A rationally designed bifunctional oxygen electrocatalyst based on Co_2P nanoparticles for Zn-air battery

Qing Shi[a,b], Yapeng Zheng[b], Weijun Li[b], Bin Tang[a], Lin Qin[*,a], Weiyou Yang[b], Qiao Liu[*,b]

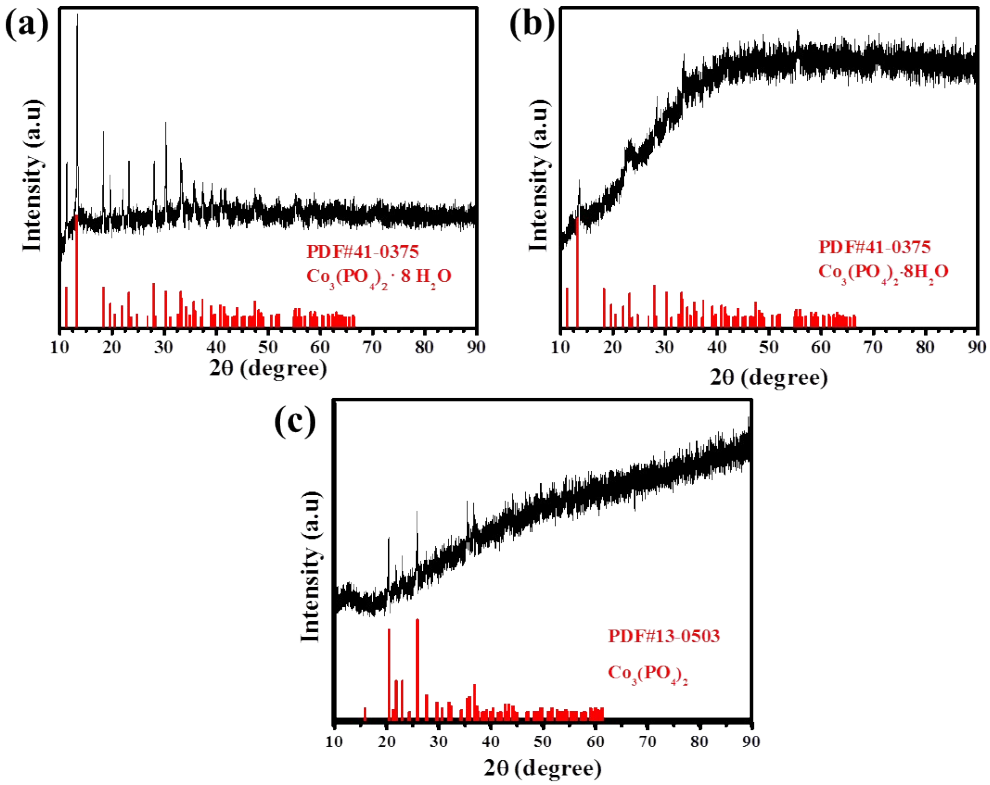

Fig. S1 Typical XRD patterns of intermediates: (a) $Co_3(PO_4)_2 \cdot 8H_2O$, (b) $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC, (c) $Co_3(PO_4)_2$.

The sample of $Co_3(PO_4)_2 \cdot 8H_2O$ was prepared via the following procedure: First, adding 25 mL of Na_2HPO_4 (0.4 M) solution into 300 mL of DI water, then 10 mL of $CoCl_2$ solution (24 mg mL^{-1}) was added into the above mixture that kept stirring for 12 h; finally, the solids were collected by centrifuging, washing and freeze-drying.

The sample of $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC is the precursor of Co_2P-NPC/CF, and the sample of $Co_3(PO_4)_2$ is product of pyrolysis $Co_3(PO_4)_2 \cdot 8H_2O$ under Ar atmosphere at 900 °C for 3 h.

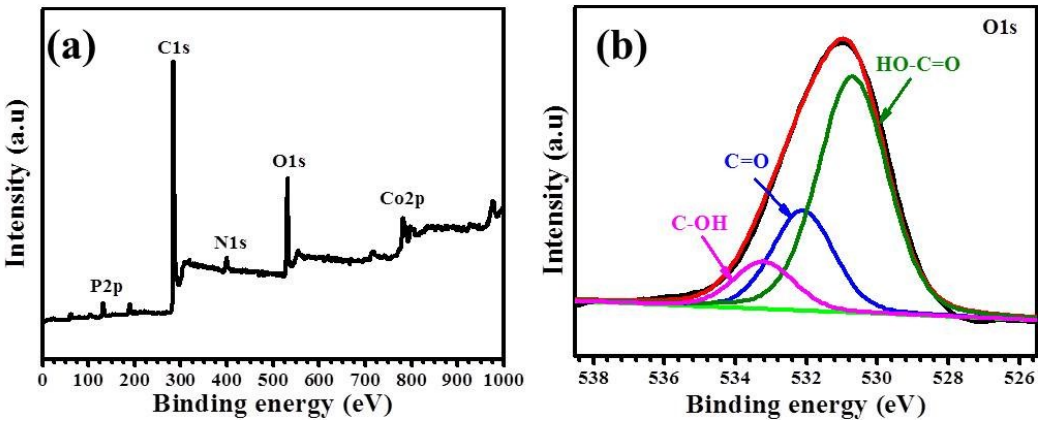

Fig. S2 (a) The XPS survey spectrum and (b) high-resolution O 1s spectrum of Co_2P-NPC/CF.

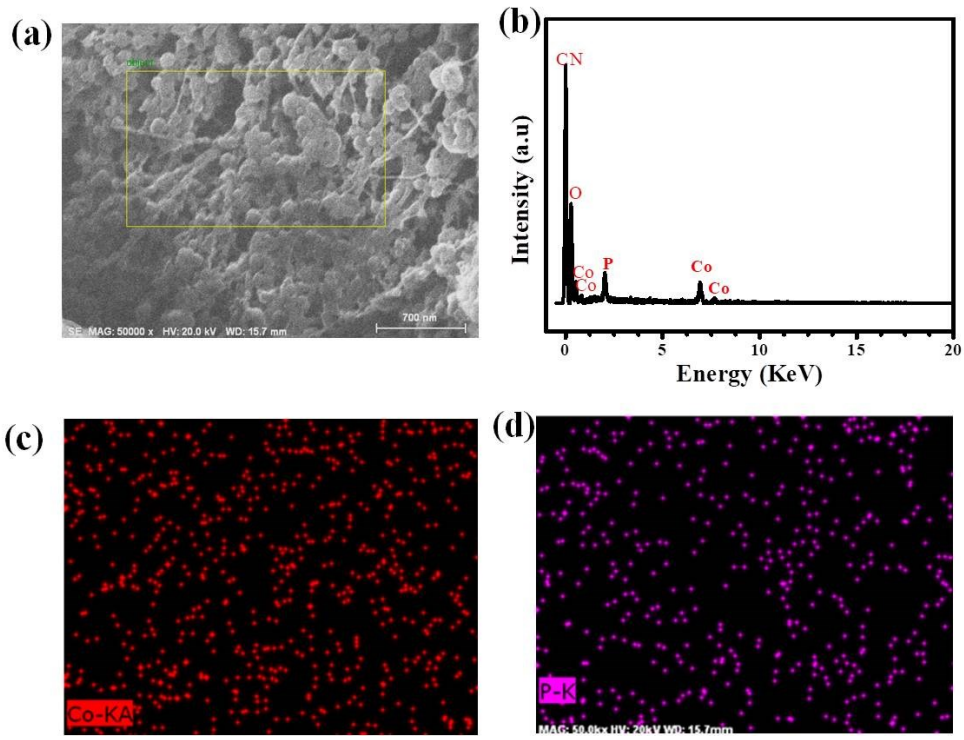

Figure S3 (a) SEM image and (b) EDS spectrum of $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC.

In order to probe the P source for the doping of resultant carbon, the sample of $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC was investigated by EDS test. If the phosphorus source for the doping of carbon comes from Na_2HPO_4, the $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC sample should contain a large number of adsorbed Na^+ and HPO_4^{2-} ions. In fact, before the pyrolysis transformation, $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC underwent the repetitive rinsing by deionized water, and the soluble species adsorbed in PDA/BC matrix can be completely removed. EDS spectrum shown in Figure S3b supports this assumption, where the Na^+ signal is absent, which suggests that the excessive Na_2HPO_4 has been washed away from $Co_3(PO_4)_2 \cdot 8H_2O$/PDA/BC.

To further determine whether there is residual HPO_4^{2-} absorbant, we have also carried out elemental mapping on this sample, as shown in Figure S3c-d, It is found that the elemental distribution of P is not more scattered but almost the same as that of Co, indicating that the main form of existed P atoms lies in $Co_3(PO_4)_2$ rather than

adsorbed HPO_4^{2-} ions on PDA and/or BC. Therefore, it can be concluded that the major contributor of P doping in carbon comes from phosphorus in $Co_3(PO_4)_2$.

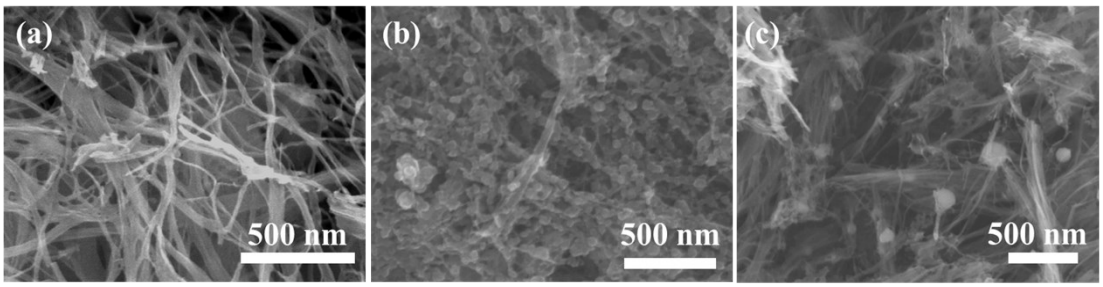

Fig. S4 The SEM images of as-fabricated materials: (a) CF, (b) NC/CF, and (c) Co_2P/CF.

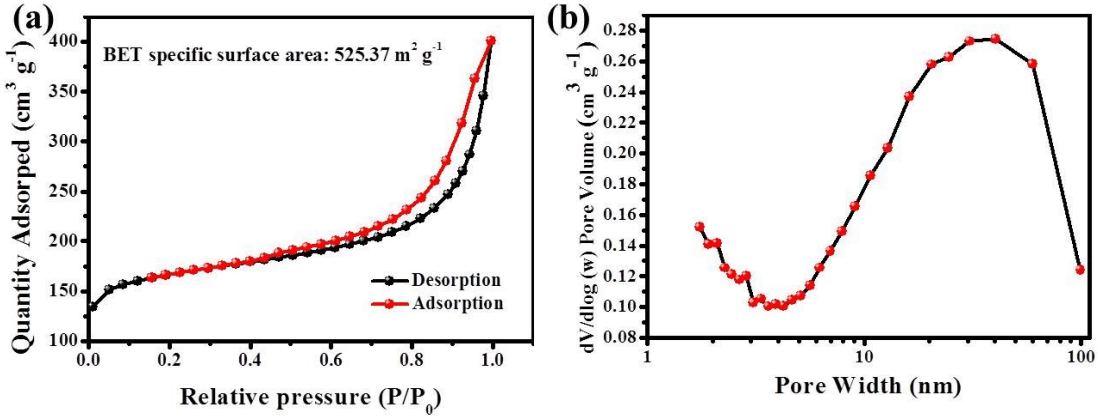

Fig. S5 (a) N_2 adsorption-desorption isotherm and (b) pore size distribution of Co_2P-NPC/CF.

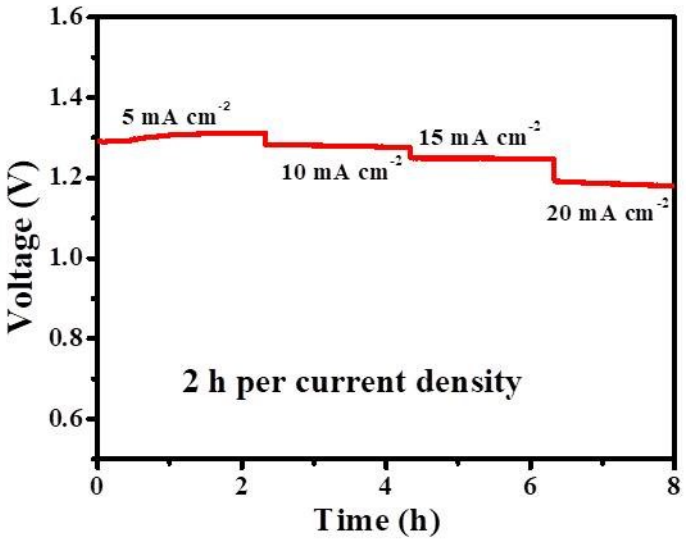

Fig. S6 Rate capability of Co_2P-NPC/CF

Table S1 The ORR performance of the as-fabricated materials and commercial Pt/C.

Catalysts	E_{onset} **(V)**	$E_{1/2}$ **(V)**	**Tafel slope (mV dec^{-1})**
CF	0.66	0.51	102
NC/CF	0.85	0.64	90
Co_2P/CF	0.78	0.70	88
Co_2P-NPC/CF	**0.94**	**0.85**	**52**
Pt/C	0.95	0.82	80

Table S2 Overview of bifunctional activity of recently reported Co-containing carbon electrocatalysts towards ORR and OER in 0.1 M KOH.

Catalysts	$E_{j=10}$ **(V vs. RHE)**	$E_{1/2}$ **(V vs. RHE)**	$\triangle E$ **(V)**	**Ref.**
Co_2P@CoNPG	1.73	0.81	0.92	1
NC@Co-NGC	1.64	0.82	0.82	2
CoNC@GF	1.66	0.87	0.79	3
Co_2P/CoN-in-NCNTs	1.65	0.85	0.80	4
CoPNi-N/C	1.63	0.81	0.79	5
CoFe/N-GCT	1.67	0.79	0.88	6
Co-NC@CoP-NC	1.56	0.78	0.78	7
CoNP@NC/NG	1.62	0.78	0.84	8
Co_2P@CNF	1.69	0.803	0.887	9
Cu-Co_2P@2D-NPC	1.57	0.835	0.735	10
Co_2P-NPC/CF	**1.59**	**0.85**	**0.75**	**This work**

Table S3 The OER performance of the as-fabricated materials and commercial RuO_2.

Catalysts	E_{j10} **(V)**	**Tafel slope (mV dec^{-1})**	R_{ct} **(Ω)**
CF	Not reach	110	183.7
NC/CF	1.69	99	96
Co_2P/CF	1.63	93	42.6
Co_2P-NPC/CF	**1.60**	**66**	**17.7**
RuO_2	1.62	83	23.4

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