Supporting Information

Uniform copper-cobalt phosphides embedded in N-doped carbon framework as efficient bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries

Hang Zhang,[a,c,d] Zhao Yang, [a,c,d] Xuemin Wang, [a,c,d] Sihao Yan, [a,c,d] Tianyou Zhou,[b] Cui Zhang,[*,a,c,d]

Shane G. Telfer,[*,b] and Shuangxi Liu[*, a,c,d]

a. *Institute of New Catalytic Materials Science, School of Materials Science and Engineering, Nankai University, Tianjin 300350, PR China. *E–mail: zhangcui@nankai.edu.cn; sliu@nankai.edu.cn*
b. *Institute of Fundamental Sciences, Massey University, Palmerston North 4442, New Zealand. *E–mail: S.Telfer@massey.ac.nz*
c. *National Institute of Advanced Materials, Nankai University, Tianjin 300350, PR China.*
d. *Tianjin Collaborative Innovation Center for Chemistry & Chemical Engineering, Tianjin 300072, PR China*

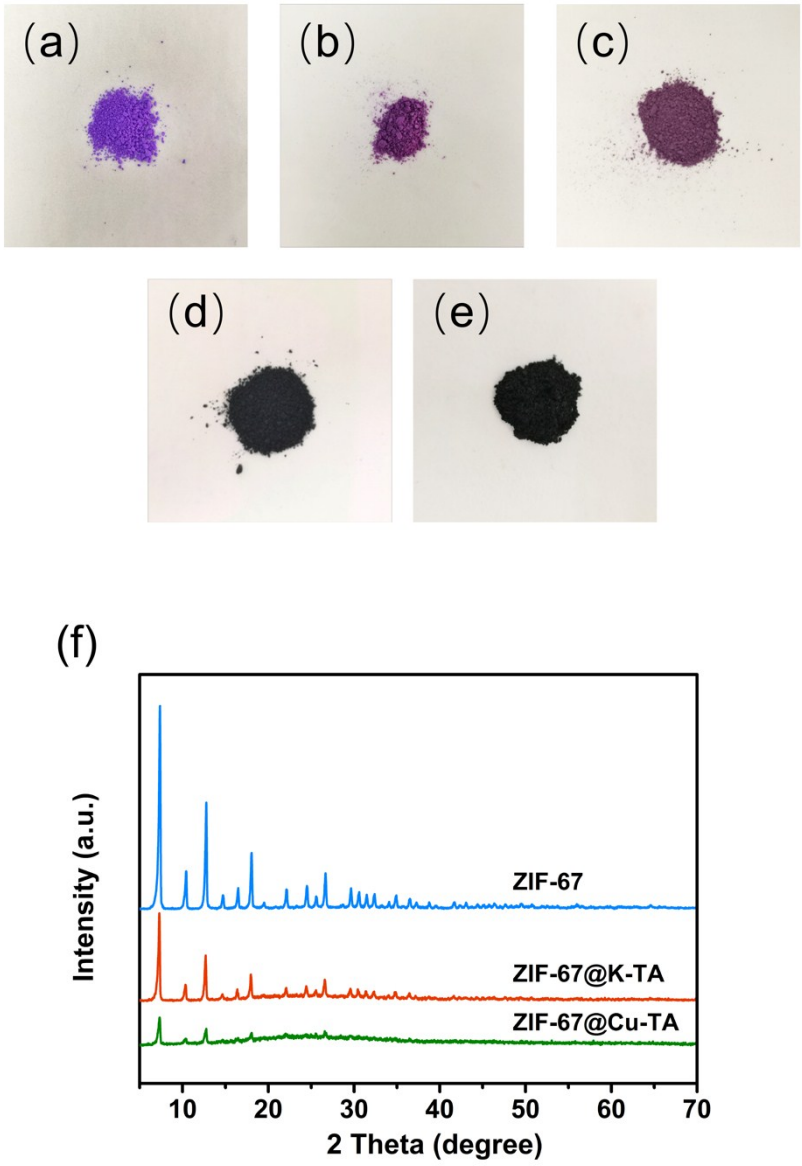

Fig. S1 The photographs of the (a) ZIF-67, (b) ZIF-67@K-TA, (c) ZIF-67@Cu-TA, (d) CuCo-NC-700 and (e) CuCoP-NC-700. (f) XRD patterns of the ZIF-67, ZIF-67@K-TA and ZIF-67@Cu-TA.

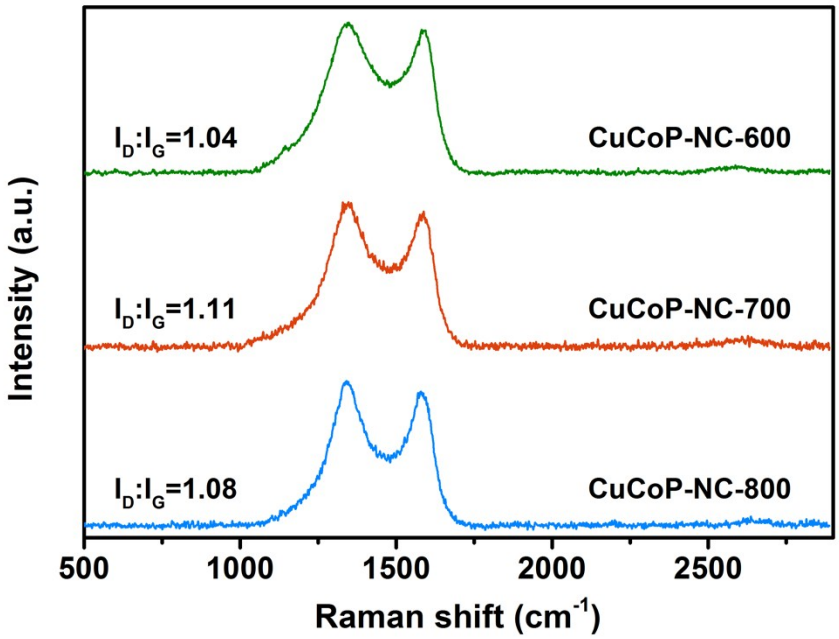

Fig. S2 Raman spectra of CuCoP-NC-X.

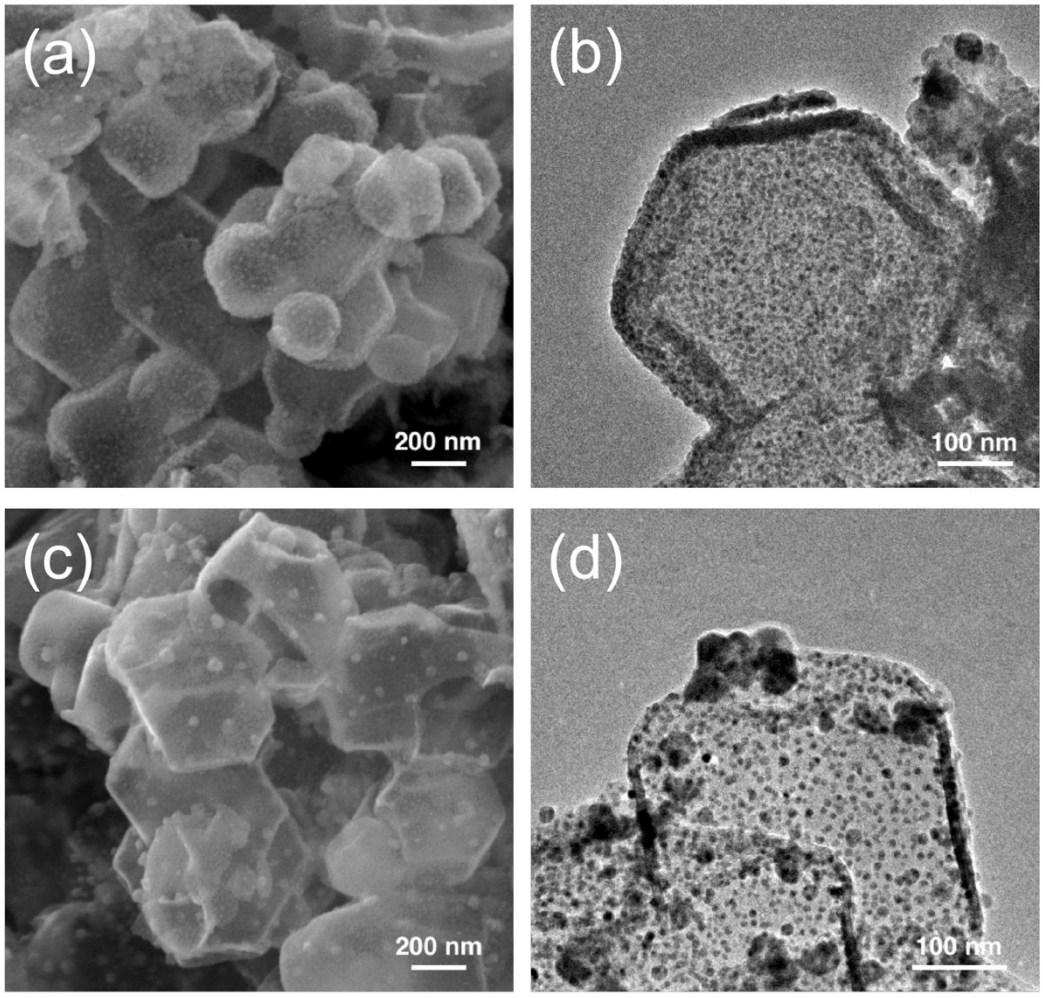

Fig. S3 SEM and TEM images of (a, b) CuCoP-NC-600 and (c, d) CuCoP-NC-800.

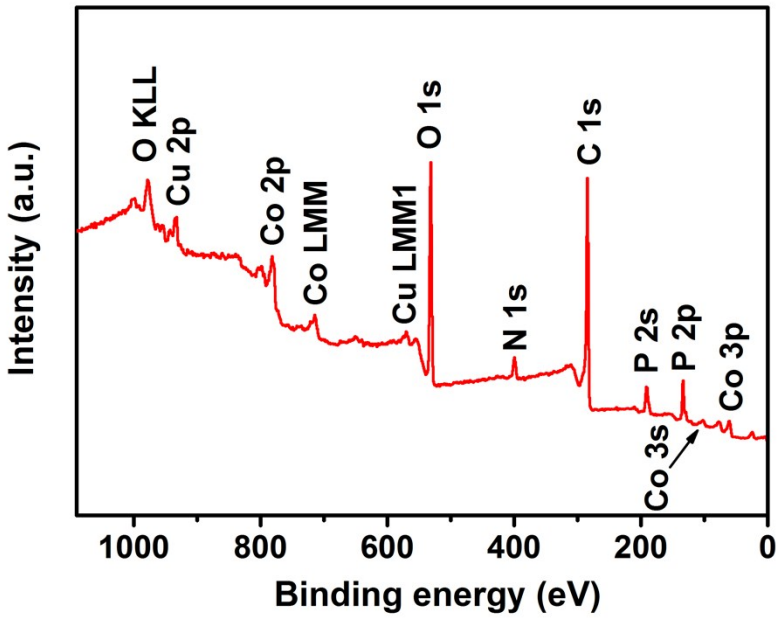

Fig. S4 Survey XPS spectrum of CuCoP-NC-700.

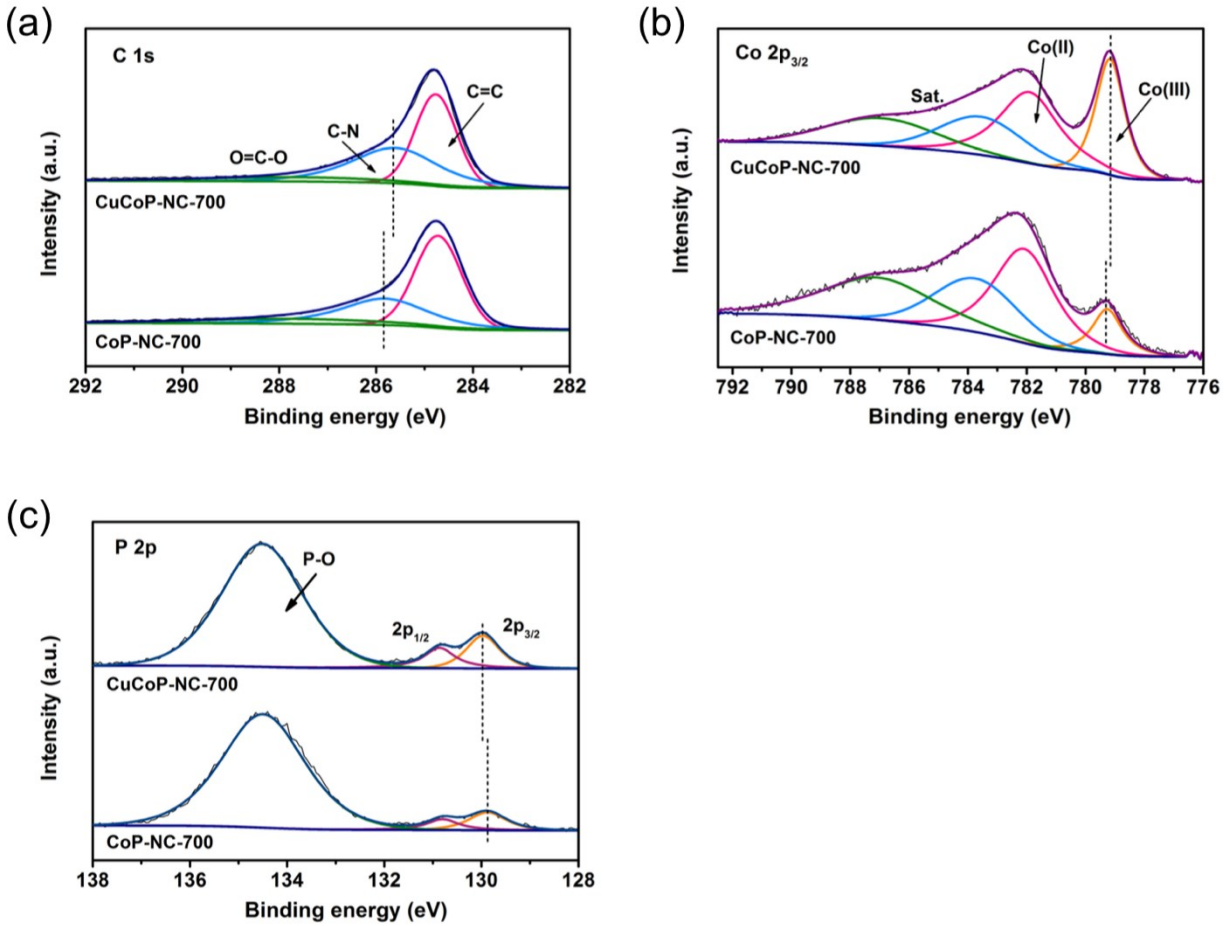

Fig. S5 XPS spectra of CuCoP-NC-700 and CoP-NC-700 for (a) C 1s, (b) Co $2p_{3/2}$ and (c) P 2p.

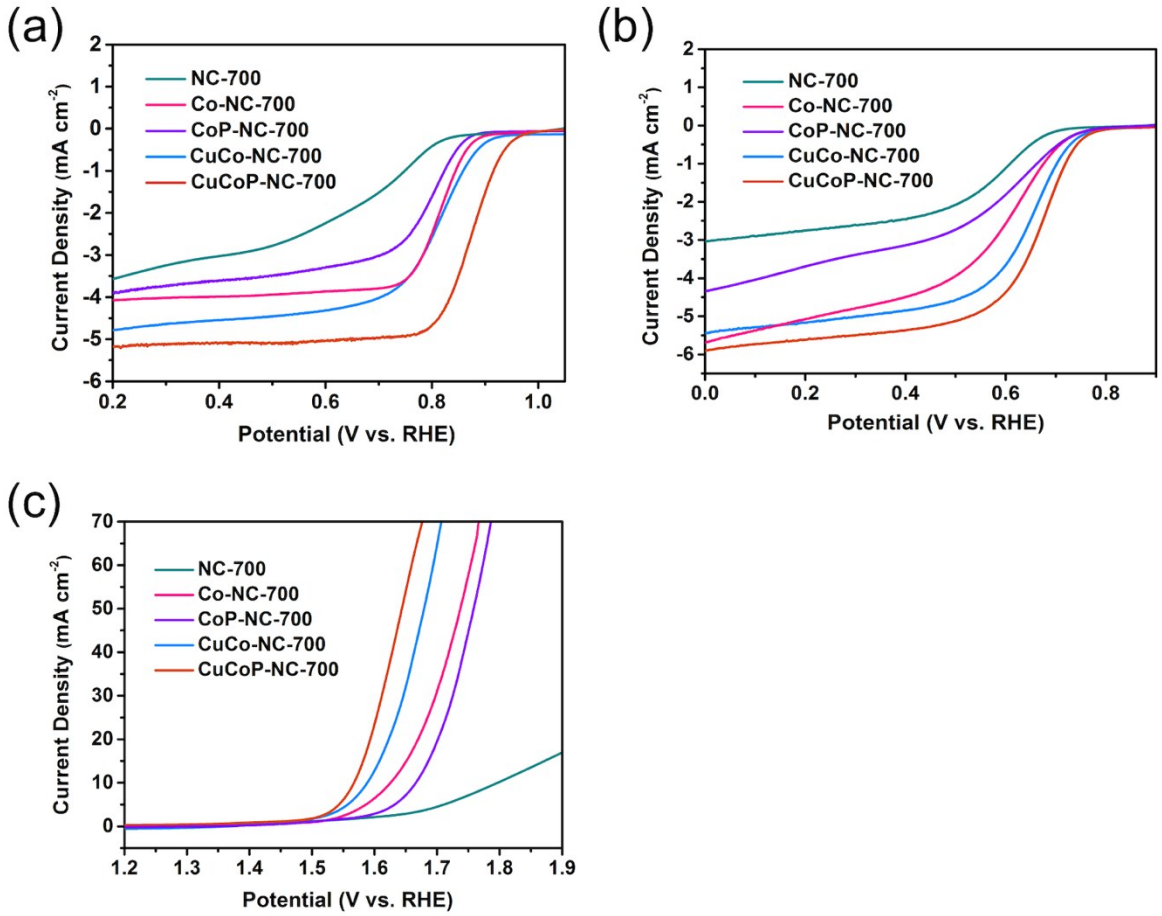

Fig. S6 LSV curves of NC-700, Co-NC-700, CoP-NC-700, CuCo-NC-700 and CuCoP-NC-700 at a scan rate of 10 mV s^{-1} and a rotating speed of 1600 rpm in O_2 saturated (a) 0.1 M KOH solution and (b) 0.5 M H_2SO_4 solution towards ORR. (c) LSV curves of NC-700, Co-NC-700, CoP-NC-700, CuCo-NC-700 and CuCoP-NC-700 at a scan rate of 10 mV s^{-1} in 1 M KOH solution towards OER.

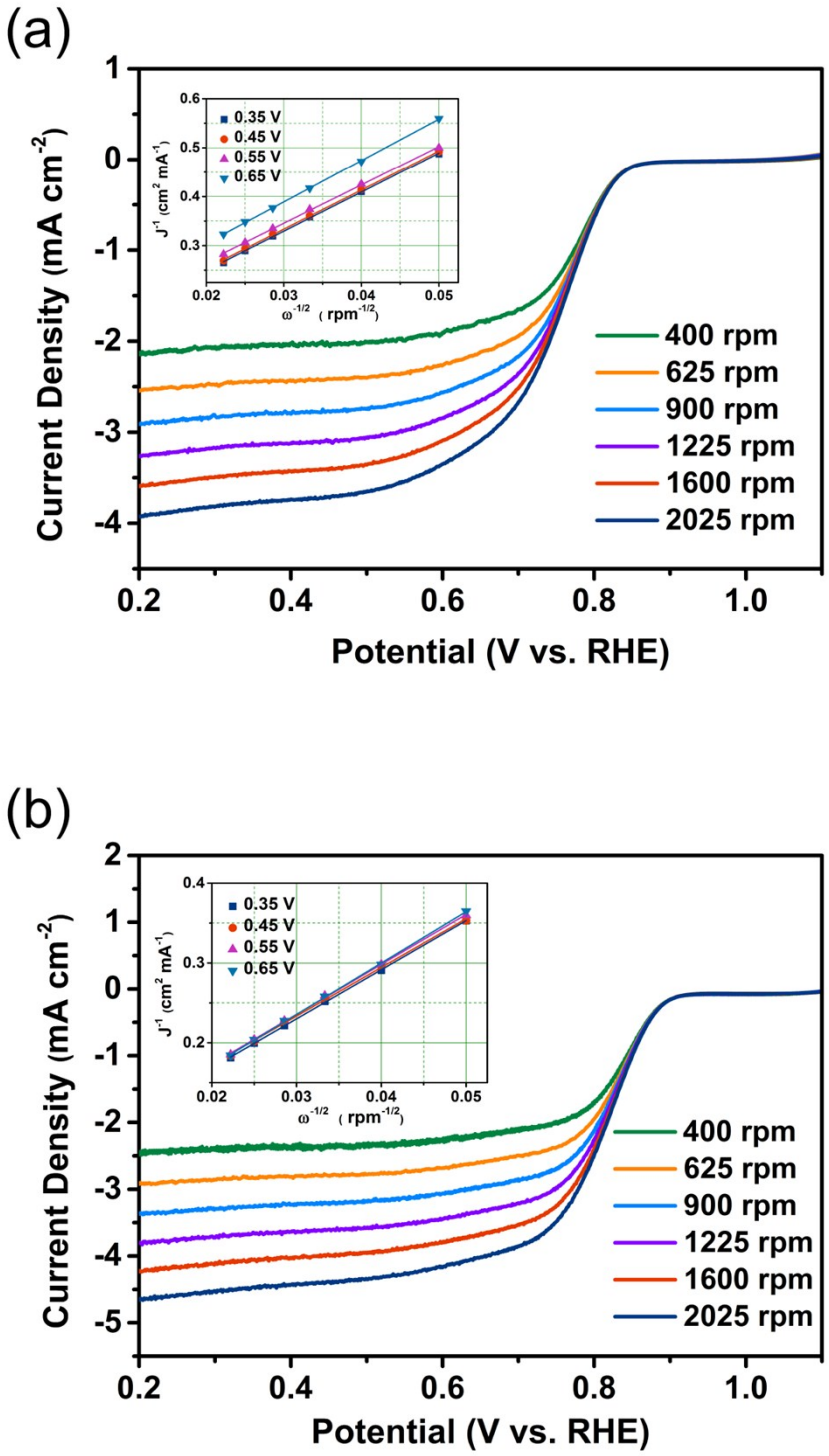

Fig. S7 LSV curves of (a) CuCoP-NC-600 and (b) CuCoP-NC-800 under different rpms ranging from 400 to 2025 rpm in O_2 saturated 0.1 M KOH solution and K-L plots of CuCoP-NC-600 and CuCoP-NC-800 at various potentials (inset).

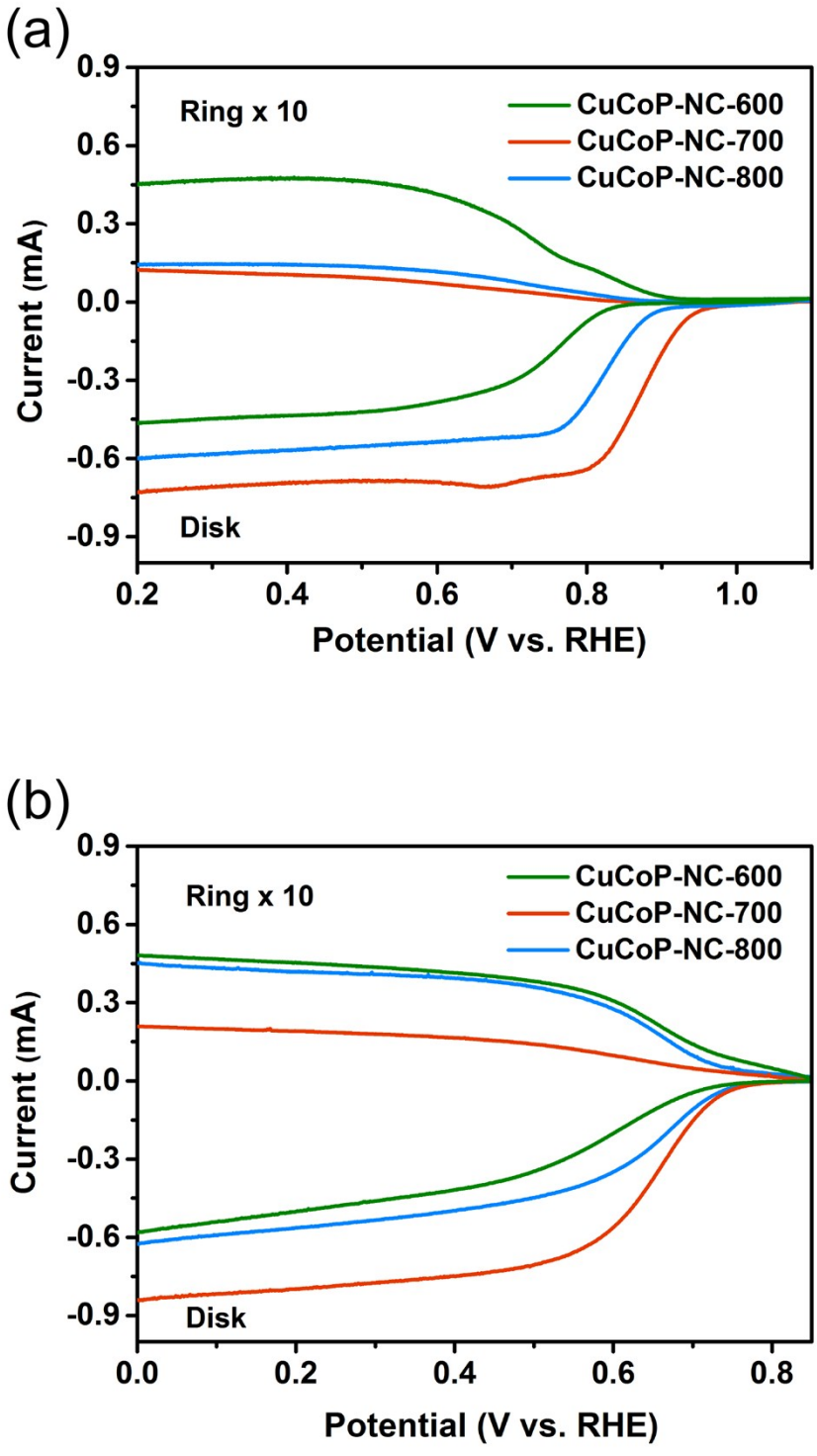

Fig. S8 RRDE voltammograms and amperometric responses were measured with a rotating speed of 1600 rpm and in O_2 saturated (a) 0.1 M KOH solution and (b) 0.5 M H_2SO_4 solution at a scan rate of 10 mV s^{-1} of CuCoP-NC-X.

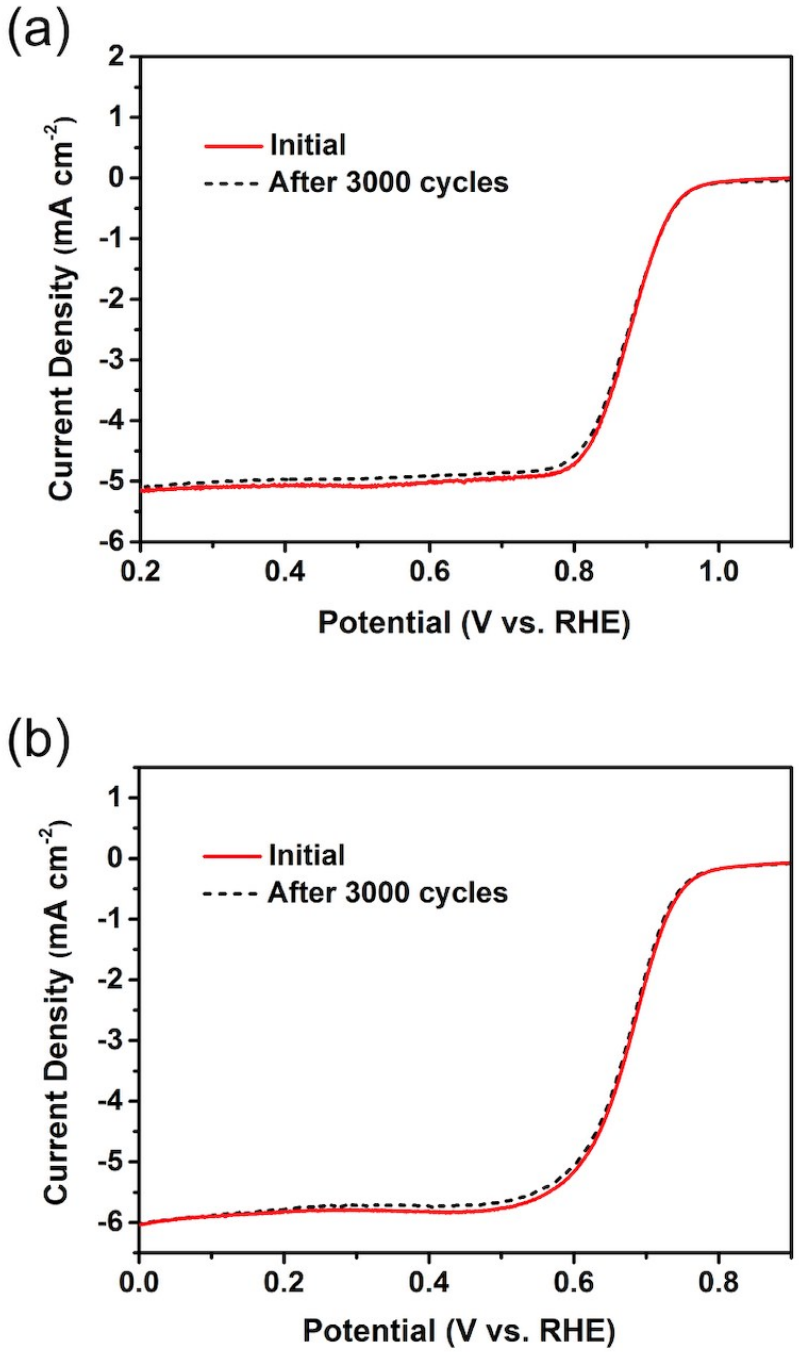

Fig. S9 LSV curves of CuCoP-NC-700 before and after 3000 cycles tests in O_2 saturated (a) 0.1 M KOH solution and (b) 0.5 M H_2SO_4 solution towards ORR durability evaluation.

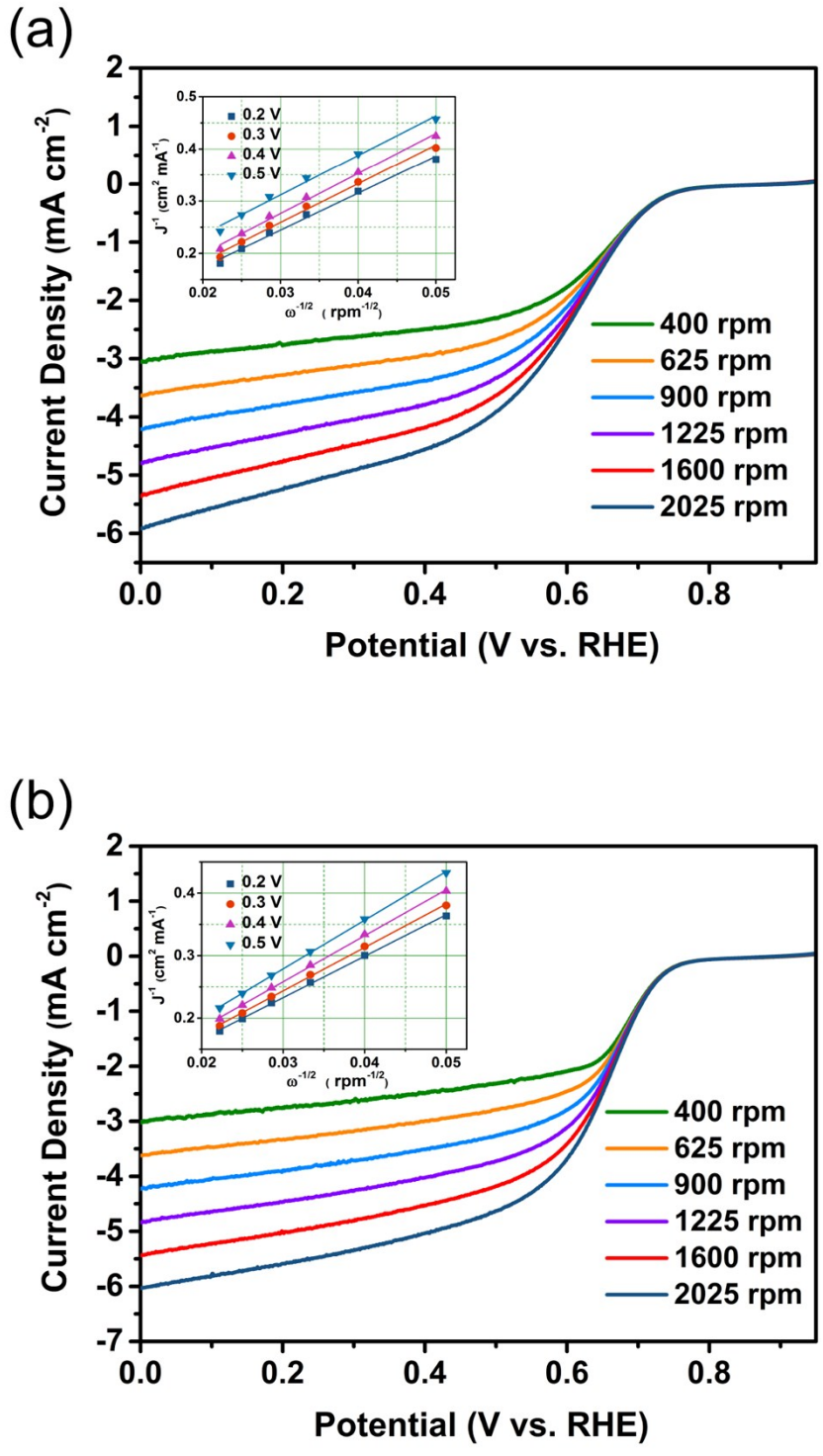

Fig. S10 LSV curves of (a) CuCoP-NC-600 and (b) CuCoP-NC-800 under different rpms ranging from 400 to 2025 rpm in O_2 saturated 0.5 M H_2SO_4 solution and K-L plots of CuCoP-NC-600 and CuCoP-NC-800 at various potentials (inset).

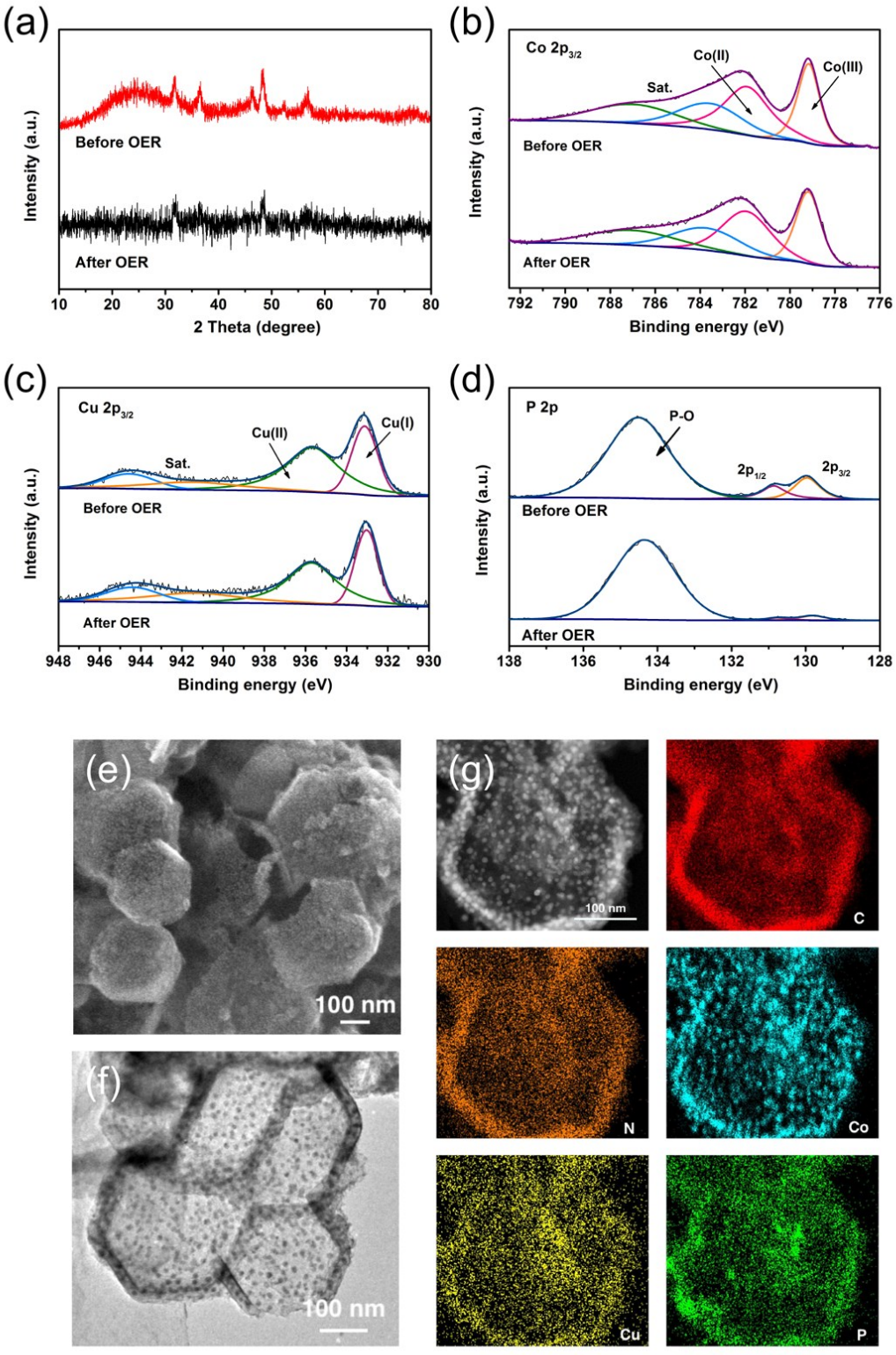

Fig. S11 (a) XRD patterns, XPS spectra for (b) Co $2p_{3/2}$, (c) Cu $2p_{3/2}$, and (d) P 2p of CuCoP-NC-700 before and after OER durability measurement. (e) SEM image, (f) TEM image and (g) elemental mapping images of CuCoP-NC-700 after OER durability measurement.

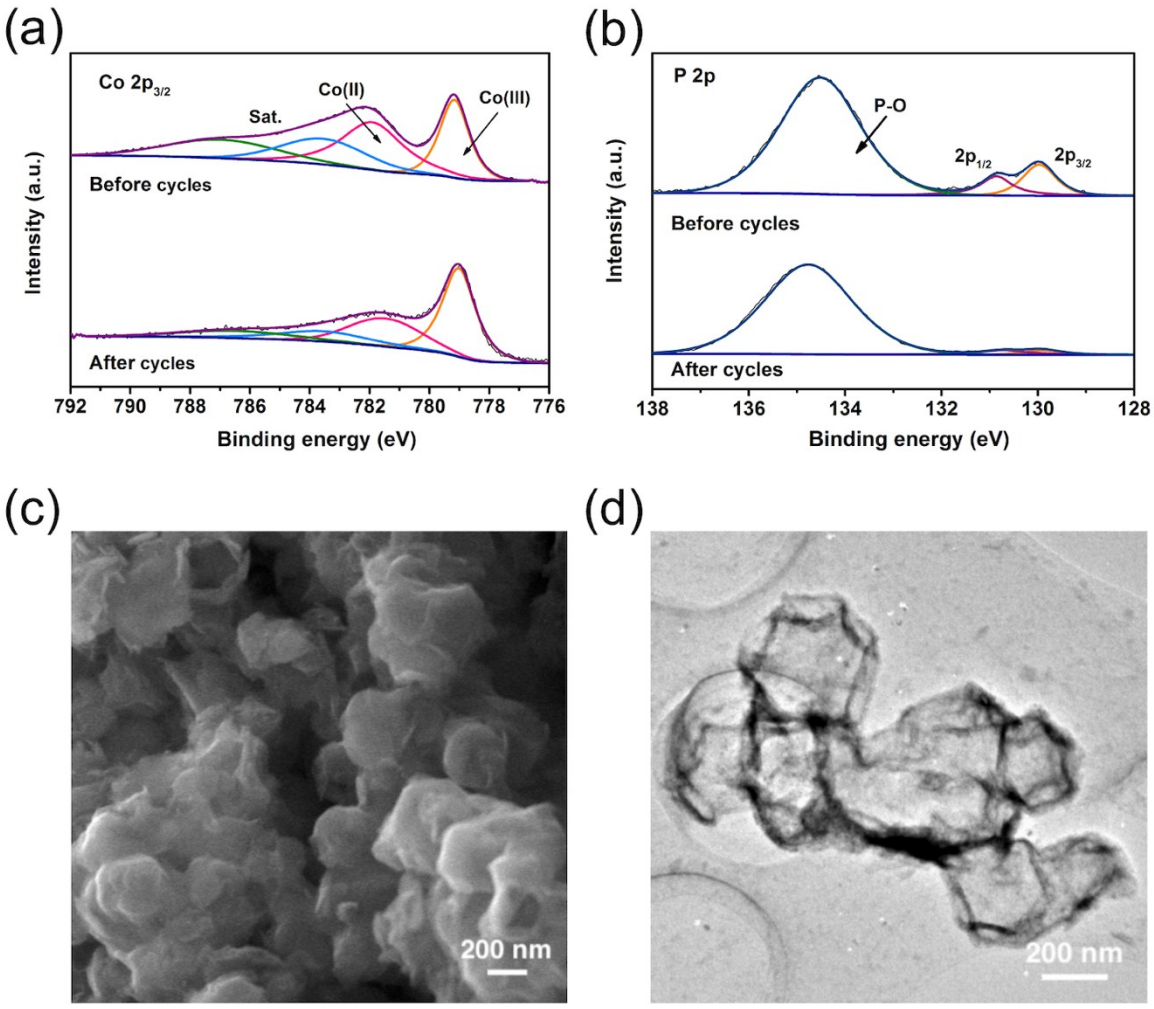

Fig. S12 XPS spectra for (a) Co $2p_{3/2}$ and (b) P 2p of CuCoP-NC-700 before and after charge-discharge cycles measurements of the Zn-air battery. (c) SEM image and (d) TEM image of CuCoP-NC-700 after charge-discharge cycles measurements of the Zn-air battery.

Table S1 ICP data and the atom ratios of Co/Cu of CuCoP-NC-X.

Sample	Co contents (mg L^{-1})	Cu contents (mg L^{-1})	Atom ratios of Co/Cu
CuCoP-NC-600	0.3586	0.0960	3.74/1
CuCoP-NC-700	0.5337	0.1467	3.64/1
CuCoP-NC-800	0.3670	0.1031	3.56/1

Table S2 The relative contents and ratios of Co and Cu species in CuCoP-NC-X by XPS spectra of Co $2p_{3/2}$ and Cu $2p_{3/2}$.

Sample	Relative contents (%)				Contents ratios	
	Co(III)	Co(II)	Cu(I)	Cu(II)	Co(III)/Co(II)	Cu(I)/Cu(II)
CuCoP-NC-600	9.5	24.1	16.6	47.8	0.39/1	0.35/1
CuCoP-NC-700	24.9	32.5	29.1	45.2	0.77/1	0.64/1
CuCoP-NC-800	21.7	34.0	41.4	40.7	0.64/1	1.02/1

Table S3 The relative contents (%) of pyridinic N, pyrrolic N and graphitic N in CuCoP-NC-X by XPS spectra of N1s.

Sample	Pyridinic N	Pyrrolic N	Graphitic N
CuCoP-NC-600	21.3	25.5	53.2
CuCoP-NC-700	35.7	18.2	46.1
CuCoP-NC-800	25.9	19.6	54.5

Table S4 The ORR electrocatalytic performance of non-precious metal materials in the recent literatures.

Materials	Electrolyte	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	References
CuCoP-NC-700	0.1 M KOH	0.978	0.872	**This work**
CuCoP-NC-700	0.5 M H_2SO_4	0.801	0.670	**This work**
CoOP@bio-C	0.1 M KOH	0.91	0.81	*J. Mater. Chem. A* **2018**, 3, 546
Co-BNCBNTs-900	0.1 M KOH	0.93	0.82	*J. Mater. Chem. A* **2018**, 6, 24071
CuCo@NC	0.1 M KOH	0.96	0.884	*Adv. Energy Mater.* **2018**, 7, 170019
Cu_3P@NPPC-650	0.1 M KOH	/	0.78	*Adv. Mater.* **2017**, 29, 1703711
Fe/Co-N/S-Cs	0.1 M KOH	/	0.832	*Appl. Catal B-Environ* **2019**, 241, 95
N-NC@G-900	0.1 M KOH	1.0	0.85	*Angew. Chem. Int. Ed.* **2018**, 130, 16749
N-NC@G-900	0.5 M H_2SO_4	0.80	0.65	*Angew. Chem. Int. Ed.* **2018**, 130, 16749
CoP-DC	0.1 M KOH	/	0.81	*Adv. Energy Mater.* **2018**, 8, 1703623

Table S5 The OER electrocatalytic performance of non-precious metal materials in the recent literatures.

Materials	Electrolyte	Overpotential at 10 mA cm^{-2} (mV)	References
CuCoP-NC-700	1 M KOH	338	**This work**
Fe_1Co_1-P/C	1 M KOH	362	*Small methods* **2018,** 353, 1800214
15% PANI/ZIF-67	0.1 M KOH	330	*Carbon* **2018**, 132, 580
Cu@CuO-C	1 M KOH	340	*J. Mater. Chem. A* **2018**, 6, 19176
NGO/Ni_7S_6	0.1 M KOH	380	*Adv. Funct. Mater.* **2017**, 27, 1700451
NC@Co-NGC DSNC	0.1 M KOH	410	*Adv Mater.* **2017**, 11, 1700874
$MnCo_2O_4$	0.1 M KOH	400	*Angew. Chem. Int. Ed.* **2017**, 27, 6834
Mn_3Co_7 – $Co_2Mn_3O_8$@CNTs/CNFs-1000	1 M KOH	374	*Energy Environ. Sci* .**2017**, 10, 321
CoP_3 CPs	1 M KOH	343	*Phys. Chem. Chem.Phys.* **2017***,* 19, 2104

Table S6 The performance of Zn-air batteries of non-precious metal materials in the recent literatures.

Materials	Open-circuit voltage (V)	Power density (mW cm^{-2})	Durability@ J (mA cm^{-2})	References
CuCoP-NC-700	1.51	116.5	Cycle time over 80h@10	**This work**
$Mn_{0.9}Fe_{2.1}C$/NC	1.5	160	Cycle number over 1000@5	*ACS Appl. Energy Mater.* **2019**, 2, 1747
Co_4N@NC-m	1.49	98.6	Cycle number over 200@10	*Carbon* **2019**, 151, 10
Co-NiO	1.446	93	Cycle time over 100h@2	*Appl. Catal B-Environ* **2019**, 250, 71
Co-POC	/	78.0	Cycle time over 25h@2	*Adv. Mater.* **2019**, 31, 1900592
Co@SNHC	1.48	105.8	Cycle time over 70h@5	*J. Mater. Chem. A* **2019**, 7, 14291
Ag-MnO_2	/	273.2	Cycle number over 3200@10	*Chemical Engineering Journal* **2019**, 366, 631
Cu-Fe-N-C	1.48	92	/	*Adv. Funct. Mater.* **2018**, 28, 1802596
Cu_3P@NPPC-650	1.46	110.8	Cycle time over 35h@5	*Adv. Mater.* **2017**, 29, 1703711