

Electronic Supplementary Information

N-doped Graphitic Layer Encased Cobalt Nanoparticles as Efficient Oxygen Reduction Catalysts in Alkaline Media

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Experimental and characterization details

Materials Nafion (5 wt%) were purchased from Sigma-Aldrich. 20 wt% Pt/C commercial electrocatalysts were purchased from Johnson Matthey. Cyanamide (50 wt%) and cobalt nitrate hexahydrate were purchased from Aladdin Industrial Inc. All other chemicals were purchased and used without any further purification. The double distilled water was used for solution preparation.

Synthesis of catalysts

For the synthesis of N-C@Co-2, 1.40g cobalt nitrate hexahydrate, 6 mL double distilled water and 4 mL cyanamide aqueous solution (50 wt%) were mixed under stirring, then the mixed solution was heated to 80 °C until completely dry to form royalblue powders. The obtained powders were calcined at 800 °C with a heating rate of 4 °C min⁻¹ in a tubular furnace protected by N₂ for 3 h. After etched in 2 M HCl solution at 80 °C for 12 hours, washed with double distilled water and ethanol, and finally dried, N-C@Co-2 (0.3g) was obtained. The N-C@Co-1 and N-C@Co-3 samples were prepared with the same synthesis conditions as that for N-C@Co-2, except using different addition of cyanamide, 2 mL and 6 mL, respectively. To prove the protection effect of the carbon shell, N-C@Co-2-ue was prepared on the same process without etch as a contrast sample. Sample N-C was synthesized using 4 mL cyanamide aqueous solution (50 wt%) as the precursor. Meanwhile, Sample CoO was synthesized using 1.40g cobalt nitrate hexahydrate as the precursor.

Characterization

The morphology characterizations were performed *via* scanning electron microscopy (SEM) (XL-30 ESEM, Philips Company). The samples were cast on indium tin oxide glass for SEM

measurement. Transmission electron microscopy (TEM) images recorded on a JEM-2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. Raman spectroscopy patterns were obtained using a confocal microprobe Raman system (HR800, Jobin Yvon). The X-ray diffraction (XRD) patterns were measured using an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu K α radiation ($\lambda = 0.15406$ nm). The specific surface areas of the samples are analyzed with a surface area analyzer (ASAP 2020, Micromeritics, USA) using physical adsorption/desorption of N₂ at the liquid-N₂ temperature. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore size distribution plot was derived from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) model. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer (Thermo Electron Corp.) with Al K α radiation (1486.6 eV) as the excitation source.

Electrochemical Measurements

Cyclic voltammetry (CV) experiments were performed with a CHI660C Electrochemical Analyzer (CH Instruments, China). Rotating disk electrode (RDE) voltammetry experiments were performed using a PARSTAT 2273 Electrochemistry Workstation. Rotating ring-disk electrode (RRDE) voltammetry experiments were performed using a speed control unit-Princeton Applied Research Model 636 Electrode Rotator and a PINE RRDE with Glassy carbon (GC) disk and Pt ring.

All electrochemical measurements were performed at room temperature in 0.1 M KOH solution. The three-electrode cell consisted of an Ag/AgCl electrode (in saturated KCl solution) as the

reference electrode, a platinum electrode as the counter-electrode, and a glassy carbon electrode (GC, 3.0 mm in diameter, 0.07065 cm² in geometric surface area for the examination for CV, 5.0 mm in diameter, 0.19625 cm² in geometric surface area for the examination for RDE, 5.61 mm in diameter, 0.24706 cm² in geometric surface area for the examination for RRDE.) with catalysts as the working electrode. The working electrode was polished mechanically before each experiment with 1, 0.3 and 0.05 mm alumina powder, respectively. The electrodes were then sonicated with double distilled water, rinsed thoroughly with double distilled water and dried under a gentle nitrogen stream. In the typical procedure for ink preparation, 6 mg catalyst was dispersed in 1.8 mL double distilled water and 0.2 mL of Nafion (5%) by ultrasonication for 30 min to obtain a well-dispersed suspension. The electrode was dried under an infrared lamp for 10 min after 5 μ L of the suspension was dropped onto the GC (3.0 mm) electrode surface. For RDE and measurements, 14 μ L of the suspension was dropped onto the GC (5.0 mm) electrode surface. 17.6 μ L of the suspension was dropped onto the GC (5.61 mm) electrode surface for RRDE measurements. The final catalyst loading for all as-prepared catalysts was 213.3 μ g cm⁻² in every electrochemical measurement.

The 0.1 M KOH solution was saturated with oxygen by bubbling O₂ for 15 min prior to each ORR test. All the CV measurements were carried out in the potential range from 1.365 to 0.165 V at a scanning rate of 50 mV s⁻¹. The LSV curves were recorded from 1.165 to 0.265 V at varying rotating speeds from 100 to 2025 rpm and a scanning rate of 5 mV s⁻¹. For the RRDE test, the disc electrode was scanned at 5 mV s⁻¹ with a rotation rate of 900 rpm, while the ring electrode was held at 1.465 V vs. RHE. The chronoamperometric measurements were performed at 0.565 V (vs. RHE reference electrode). All potentials in this paper are referred to reversible hydrogen electrode

(the potentials recorded and referred to Ag/AgCl in each experiment were calculated using the formula $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.198 \text{ V}$, where E_{RHE} is the potential vs. reversible hydrogen electrode (RHE), $E_{\text{Ag/AgCl}}$ is the potential vs. Ag/AgCl electrode, and pH is the pH value of electrolyte).^{1, 2}

The electron transfer number per oxygen molecule (n) calculated from Koutecky-Levich plots were determined by follow equation:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}} \quad \text{Equation 1}$$

$$B = 0.2nFC_{O_2} \left(D_{O_2}\right)^{2/3} \nu^{-1/6} \quad \text{Equation 2}$$

Where J is the measured current density, J_k is the kinetic current density, ω is the electrode rotation rate, n is the number of electrons exchanged per oxygen molecule for the electrochemical reaction, F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), C_{O_2} is the bulk concentration of oxygen ($1.2 \times 10^{-3} \text{ mol L}^{-1}$), D_{O_2} is the oxygen diffusion coefficient ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and ν is the kinematic viscosity of the electrolyte ($1.13 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

The electron transfer number and the amount of HO_2^- generated during ORR from RRDE experiment were determined by equation given blow:

$$\text{HO}_2^- (\%) = \frac{200I_R}{I_D N + I_R} \quad \text{Equation 3}$$

$$n = \frac{4I_D}{I_D + I_R / N} \quad \text{Equation 4}$$

Where I_R is the ring current, I_D is the disk current, N is the collection efficiency with a value of 0.37.

Supplementary Results

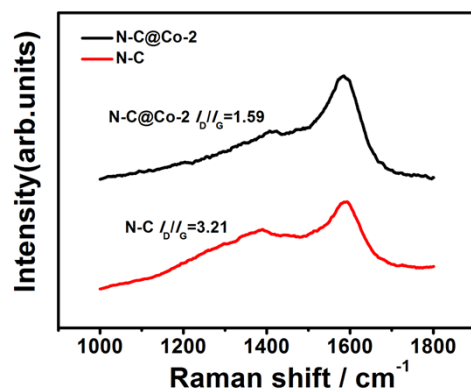


Fig. S1 Raman spectra of N-C and N-C@Co-2

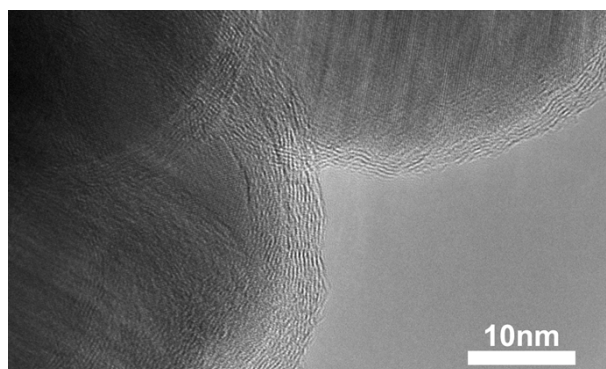


Fig. S2 HRTEM image of N-C@Co-2

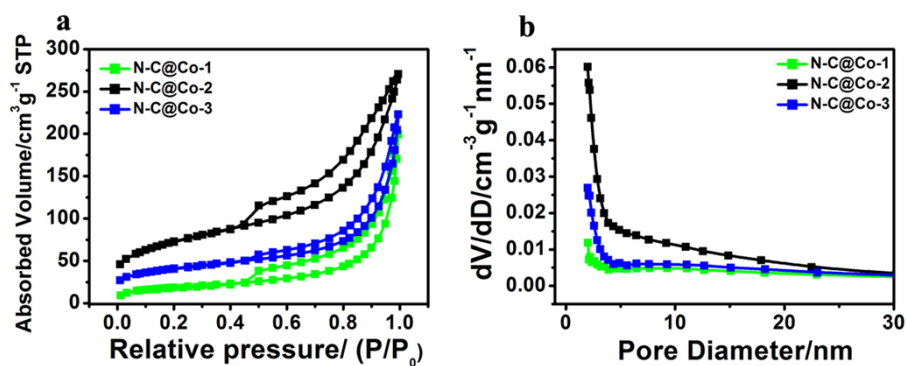


Fig. S3 (a) Nitrogen adsorption-desorption isotherms of N-C@Co-1, N-C@Co-2 and N-C@Co-3. (b) Pore size distributions of N-C@Co-1, N-C@Co-2 and N-C@Co-3.

Table S1. The chemical structure and composition of the N-C@Co-X materials

Catalyst	Addition of 50% cyanamide (mL)	Elementary content (at %)				N 1s (at %)				Co 2p _{3/2} (at %)		
		C	O	N	Co	N1	N2	N3	N4	Co1	Co2	Co3
N-C@Co-1	2	82.46	11.33	5.12	1.09	21.91	40.47	28.64	8.98	24.52	36.71	38.77
N-C@Co-2	4	84.79	8.82	5.54	0.85	33.81	23.53	32.64	10.02	53.07	19.03	27.90
N-C@Co-3	6	85.34	8.45	5.68	0.53	37.02	39.72	18.00	5.26	61.55	5.79	32.66

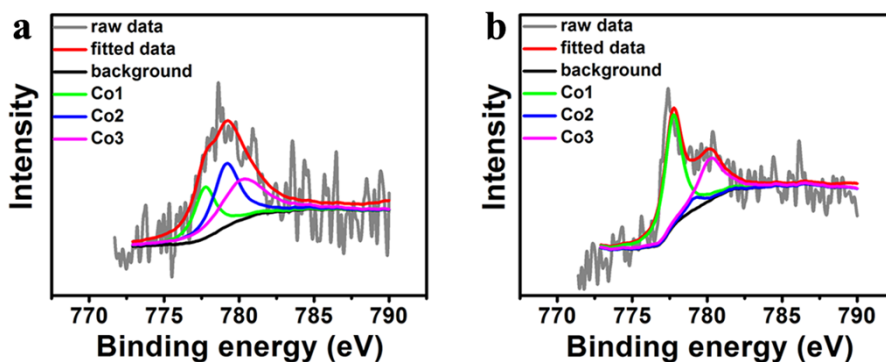


Fig. S4 High-resolution Co 2p_{3/2} XPS spectra of N-C@Co-1 (a) and N-C@Co-3 (b).

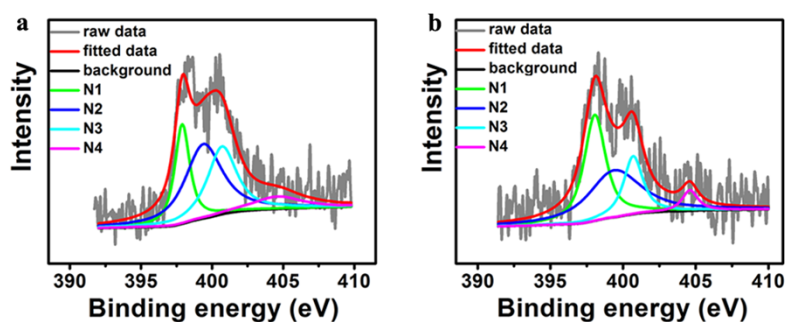


Fig. S5 High-resolution N 1s XPS spectra of N-C@Co-1 (a) and N-C@Co-3 (b).

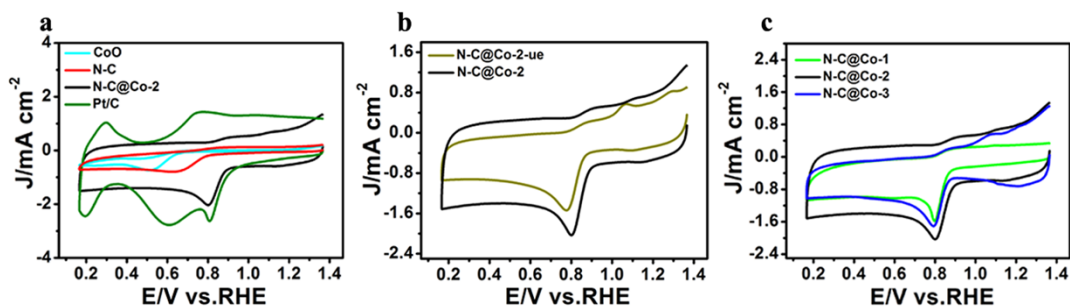


Fig. S6 (a) CV curves of CoO, N-C, N-C@Co-2 and Pt/C in O₂-saturated 0.1 M KOH solution. (b) CV curves of N-C@Co-2 and N-C@Co-2-ue in O₂-saturated 0.1 M KOH solution. (c) CV curves of N-C@Co-1, N-C@Co-2 and N-C@Co-3 in O₂-saturated 0.1 M KOH solution. Scan rate: 50 mV s⁻¹.

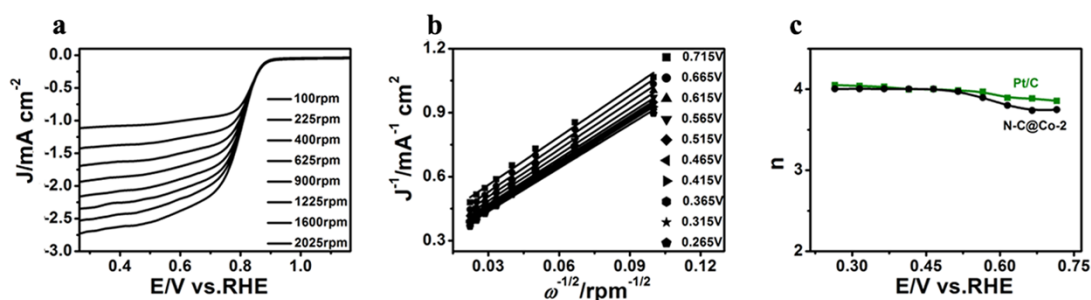


Fig. S7 (a) LSV curves at various rotation rates recorded for ORR at N-C@Co-2 electrode in oxygen-saturated 0.1 M KOH. Scan rate: 5 mV s⁻¹. Rotation rate: 100, 225, 400, 625, 900, 1225, 1600 and 2025 rpm. (b) Koutecky-Levich plots of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials from 0.715 to 0.265 V for N-C@Co-2. (c) The dependence of electron transfer number n on potential for N-C@Co-2 and Pt/C.

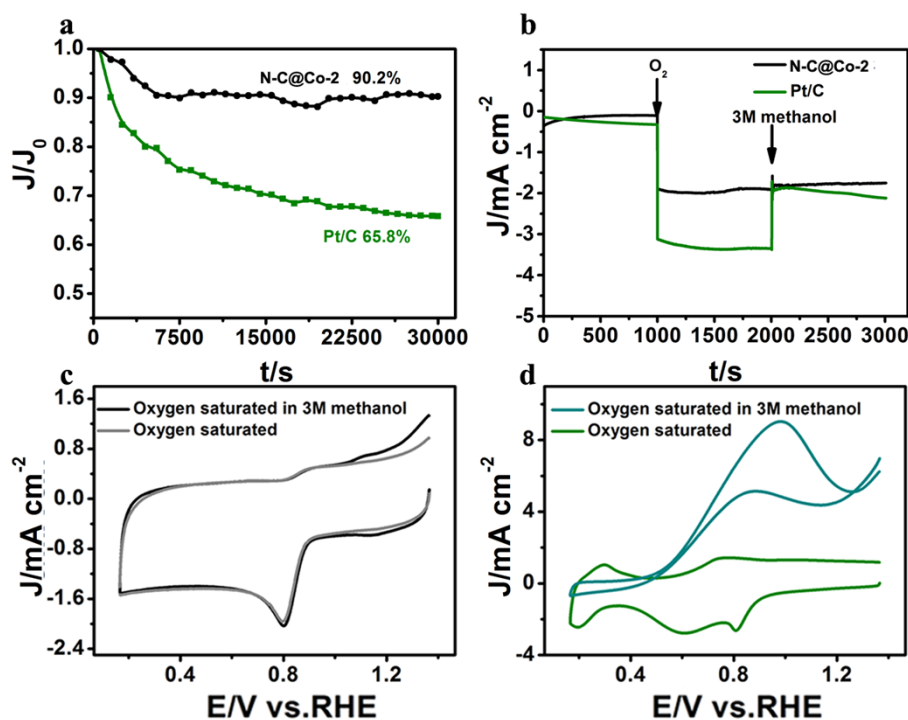


Fig. S8 (a) Chronoamperometric responses of N-C@Co-2 and Pt/C catalysts at 0.565 V in O_2 -saturated 0.1 M KOH at 900 rpm, which are normalized to the initial current responses. (b) Current-time chronoamperometric responses of N-C@Co-2 and Pt/C kept at 0.565 V vs. RHE at 900 rpm in 0.1 M KOH. The arrow indicates the introduction of O_2 and 3M methanol. (c) CVs of N-C@Co-2 in O_2 -saturated 0.1 M solution of KOH and O_2 -saturated 0.1 M solution of KOH injected 3 M CH_3OH at a scan rate of 50 mV/s. (d) CVs of Pt/C in O_2 -saturated 0.1 M solution of KOH and O_2 -saturated 0.1 M solution of KOH injected 3 M CH_3OH at a scan rate of 50 mV/s.

1. W. Luo, Z. Yang, Z. Li, J. Zhang, J. Liu, Z. Zhao, Z. Wang, S. Yan, T. Yu and Z. Zou, *Energy Environ. Sci.*, 2011, **4**, 4046-4051.
2. M. Li, X. Bo, Y. Zhang, C. Han and L. Guo, *J. Power Sources*, 2014, **264**, 114-122.