Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

Experimental Section

Materials: Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$), zinc(II) nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$), and 2-methylimidazole (2-mlm) with purity > 99.5% were obtained from Sigma-Aldrich and used without further purification. The Pt loading of commercial Pt/C catalyst was 20 wt%. Nafion was acquired from Sigma-Aldrich.

Synthesis of Co_xZn_{1-x}-ZIF nanoleaves (x represents the molar ratio of $Co^{2+}/(Co^{2+}+Zn^{2+})$): Co_xZn_{1-x}-ZIF nanoleaves (x represents the molar ratio of $Co^{2+}/(Co^{2+}+Zn^{2+})$ in the original ZIF nanoleaves) were prepared at room temperature. Typically, mixture solutions containing $Zn(NO_3)_2\cdot 6H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ (total mass is 280 mg, with well-defined molar ratios of $Co^{2+}/(Co^{2+}+Zn^{2+})$ from 0 %, 20%, 60% and 100%) were dissolved 20 mL of deionized water. In a separate container, 450 mg of 2-mlm was dissolved in 20 mL of deionized water. Next, the two solutions were quickly mixed and vigorously stirred at room temperature for 2 h. The precipitates were separated by centrifugation and thoroughly washed with fresh deionized water for 3 times and with absolute ethanol twice. Then, the purple products were dried in vacuum at 60 °C for 24 h. When the ratio of $Co^{2+}/(Co^{2+}+Zn^{2+})$ is 0 %, the prepared ZIF sample was labeled as Zn-ZIF nanoleaves and those prepared with $Co^{2+}/(Co^{2+}+Zn^{2+})$ molar ratios of 20% and 60% were labeled as Co_xZn_{1-x}-ZIF nanoleaves (where x represents the molar ratio of $Co^{2+}/(Co^{2+}+Zn^{2+})$), when the ratio of $Co^{2+}/(Co^{2+}+Zn^{2+})$ is 100 %, the prepared ZIF sample was named as Co-ZIF nanoleaves. In contrast, 3D $Co_{0.6}Zn_{0.4}$-ZIF particles were synthesized by using methanol to replace deionized water during the synthesis process, followed by same purification procedures.

Synthesis of Co_x-N/C-T : The purple Co_xZn_{1-x}-ZIF powder was heated to the desired temperature (700~900 °C) with a heating rate of 2 °C min^{-1}, for 2 h under N_2 atmosphere in a tube furnace. The pyrolyzed products were soaked in 0.5 M H_2SO_4 solution at 80 °C for 8 h to remove zinc residues, followed by a secondary heat treatment to obtain the Co_x-N/C catalysts. Finally, the products were vacuum-dried at 60 °C for overnight prior to use. The 3D $Co_{0.6}$-N/C-800 catalyst was prepared by using 3D $Co_{0.6}Zn_{0.4}$-ZIF as the precursor.

Synthesis of N/C-800 : The Zn-ZIF powder was pyrolyzed at 800 °C with a heating rate of 2 °C min^{-1}, for 2 h under N_2 atmosphere in a tube furnace. The pyrolyzed sample was soaked in 0.5 M H_2SO_4 solution at 80 °C for 8 h to remove residual zinc species, followed by subsequent heat treatment to obtain the N/C-800 catalyst.

Finally, the product was dried in vacuum at 60 °C for overnight prior to use.

Materials characterization: The field emission scanning electron microscopy (FE-SEM) images were obtained using Hitachi S-4800 microscope with an acceleration voltage of 30 kV. Transmission electron microscopy (TEM) images were captured on a JEM-2100 instrument microscope at an acceleration voltage of 200 kV. HRTEM (Philips Tecnai G2), and STEM (FEI Tecnai G2 F30 S-TWIN). The specific surface area, pore size distribution, and pore volume were characterized with a Micrometrics ASAP2020 analyzer (USA) at 77 K. X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker D8 X-ray diffraction meter with monochromatic Cu Kα radiation (λ = 0.154056 nm). The exact Co content in the pyrolyzed Co_x-N/C samples was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Nippon Jarrel-Ash Co., IRIS Advantage). XPS measurements were carried out on Kratos AXIS Ultra spectrometer with a source gun of Al Kα and spot size of 400 μm.

ORR measurements: CHI 760E electrochemical workstation (Shanghai Chenhua, China) with a three-electrode system was used for the ORR measurements. This consists of a glassy carbon rotating disk electrode (with diameter of 5 mm) as the working electrode, platinum foil as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The catalyst ink was prepared by dispersing 5 mg of the catalyst in isopropanol (containing 0.025 wt% Nafion), followed by sonication for 30 minutes to form a well-dispersed black ink. Then, 10 μL of the catalyst ink and 12.5 μL of the Pt/C ink were dropped onto the glassy carbon electrode of RDE or RRDE to give catalyst and Pt/C loading of 0.254 and 0.125 mg cm^{-2}, respectively. All electrochemical measurements were performed in *0.1 M KOH solution*. The measured potential E_{SCE} was calibrated by the reversible hydrogen potential E_{RHE} based on the equation: $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.241 + 0.059 * \mathrm{pH}$

The LSV curves obtained in O_2-saturated electrolyte were corrected by deducting the current response detected in the N_2-saturated electrolyte. The H_2O_2 yield (% H_2O_2) and electron transfer number (n) were calculated based on the following equations:

$$\% H_2O_2 = 200 \times \frac{I_R/N}{I_D + I_R/N} \tag{1}$$

$$n = 4 \times \frac{I_D}{I_D + I_R/N} \tag{2}$$

where I_{D} and I_{R} are disk current and ring current, respectively, and N is the collection efficiency of the ring electrode (0.37 in this work). RDE measurements were used to calculate the kinetic current density (J_K)

according to the Koutecky–Levich equation given below :

$$J^{-1} = J_k^{-1} + (B\omega^{0.5})^{-1} \qquad (3)$$

$$B = 0.2nF\left(D_{O_2}\right)^{2/3}\tau^{-1/6}C_{O_2} \qquad (4)$$

where J_K is the kinetic current and ω is the electrode rotating rate. B *is* the slope of the K–L plots, n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C mol^{-1}), D_{O2} is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}), τ is the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}), and C_{O2} is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

Zinc-air battery test: For the primary liquid zinc-air battery test, the catalysts ink uniformly dispersed on a hydrophobic carbon paper (2.0 × 2.0 cm^{-2}) with a catalyst loading of 0.5 mg cm^{-2} was used as the air cathode, a polished Zn foil was used as the anode and and a 6 M KOH solution was employed as the electrolyte. The CHI760E electrochemical workstation and the LAND testing system was used to carry out the polarization (V-I) and galvanostatic discharge tests at current densities of 5 and 20 mA cm^{-2}, respectively.

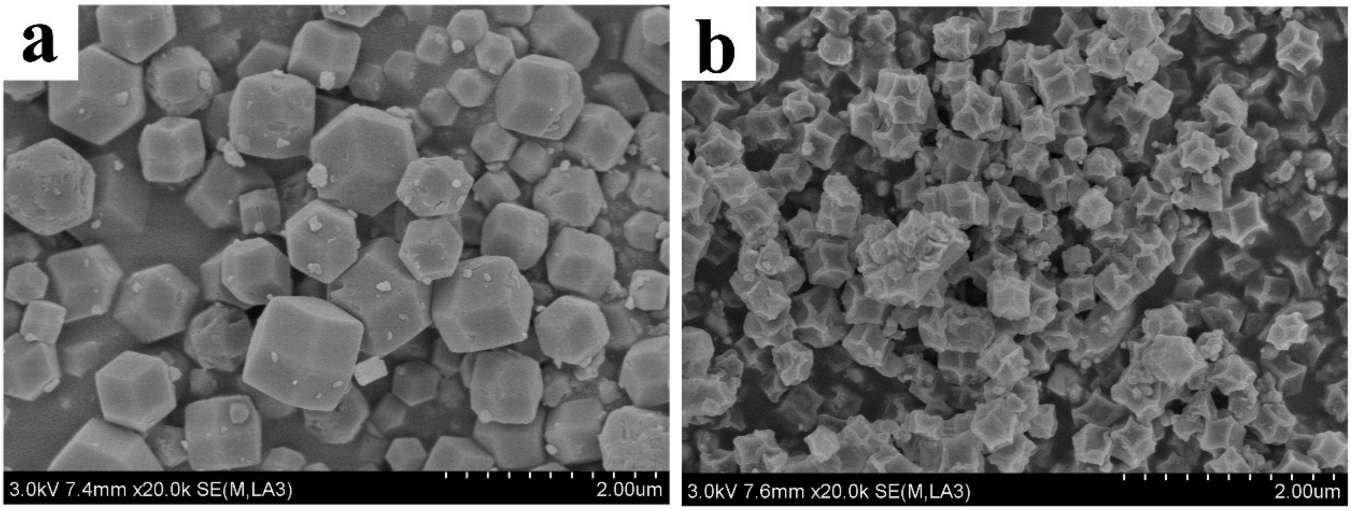

Fig. S1. SEM images of (a) 3D Co$_{0.6}$Zn$_{0.4}$-ZIF and (b) 3D Co$_{0.6}$-N/C-800.

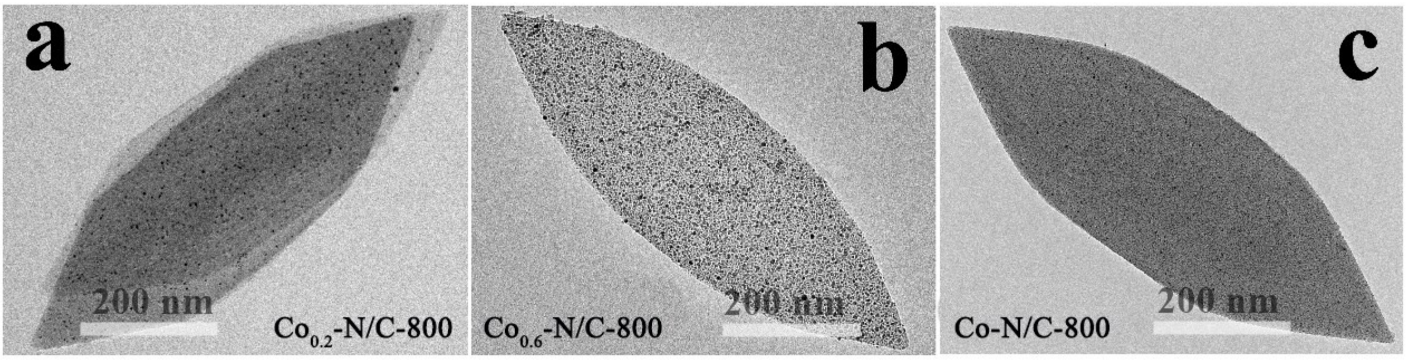

Fig. S2. TEM images of 2D Co$_{0.2}$-N/C-800 (a), Co$_{0.6}$-N/C-800 (b), and Co-N/C-800 (c).

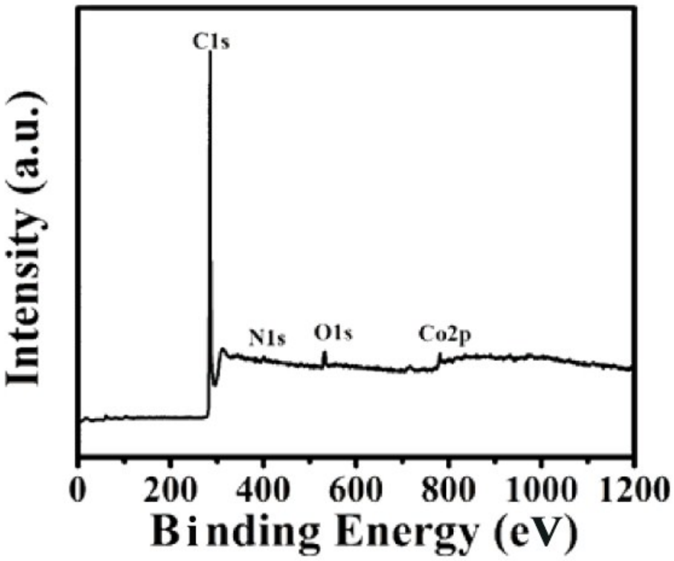

Fig. S3. XPS survey spectrum of Co$_{0.6}$-N/C-800.

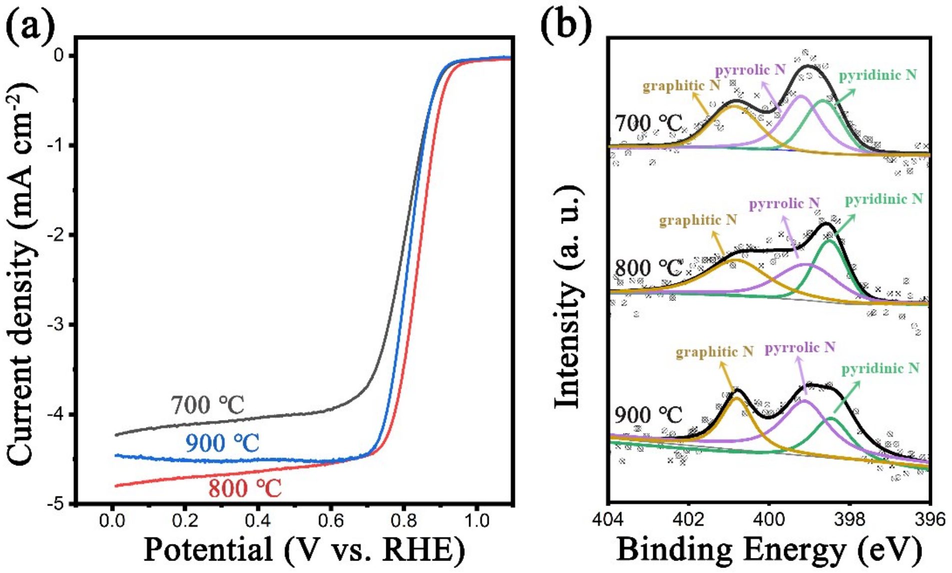

Fig. S4. (a) ORR polarization curves of $Co_{0.6}$-N/C-*T* catalysts synthesized at different temperatures. (b) $N1_S$ spectra of $Co_{0.6}$-N/C-*T* at different pyrolysis temperatures.

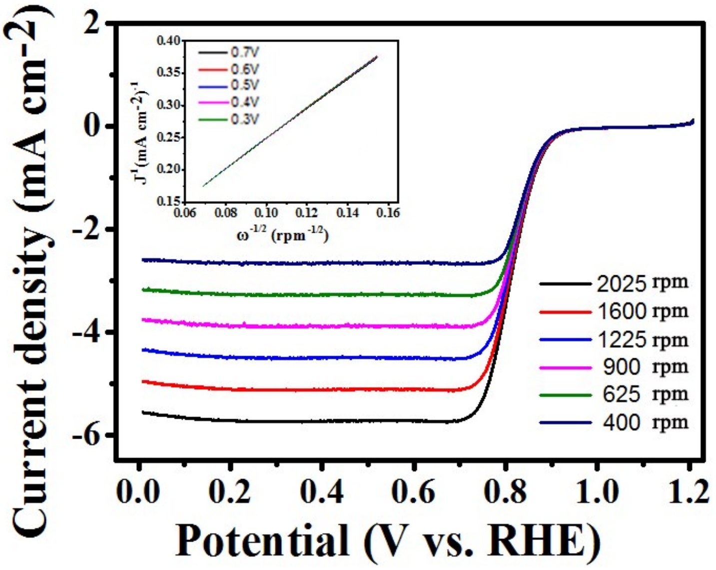

Fig. S5. LSV plots of $Co_{0.6}$-N/C-800 at different rotation speeds (inset: K-L plots).

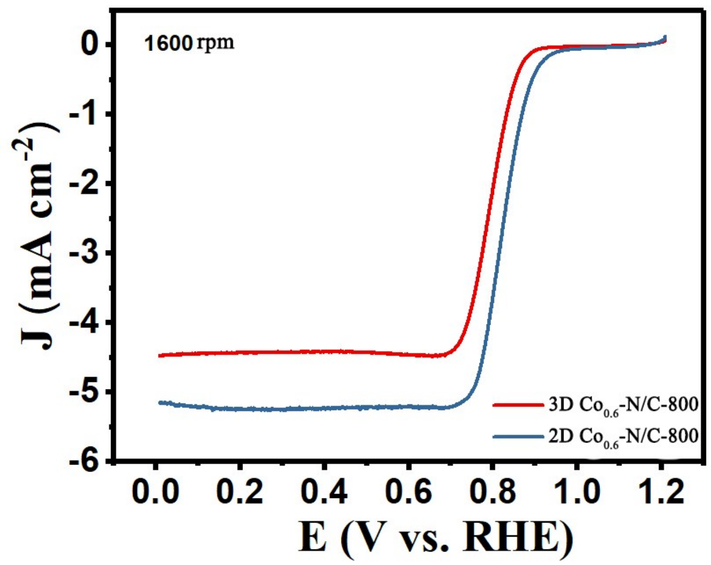

Fig. S6. LSV plots of 3D Co$_{0.6}$-N/C-800 and 2D Co$_{0.6}$-N/C-800.

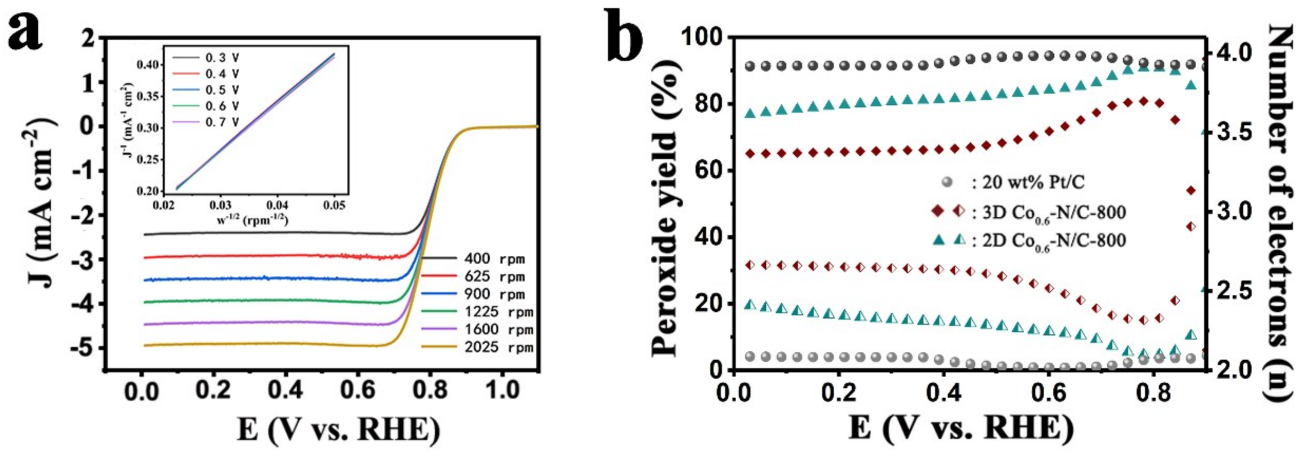

Fig. S7. (a) LSV plots of 3D Co$_{0.6}$-N/C-800 at different rotation speeds. (b) Peroxide yield and electron transfer number of 3D Co$_{0.6}$-N/C-800, 2D Co$_{0.6}$-N/C-800, and 20 wt.% Pt/C in O_2-saturated 0.1 M KOH at a scan rate of 5 mV s^{-1} under a rotation speed of 1600 rpm.

Table S1. Summary of various electrocatalysts for ORR.

Catalyst	**Half-wave Potential (V vs. RHE)**	**Current density (mA cm^{-2})**	***n* [Average number of electron transfer at 0.3 V～0.8V]**	**References**
Co$_{0.6}$-N/C-800	0.825	-5.2	3.90	This Work
20 wt% Pt/C	0.811	-5.5	3.99	This Work
ZCP-CFs-900	0.805	-5.6	3.97	*J. Mater. Chem. A, 2017,5, 1211-1220*
NC@Co-NGC DSNC	0.82	-4.5	4	*Adv. Mater. 2017, 1700874*
Co@ Co3O4/NC	0.8	-4.5	/	*Angew. Chem. Int. Ed. 2016, 55, 4087- 4091*
Co@ Co3O4@C-CM	0.81	-4.6	3.9	*Energy Environ. Sci. 2015, 8, 568- 576*
Co@NPCM/CNF-850	/	-5.7	3.8	*ACS Appl. Mater. Interfaces 2017, 9, 21747.*
Co/N-MC-2-750	/	-5.8	3.96	*J. Mater. Chem. A, 2017, 5,14763*
ZIF-derived porous carbon	0.76	-5.15	3.9	*Adv. Mater. 2014, 26, 1093*
Ordered mesoporous carbon	0.69	-4.8	3.1	*Angew. Chem. Int. Ed. 2015, 54 ,9907*