

Supplementary Materials

Atomic cobalt catalysts for efficient oxygen evolution reaction

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Materials and reagents

Graphite powder (SP), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sulfuric acid (H_2SO_4 , 98%), hydrochloric acid (HCl , 36%), potassium hydroxide (KOH), hydrogen peroxide (H_2O_2 , 28%) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). NH_3 (99.99%) and Ar (99.99%) were purchased from Juyang Gas (Changchun, China). All chemicals were analytical grade and used as purchased without further purification. Solutions were prepared using high purity water (Millipore Milli-Q purification system, resistivity $> 18 \text{ M}\Omega \cdot \text{cm}$).

Preparation of materials

Graphene oxide (GO) was prepared by a modified Hummers method.¹ Cobalt ions were introduced into the matrix of the graphene by high temperature treatment. In a typical synthesis, 100 mg GO was thoroughly dispersed in 50 mL water by sonication for 2 h. Then, 2.8 mg $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (initial Co content: 0.7 wt%) was added to the mixture. After stirring for 30 min, the water was dislodged by vacuum-rotary evaporation procedure. The residual solid was annealed under an Ar or NH_3 atmosphere at 750 °C for 2 h to obtain 0.7-Co@G-750, and 0.7-Co@NG-750, respectively. For comparison, a series of 0.7-Co@NG-T (T: annealing temperature) samples annealed under different temperature were fabricated by a similar synthetic procedure with the synthesis of Co@NG-750 except the different annealing temperature (i.e. 450, 550, 650, and 850 °C). And a series of c-Co@NG-750 samples

with different initial cobalt contents were fabricated by a similar synthetic procedure with the synthesis of Co@NG-750 except the different initial cobalt contents (i.e. 0.1, 0.3, 0.5, 0.7, and 0.9 wt.%). For comparison, graphene (G) and N-doped graphene (NG) was prepared by annealing GO at 750 °C under an Ar atmosphere and a NH₃ atmosphere for 2 hours, respectively.

Electrochemical measurement

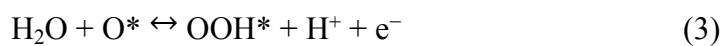
All electrochemical measurements were performed in a three-electrode system with a glassy carbon electrode (GCE) as the substrate for the working electrode, a graphite rod as the counter electrode and a saturated calomel electrode as the reference electrode. The reference electrode was calibrated with respect to a reversible hydrogen electrode before each experiment. The glassy carbon electrode was pre-polished using 0.05 μm alumina and distilled water. To prepare the working electrode, 2 mg of the catalyst was dispersed in a 0.5 mL mixed solvent of ethanol and Nafion (0.25 wt%) and sonicated to obtain a homogeneous ink. A certain amount of the catalyst ink was drop-casted on the glassy carbon electrode (catalyst loading: $\sim 0.28 \text{ mg}\cdot\text{cm}^{-2}$) and dried at room temperature.

For OER, the working electrode was first activated by steady-state cyclic voltammetry (CV) performed in the potential range from 0.2 to 1.5 V vs RHE at a scan rate of 50 mV s^{-1} for 50 cycles. Linear scan voltammetry (LSV) curves were then collected at a scan rate of 1 mV s^{-1} . All of the potentials in the LSV polarization curves were without iR compensation unless specifically illustrated.

Computational methods

Density functional theory (DFT) was employed in this work to evaluate the overpotential of OER on Co@NG catalysts. We used the Vienna ab initio simulation package (VASP) code² with electron correlation treated within the generalized gradient approximation using the PBE exchange-correlation functional.³ The one-electron states were expanded in a plane-wave basis with a kinetic cut-off energy of 400 eV, and the PAW method⁴ was used to take into account the effect of the inner cores on the valence states. Suitable Monkhorst-Pack meshes⁵ have been used to sample the reciprocal space for different models. The DFT+U method was applied to 3d orbitals of Co to correct the on-site Coulomb interactions.⁶ The value of U_{eff} was chosen to be 5.9 according to a previous linear response method.⁷ DFT+U method was previously found incapable of reaching the accuracy of quantum chemical coupled-cluster calculations by adjusting the U value.⁸ However, it may be the only method that can correct self-interaction error within affordable computational cost when large atomic models are considered. Besides, we believe DFT+U can predict relative shift of overpotentials on different models that are interested in this study more accurately. The structural models are considered fully relaxed until forces on the relaxed atoms were smaller than 0.05 eV/Å. All calculations are spin-polarized. The Brillouin zone was sampled with a $2 \times 2 \times 1$ k-point mesh for the Co@NG catalysts.

The theoretical overpotentials for oxygen evolution reaction (OER) on Co@NG catalysts are calculated using the computational hydrogen electrode model.⁹ The method has previously been successful in predicting trends in electrochemical activity on oxide surfaces.¹⁰ Briefly, we used DFT calculations to evaluate the binding energies of O*, OH* and OOH* on the Co sites of the Co@NG catalysts. Based on the calculated binding energies, the Gibbs free energy changes of electrochemical elementary steps are calculated along the OER reaction coordinate of a four-step reaction mechanism:



We assume standard conditions in calculating the Gibbs free energy changes. With this approach, the theoretical overpotential (η^{OER}) at standard conditions is defined as:

$$\eta^{\text{OER}} = (G^{\text{OER}}/\text{e}) - 1.23 \text{ V} \quad (5)$$

Where G^{OER} is the potential determining step defined as the highest free energy step in the process of OER.

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 α radiation ($\lambda = 1.5406 \text{ \AA}$). The infrared spectra (IR) of various samples were recorded at room temperature using a NICOLET Impact 410 spectrometer. N₂ adsorption–desorption isotherms were obtained on a Micromeritics ASAP 2010 system at liquid N₂ temperature. Before measurements, the samples were outgassed at 200 °C for 6 h. The specific surface area was calculated by using Brunauer–Emmett–Teller (BET) method. 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 resolution TEM (HRTEM) images were recorded on a JEM-2100 transmission electron microscope (Tokyo, Japan) at 200 kV. High angle annular dark field imaging (HAADF) was 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 α 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 content of cobalt 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 catalyst 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.

Calibration of SCE and conversion to RHE

The reference electrode SCE was calibrated according to the method reported previously.¹¹ Calibrations were carried out by using a reversible hydrogen electrode (RHE). First, two Pt electrodes were cleaned by cycling in 1 M H₂SO₄ between -2 and 2 V for 2 hours. Then, they were used as working electrode and counter electrode, respectively. Before the calibration, the electrolytes 0.1 M KOH and 0.5 M H₂SO₄ should be saturated with H₂ by continuous bubbling H₂. During the calibration, hydrogen was bubbled over the working electrode. A series of controlled-potential chronoamperometric curves were measured for 300 s to get the current interconvert between the hydrogen oxidation and hydrogen evolution reaction. The resulting potential is the potential of zero net current. In this work, the potential of zero net current was found at -1.038 V versus the SCE electrode in 1.0 M KOH. Thus, the potentials, measured against SCE, were converted into the potentials versus RHE by using the equation 6:

$$\text{In 1.0 M KOH: } E_{\text{vs.RHE}} = E_{\text{vs.SCE}} + 1.038 \text{ V} \quad (6)$$

Electrochemically active surface area (ECSA)

To determine the effective electrochemical active surface area (ECSA) of samples, a series of cyclic voltammetry (CV) curves were tested at various scan rates (10, 20, 40, 60, 80 and 100 mV/s) in the potential window between 1.038 and 1.138 V vs. RHE. The sweep segments of the measurements were set to 10 to ensure consistency. The geometric double layer capacitance (C_{dl}) was calculated by plotting the difference of current density $\Delta J = (J_{anodic} - J_{cathodic})/2$ at 1.088 V vs. RHE against the scan rate, and the slope of the linear trend was C_{dl} . Finally, the ECSA of catalyst on GCE is estimated according to the equation 7:

$$ECSA = \frac{C_{dl}}{C_s} \quad (7)$$

where C_s is the specific capacitance of a flat standard electrode with 1 cm² of real surface area, which is generally in the range of 20 to 60 $\mu\text{F cm}^{-2}$.¹² In this work, the averaged value of 40 $\mu\text{F cm}^{-2}$ was adopted for the flat electrode.

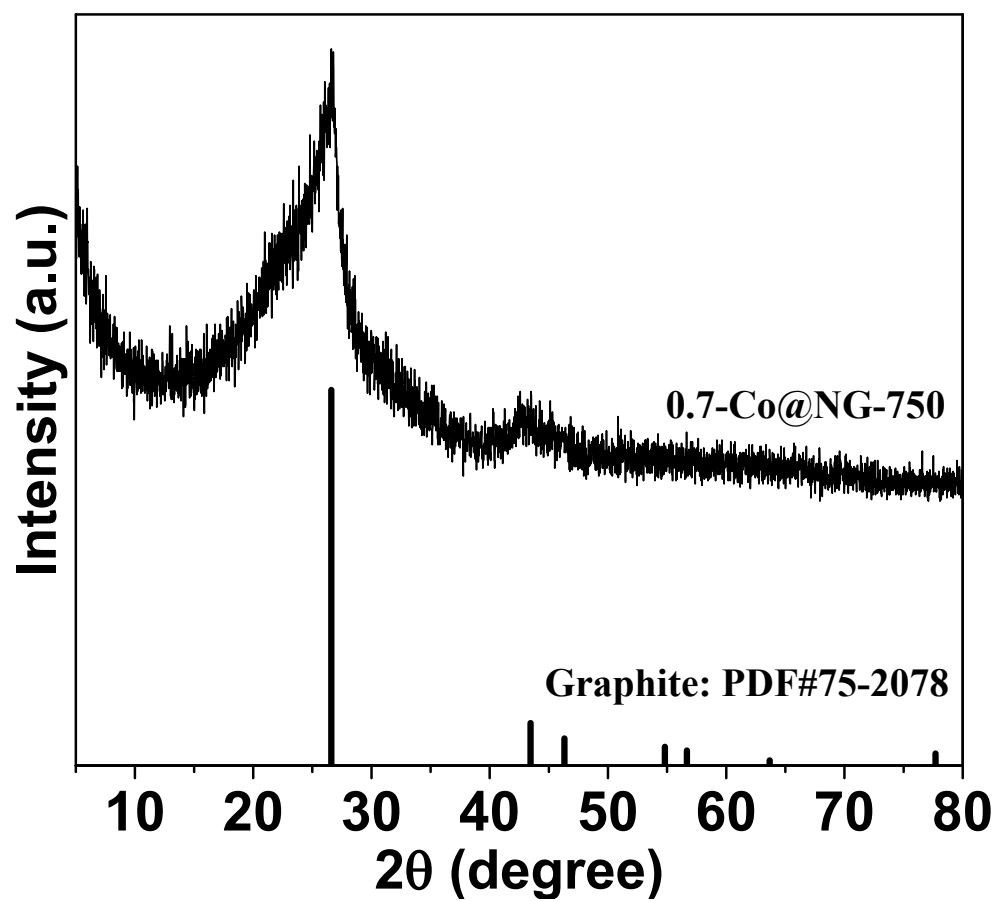


Figure S1. XRD patterns of 0.7-Co@NG-750 and referred graphite sample.

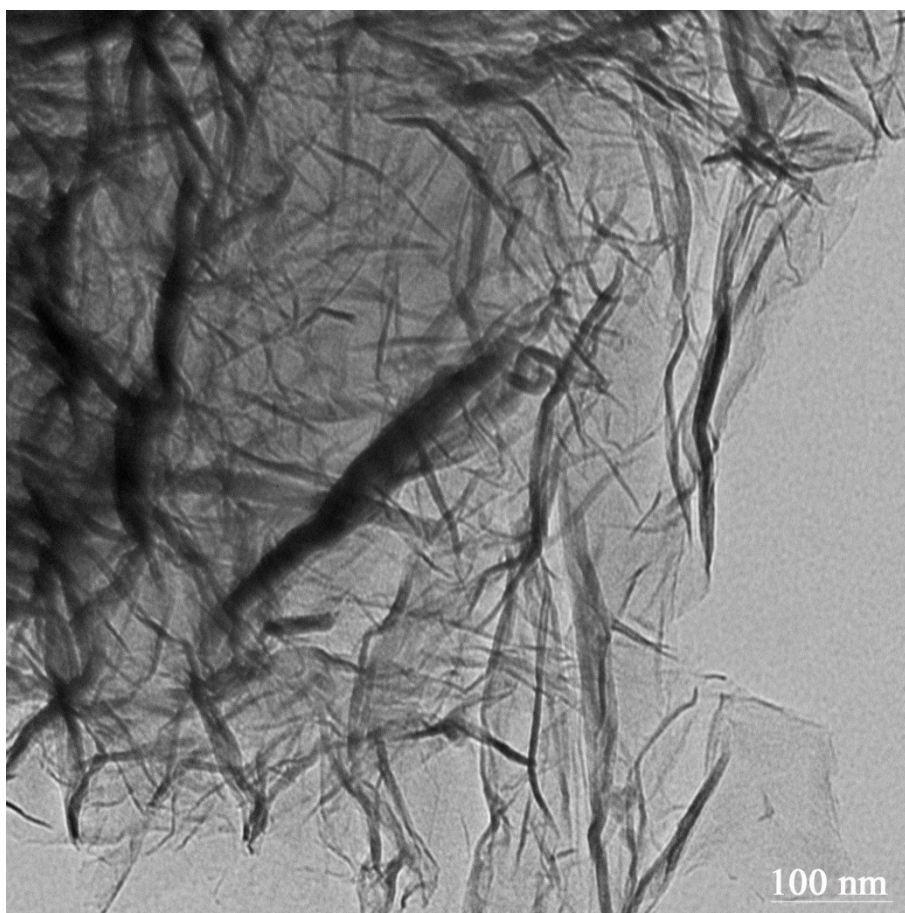


Figure S2. TEM image of 0.7-Co@NG-750.

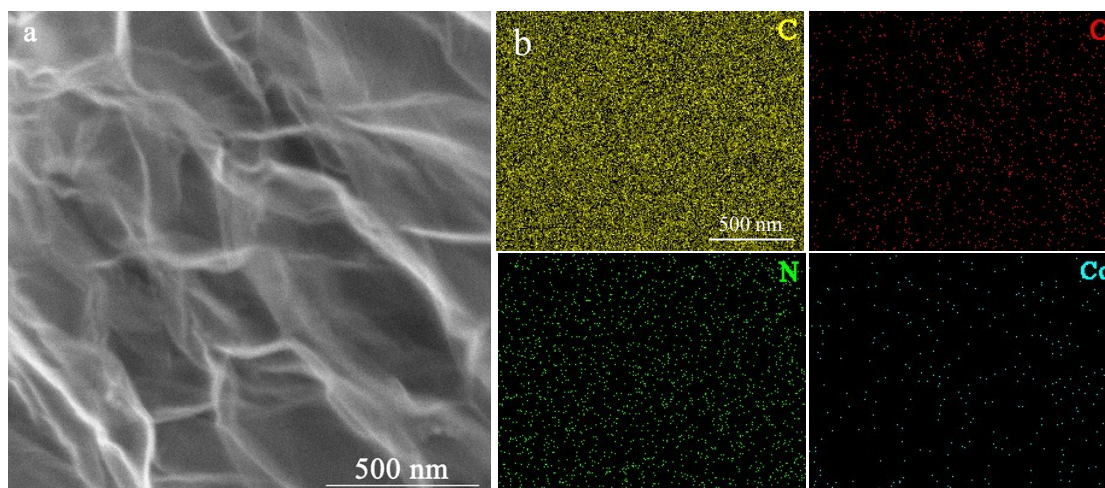


Figure S3. SEM image used in the EDS mapping test, (b) the corresponding EDS mapping of 0.7-Co@NG-750.

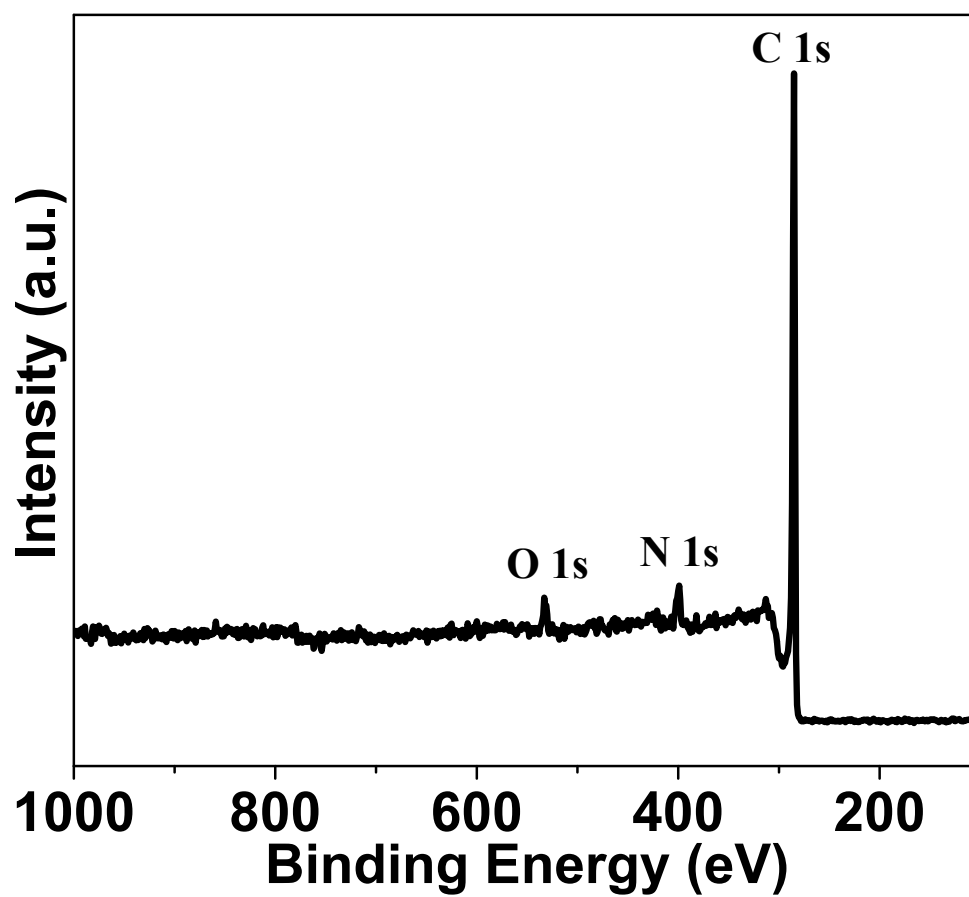


Figure S4. XPS survey spectrum of 0.7-Co@NG-750.

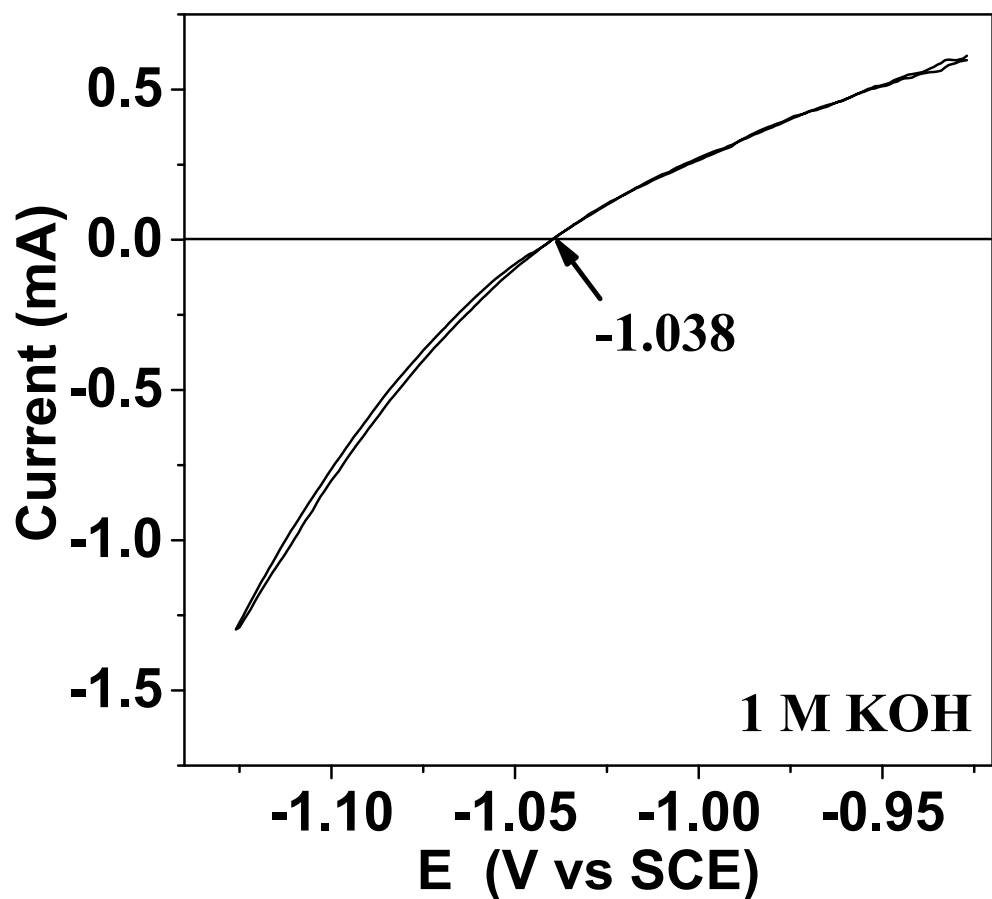


Figure S5. The current as a function of the applied potentials for the calibration of SCE reference electrode in 1.0 M KOH.

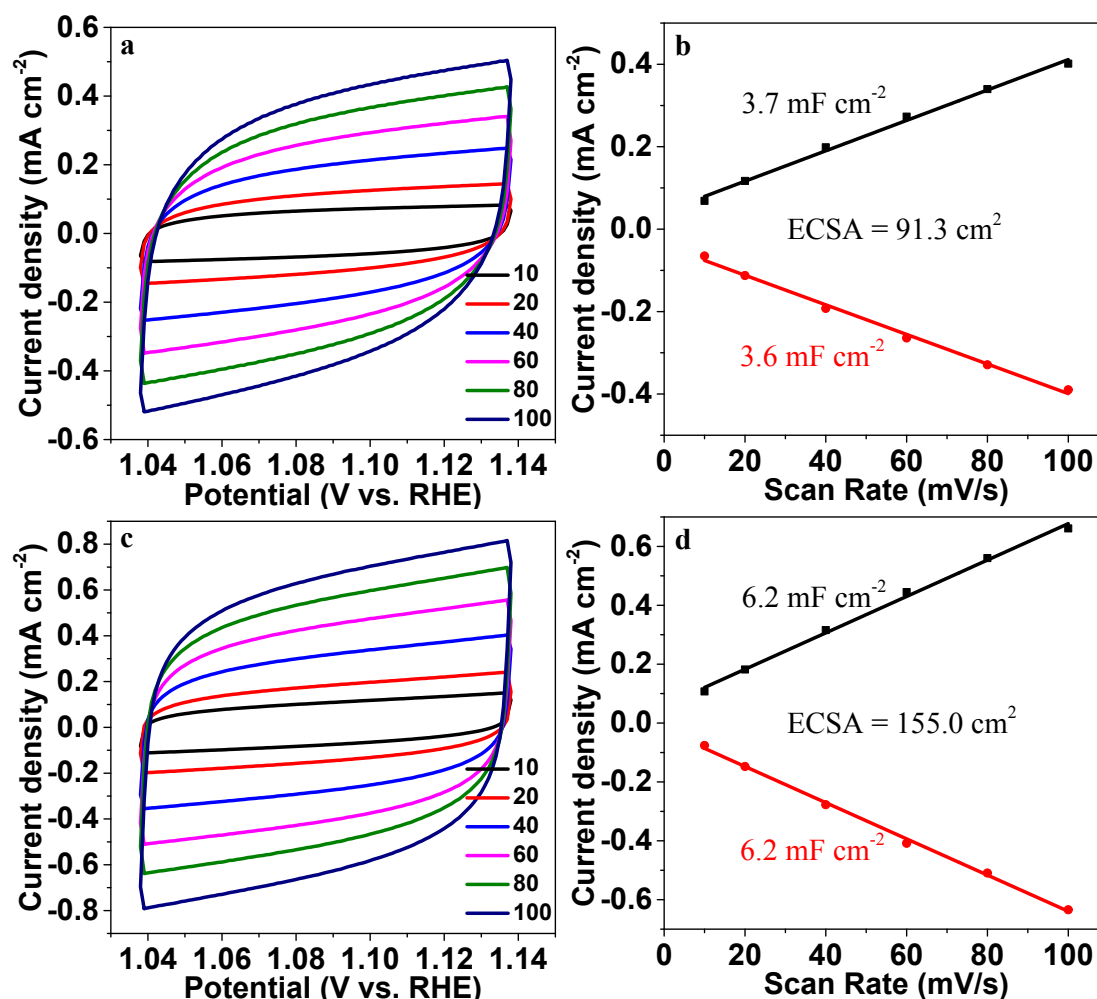


Figure S6. Double-layer capacitance measurements for determining the electrochemical active surface area for the 0.7-Co@G-750 (a, b) and 0.7-Co@NG-750 (c, d). (a, c) CVs measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹. (b, d) The cathodic (black) and anodic (red) currents measured at 1.088 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.

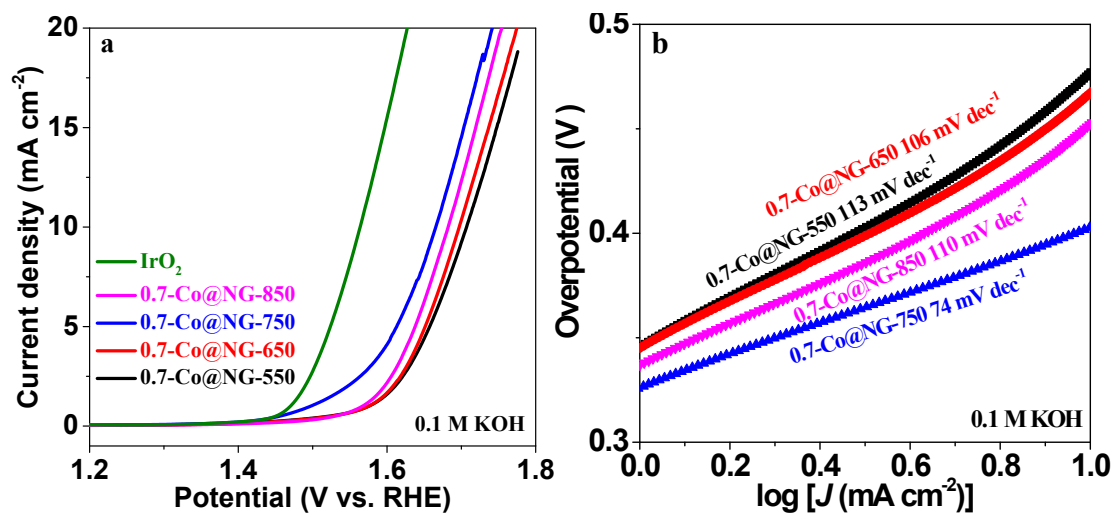


Figure S7. (a) LSV curves of 0.7-Co@NG-T and IrO_2 in 0.1 M KOH. (b) Tafel plots for 0.7-Co@NG-T .

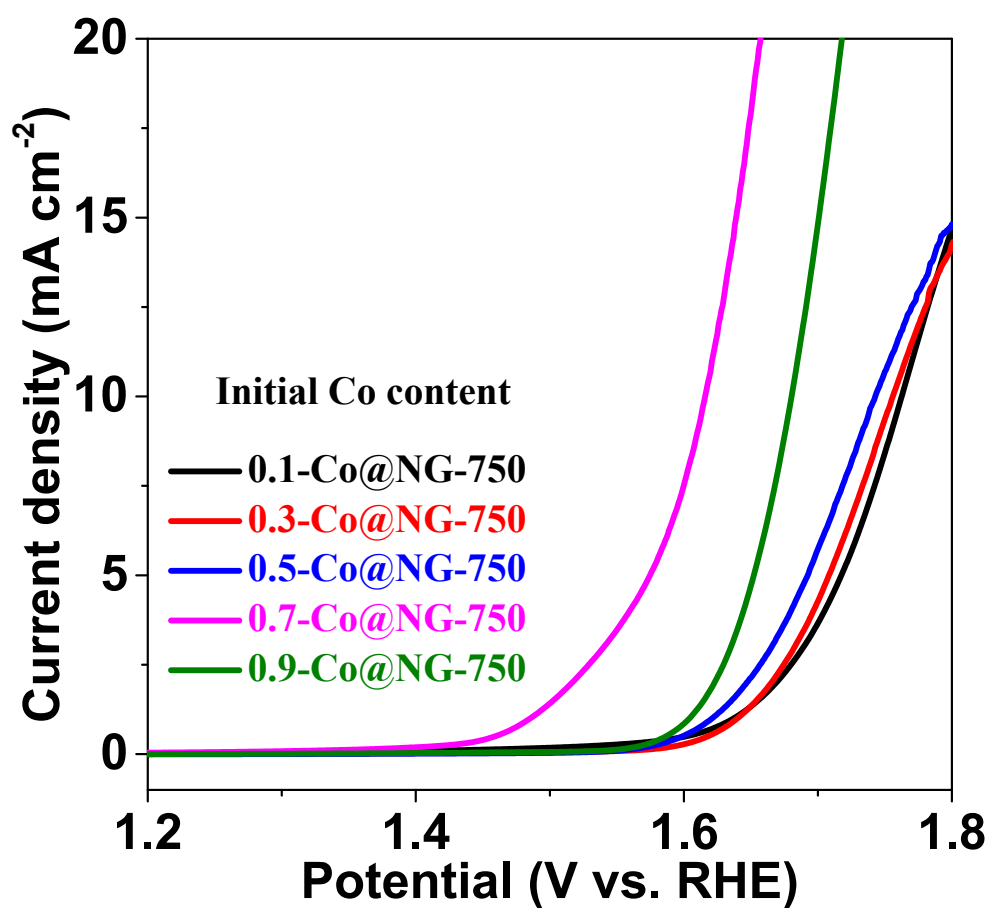


Figure S8. LSV curves of c-Co@NG-750 in 1.0 M KOH.

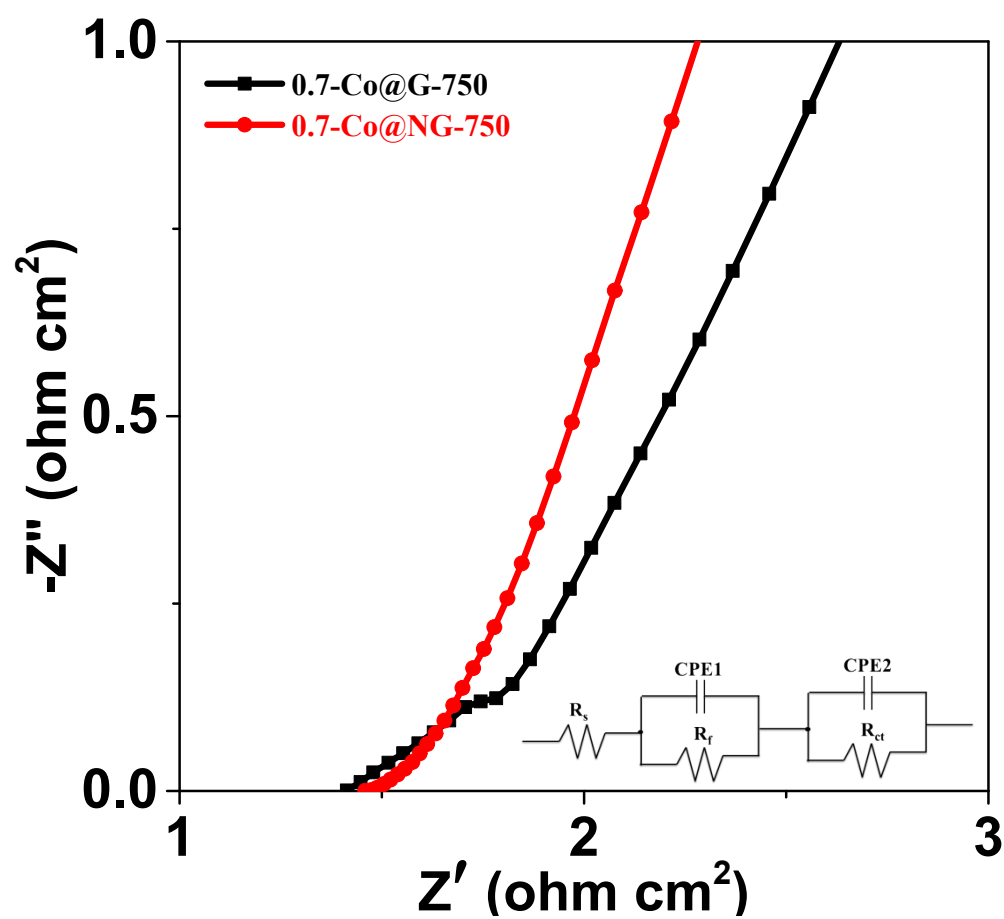


Figure S9. Nyquist plots of the EIS test for the 0.7-Co@G-750 and 0.7-Co@NG-750.

The solid lines are the fits to the data using the simplified Randles circuit shown in the inset.

References

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