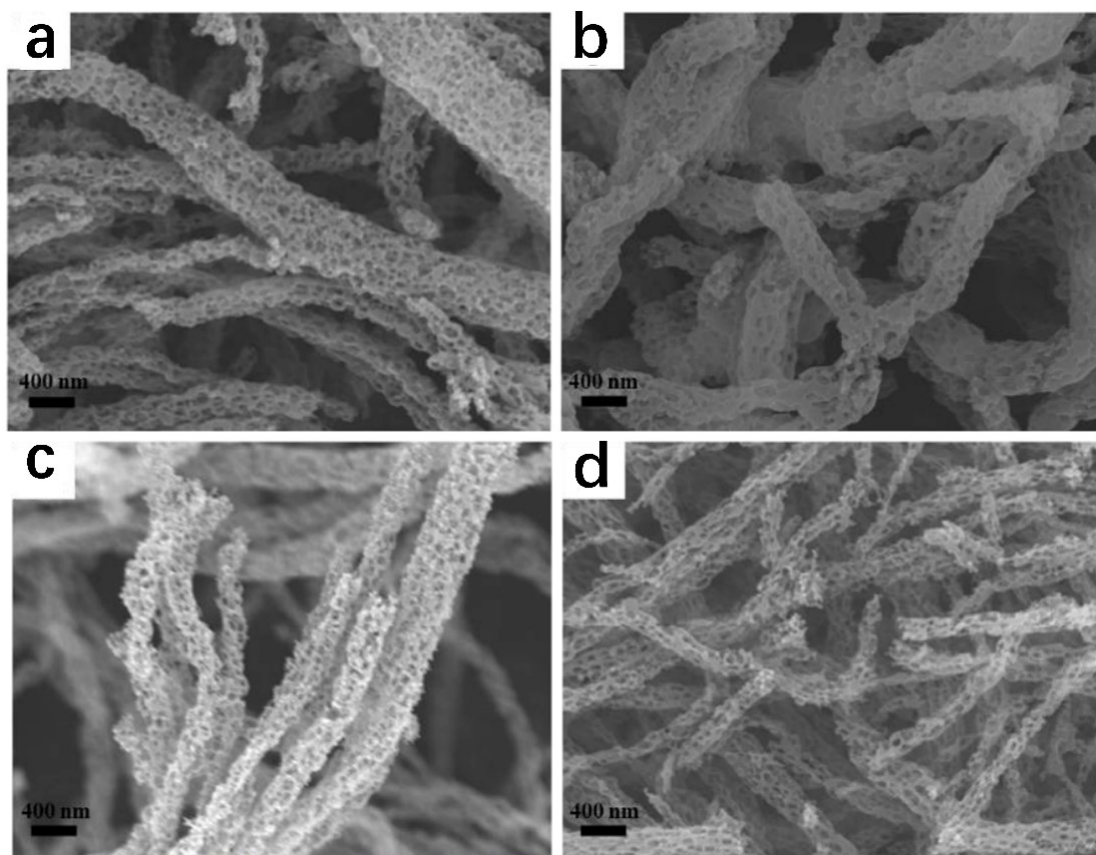


**Fig. S3** The XRD spectra of Co@PCNFs prepared at various carbonation temperatures .

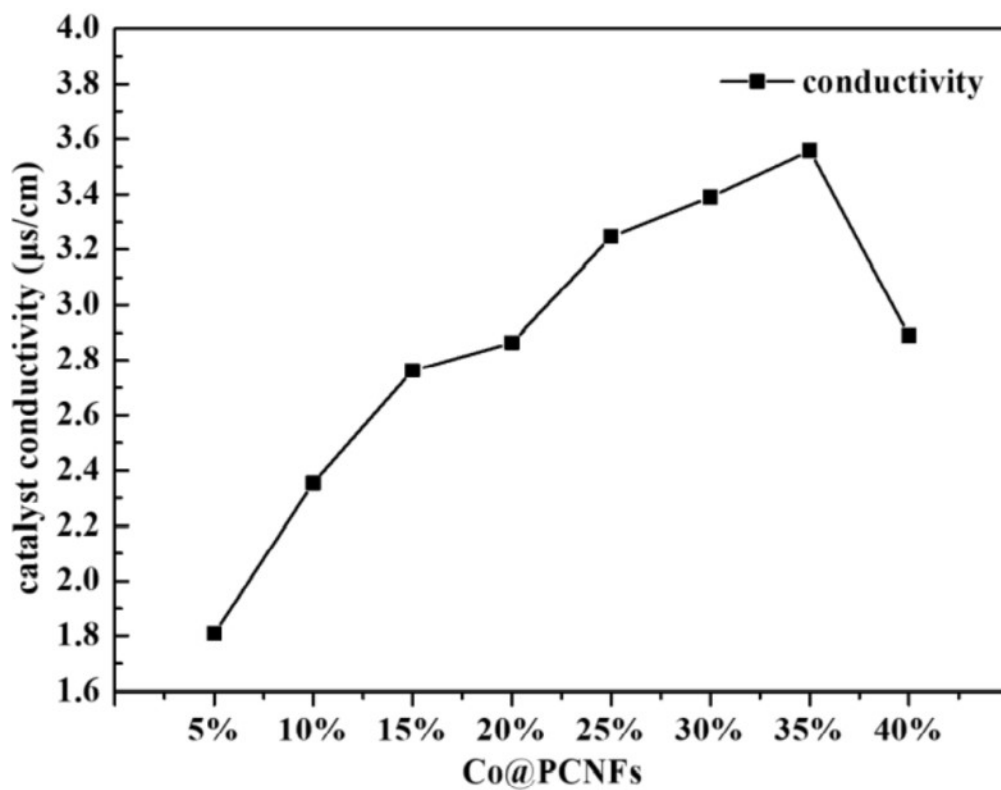


**Fig. S4** SEM images of the catalytic samples with different ratios of CoP@PCNFs. **(a)** CoP@PCNFs-5%; **(b)** CoP@PCNFs-10%; **(c)** CoP@PCNFs-15%; **(d)** CoP@PCNFs-20%; **(e)** CoP@PCNFs-25%; **(f)** CoP@PCNFs-30%; **(h)** CoP@PCNFs-35%; **(i)** CoP@PCNFs-40%.

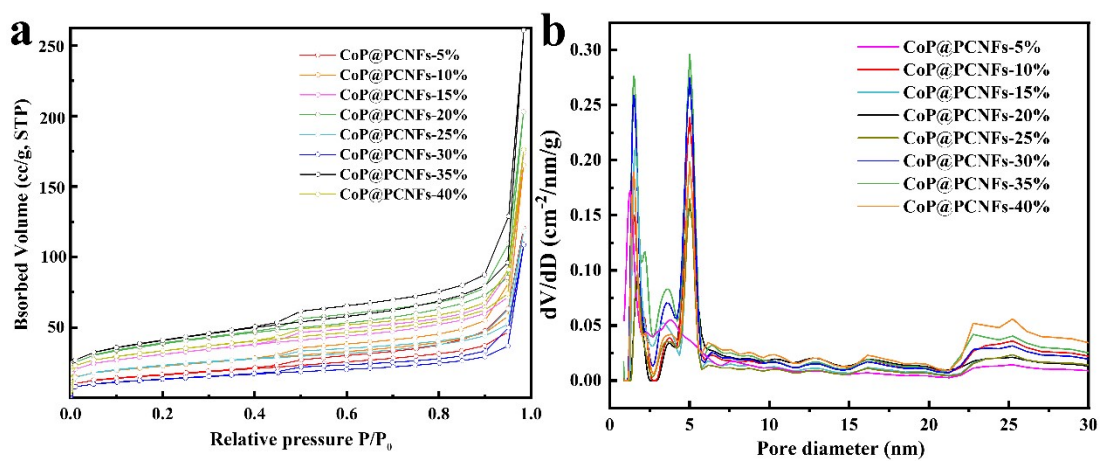




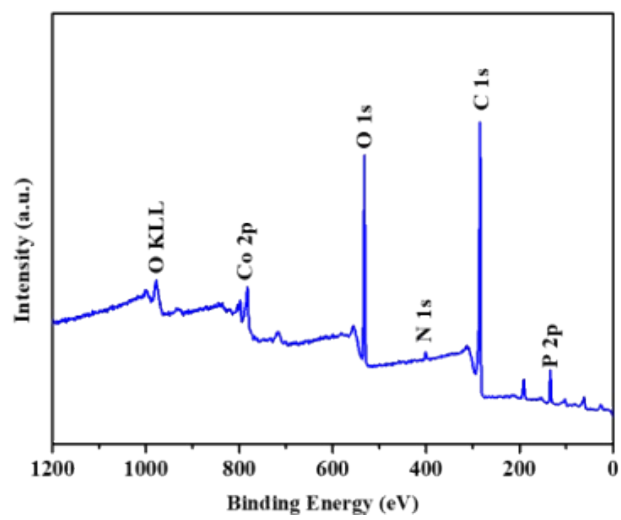
**Fig. S5** SEM images of different ZIF-67 doping amounts, where mass ratios of the ZIF67/PVP= (a) 1:20, (b) 3:20, (c) 5:20 and (d) 7:20.



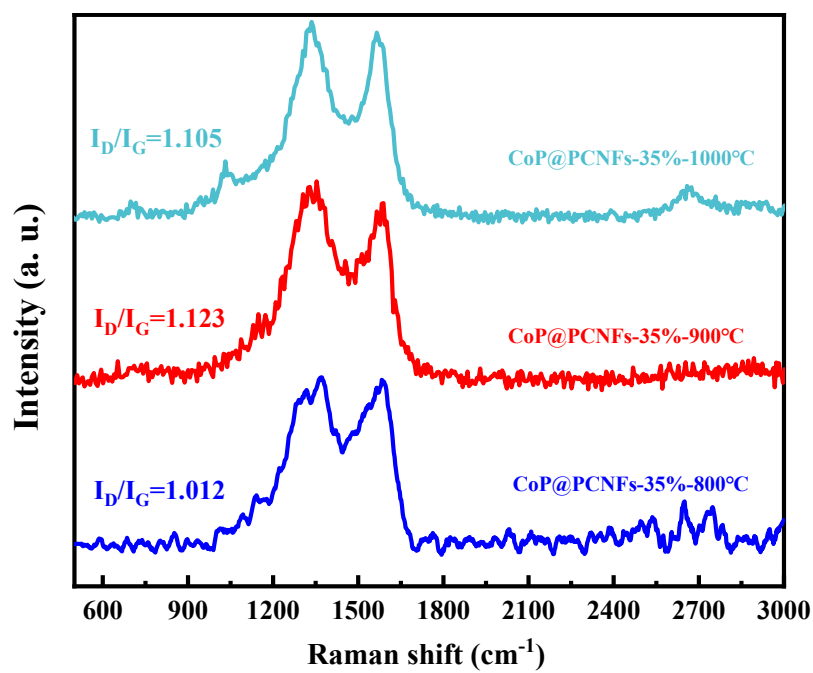
**Fig. S6** Conductivity of catalysts obtained by using the nanofibers doped with different proportions of ZIF-67 at 900°C.



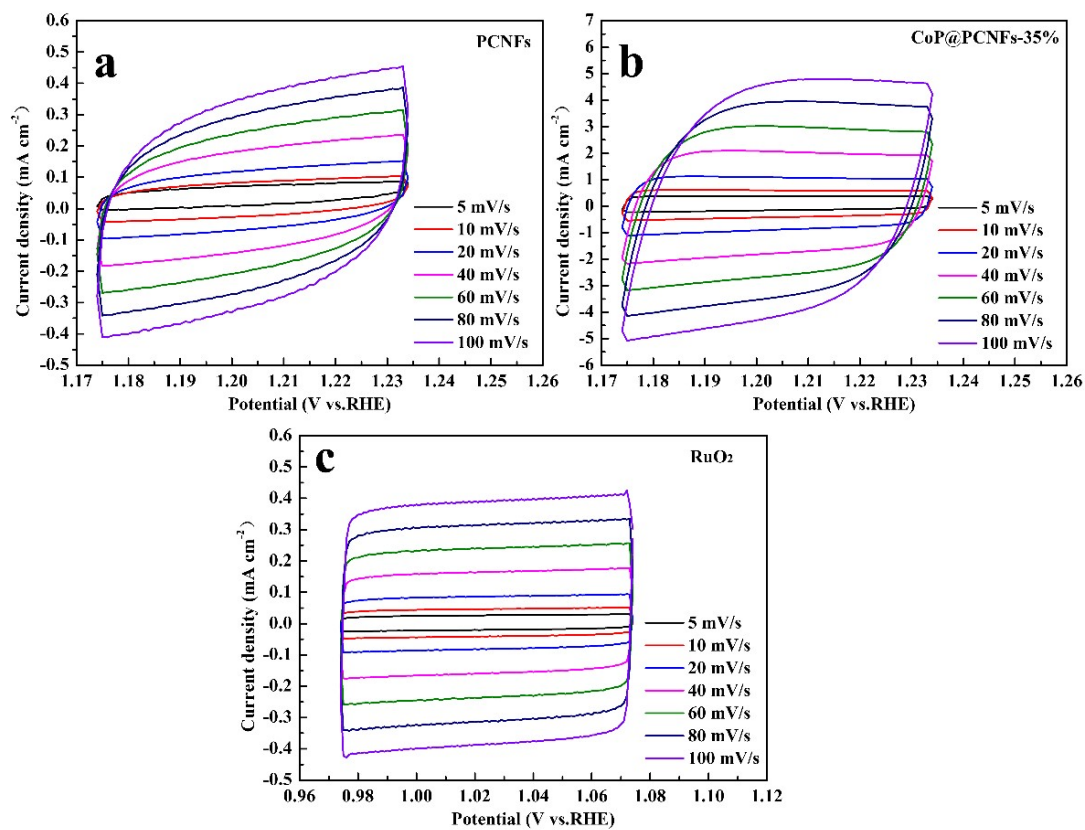
**Fig. S7 (a)** The N<sub>2</sub> adsorption-desorption isotherm curves and **(b)** pore size distribution maps of CoP@PCNFs with different doping levels.



**Fig. S8** The XPS full spectra of CoP@PCNFs.



**Fig. S9** Raman spectra of CoP@PCNFs-35% at different carbonization temperatures (800°C, 900°C and 1000°C).



**Fig. S10** (a) CV plots of PCNFs catalysts; (b) CV plots of CoP@PCNFs-35% catalysts; (c) CV plots of RuO<sub>2</sub> catalysts;

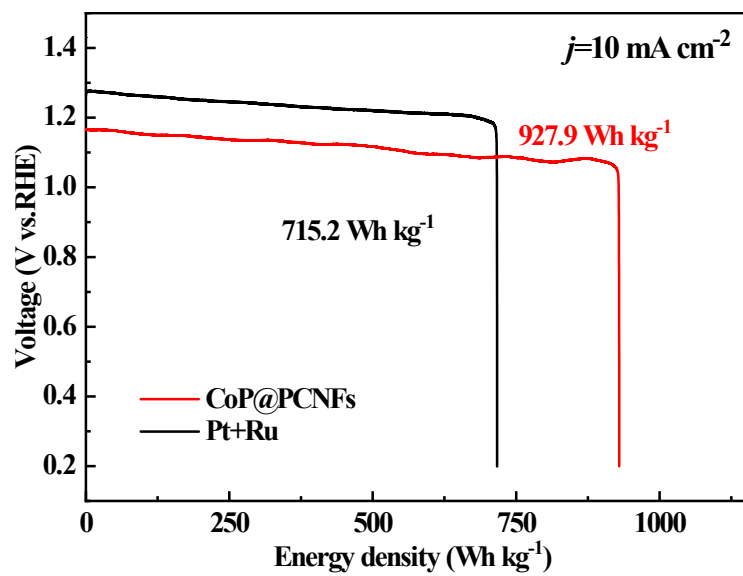


Fig. S11 energy density curves at a current density of 10 mA cm<sup>-2</sup> test.

**Table S1.** Specific surface area (SSA) based on BET testing

<b>Catalysts</b>	<b>SSA (m<sup>2</sup>/g)</b>
CoP@PCNFs-5%	68.526
CoP@PCNFs-15%	70.125
CoP@PCNFs-20%	72.384
CoP@PCNFs-25%	80.145
CoP@PCNFs-30%	86.149
<b>CoP@PCNFs-35%</b>	<b>94.430</b>
CoP@PCNFs-40%	90.367
PCNFs	572.558



**Table S2.** Compare the potential difference ( $\Delta E$ ) of CoP@PCNFs with the current mainstream CoP-based bifunctional electrocatalysts for ZABs.

Catalysts	References	$\Delta E$ (V vs. RHE)
CoP@PNC	S1	0.781
Bi-CoP/NP-DG	S2	0.790
N/P-C-CoP-850	S3	0.715
Co-Co <sub>2</sub> P@NC	S4	0.740
C <sub>3</sub> N <sub>4</sub> /Co (N/CNTs/Co)	S5	0.816
CoP/NC	S6	0.740
<b>CoP@PCNFs-35%</b>	<b>(This study)</b>	<b>0.670</b>

## Reference

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