

Supporting Information

A High-Performance Electrocatalyst for Oxygen Reduction Based on Reduced Graphene Oxide Modified with Oxide Nanoparticles, Nitrogen Dopants, and Possible Metal-N-C Sites

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Chemicals: Iron (III) chloride (FeCl_3) and cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were purchased from AcrosOrganics Chemical Reagent Co. 1,10-phenanthroline (phen), melamine, potassium permanganate (KMnO_4), phosphorus (V) oxide (P_2O_5), sodium nitrate (NaNO_3), sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2), sulphuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Graphite powder (99+%) was purchased from Alfa Aesar. VXC-72 was supplied by Cabot Corp. (USA) and carbon nanotubes (CNTs) were from Ningbo institute of materials technology & engineering, China. All aqueous solutions were prepared with ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$ at $25 \text{ }^\circ\text{C}$) produced from a Millipore water system (Synergy® UV, France).

Synthesis of graphene oxide: Graphene oxide (GO) was synthesized from natural graphite flakes by a modified Hummers method.¹ Graphite powder (3 g, 100 mesh) was placed into a mixture of concentrated H_2SO_4 (12 mL), $\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$ (3.26 g) and P_2O_5 (2.5 g). The mixture was incubated at $80 \text{ }^\circ\text{C}$ for 4.5 h. Next, the mixture was cooled down to room temperature and diluted with 0.5 L of H_2O and left overnight. In the following, the mixture was filtered and washed using a $0.45 \text{ }\mu\text{m}$ millipore-filter to remove the residual acid. The product was dried under ambient condition. This pre-oxidized graphite was then subjected to oxidation by the following steps. The pretreated graphite powder was placed into concentrated H_2SO_4 ($0 \text{ }^\circ\text{C}$, 120 mL). Next, KMnO_4 (15 g) was added gradually under stirring and the temperature of the mixture was kept to be below $20 \text{ }^\circ\text{C}$. Next, the mixture was stirred at $35 \text{ }^\circ\text{C}$ for 2 h, followed by the additional of 0.7 L H_2O . Shortly, 20 mL of 30% H_2O_2 was added to the mixture. The resulting brilliant-yellow mixture was filtered and washed with 10 wt% HCl aqueous solution (1 L) and then washed repeatedly with H_2O until the pH of the filtrate was neutral. The GO slurry was dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ and purified by dialysis for one week.

Synthesis of $\text{Fe}_3\text{Co-rGO}$ Electrocatalyst: Phen (105 mg) and melamine (66 mg) at 1:1 molar ratio were added to 100 mL of water in a round-bottom flask and the mixture was incubated at $80 \text{ }^\circ\text{C}$. 10 mL of 41 mM FeCl_3 and 10 mL of 13 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was mixed at Fe/Co molar ratio of about 3:1 and heated to $80 \text{ }^\circ\text{C}$. 100 mL of 2 mg/mL GO aqueous solution was prepared under sonication at $80 \text{ }^\circ\text{C}$. In this case, the mass loading of transition metal salts on GO is 32 wt%.

Initially, the three stock solutions were mixed together and stirred for 30 min at 80 °C, followed by cooling down to room temperature in about 80 min to form dark-yellow precipitates. Next, 50 mL of 8 mg/mL NaBH₄ aqueous solution was added. The dark-yellow precipitates gradually turned into black, indicating the completion of the reduction of GO. The black precipitates were filtered, washed with water, and dried overnight at 65 °C. Next, the sample was heat-treated in argon (80 mL/min) at 800 °C with a heating rate of 4 °C min⁻¹ for 2 h. Finally, the heat-treated sample was leached in 0.5 M H₂SO₄ aqueous solution at 80 °C for 30 min to remove unstable species. Next, the product was repeatedly washed with water until the filtrate pH reached 7. Finally, the sample was dried again at 65 °C prior to being used for further measurements. Controlled experiments were carried out by varying one parameter each time while keep all the others the same, including phen/melamine molar ratio (phen alone, 1:0.75, 1:1, 0.75:1, melamine alone), support type (VXC-72, rGO, carbon nanotubes), Fe/Co molar ratio (Fe alone, 1:1, 3:1, 1:3, Co alone), and heating temperature (450, 650, 775, 800, 850, and 900 °C).

Electron Microscopy and X-ray Diffraction Studies: The X-ray diffraction (XRD) spectrum was recorded in transmission geometry with Cu K α radiation ($\lambda = 0.15432$ nm) in the range of 10-80° on Rigaku D/Max 2400 with 2 θ scan mode at a scanning rate of 5° min⁻¹. XPS (Thermo ESCALAB 250Xi), SEM (HITACHI S5500, 30 KeV), TEM (FEI Tecnai G2 Spirit, 120 KeV), HRTEM and HAADF STEM (FEI Tecnai G2 F30 S-Twin, 300 KeV) were performed on obtained electrocatalysts. The samples for electron microscopy analysis were prepared by adding drops of colloidal suspensions onto a standard copper grid and wicking away the excess liquid with a tissue paper. The grids were air-dried for at least 2 h before imaging.

Electrochemical Measurements: Electrochemical measurements of cyclic voltammetry (CV), rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) were carried out by a potentiostat (760D, CH Instruments, Shanghai, China) with a conventional three-electrode electrochemical cell installed with a platinum mesh as the counter electrode and a Hg/HgO (1 M NaOH) as the reference electrode. For the preparation of working electrodes, an electrocatalyst was dispersed with the aid of sonication in a mixed solution consisted of water, ethanol, and Nafion solution (5 wt%, Dupont) ($V_{\text{water}}:V_{\text{ethanol}}:V_{\text{Nafion}}=1:9:0.1$) to form a catalyst ink (3.9 mg/mL). Next, 60 μ L of the catalyst ink was dropped on the surface of glassy carbon RDE (0.19625 cm², PINE Instruments) and then evaporated in air. For comparison, working electrodes of 20 wt% commercial Pt/C (Johnson Matthey-JM) were prepared in a similar manner. Cyclic voltammetry (CV) characterization of catalysts was carried out in N₂-purged alkaline solution (0.1 M KOH) with a potential range of -0.8 to 0.2 V (vs. Hg/HgO) at a positive scanning rate of 100 mV s⁻¹. The oxygen reduction reaction (ORR) polarization curves of RDE and RRDE (disk area: 0.2475 cm², ring area: 0.1886 cm², PINE Instrument) were obtained in O₂-saturated 0.1 M KOH aqueous solution with a scanning range of -0.8 to 0.2 V (vs. Hg/HgO) and a positive scanning rate of 5 mV s⁻¹ at 1600 rpm. The ring potential of RRDE was kept constant at 0.2 V (vs. Hg/HgO). The peroxide percentage (%HO₂⁻) and electron transfer number (n) were evaluated based on the following equations:

$$j_{\text{lim}} = 0.62nFD^{2/3}\nu^{-1/6}C_o\omega^{1/2} \quad (1)$$

$$\%HO_2^- = 200 \times \frac{I_r/N}{(I_r/N) + I_d} \quad (2)$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}} \quad (3)$$

In equation (1), j_{lim} is the limiting current density; n is the number of electrons transferred per oxygen molecule; $F(96485 \text{ C mol}^{-1})$ is the Faraday constant; $D (1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$ is the diffusion coefficient of O_2 in 0.1 KOH and $C_0 (1.2 \times 10^{-6} \text{ mol cm}^{-3})$ is the concentration of O_2 in the electrolyte. ν is the kinetic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$); and ω is the electrode rotation rate (rad s^{-1}). In equation (2) and (3), I_r and I_d is the ring and disk current, respectively. The manufacturer's value of N (ring collection efficiency) is 37%. For durability test, potential cycling were conducted under a harsh degradation condition in the range of -0.4 to 0.2 V (vs. Hg/HgO) for a total number of 1500 cycles in O_2 -saturated 0.1 M KOH. The potential sweep rate was 100 mV s^{-1} . After certain cycling numbers, ORR polarization curve was collected to track the degradation of electrocatalysts.

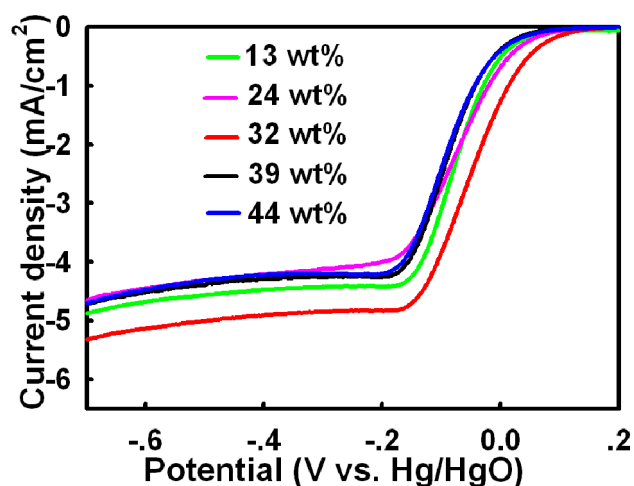


Figure S1. The ORR polarization curves of electrocatalyst at different theoretical loadings (transition metal salts on GO) obtained at a positive scanning rate of 5 mVs^{-1} and 1600 rpm in O_2 -saturated 0.1 M KOH aqueous solution.

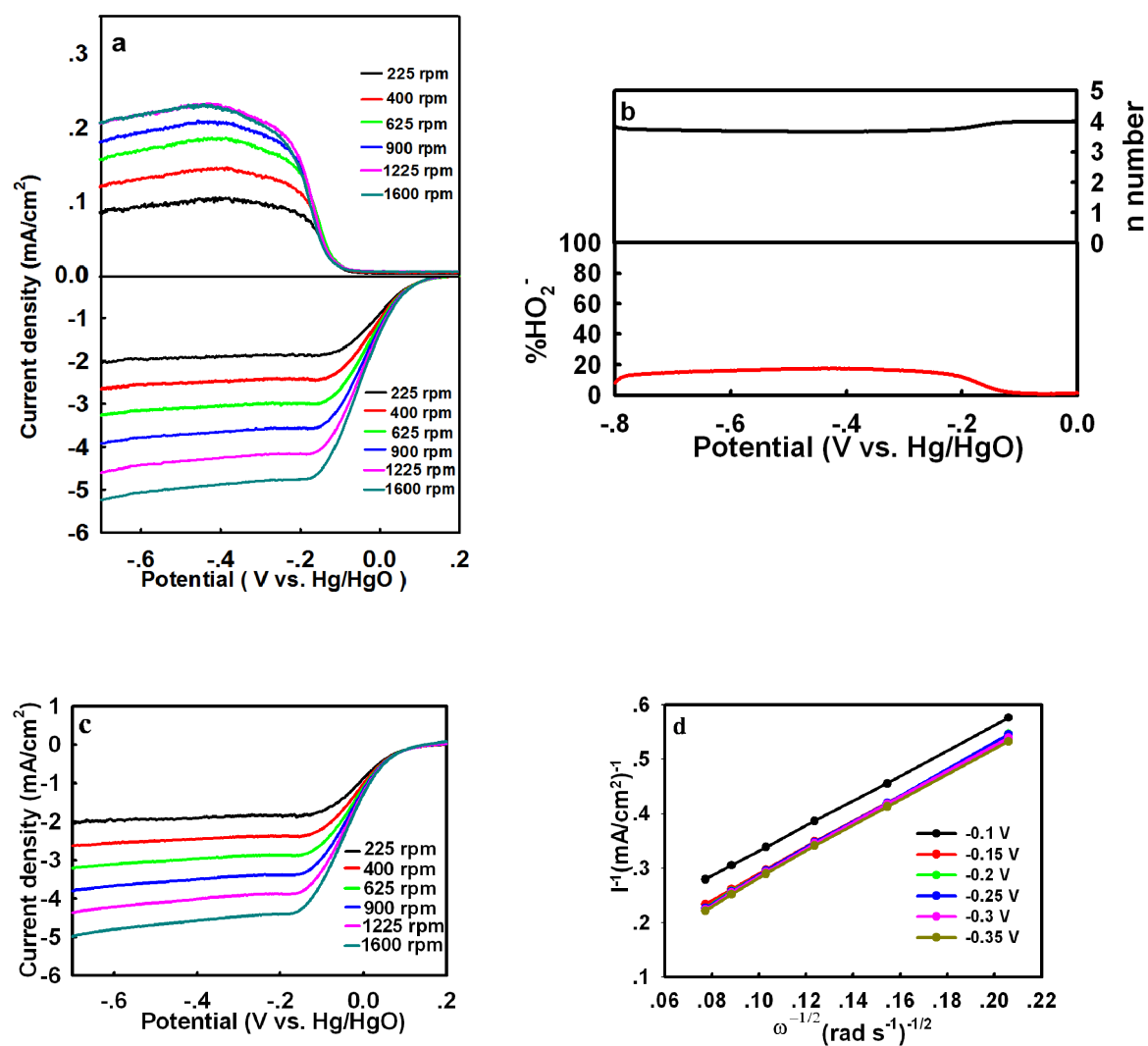


Figure S2.(a) Ring current density and disk current density of the Fe₃Co-rGO obtained at different rpm and (b) n number and %HO₂ at 1600 rpm in O₂-saturated 0.1 M KOH aqueous solution with a positive scanning rate of 5 mVs⁻¹; (c) ORR polarization curves of the Fe₃Co-rGO (repeated) recorded in O₂-saturated 0.1 M KOH at different scan rates (225-1600 rpm); (d) K-L plots (repeated) at different potentials derived from the ORR polarization curves in (c).

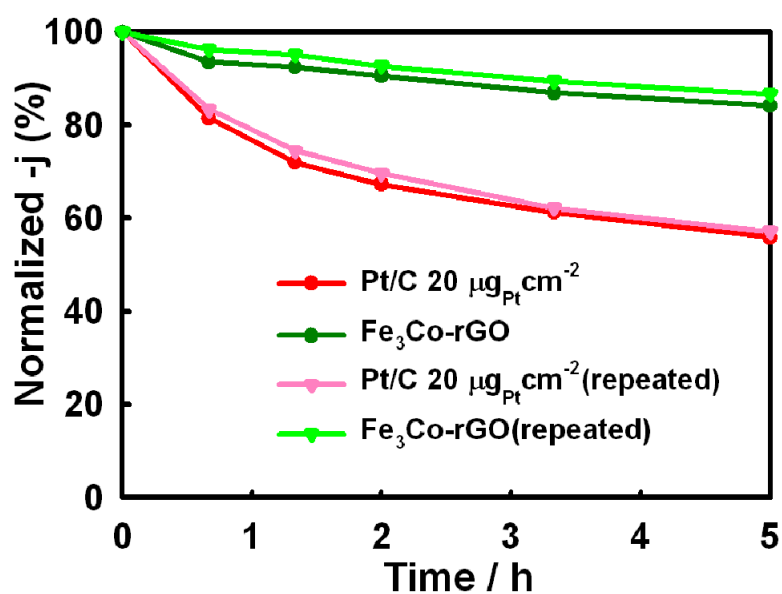


Figure S3. Current density degradation at 0 V (vs. Hg/HgO) in the potential cycling process from -0.4 to 0.2 V at a scan rate of 100 mV s⁻¹.

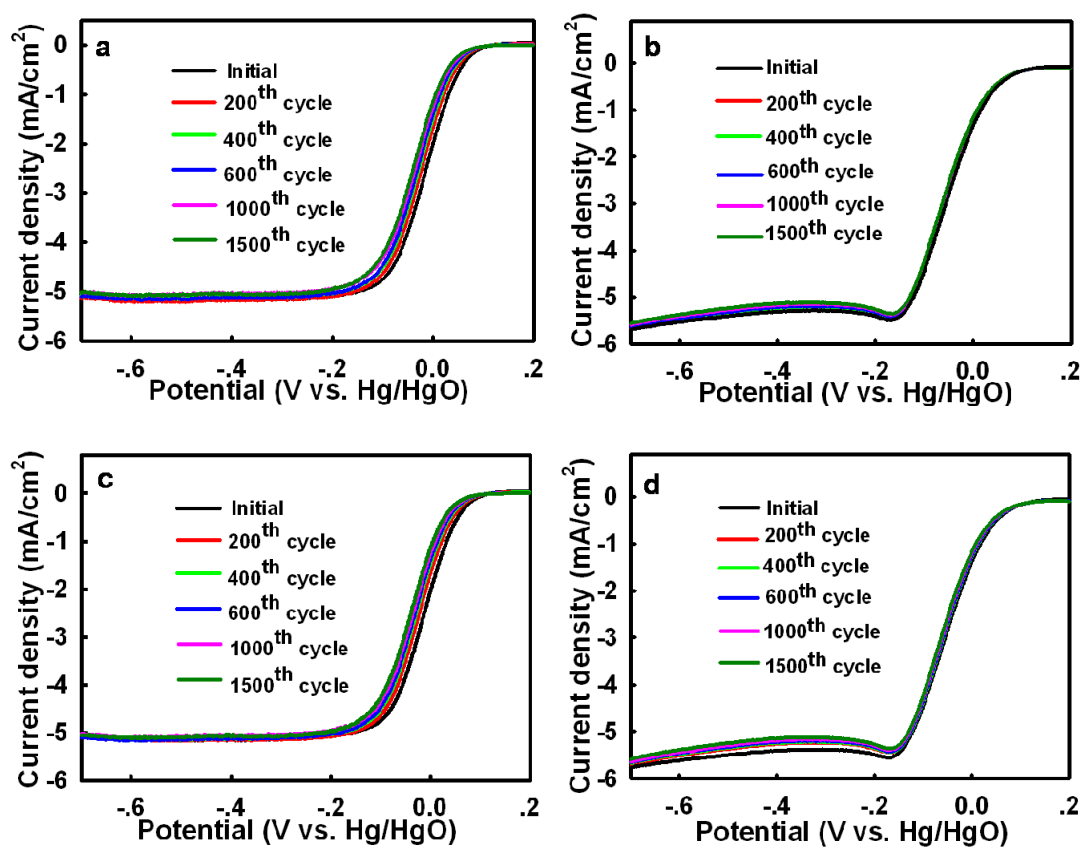


Figure S4. The ORR polarization curves of (a) the 20 wt% Pt/C, (b) the $\text{Fe}_3\text{Co-rGO}$ (c) 20 wt% Pt/C (repeated) and (d) $\text{Fe}_3\text{Co-rGO}$ (repeated) obtained after certain potential cycling numbers (0, 200, 400, 600, 1000 and 1500) with a positive scanning rate of 5 mVs⁻¹ at 1600 rpm in O₂-saturated 0.1 M KOH aqueous solution.

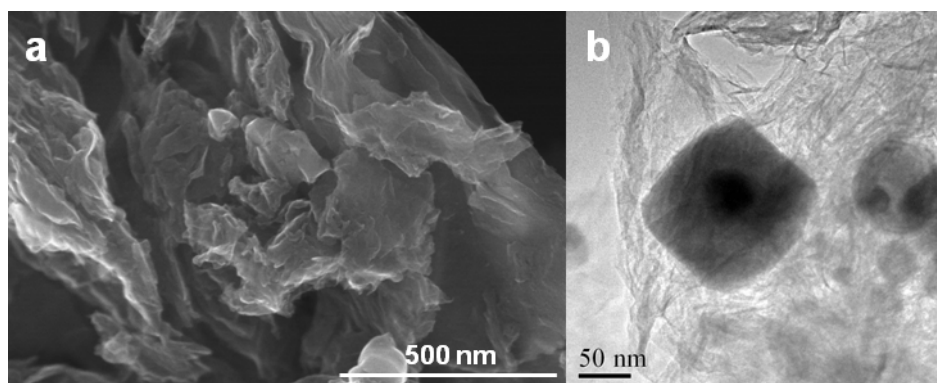


Figure S5. SEM (a) and TEM (b) image of the electrocatalyst $\text{Fe}_3\text{Co-rGO}$.

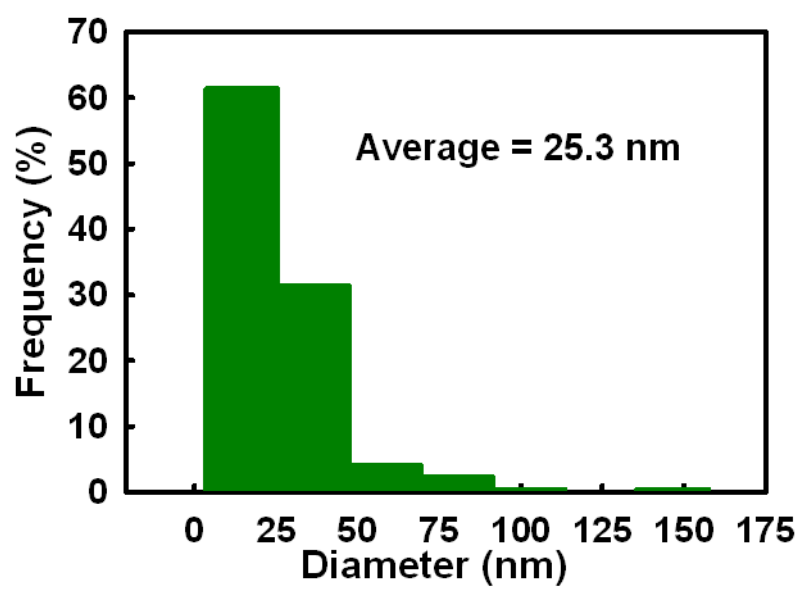


Figure S6. The size distribution of nanoparticles on rGO of the $\text{Fe}_3\text{Co-rGO}$ by measuring randomly selected 220 individual nanostructures.

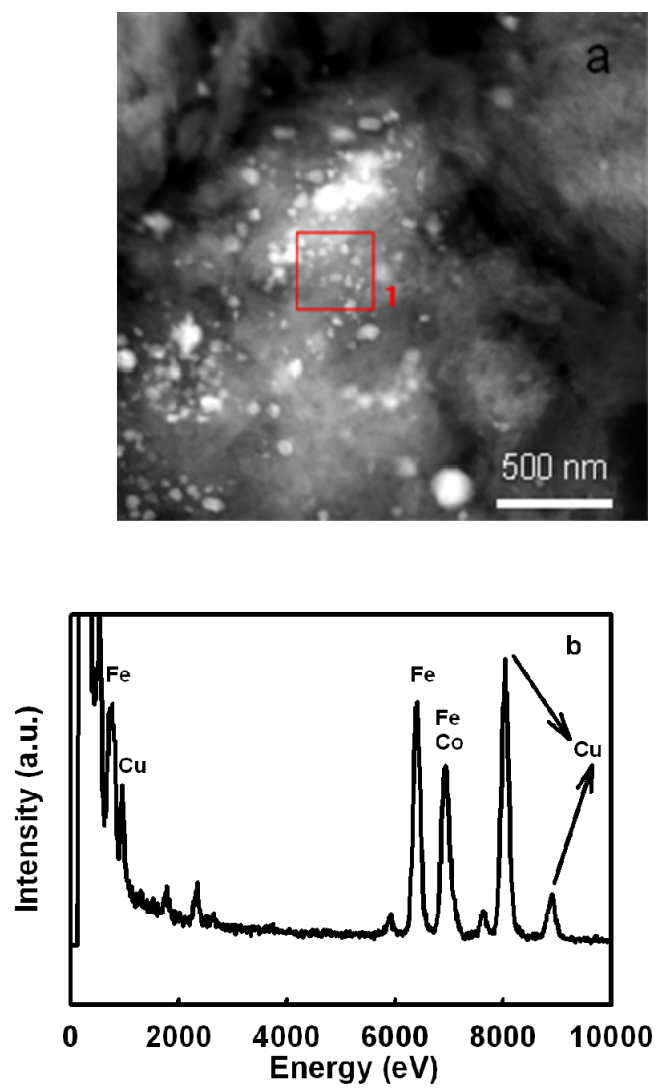


Figure S7. (a) HAADF STEM image of the $\text{Fe}_3\text{Co-rGO}$; (b) EDX of the $\text{Fe}_3\text{Co-rGO}$ for the selected area in (a).

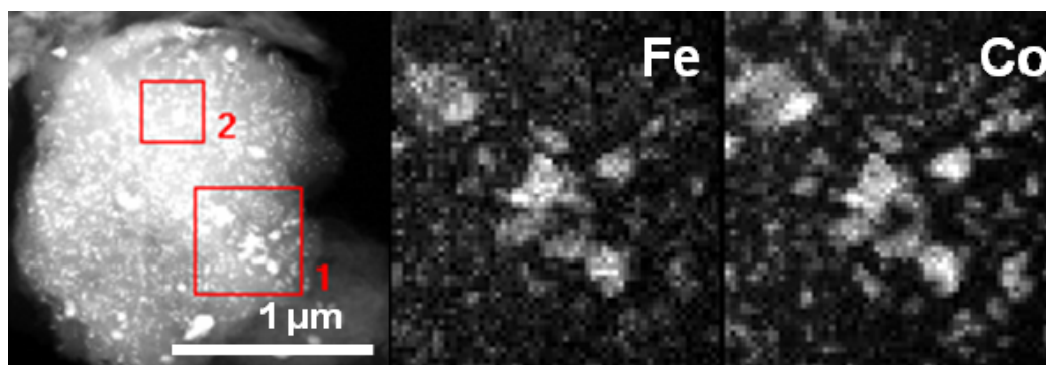


Figure S8. Fe and Co EDX mapping of selected area 1 for the $\text{Fe}_3\text{Co-rGO}$.

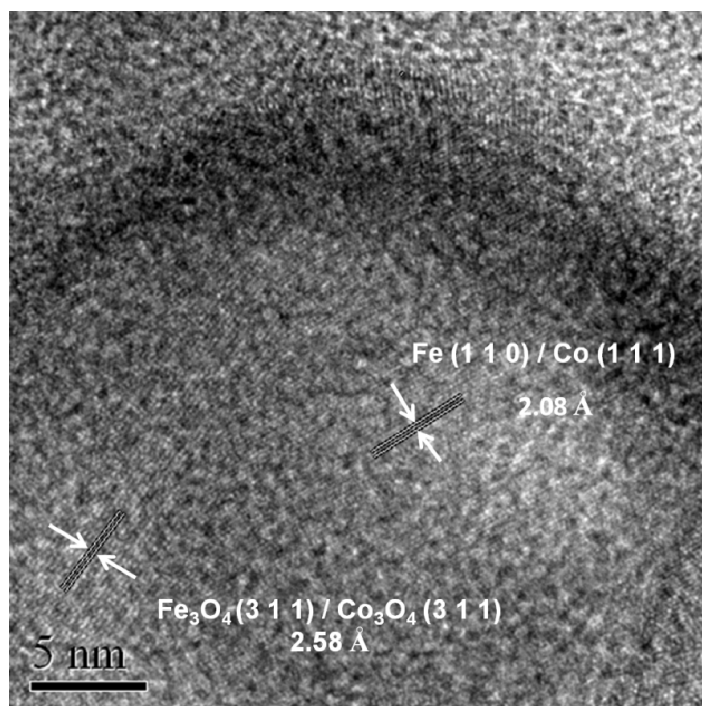


Figure S9.HR-TEM image for Fe₃Co-rGO.

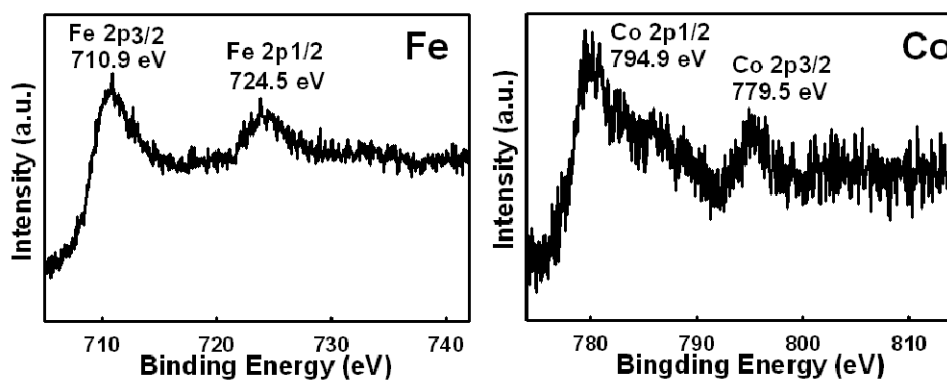


Figure S10.High resolution XPS of Fe and Co for the Fe₃Co-rGO.

Table S1. ORR activity of recently reported highly active non-noble metal electrocatalysts in alkaline solutions compared with the 20 wt% commercial Pt/C at a metal loading of 20 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$

Literature	C_{KOH} (M)	RDE (rpm/mVs ⁻¹)	$\Delta E_{\text{onset potential}}$ (mV)	$\Delta E_{1/2}$ (mV)	H ₂ O ₂ (%)
This study	0.1	1600/5	5	-23	~18
Nat. Mater., 2011, 10, 780	0.1	1600/5	unknown	-30	~6
J. Am. Chem. Soc., 2012, 134, 15849	1	1600/5	unknown	-35	~12
J. Am. Chem. Soc., 2012, 134, 3517	0.1/1	1600/5	unknown	-20	~10
Angew. Chem. Int. Ed., 2011, 50, 3257	1	1600/5	10	unknown	unknown

References:

- 1 a) C. Vallés, C. Drummond, H. Saadaoui, C. A. Furtado, M. He, O. Roubeau, L. Ortolani, M. Monthieux, A. Pénicaud, *J Am. Chem. Soc.*, 2008, **130**, 15802; b) W. S. Hummers, R. E. Offeman, *J Am. Chem. Soc.*, 1958, **80**, 1339.
- 2 S. Wang, D. Yu, L. Dai, D. W. Chang, J. B. Baek, *ACS Nano*, 2011, **5**, 6202.