

Supporting Information

***In Situ* Hybridization of CoO_x Nanoparticles on N-Doped Graphene Through One Step Mineralization of Co-Responsive Hydrogels**

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- **General experimental**

4-pyridine carboxaldehyde was purchased from Xiensi Reagent (Tianjin, China), L/D-typtophan, $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ and sodium borohydride were purchased from Xiya Reagent (Chengdu, China). 20% Pt/C commercial catalyst (Johnson-Matthey HiSPEC 3000) was used for comparison. All other reagents were of analytical grade and deionized water (MillQ, 6.8M Ω) was used.

CV measurements were performed on the CHI 650D electrochemical workstations (Shanghai, China). RDE tests were used by a Pine Modulated Speed Rotator (AFMSRCE, America) at a scan rate of 5 mV s⁻¹ with various rotating speed from 400 to 1600 rpm. A FEI HELIOS NanoLab 600i scanning electron microscope (SEM), a Veeco dimension 3100 atomic force microscopic (AFM) and a FEI Titan G2 60-300 transmission electron microscope (TEM) at an accelerating voltage of 200 kV were used to investigate morphological properties of the prepared samples. XRD measurements were performed on a D/max 2550 X-ray power diffractometer (Bruker/AXS D8 Advance) to detect the structurally characteristic of the samples. Moreover, energy-dispersive X-ray (EDX) and EDX-STEM mapping analyses were obtained from TEM (FEI Titan G2 60-300, America). Raman measurement was performed using an in Via-reflex spectrometer (Renishaw) equipped with a microscope under 532 nm laser radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out at an ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Fisher-VG Scientific, America). Annealing processes were carried out at an OTF-1200X-L tube furnace (Kejing, Hefei).

- **Electrochemical measurements**

Cyclic voltammetry (CV): 0.5 mg of catalyst dispersed in 1mL of Mili-Q water by sonicating the mixture for 30 minutes in an ultrasonic bath to achieve a homogenous ink. 6 μL of catalyst ink was drop cast on the glassy carbon electrode (GCE) resulting in a deposition of 0.3 cm in diameter (the loading of all nonprecious catalyst is $\sim 42 \mu\text{g cm}^{-2}$) and dried at 50°C for ~ 20 minutes. CV measurements were performed on the CHI 650D electrochemical workstations (Shanghai, China), Pt as counter electrode, Ag/AgCl electrode as reference electrode and GCE as working electrode. Before the implementation of the experiments, the electrolyte solution (0.1M KOH) was saturated with oxygen or nitrogen (control experiment) by aerating the gas into the electrolyte for at least 30 minutes. In order to ensure the gas has been in a saturated state in the electrolyte, purging was continued throughout the experimental process. CVs were tested at a scan rate of 100 mV s⁻¹ after 3 cycles during a potential range of 0.2 to -0.8 V vs. Ag/AgCl. When the methanol tolerance ability was detected, the electrolyte was changed to a mixed solution of 0.1 M KOH and 1 M CH₃OH. The potentials in all electrochemical experiments were converted to the standard hydrogen electrode potential according to the following formula:

$$ERHE = E_{\text{Ag/AgCl}} + 0.05916 * pH + E_{\theta\text{Ag/AgCl}} \quad (1)$$

where $E_{\text{Ag/AgCl}}^{\theta}$ is the standard potential of the Ag/AgCl electrode at room temperature (15°C, $E_{\text{Ag/AgCl}}^{\theta}=0.2089$ V). 20% Pt/C commercial catalyst (Johnson-Matthey HiSPEC 3000) was used for comparison.

Rotating disk electrode (RDE) measurements: RDE tests were used by a Pine Modulated Speed Rotator (AFMSRCE, America) at a scan rate of 5 mV s⁻¹ with various rotating speed from 400 to 1600 rpm. The similar

method with CV has been carried out for prepared catalysts for RDE measurements. Koutecky-Levich plots were employed to describe ORR kinetics characteristics and provide mechanisms of prepared catalysts.

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (2)$$

Where J is the experimental current density, J_K and J_L are the kinetic limiting current density and diffusion limiting current density respectively. ω is the angular velocity, and B and J_K can be calculated by the following formulas, respectively:

$$B = 0.62nFC_o(D_o)^{2/3}\nu^{-1/6} \quad (3)$$

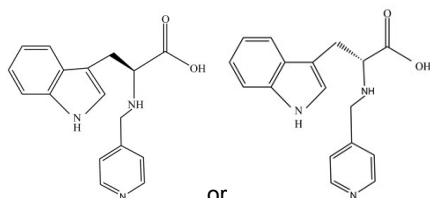
$$J_K = nFkC_o \quad (4)$$

Where n is transferred electron number, F is the Faraday constant ($96,485\text{C mol}^{-1}$), C_o is the bulk concentration of O_2 ($1.15 \times 10^{-6}\text{ mol cm}^{-3}$), D_o is the diffusion coefficient of O_2 ($1.90 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($0.01\text{ cm}^2\text{ s}^{-1}$).

• General procedure for the aerogel preparation

Synthetic route of GO: The GO was synthesized through a modified Hummers method.^[1] Modified Hummers methods could yield well-distributed GO solution. However, we usually perform a 48 hours' dialysis toward GO after reducing it to obtain ultrathin graphene is tricky and laborious.

Synthesis of PT: The synthetic method of PT is referred to the reported literature.^[2] To an aqueous solution (10 mL) of L/D-tryptophan (1g, 5 mmol) containing KOH (0.28 g, 5 mmol), 4-pyridinecarboxaldehyde (0.54 g, 5 mmol) in MeOH (5 mL) was added slowly. The solution was stirred for 2 h at room temperature. Then the solution was cooled in an ice bath. NaBH_4 (0.23 g, 6 mmol) was added to the solution slowly. The mixture was stirred for 3 h, and 50% acetic acid was used to neutralize the basic (pH~10) reaction mixture and adjusted the pH to 4.0-5.0. The mixture system was stirred further for 2 h. The resulting solid was filtered off, and washed with methanol and water, dried, and recrystallized from water/methanol (3:1). The molecular formula of PT is



Synthesis method of PT- Co^{2+} /GO hybrid hydrogels: To begin with, PT- Co^{2+} /GO hybrid hydrogels were obtained by mixing the PT solution and cobalt (II) acetate solution with GO suspending liquid (1 mg mL⁻¹ PT solution, 1 mg mL⁻¹ cobalt (II) acetate solution and 1 mg mL⁻¹ GO solution, Scheme 1a and b), and the pH was adjusted to 7-8 with aqueous ammonia. The solution changes into a hydrogel after sonication for several seconds.

Synthesis method of the CoO_x NPs on N-doped graphene aerogels: The procedure for preparing the CoO_x NPs on N-doped graphene aerogels is briefly explained in Scheme 1. After hydrothermal treatment with self-assembly (at 180°C for 12 h), PT- Co^{2+} /GO hydrogels became shrinkable supramolecular hybrid hydrogels. Afterwards, the supramolecular hybrid hydrogels were subjected to vacuum freeze drying (the materials were denoted as $\text{CoO}_x/\text{N-rGO}$ after vacuum freeze drying) and further high temperature annealing treatment (heated at 600, 700 and 800°C respectively for 3h with argon protection and yielded nitrogen-enriched graphene with incorporation of CoO_x NPs and these were named $\text{CoO}_x/\text{N-rGO600}$, $\text{CoO}_x/\text{N-rGO700}$ and $\text{CoO}_x/\text{N-rGO800}$, respectively.) to produce the CoO_x NPs on N-doped graphene aerogels (Scheme 1c and d). Moreover, pure CoO_x was prepared only using $\text{Co}(\text{CH}_3\text{CO}_2)_2$ and N-rGO was prepared using a similar approach with $\text{CoO}_x/\text{N-rGO}$ samples by excluding $\text{Co}(\text{CH}_3\text{CO}_2)_2$ precursors, respectively.

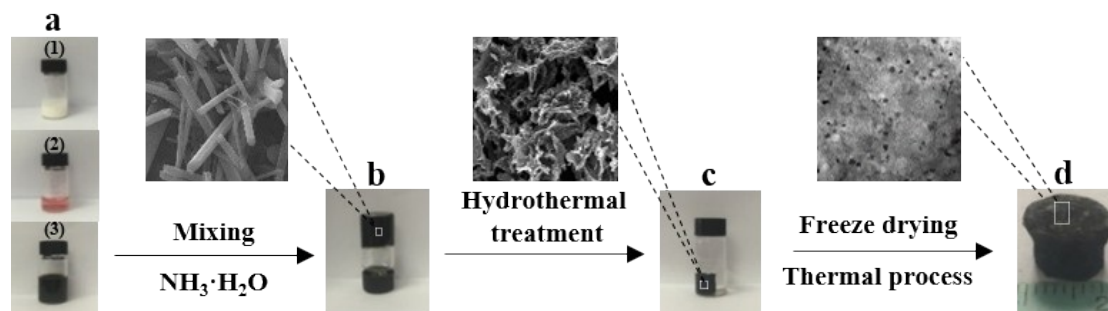


Figure S1 The preparation process for the CoO_x NPs on N-doped graphene aerogels and corresponding electron microscopic images.

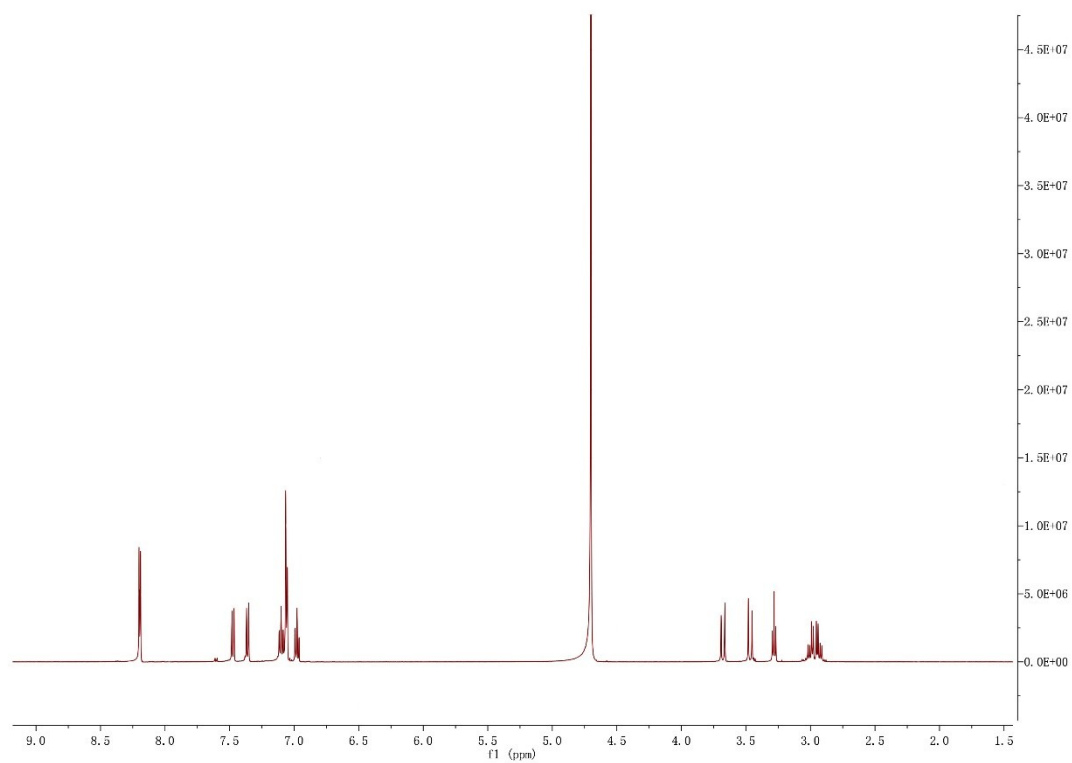


Figure S2 ^1H NMR (500 MHz) Spectra of PT in D_2O .

^1H NMR (500 MHz, D_2O , ppm): $-\text{CH}_2$ (2.97, dd, 2H), $-\text{CH}$ (3.29, t, $J = 6.7$ Hz, 1H), $-\text{CH}_2$ (3.66, dd, 2H), In-H (6.98-7.13, m, 6H), py-H (7.42, dd, 2H), py-H (8.28, dd, 2H).

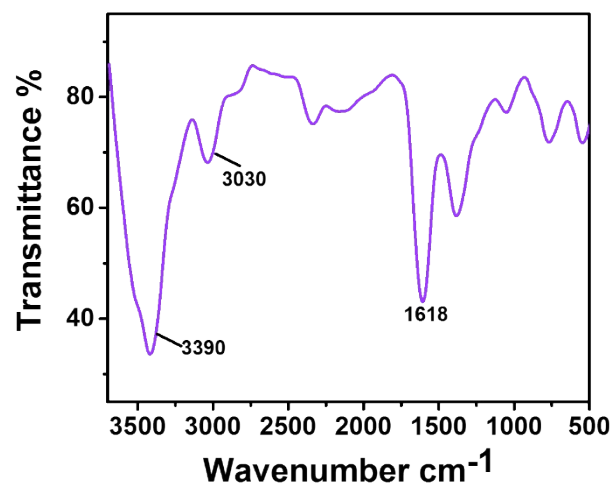


Figure S3 The FT-IR spectra of PT.

The peak at 1618 cm⁻¹ demonstrated the exist of pyridine ring skeleton stretching vibration. The peaks at 3390 cm⁻¹ and 3030 cm⁻¹ suggested the attendance the carboxyl.

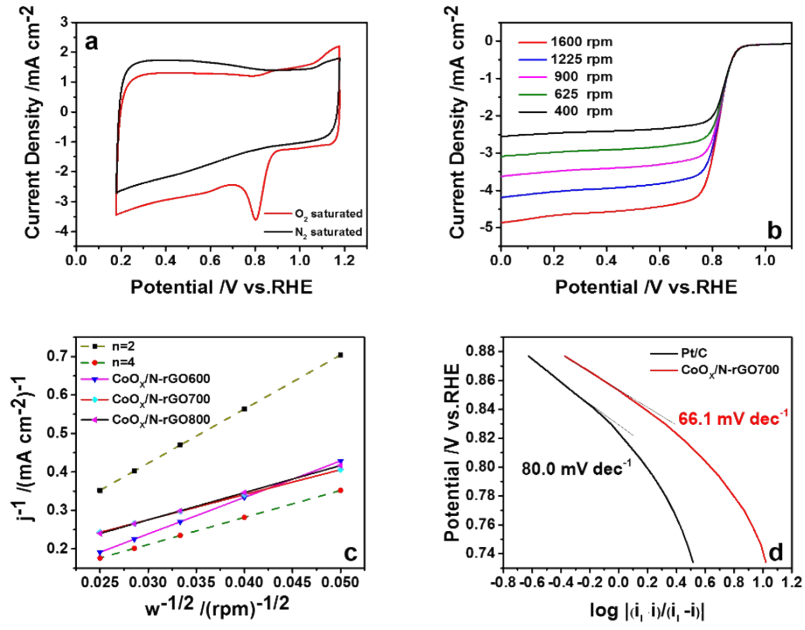


Figure S4 Electrochemical characteristics of aerogels. (a) CVs of CoO_x/N-rGO700 as the catalyst for ORR in N₂-saturated and O₂-saturated 0.1 M KOH at a scan rate of 100 mV s⁻¹, respectively; (b) LSVs of CoO_x/N-rGO700 in O₂-saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹ at different RDE rotation rates (in rpm); (c) The Koutecky–Levich plots of CoO_x/N-rGO600, CoO_x/N-rGO700 and CoO_x/N-rGO800 derived from RDE tests at 0.47 V; (d) Tafel plots obtained from the RDE measurements on Pt/C catalyst and CoO_x/N-rGO700.

Table S1 The ORR performance of CoO_x/N-rGO samples in 0.1 M KOH.

Sample	Onset potential /V ^[a]	Half wave potential /V ^[a]	Peak potential /V ^[a]	Peak current density /mA cm ⁻²	Electron transfer number at -0.47 V ^[a]
CoO _x /N-rGO600	0.877	0.810	0.763	2.24	2.96
CoO _x /N-rGO700	0.927	0.840	0.802	2.35	3.98
CoO _x /N-rGO800	0.925	0.829	0.783	1.96	3.63
Pt/C	0.949	0.836	0.781	2.23	3.96

[a]: V vs. RHE.

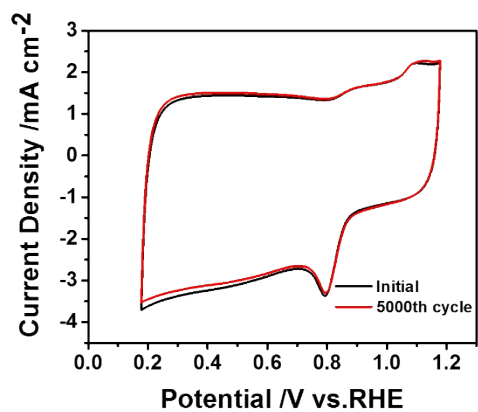


Figure S5 The stability of CoO_x/N-rGO700. CoO_x/N-rGO700 as the catalyst for ORR in O₂-saturated 0.1 M KOH at a scan rate of 100 mV s⁻¹ and after 5000 cycles.

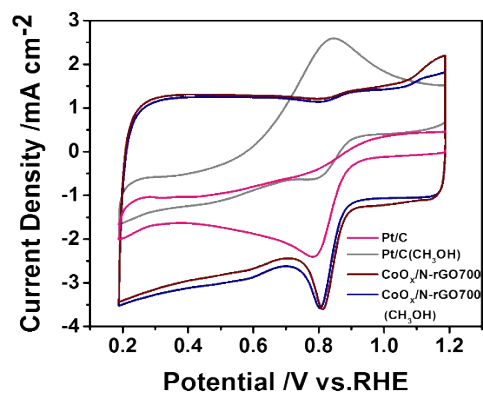


Figure S6 The methanol tolerance ability of CoO_x/N-rGO700 and Pt/C catalyst. (a) CVs of the CoO_x/N-rGO700 and (b) Pt/C modified electrodes in 0.1 M KOH saturated with O₂ and 0.1 M KOH+1 M CH₃OH saturated with O₂ at a scan rate of 100 mV s⁻¹, respectively.

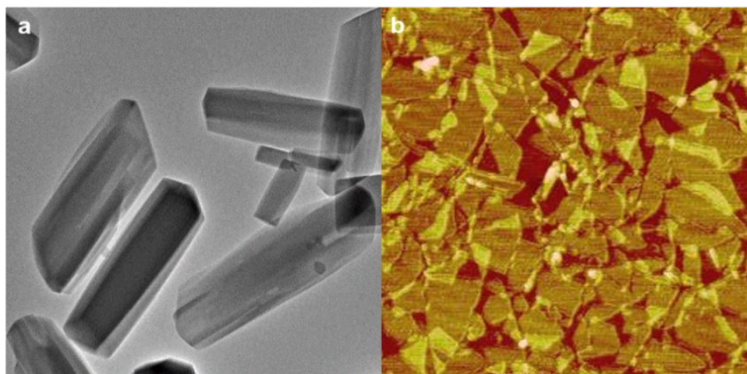


Figure S7 The TEM image of 1 mg mL^{-1} PT solution (a) and AFM image of 1 mg mL^{-1} GO solution (b).

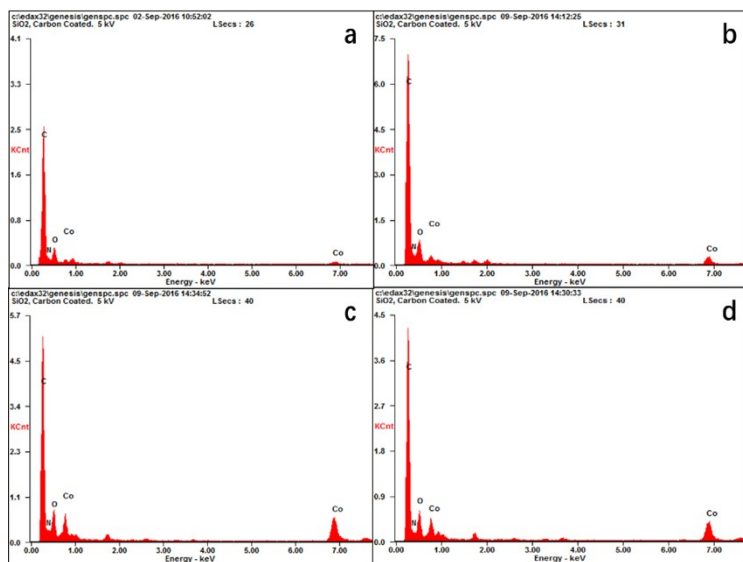


Figure S8 TEM EDS analyses of CoO_x/N-rGO(a), CoO_x/N-rGO600(b), CoO_x/N-rGO700(c) and CoO_x/N-rGO800(d).

Table S2 The elements content of CoO_x/N-rGO samples from TEM EDS.

Sample	C at%	N at%	O at%	Co at%
CoO _x /N-rGO	90.40	3.80	5.40	0.40
CoO _x /N-rGO600	90.50	3.00	5.80	0.60
CoO _x /N-rGO700	86.50	4.60	6.70	2.20
CoO _x /N-rGO800	88.40	3.50	6.30	1.80

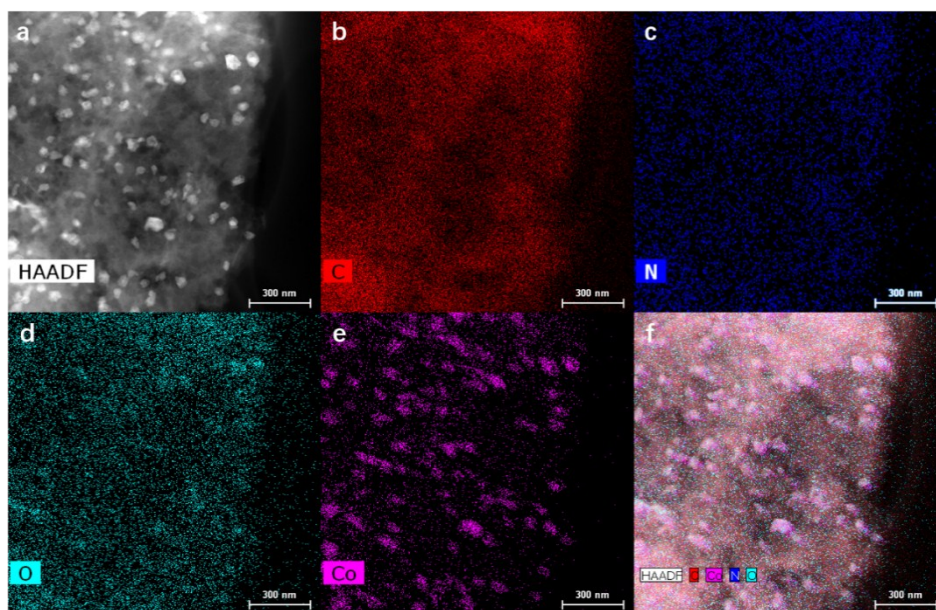


Figure S9 Elemental Mapping of $\text{CoO}_x/\text{N-rGO700}$: (a) HAADF-STEM image and (b-f) corresponding HAADF-STEM-EDS maps of different elements, showing the distribution of various elements in $\text{CoO}_x/\text{N-rGO700}$.

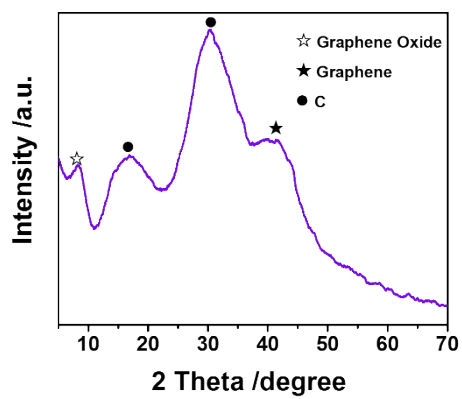


Figure S10 The XRD pattern of PT-Co²⁺/GO hydrogel.

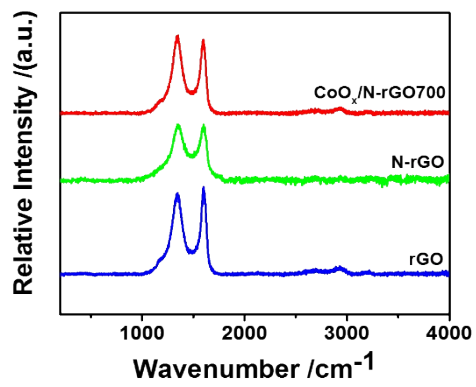


Figure S11 Raman spectra of rGO (blue), N-rGO (green), and CoO_x/N-rGO700 (red).

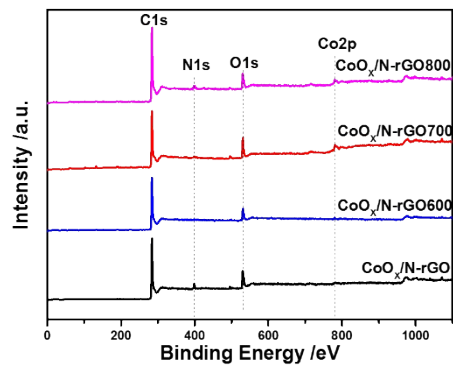


Figure S12 XPS spectra recorded from 0 to 1100 eV of CoO_x/N-rGO (black), CoO_x/N-rGO600 (blue), CoO_x/N-rGO700 (red) and CoO_x/N-rGO800 (magenta).

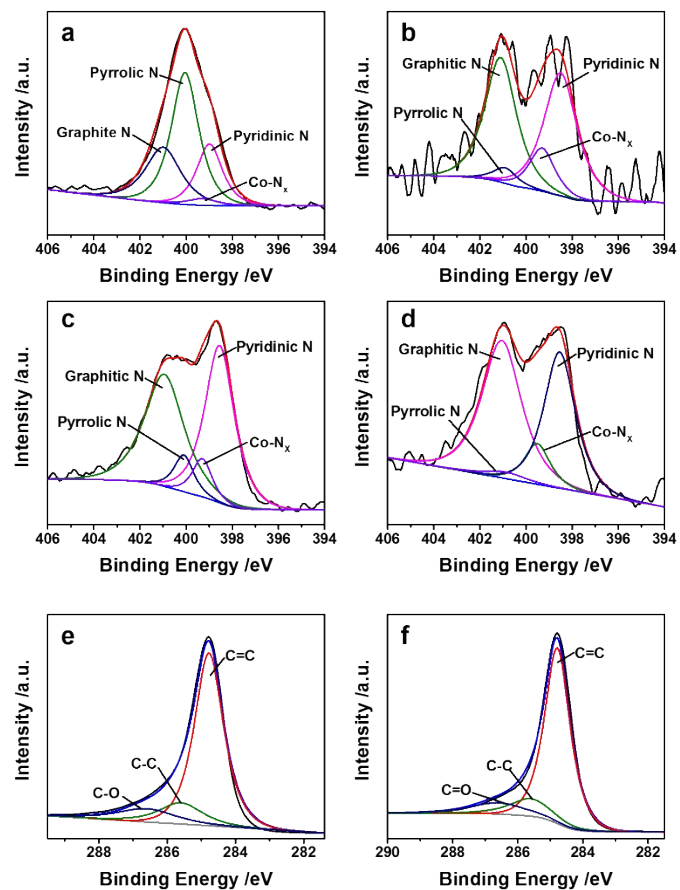


Figure S13 The N1s XPS spectra of (a) CoO_x/N-rGO, (b) CoO_x/N-rGO600, (c) CoO_x/N-rGO700 and (d) CoO_x/N-rGO800; (e) C1s XPS spectra of CoO_x/N-rGO700 samples; (f) C1s XPS spectra of rGO samples.

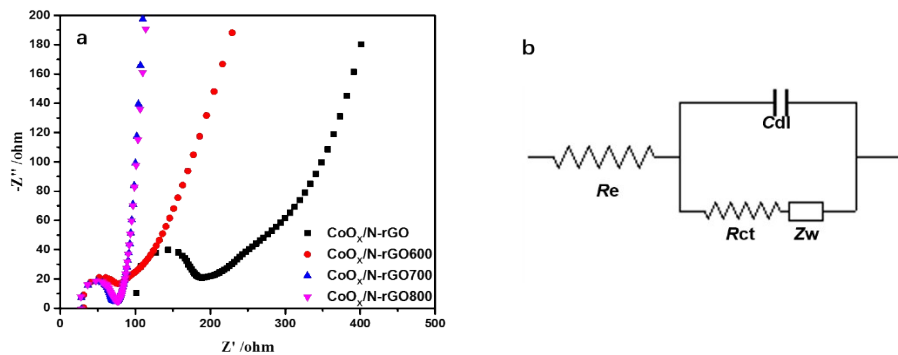


Figure S14 (a) Nyquist plots of the CoO_x/N-rGO (black), CoO_x/N-rGO600 (red), CoO_x/N-rGO700 (blue) and CoO_x/N-rGO800 (magenta); (b) The electrical equivalent circuit used for fitting impedance spectra. Re is the electrolyte resistance, Cdl and Rct are the double-layer capacitance and charge-transfer resistance, respectively, Zw is the Warburg impedance.

References

- [1] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- [2] X. Wang, T. He, L. Yang, H. Wu, R. Zhang, Z. Zhang, R. Shen, J. Xiang, Y. Zhang, C. W. Wei, *Nanoscale*, 2016, **8**, 6479.