Supporting information

Sponge-templated sandwich-like cobalt-embedded nitrogen-doped carbon polyhedrons/graphene composite as a highly efficient catalyst for Zn-air batteries

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Characterization

The scanning electron microscope (SEM) was conducted on FEI HELIOS NanoLab 600i to investigate the surface morphologies and structures of the samples at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) was carried out on a FEI Tecnai G2 F20 field emission transmission electron microscope operated with an electron acceleration energy of 200 kV. X-ray diffraction (XRD) patterns were acquired on D/max-RB diffractometer using a Cu K α X-ray source operating (40 kV, 20 mA, $\lambda = 1.54$ Å) at a scanning rate of 2° min⁻¹. Raman spectra were collected on Renishaw RM 1000 spectromicroscopy system. The chemical components and the effect of N doping of the samples were recorded with Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). The specific surface area and pore size distributions were investigated by nitrogen adsorption–desorption isotherms using a QUADRASORB SI analyzer.

Electrochemical measurements

All of electrocatalytic measurements was examined by a standard three-electrode system using a CHI 760E electrochemical workstation_at room temperature, with a platinum mesh as the counter electrode, Ag/AgCl prefilled with 3.5 mol L⁻¹ KOH (0.98 V relative to reversible hydrogen electrode, RHE) as the reference electrode, and a rotating ring-disk electrode (RRDE) covered with prepared catalyst as the working electrode. 2.5 mg of the sample was dispersed on the mixed solution of

ethanol (0.5 mL), deionized water (0.485 mL) and Nafion (0.015 mL, 5 wt.%), sonicating for 30 min to form homogenous (5 mg mL⁻¹), whose volume ratio was 5:5:0.3. Then 20 μ L of the suspension was pipetted on the surface of the RRDE with a mass loading of 0.16 mg cm⁻² for all samples including commercial Pt/C (20 wt%). forming the working electrode at room temperature. The diameter of the RRDE is 5.61 mm. The cyclic voltammetry (CV) measurements were accomplished within a potential range from 0 V to 1.2 V (vs. RHE) in N₂ or O₂-saturated 0.1 mol L⁻¹ KOH at a scan rate of 50 mV s⁻¹. Prior to the test, working electrode was fully cycled to activate the catalyst. The staircase voltammetry (SCV) was used to measure the electrochemical activity for ORR with a potential step of 50 mV at intervals of 30 s from 0 V to 1.2 V vs. RHE in O₂-saturated 0.1 mol L⁻¹ KOH at 1600 rpm. Electrochemical impedance spectroscopy (EIS) measurement was performed in the frequency range from 50 kHz to 1 Hz with an amplitude of 5 mV and recorded at 1.60 V vs. RHE in an O_2^- saturated electrolyte at a rotation rate of 1600 rpm. The long-time stability behavior of the catalyst was evaluated by consecutive 5000 voltammetry cycles within the potential range of 0.6 to 1 V (vs. RHE) and Current-time (i-t) chronoamperometric responses at constant potential of 0.8 V with a rotation speed of 1600 rpm. The tolerance of catalyst to methanol cross-over was performed by chronoamperometric measurement in the presence of methanol (3 mL, 0.1 M) in O₂saturated KOH solution (100 mL, 0.1 M). The electron transfer number (n) can be calculated by the Koutecky–Levich (K–L) equation, which is measured by a series of SCV curves with increasing rorating speeds, the K-L equations shown as follows:

$$\frac{1}{I} = \frac{1}{I_K} + \frac{1}{I_D}$$
$$I_D = 0.62nFC_0(D_0)^{2/3}\omega^{1/2}v^{-1/6}$$

where I is the measured current density, Ix and ID are the kinetic and diffusion-limiting current, respectively. F is Faraday constant (96485 C mol⁻¹), n is transferred electron number, C₀ is the bulk concentration of O₂ (1.2×10^{-3} mol L⁻¹), D₀ is the diffusion coefficient of O₂ (1.9×10^{-5} cm² s⁻¹) and v is the kinetic viscosity of the electrolyte (0.01 cm² s⁻¹). When expressing the rotation speed in rpm, the constant 0.2 is applied.

RRDE measurements were also employed to determine the reaction pathway (electron transfer number) by detecting the HO₂- formation. The electron transfer number (n) and hydrogen peroxide yield (%H₂O₂) can be calculated according to the following equation:

$$n = 4 * \frac{I_D}{I_D + \frac{I_R}{N}}$$

% $H_2O_2 = 2 * \frac{\frac{I_R}{N}}{I_D + \frac{I_R}{N}}$

Where I_D and I_R are the disk and ring currents, respectively, N is the ring current collection efficiency (~ 37%).

Zn-air battery tests: The catalysts were measured in a Zn–air battery at room temperature. The assembly and measurement of Zn-air battery were operated under the follow procedure. The air cathode was prepared by mixture of s-Co@NCP/rGO or Pt/C (2.5 mg), acetylene black (1 mg), activated carbon (4 mg), and Nafion (5 wt%, 8

ml) in 200 ml of isopropyl alcohol to form a homogeneous catalyst ink. Ni foam as the substrate was immersed in 1 M HCl solution and then washed with ethanol and ultrapure water. The catalyst ink was dropped onto the Ni foam with a mass loading of 2 mg cm² followed by drying in vacuum at 60 °C for 24 h. A commercial gas diffusion layer was used next to the Ni catalyst layer to make gas accessible and prevent electrolyte leakage. Polished zinc foil was used as the anode, and 6 M KOH solution was employed as the electrolyte. The polarization curves were conducted using a CHI760E electrochemical workstation. Galvanostatically test was operated for the discharge polarization curves at 10 mA cm⁻² using a NEWWARE battery tester.



Figure S1. SEM image of (a) GO and (b) rGO-800.



Figure S2. SEM image of Co@NCP/rGO-800 catalyst.



Figure S3. SEM images of (a) ZIF-67 precursor (b) Co@NCP-800.



Figure S4. SEM images of the catalysts calcined at different temperatures.

(a) s-Co@NCP/rGO-600, (b) s-Co@NCP/rGO-700, (c) s-Co@NCP/rGO-800,

(d) s-Co@NCP/rGO-900.



Figure S5. XRD pattern of (a) ZIF-67 and (b) the catalysts calcined at different temperatures.



Figure S6. Raman spectra of the catalysts calcined at different temperatures.



Figure S7. XPS full spectra of (a) Co@NCP-800, s-Co@NCP/rGO-800, rGO-800 and (b) s-Co@NCP/rGO catalysts with different pyrolysis temperatures.



Figure S8. High-resolution C 1s XPS spectra of (a) s-Co@NCP/rGO-600, (b) s-

Co@NCP/rGO-700, (c) s-Co@NCP/rGO-800, (d) s-Co@NCP/rGO-900.



Figure S9. High-resolution N 1s XPS spectra of (a) s-Co@NCP/rGO-600, (b) s-Co@NCP/rGO-700, (c) s-Co@NCP/rGO-800, (d) s-Co@NCP/rGO-900.



Figure S10. High-resolution Co 2P XPS spectra of (a) s-Co@NCP/rGO-600, (b) s-





Figure S11. (a) N_2 adsorption-desorption isotherms curves and (b) pore size distributions of s-Co@NCP/rGO with different pyrolysis temperatures.



Figure S12. (a) N_2 adsorption-desorption isotherms curve and (b) pore size distribution of Co@NCP/rGO-800.



Figure S13. SCV curves of the samples with different pyrolysis temperatures as reference obtained in O_2 -saturated 0.1 mol L⁻¹ KOH electrolyte with a rotating speed of 1600 rpm.



Figure S14. EIS Nyquist plots of s-Co@NCP/rGO-800 and Co@NCP-800.



Figure S15. SCV curves of s-Co@NCP/rGO-800 and s-Co@NCP/rGO-acid in O_2 -saturated 0.1 mol L⁻¹KOH electrolyte with a rotating speed of 1600 rpm.



Figure S16. Long-term durability test for (a) Pt/C and (b) Co@NCP/rGO-800 by recording the SCV curves before and after 5000 cycles.



Figure S17. TEM images of (a) s-Co@NCP/rGO, (b) s-Co@NCP/rGO after long-term durability test, (c) Pt/C and (d) Pt/C after long-term durability test.



Figure S18. SCV curves of (a) Pt/C and (b) s-Co@NCP/rGO-800 in O_2 -saturated 0.1 mol L⁻¹ KOH electrolyte with and without methanol.

Table S1.	Element analy	vsis of s- (Co@NCP/rGO-	X (X=600,	700, 800,	900 °C) catalysts
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Samples	%C	%N	%O	%Co
s-Co@NCP/rGO-600	73.36	7.69	11.13	5.83
s-Co@NCP/rGO-700	82.41	3.42	10.41	3.76
s-Co@NCP/rGO-800	89.36	3.39	5.32	1.93
s-Co@NCP/rGO-900	89.05	1.77	6.81	2.37

Table S2. N 1s peak fitting results of the samples pyrolysis at different temperatures

Samples %	Total-N	Pyridinic-N	Pyrrolic-N	Graphitie-N	Co-N _x
s-Co@NCP/rGO-600	7.69	24.39	31.16	14.76	29.68
s-Co@NCP/rGO-700	3.42	23.74	21.00	21.34	33.92
s-Co@NCP/rGO-800	3.39	17.46	17.95	38.24	26.34
s-Co@NCP/rGO-900	1.77	16.39	6.13	46.80	30.68

Samples	s- Co@NCP/r GO-800	Co@NC P-800	rGO-800	Co@NCP /rGO-800	Pt/C
onset potentials (V)	0.94	0.94	0.94	0.94	1.03
half-wave	0.85	0.80	0.76	0.81	0.86
potential (V)					
limiting current density (mA cm ⁻²)	4.98	4.22	4.82	4.91	5.68

Table S3. The onset potentials, half-wave potential, limiting current density of different samples.

Table S4. The onset potentials, half-wave potential, limiting current density of s-Co@NCP/rGO-X (X=600, 700, 800, 900 °C) catalysts

Pyrolysis temperature	600℃	700℃	800°C	900℃
onset potentials (V)	0.94	0.94	0.94	0.89
half-wave	0.84	0.83	0.85	0.79
potential (V)				
limiting current density (mA cm ⁻²)	4.61	4.46	4.98	3.37

catalyst	E _{1/2} vs. RHE / V	Maximum power density/mW cm ⁻²	reference
NDGs-800	0.85	115	Wang_ACS Energy Lett2018 ¹
C-MOF-C2-900	0.82	105	Zhang_Adv. Mater. _2018 ²
MnO@Co-N/C-700	0.83	130	Chen-J. Mater. Chem. A-2018 ³
HP-Fe-N/CNFs	0.80	135	Zhao_ACS Appl. Mater. Interfaces_2018 ⁴
NPS-G-2-900	0.857	151	Zheng_ Appl Catal B: Environ_2019 ⁵
Ni-MnO/rGO	0.78	123	Fu_Adv. Mater2018 ⁶
Co ₂ P/CoN-in-NCNTs- 1000	0.85	194	Guo_Adv. FunctMater. 2018 ⁷
CoIn ₂ S ₄ /S-rGO	0.83	133	Fu_Adv. Energy Mater 2018 ⁸
3DOM-Co@TiO _x Ny	0.84	110	Liu_ Adv. Mater. _2019 ⁹
FeCo/FeCoNi@NCNTs- HFs-900	0.85	156	Wang_Appl. Catal. B: Environ. 2019 ¹⁰
s-Co@NCP/rGO-800	0.85	186	This work

Table S5. Comparison of ORR performance and power density of zinc-air batteries under alkaline conditions for our synthesized sample with other reported catalysts

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