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Electronic Supplementary Information

In situ directional formation of Co@CoO_x-embedded 1D carbon nanotubes as an efficient oxygen electrocatalyst for ultra-high rate Zn–air batteries

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Calculation details for electron transfer number, peroxide yield and thickness of EDL

For the RDE tests, the polarization curves were collected at disk rotation rates of 400, 900, 1225, 1600 and 2025 rpm. For the calculation of the electrons transfer number (n), we analyzed the kinetic parameters based on the Koutecky-Levich equations:

$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\varpi^{1/2}}+\frac{1}{J_K}$$

$$B=0.62nFC_0(D_o)^{2/3}\nu^{-1/6}$$

where J is the measured current density, J_L and J_k are the diffusion-limiting current density and kinetic current density. ω is the angular velocity, F is the Faraday constant (96500 C/mol), C_o is the bulk concentration of O_2 (1.2×10^{-6} mol/cm^3), D_o is the diffusion coefficient of O_2 in 0.1M KOH solution (1.9×10^{-5} cm^2/s), ν is the kinematic viscosity of the electrolyte (0.01 cm^2/s) and k is the electron transfer rate constant.

For the Tafel plot, the kinetic current was calculated as follows:

$$J_K = \frac{J_L \times J}{J_L - J}$$

For the RRDE tests, the polarization curves were collected at disk rotation rates of 1600 rpm. The electron transfer number (n) and the peroxide yield (HO_2^-%) was calculated as follows:

$$\text{n} = 4 \times \frac{I_d}{I_d + I_r / N}$$

$$HO_2^- \% = 200 \times \frac{I_r / N}{I_d + I_r / N} \%$$

The I_d and I_r are disk current and ring current in RRDE test. The N is the collecting efficiency (0.37).

The thickness of the EDL (i.e. Debye length) was calculated as follows:

$$\kappa^{-1} = \frac{1}{3.29 \times 10^7 \times C^{*1/2}}$$

where C* is the bulk electrolyte concentration in mol L^{-1} and κ^{-1} is given in cm.

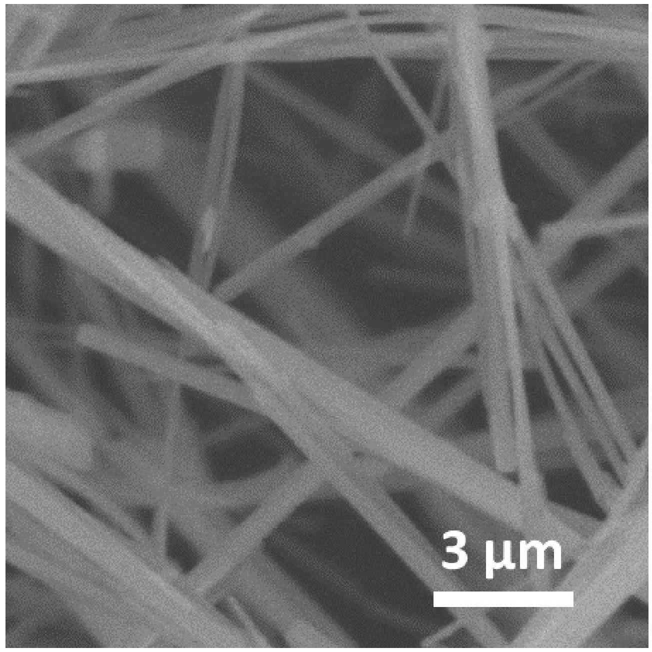

Figure S1. (a) SEM image of ZnO NWs.

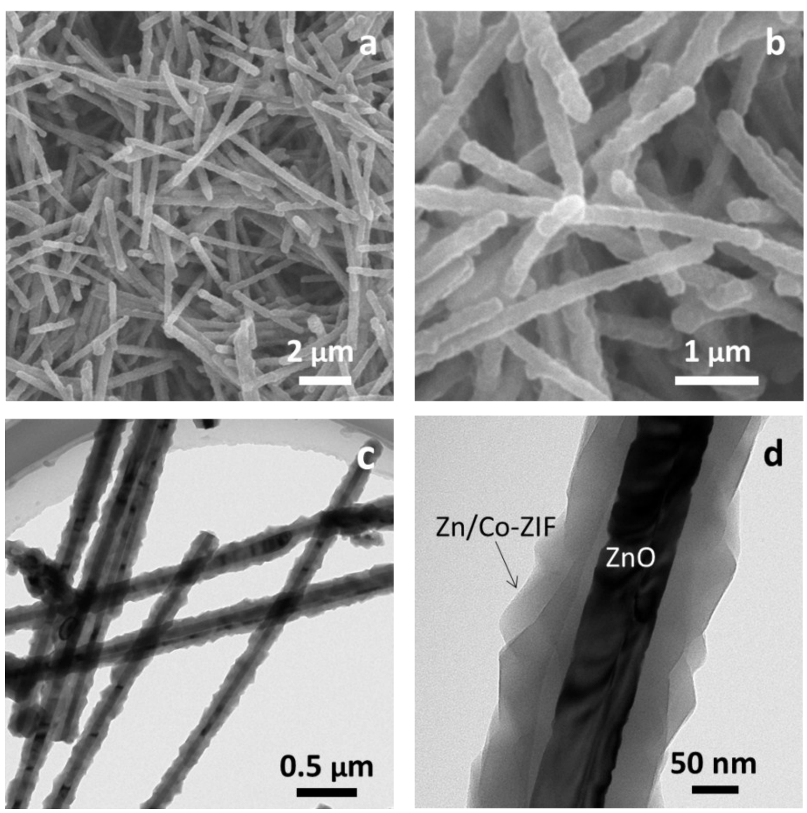

Figure S2. SEM (a, b) and TEM (c, d) images of ZnONWs@Zn/Co-ZIF.

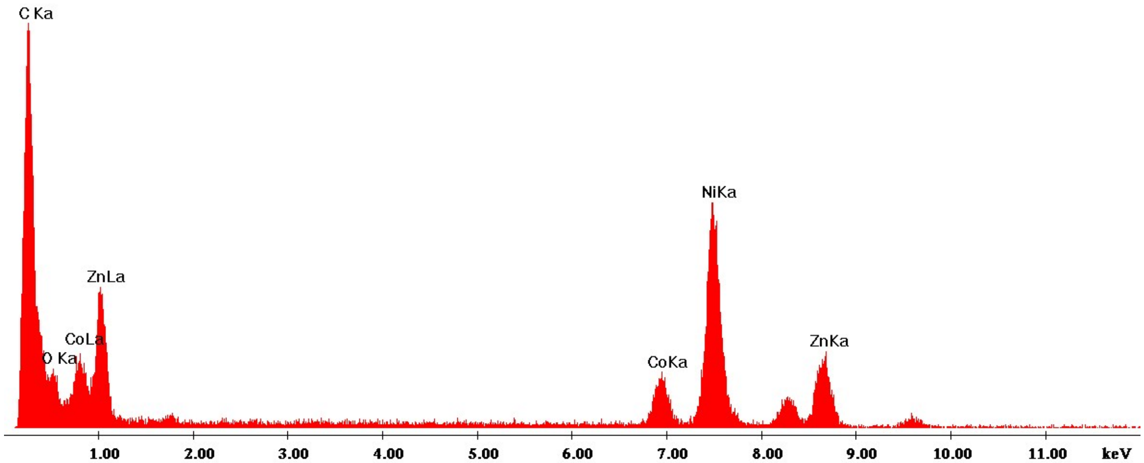

Figure S3. EDS data of ZnONWs@Zn/Co-ZIF. Ni signal was from Ni based TEM grid.

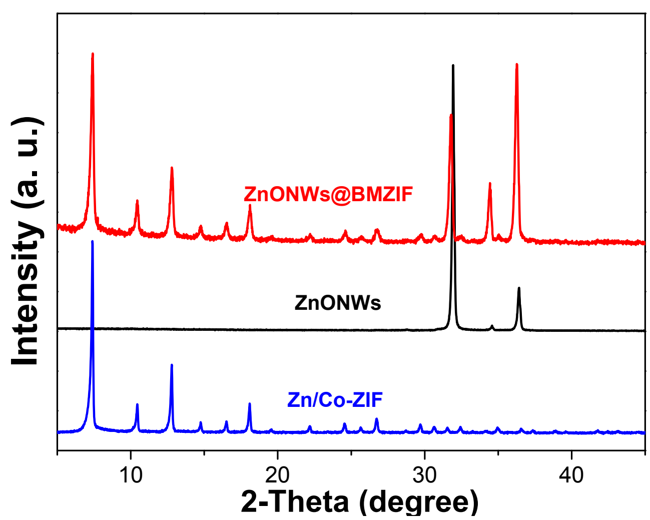

Figure S4. XRD patterns of ZnONWs@BMZIF, ZnONWs and Zn/Co-ZIF.

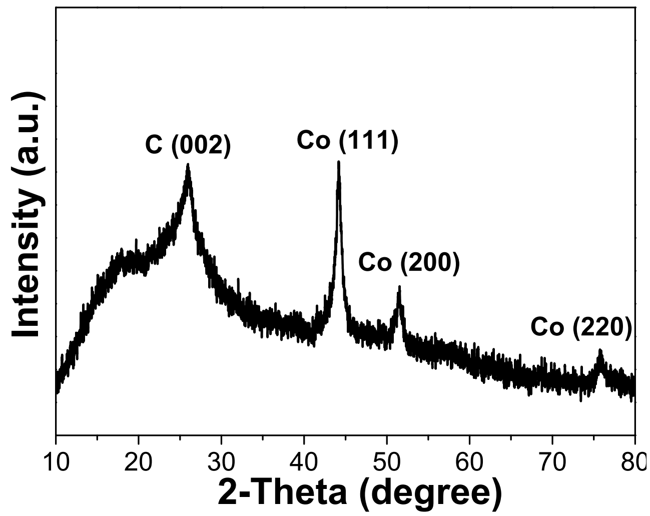

Figure S5. XRD pattern of Co/NCP.

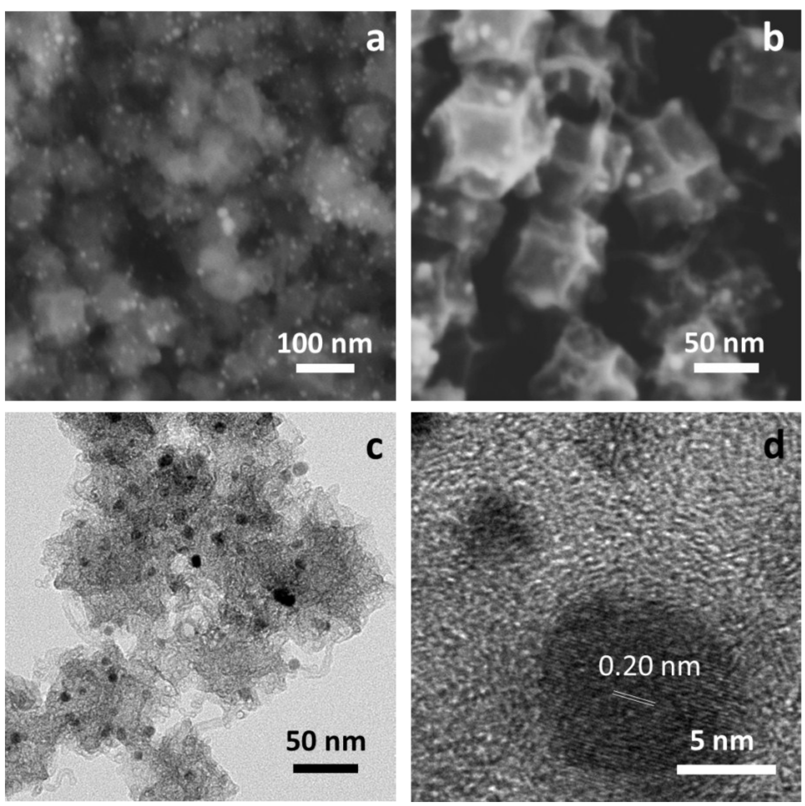

Figure S6. (a, b) SEM, (c) TEM and (d) HR-TEM images of Co/NCP. The lattice spacing of the CoNP was measured to be about 0.20 nm, consistent with the interplanar spacing of (111) for metallic Co.

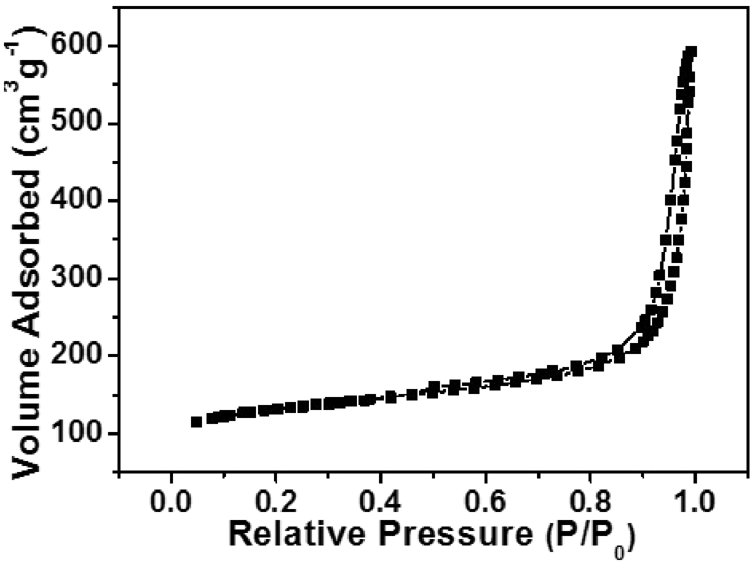

Figure S7. N_2 sorption isotherms of Co/NCP.

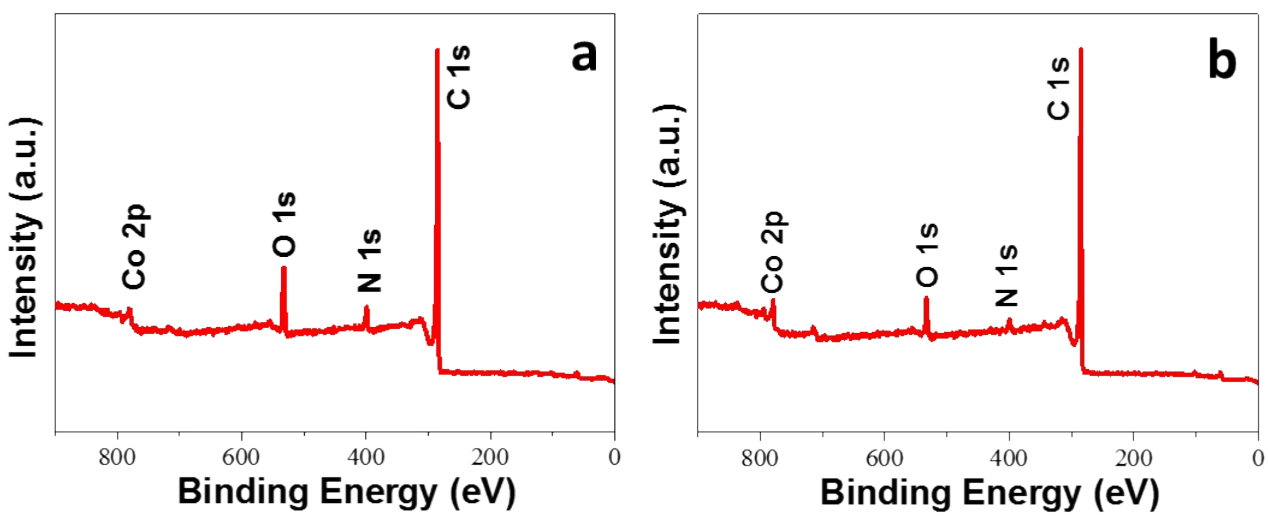

Figure S8. The survey scan spectrum of Co@CoO_x/NCNT (a) before and (b) after 6 times He ion etching cycles.

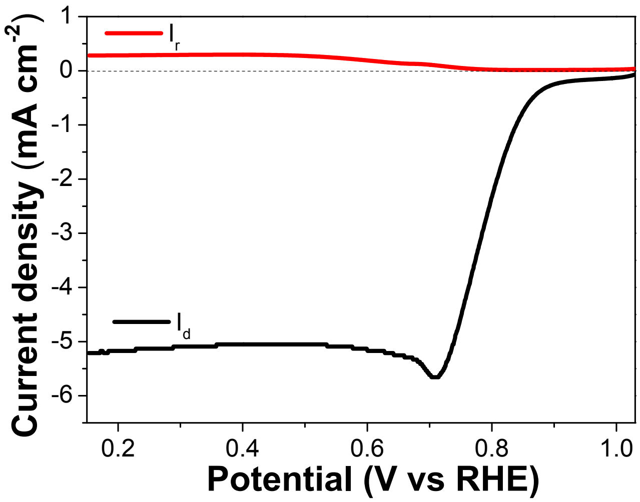

Figure S9. RRDE data of Co@CoO_x/NCNT.

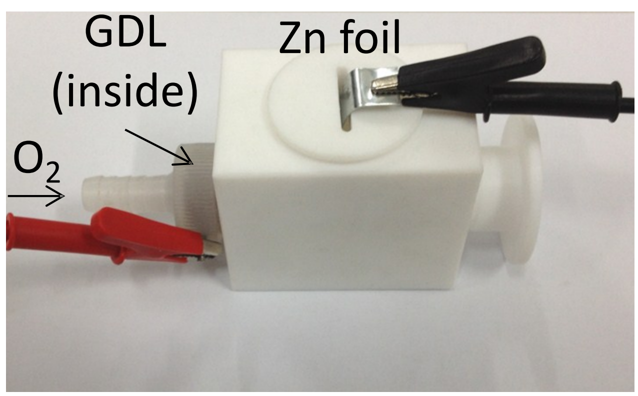

Figure S10. Detailed battery structure.

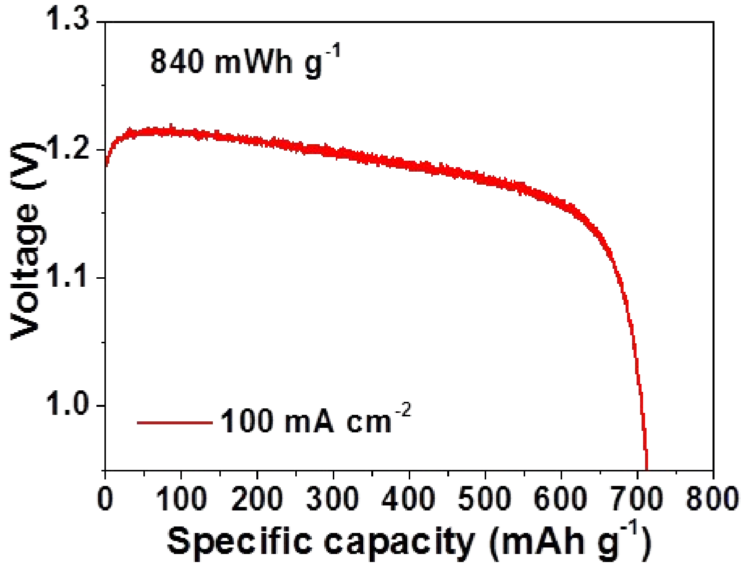

Figure S11. Specific capacity of Co@CoO_x/NCNT measured at the current density of 100 mA cm^{-2}.

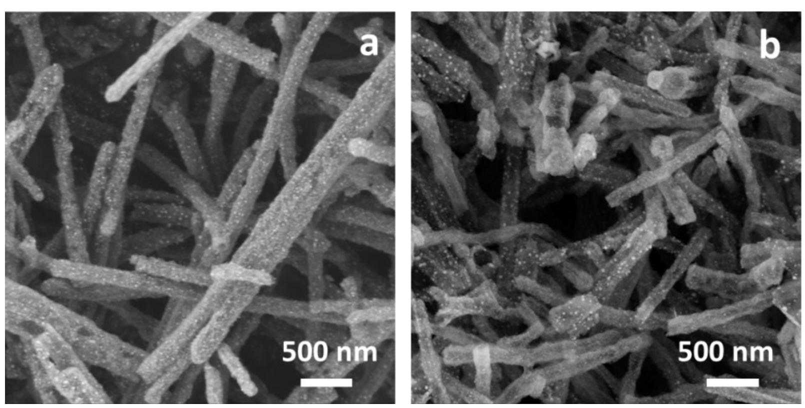

Figure S12. SEM images of Co@CoO_x/NCNT before (a) and after (b) 100 h long term discharge.

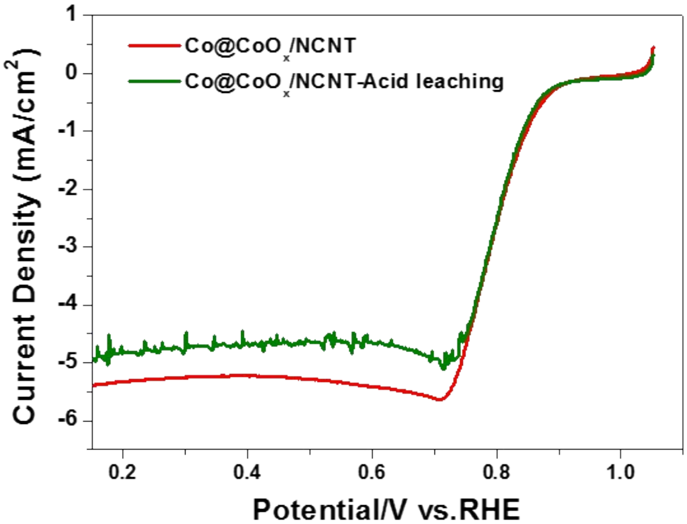

Figure S13. ORR polarization curves of Co@CoO$_x$/NCNT before (red) and after (green) acid leaching, in O_2-saturated electrolyte (scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

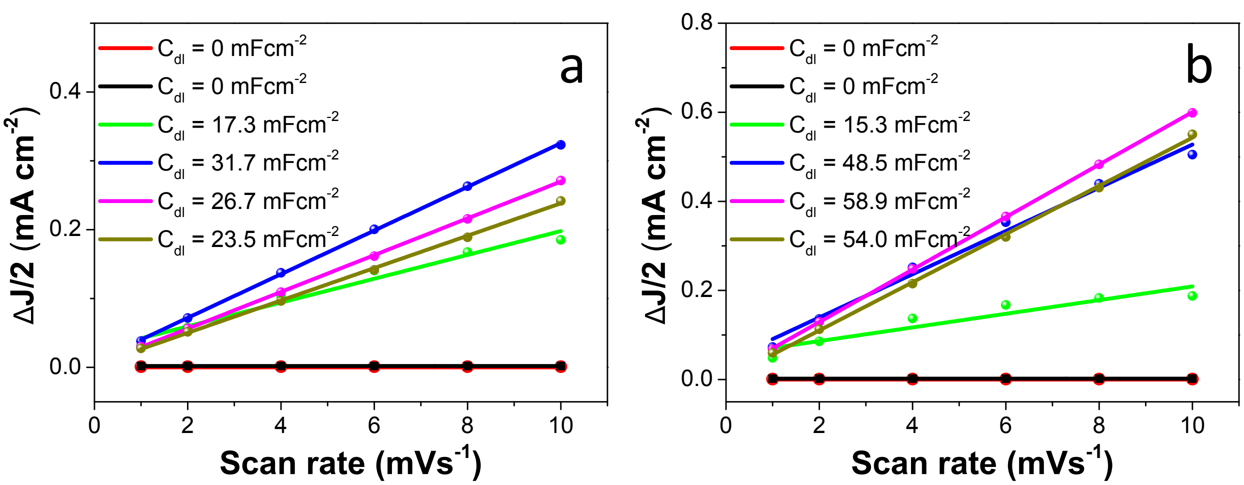

Figure S14. Linear fitting of the capacitive currents (ΔJ/2) vs. scan rates of (a) Co/NCP and (b) Co@CoO$_x$/NCNT to estimate the C_{dl} in various electrolyte concentrations.

Table S1. Comparison of ORR performance of the highly active non-precious electrocatalysts reported recently with Co@CoO_x/NCNT.

Sample	electrolyte	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Limiting current density (mA cm^{-2})	Reference
Co@CoO_x/NCNT	0.1M KOH	0.94	0.80	5.37	this work
CoO/NCNT	1 M KOH	0.93	N.A	~ 3.75	S1
Co_3O_4/N-doped-Gr	0.1 M KOH	0.88	0.83	~ 5.0	S2
Fe-P-C	0.1 M KOH	0.95	N.A	5.01	S3
Co@Co_3O_4@C-CM	0.1 M KOH	0.93	0.81	N.A	S4
NiFe@NCx	0.1 M KOH	1.03	0.86	~ 5.8	S5
Co-P-CN	0.1 M KOH	0.91	0.83	6.0	S6
Fe-N/C	0.1 M KOH	0.98	N.A	4.81	S7
Fe-N-SCCFs	0.1 M KOH	1.03	0.88	~ 5.6	S8
Fe/N-GPC	0.1 M KOH	0.94	0.82	~ 5.0	S9
Co/CoN_x/NCNT/C	0.1 M KOH	0.90	0.8	3.84	S10
Co-N-C	0.1 M KOH	0.98	0.87	~ 6.0	S11

Table S2. Comparison of the performance of the Zn-air battery using the Co@CoO_x/NCNT with the reported Zn-batteries in the literature.

Air Catalysts	OCP	V @ 10 mA/cm^2	V @ 20 mA/cm^2	V @ 25 mA/cm^2	V @ 50 mA/cm^2	V @ 100 mA/cm^2	V @ 200 mA/cm^2	V @ 300 mA/cm^2	Peak Power (mW/cm^2)	Durability (h)	Reference
Co@CoO_x/NCNT	1.52	1.33		1.31	1.27	1.21	1.12	1.01	353	100	Our work
FeCu alloy	1.4			1.2		1.1	0.9	0.62	212	110	S12
a-MnOx NW on KB	1.4						0.9		190	N/A	S13
TiCN	1.4		1.2		1.15	1.08			275	55	S14
Co@NG	1.4	1.31			1.21				400	14	S15
$Ag_{50}Cu_{50}$		1.23	1.18		1.03				90	20	S16
$NiCO_2O_4$/CNT	1.38	1.25							330	100	S17
NCNT/Co-NiO-NiCo		1.22	1.08						N/A	N/A	S18
CoO/NCNT	1.4				1.2	1.1			265	22	S19
NCNF-1000	1.48	1.24							185	18	S20
Cu-N@C		1.2							212	100	S21
GQD-GH		1.11							80	1	S22
NCT/$Co_xMn_{1-x}O$		1.28@7 mA							N/A	N/A	S23
CF/N-rGO-150-Vulcan				0.8V-1.0V @30mA					190	24	S24
AgNP-SWNT	1.2								N/A	12	S25
Fe/Fe_3C-melamine/N-KB	1.4								200	N/A	S26
CuPt-NC	1.4		1.3						250	13.9	S27
CMO/N-rGO	1.5		1.15						N/A	14	S28
Co_3O_4-SP/NGr-24h	1.5	1.25	1.2		1.1				190	28	S29
P, S-CNS	1.51	1.23							198	100	S30

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