

Supporting Information

Manuscript title: Atomically dispersed cobalt- and nitrogen-codoped graphene towards bifunctional catalysis of oxygen reduction and hydrogen evolution reactions

Authors list: Xudong Wen, Lu Bai, Min Li, Jingqi Guan

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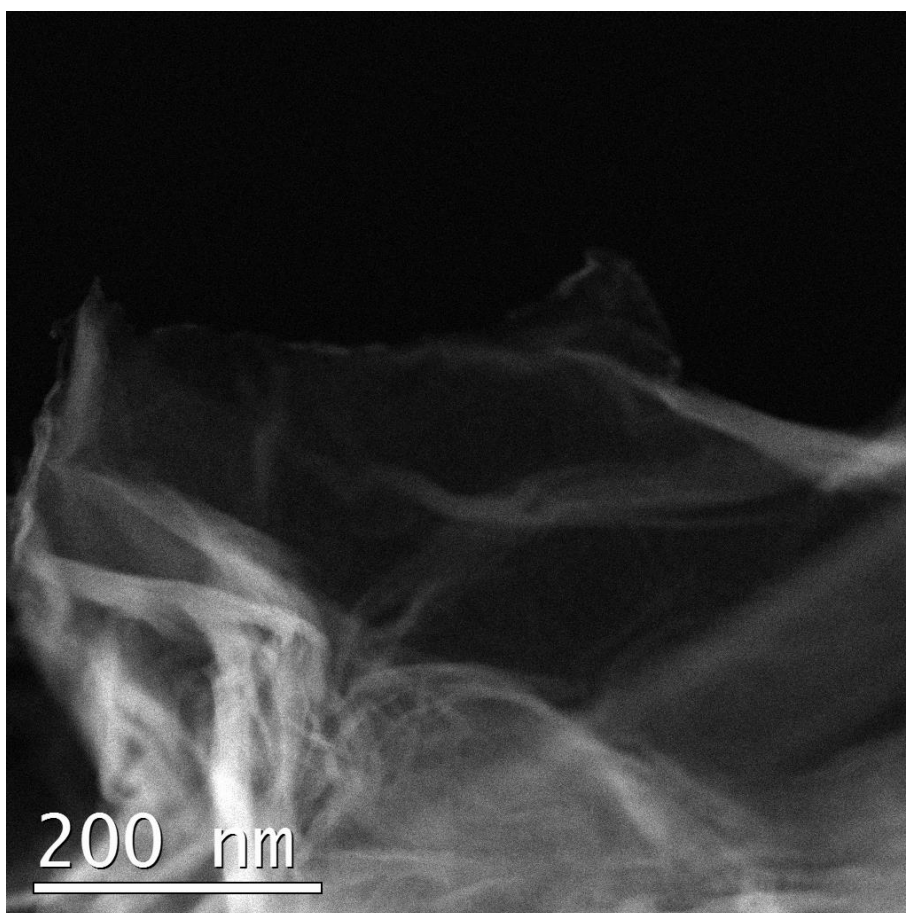


Figure S1. HAADF-STEM image of Co@NG-750 with low resolution.

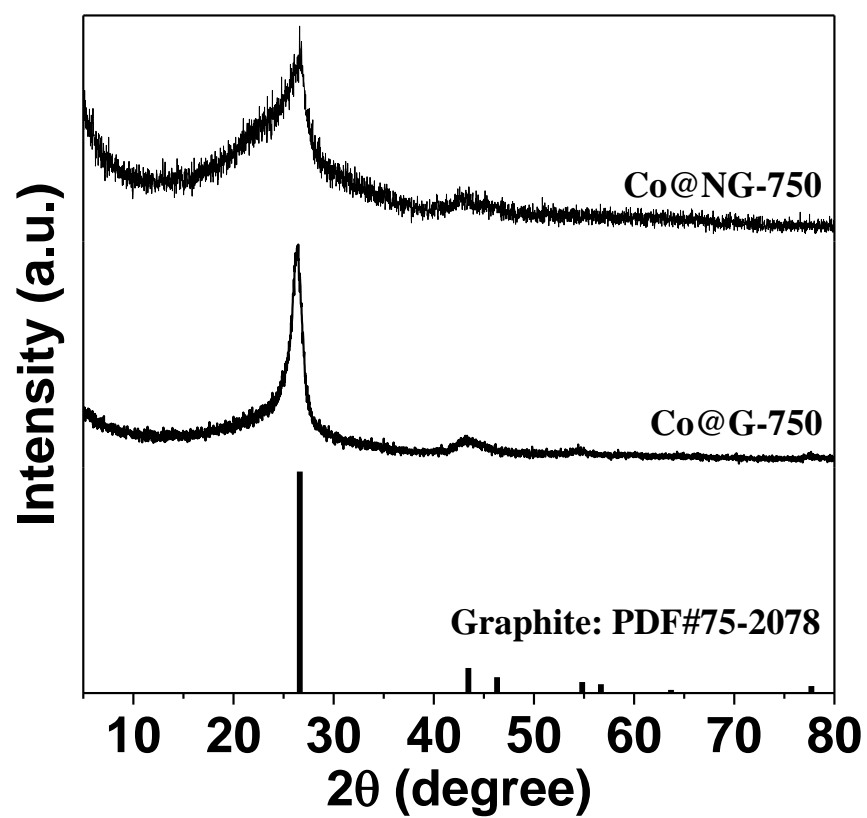


Figure S2. XRD patterns of Co@G-750 and Co@NG-750.

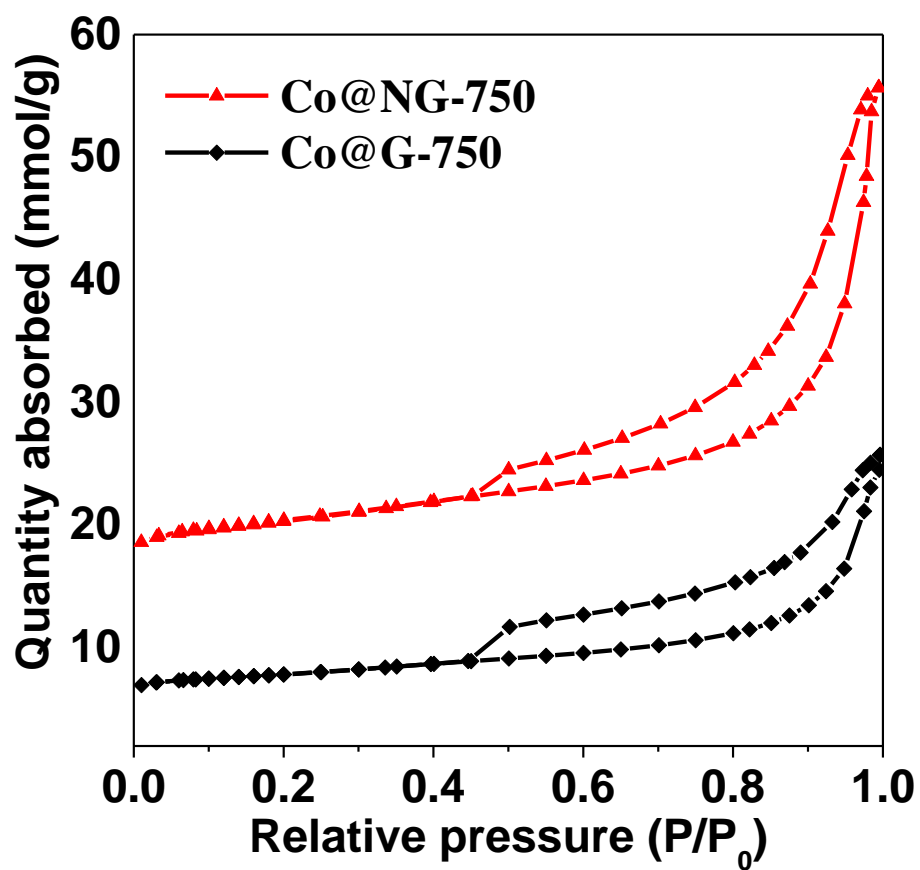


Figure S3. N₂ adsorption–desorption isotherms of Co@G-750 and Co@NG-750.

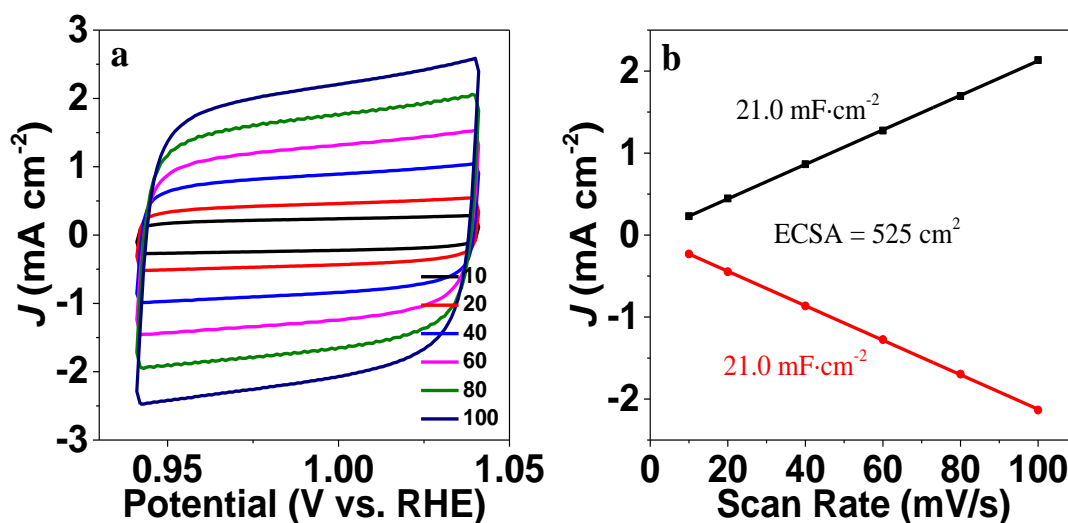


Figure S4. Double-layer capacitance measurements for determining the electrochemical active surface area for the Co@NG-450. (a) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b) The cathodic (black) and anodic (red) currents measured at 1.093 V vs RHE as a function of the scan rate. The average of the absolute value of the slope is taken as the double-layer capacitance of the electrode.

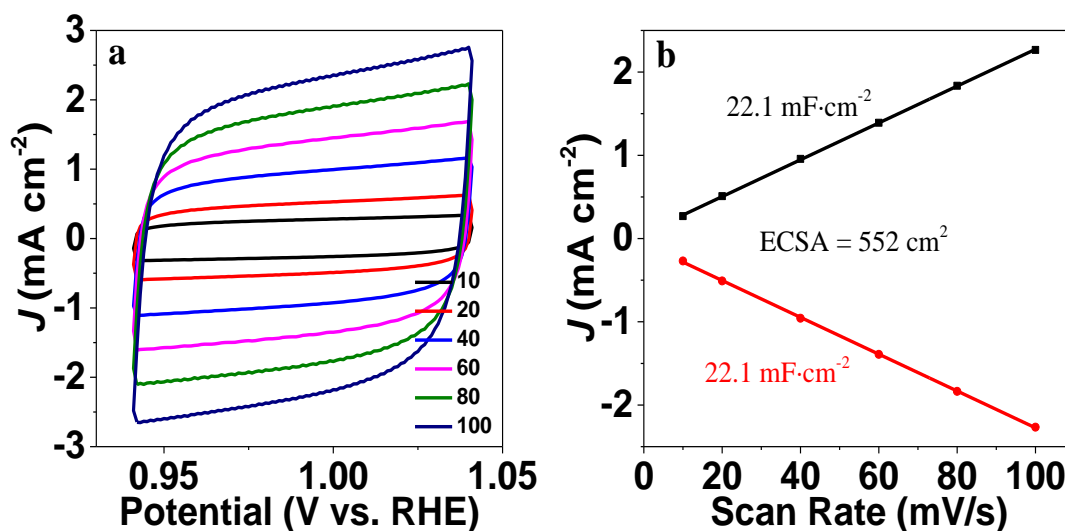


Figure S5. Double-layer capacitance measurements for determining the electrochemical active surface area for the Co@NG-550. (a) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b) The cathodic (black) and anodic (red) currents measured at 1.093 V vs RHE as a function of the scan rate. The average of the absolute value of the slope is taken as the double-layer capacitance of the electrode.

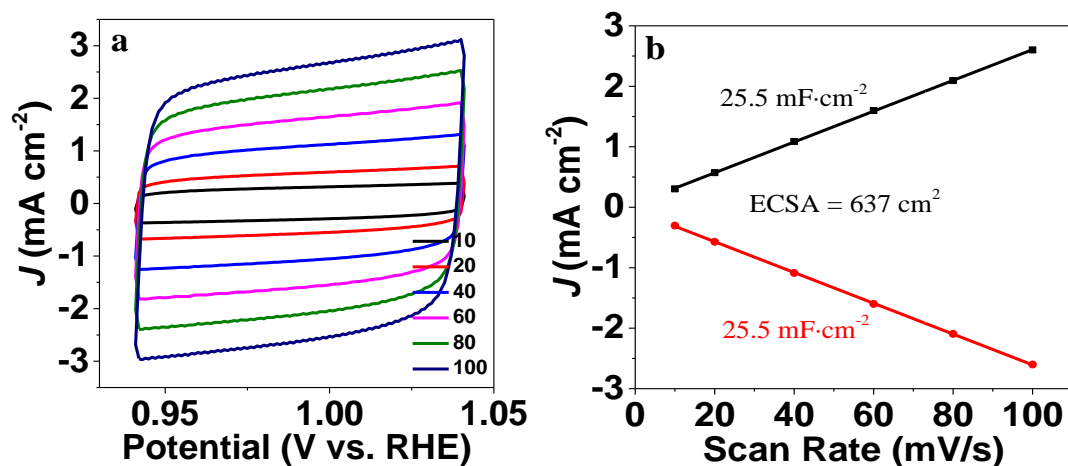


Figure S6. Double-layer capacitance measurements for determining the electrochemical active surface area for the Co@NG-650. (a) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b) The cathodic (black) and anodic (red) currents measured at 1.093 V vs RHE as a function of the scan rate. The average of the absolute value of the slope is taken as the double-layer capacitance of the electrode.

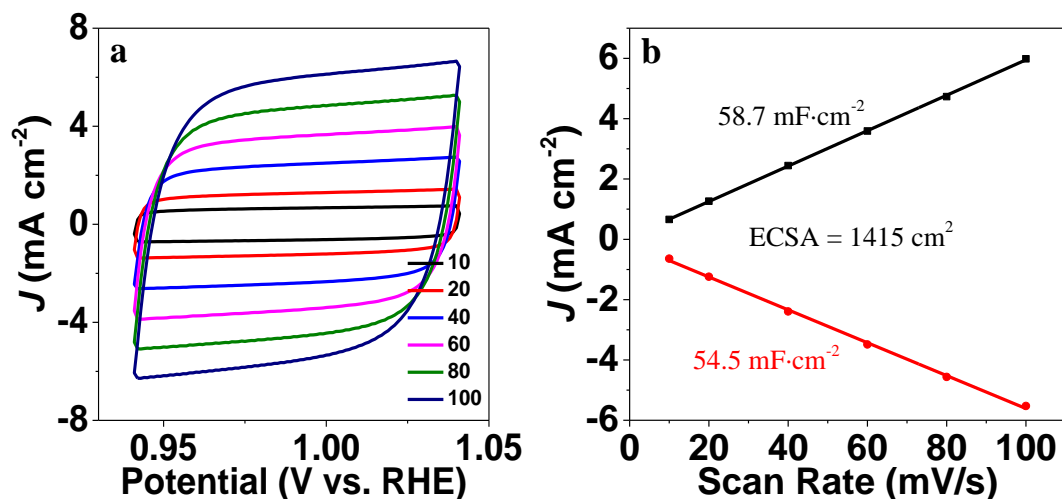


Figure S7. Double-layer capacitance measurements for determining the electrochemical active surface area for the Co@NG-750. (a) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b) The cathodic (black) and anodic (red) currents measured at 1.093 V vs RHE as a function of the scan rate. The average of the absolute value of the slope is taken as the double-layer capacitance of the electrode.

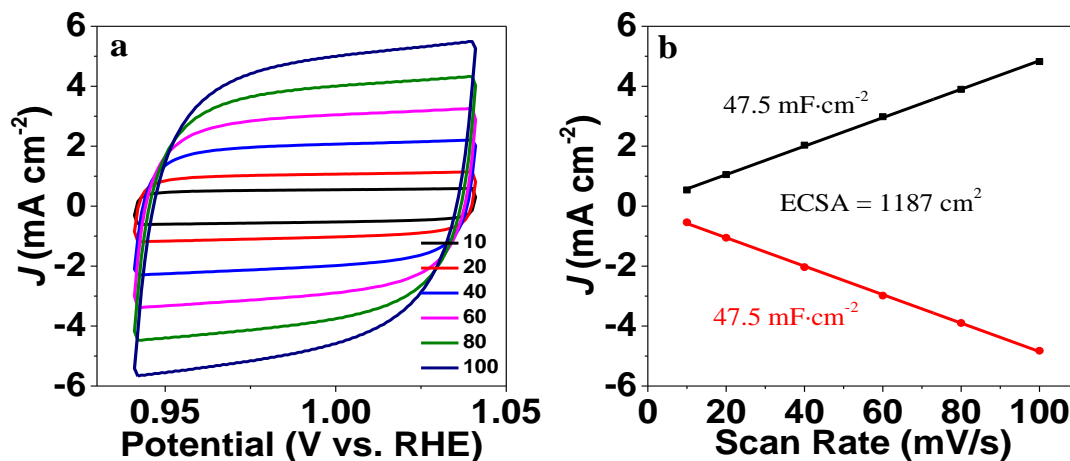


Figure S8. Double-layer capacitance measurements for determining the electrochemical active surface area for the Co@NG-850. (a) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b) The cathodic (black) and anodic (red) currents measured at 1.093 V vs RHE as a function of the scan rate. The average of the absolute value of the slope is taken as the double-layer capacitance of the electrode.

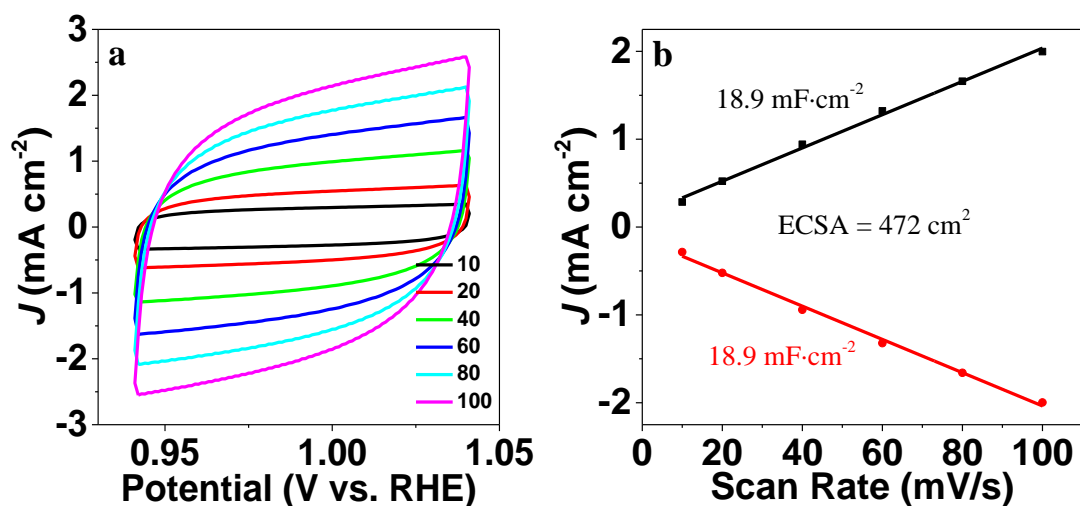


Figure S9. Double-layer capacitance measurements for determining the electrochemical active surface area for the Co@G-750. (a) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b) The cathodic (black) and anodic (red) currents measured at 1.093 V vs RHE as a function of the scan rate. The average of the absolute value of the slope is taken as the double-layer capacitance of the electrode.

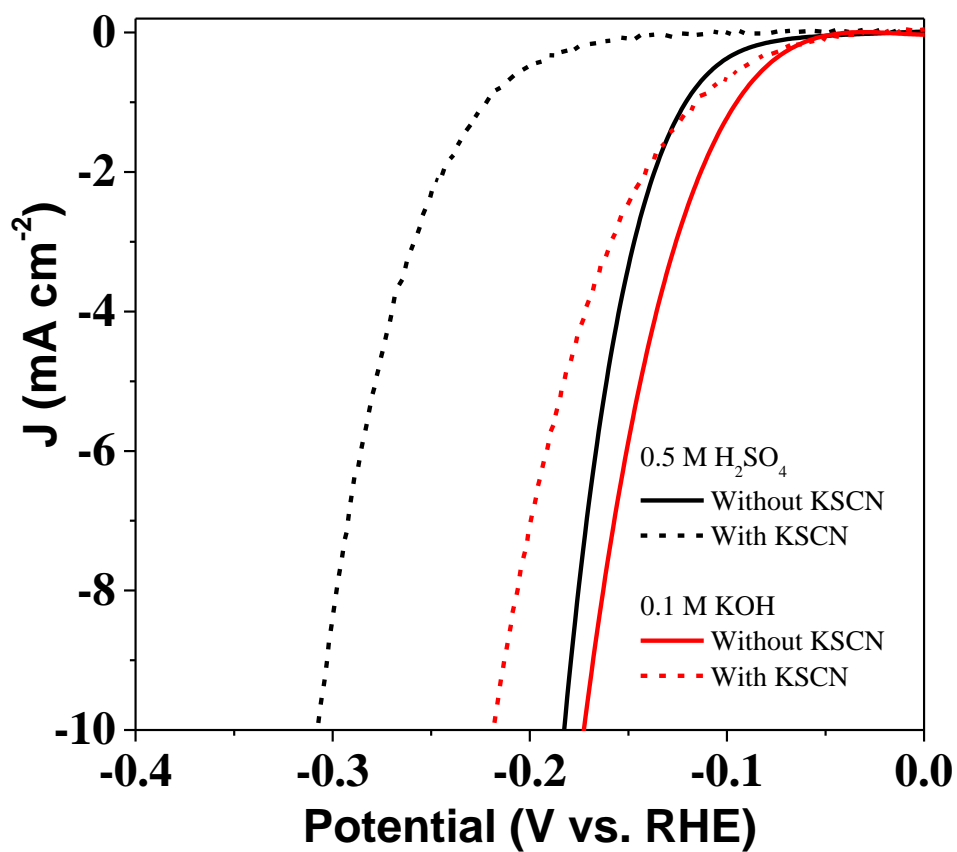


Figure S10. LSV polarization curves for HER on Co@NG-750 in 0.1 M KOH and 0.5 M H₂SO₄ with (dot line) and without (solid line) 10 mM KSCN.

Table S1 Elemental compositions of Co-G-750 and Co-NG-T annealed at different temperatures

Sample	Surface composition (<i>mol.</i> %)			
	C	N	O	Co
Co@G-750	87.55	-	12.13	0.32
Co@NG-450	87.53	4.78	7.43	0.26
Co@NG-550	88.40	5.23	6.14	0.23
Co@NG-650	87.81	6.68	5.29	0.22
Co@NG-750	88.0	7.92	3.88	0.20
Co@NG-850	92.33	6.75	3.67	0.25

Materials

Graphite powder (GP), sodium nitrate, potassium permanganate, sulfuric acid (98%), cobalt chloride hexahydrate, potassium hydroxide, ethanol and Pt/C (20 wt.% Pt) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). NH_3 (99.99%) and N_2 (99.99%) were purchased from Juyang Gas (Changchun, China). Ultrapure water (18.2 M Ω) was employed. All chemicals were used as received without further purification.

Electrochemical testing

Electrochemical HER measurements were carried out in a standard three-electrode system. 4 mg of electrocatalyst and 20 μL Nafion solution (5 wt.%) dispersed in 980 μL of ethanol under sonication for 30 min to form a uniform catalyst ink. Then, 5 μL ink was dropped on the glassy carbon electrode (GCE, 3 mm diameter) as the working electrode. A saturated calomel electrode (SCE) and a carbon plate were used as the reference electrode and the counter electrode, respectively. The electrolytes are 0.1 M KOH solution and 0.5 M H_2SO_4 solution. All potentials measured were calibrated to RHE using the equation: $E(\text{vs RHE}) = E(\text{vs SCE}) + 0.241 \text{ V} + 0.0591\text{pH}$.

Electrochemical ORR measurements were performed on an electrochemical workstation coupled with a rotating disk electrode (RDE) system (Pine Research Instrumentation, USA). The common method used to diagnose electrochemical mechanism is the Koutecky-Levich (K-L) method.¹⁴ The number of electron transfer (n) is determined by the slope of the line according to the following K-L equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{nFAkC_{\text{O}_2}} + \frac{1}{0.62nFAC_{\text{O}_2}D_{\text{O}_2}^{2/3}\nu^{-1/6}\omega^{1/2}} \quad (1)$$

where j is the rotating electrode current density, j_k is the kinetic current density, j_d is the diffusion-limiting current density, n is the electron transfer number per O_2 molecule, F is the Faraday constant (96500 C mol^{-1}), k is the electron transfer rate constant, C_{O_2} is the bulk oxygen concentration in electrolyte (0.1 M KOH, $1.2 \times 10^{-6} \text{ mol L}^{-1}$), A is the electrode geometric area ($\approx 0.247 \text{ cm}^2$), D_{O_2} is the diffusion coefficient of oxygen molecule in electrolyte (0.1 M KOH, $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte (0.1 M KOH, $0.01 \text{ cm}^2 \text{ s}^{-1}$), and ω is the electrode rotation speed (rad s^{-1}).

Characterization

X-ray diffraction (XRD) was carried out on a RIGAKU D/MAX2550/PC diffractometer at 40 kV and 100 mA with copper filtered $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the samples was obtained with JEOS JSM 6700F field-emission scanning electron microscope (SEM). Transmission electron microscope (TEM) images were observed by a Hitachi HT7700. High angle annular dark field imaging (HAADF) performed with an aberration-corrected JEM-ARM 200F microscope. X-Ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250 X-ray electron spectrometer using Al $K\alpha$ radiation. Region scans were collected using a 20 eV pass energy. Peak positions were calibrated relative to C 1s peak position at 284.6 eV. The cobalt content in the catalysts was determined using inductively coupled plasma atomic emission spectrometer (ICP-AES) on a Shimadzu ICPS-8100. Prior to ICP-AES measurement, 50 mg sample was placed in a 50 mL beaker and calcined in an oven at 520 °C for 6 h to completely remove the carbon. The residue was dissolved in nitric acid and diluted with water to test the cobalt content.