Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

(Fe, Co)@Nitrogen-doped Graphitic Carbon Nanocubes Derived from Polydopamine-encapsulated Metal-organic Frameworks as a Highly Stable and Selective Non-precious Oxygen Reduction Electrocatalyst

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Experimental

Preparation of $Fe_4[Fe(CN)_6]_3$, $Co_3[Co(CN)_6]_2$, $Fe_3[Co(CN)_6]_2$, and $Fe_3[Co(CN)_6]_2$@ PDA NCs: 3.0 g of Polyvineypirrolydone (PVP) and 0.226 g of $K_4[Fe(CN)_6]\cdot 3H_2O$ were dissolved in 40mL of HCl solution (0.01 M) and continuously stirred at room temperature for 30 min. The solution was then transferred into a Teflon-lined stainless autoclave, heated to 80 ^{o}C for 24 h to form $Fe_4[Fe(CN)_6]_3$ NCs. The products were collected by centrifugation and washed by DI water, and finally dried up. 33.2 mg of $K_3[Co(CN)_6]_2$ and 0.6 g of PVP were dissolved in 20 mL water, and then added into 20ml of $Co(CH_3COO)_2$ (37.4 mg) aqueous solution or 20 mL of $FeSO_4$ (42.0 mg) aqueous solution slowly and regularly by using a syringe to form $Co_3[Co(CN)_6]_2$ and $Fe_3[Co(CN)_6]_2$ NCs, respectively.

After stirring at room temperature for 24 h, the products were collected by centrifugation and washed by DI water, and finally dried up. 0.1 g of $Fe_3[Co(CN)_6]_2$ NCs powder was initially dispersed in 20 mL of tri buffer solution (10 mM, pH=8.5). Subsequently, 40mg of dopamine was dissolved into above dispersion, and stirred at room temperature for 18 h to form $Fe_3[Co(CN)_6]_2$@PDA NCs. The products were collected by centrifugation and washed by DI water, and finally dried up.

Preparation of Fe, Co, (Fe, Co), and (Fe, Co)@NGC NCs: The as-synthesized $Fe_4[Fe(CN)_6]_3$, $Co_3[Co(CN)_6]_2$, $Fe_3[Co(CN)_6]_2$, and $Fe_3[Co(CN)_6]_2$@PDA powder were thermally decomposed at the temperature of 600 ~ 900 ^oC for 1 h under Ar atmosphere with a heating rate of 5 ^oC min^{-1} to form Fe, Co, (Fe, Co), and (Fe, Co)@NGC NCs, respectively.

General Characterizations: The product morphologies were directly examined by scanning electron microscopy (SEM) using Nova NanoSEM 450 at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) observations were carried out on a Tecnai G2 20 microscope operating both at 200 kV. X-ray diffraction (XRD) was performed on a Philips PW-1830 X-ray diffractometer with Cu kα irradiation (λ=1.5406 Å). The step size and scan rate are set as 0.05^o and 0.025^o/s, respectively. X-ray photoelectron spectroscopy (XPS) was measured on a Perkin-Elmer model PHI 5600 XPS system with a resolution of 0.3-0.5 eV from a monochromated aluminium anode X-ray source with Kα radiation (1486.6 eV). The thermogravimetric analysis (TGA) was undertaken from 30 to 800 ^oC on a Pyris 1 TGA (PerkinElmer Instruments). The heating rate was 10 ^oC min^{-1} under an Ar airflow of 25 mL min^{-1}.

Electrochemical Characterizations: Electrochemical measurements were carried out by using a potentiostat (CHI 760E) and the rotating ring disk electrode (RRDE-3A) system in a conventional, three-electrode cell. It consisting of glassy carbon electrode (GCE) was used as the working electrode, Pt mesh was employed as the counter electrode and Hg/HgO (1.0 M NaOH) was used as the reference electrode. The electrode potential is reported relative to the reversible hydrogen electrode (RHE) potential, which was converted from the MMO reference electrode using: $E_{RHE}=E_{(Hg/HgO)}+0.9096$ V. For the rotating disk electrode (RDE) measurement, the working electrode was modified with a catalyst layer by dropping a suitable amount of catalyst ink on the GCE. The catalyst ink was prepared by ultrasonically dispersing 5 mg of the catalysts in a solution containing 0.99 mL of N, N-Dimethylformamide and 10 μL of 5 wt% Nafion solutions for 30 min to obtain a homogeneous solution. 10 μL of the dispersion was pipetted out and dropped onto a glassy carbon rotating disk electrode of 4 mm in diameter (~ 0.4 mg cm^{-2}), which was then dried in air. For all of the experiments, stable voltammogram curves were recorded after scanning at 50 mV s^{-1} in the potential region from 0.9 to 1.5 V in 0.1 M KOH solution. Cycle voltammetry (CV) experiments were conducted at room temperature in 0.1 M KOH solution saturated with nitrogen and oxygen gases at a scan rate of 10 mV s^{-1} in the potential range of 1.1 ~ 0.3 V. Linear sweep voltammograms (LSVs) and Tafel plots were carried out in O_2-saturated 0.1 M KOH solution from 1.1 to 0.4 V. The working electrode was scanned cathodically at a rate of 5 mV s^{-1} with varying rotating speed from 400 rpm to 2400 rpm. Normalized currents are given in terms of geometric weight (mA cm^{-2}). Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (n) on the basis of the Koutecky-Levich equation:

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

$$B=0.62nFC_oD_o^{2/3}\nu^{-1/6} \qquad (2)$$

$$J_k=nFkC_o \qquad (3)$$

Where J is the measured current density, J_k and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity, n is transferred electron number, F is the Faraday constant (96485 C mol^{-1}), C_o is the bulk concentration of O_2 (1.2x10^{-6} mol cm^{-3}), ν is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}), D_o is the O_2 diffusion coefficient (1.9 x 10^{-5} cm^2 s^{-1}), and k is the electron-transfer rate constant.

For the rotating ring-disk electrode (RRDE) measurement, the catalyst inks and electrodes were prepared by the same method as the RDE. The disk electrode was scanned cathodically at a rate of 5 mV s^{-1} and the ring potential was constant at 1.5 V vs. RHE. The HO_2^- % and electron transfer number (n) were determined by the followed equations:

$$\mathrm{HO_2^-}\%=200\mathrm{x}\frac{\mathrm{I_r}/N}{\mathrm{I_d}+\mathrm{I_r}/N} \qquad (4)$$

$$n=4\mathrm{x}\frac{\mathrm{I_d}}{\mathrm{I_d}+\mathrm{I_r}/N} \qquad (5)$$

Where I_d is the disk current density, I_r is the ring current density and N is current collection efficiency (N) of the Pt ring. N was measured to be 0.32 from the reduction of $K_3Fe[CN]_6$.

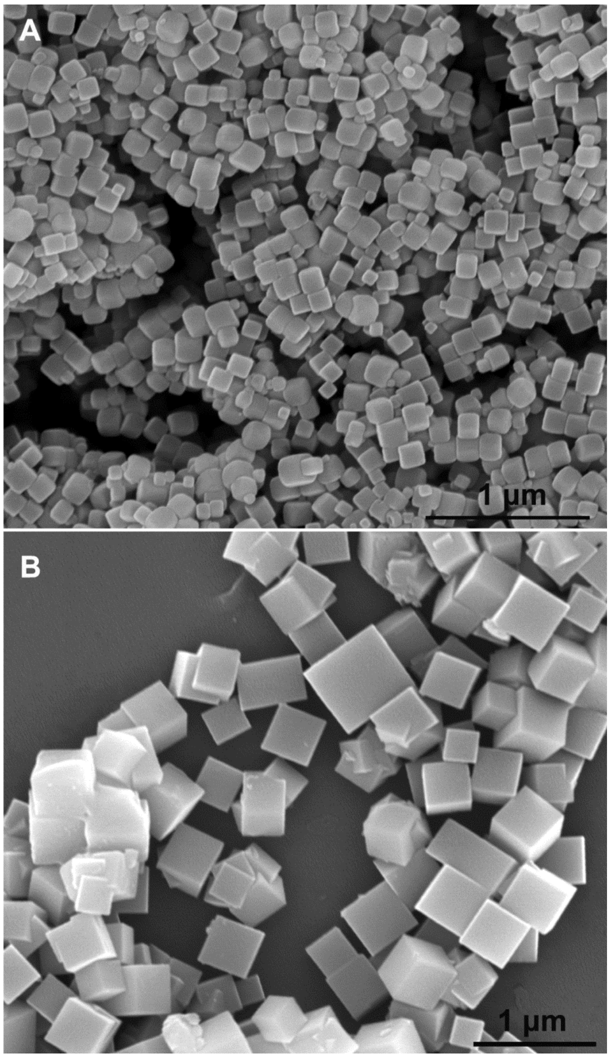

Figure S1. SEM images of (A) $Co_3[Co(CN)_6]_2$ and (B) $Fe_3[Fe(CN)_6]_2$ precursors.

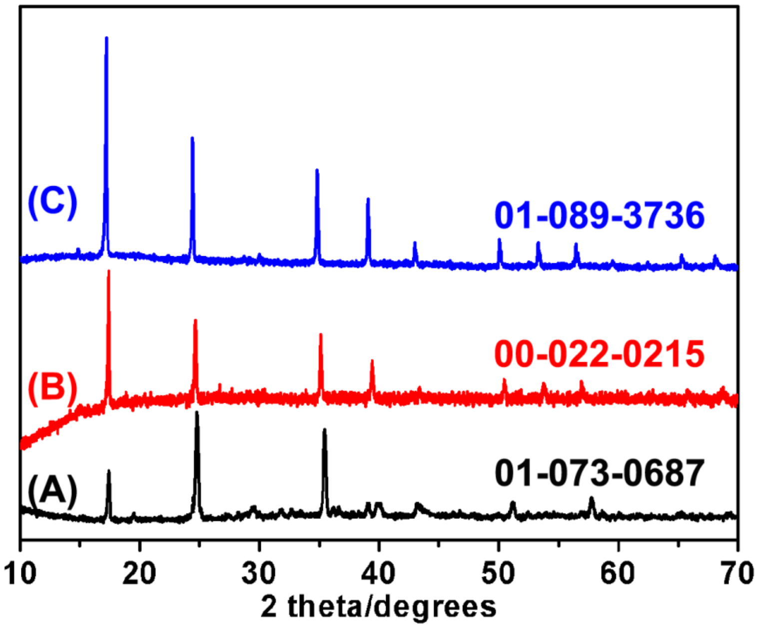

Figure S2. XRD patterns of (A) $Fe_4[Fe(CN)_3]_2$, (B) $Co_3[Co(CN)_6]_2$, and (C) $Fe_3[Co(CN)_6]_2$ precursors, which are in agreement with the standard patterns of JCPDS 01-073-0687, 00-022-0215, and 01-089-3736, respectively.

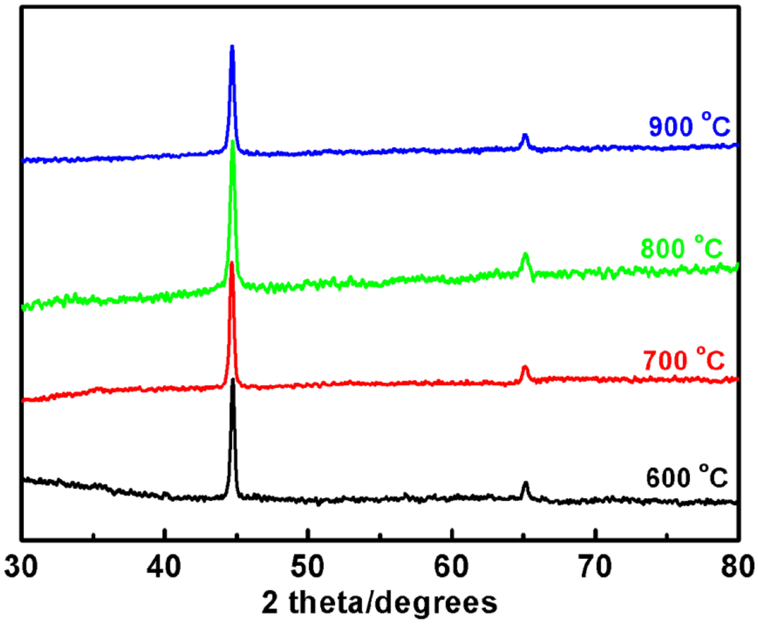

Figure S3. XRD patterns of the products transformed from $Fe_3[Co(CN)_6]_2$ NCs at 600-900 ^oC under Ar atmospheres.

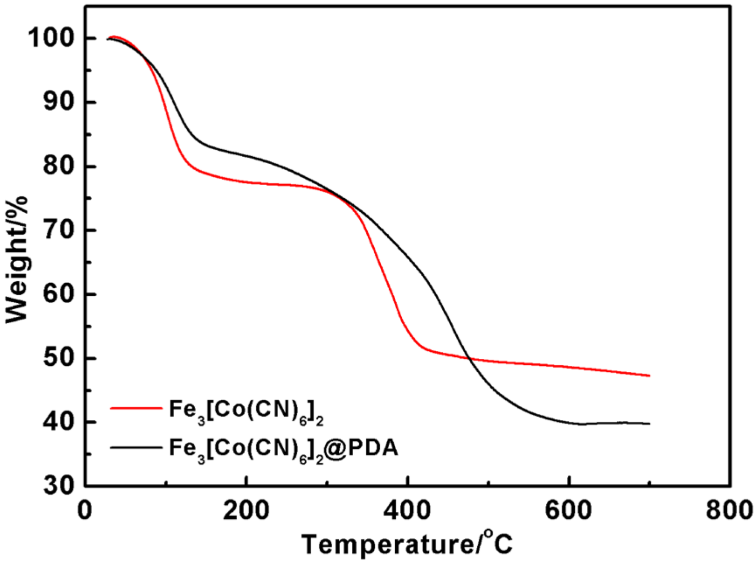

Figure S4. TGA curves of the $Fe_3[Co(CN)_6]_2$ and $Fe_3[Co(CN)_6]_2$@PDA NCs under Ar atmosphere in the temperature range of 30 ~ 700 °C with a heating rate of 10 °C min^{-1}.

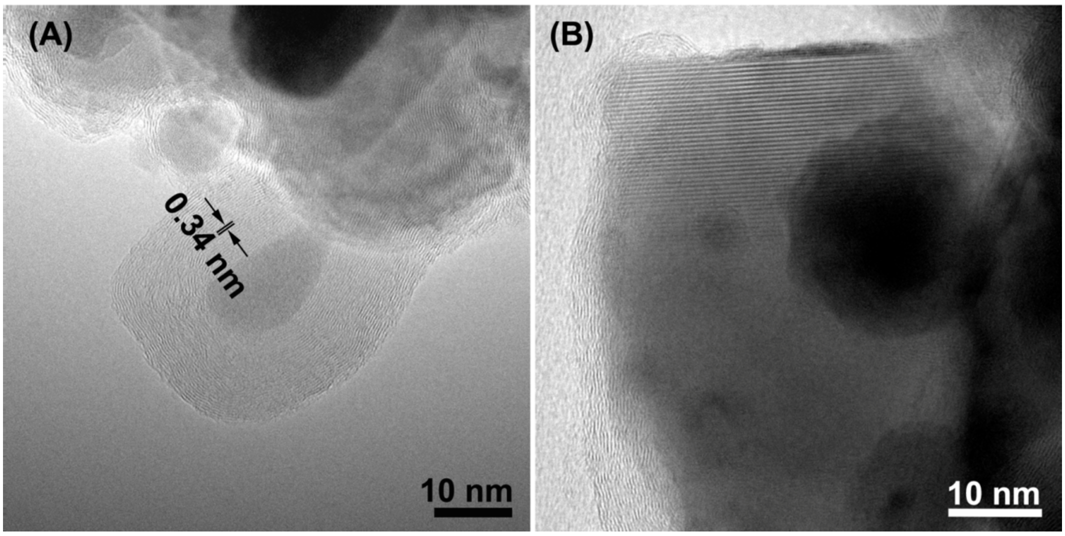

Figure S5. (A, B) High-resolution TEM (HRTEM) images of the (Fe, Co) NCs at different positions.

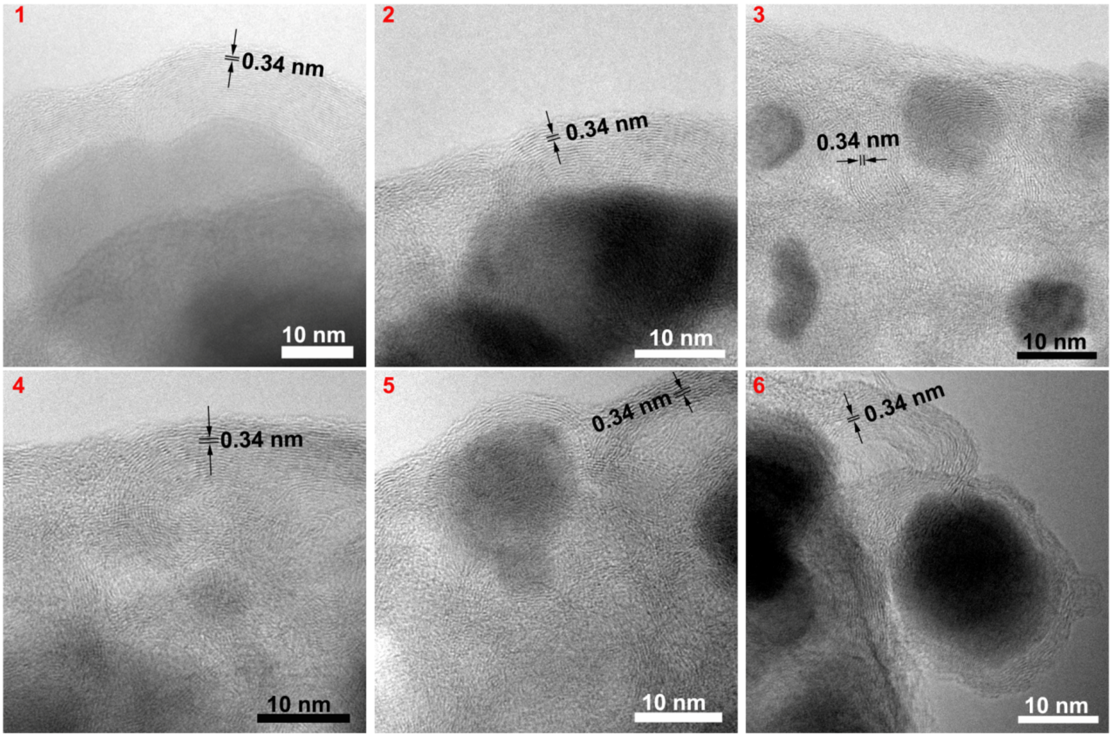

Figure S6. HRTEM images of the (Fe, Co)@NGC NCs, corresponding to six different positions in Figure 1G.

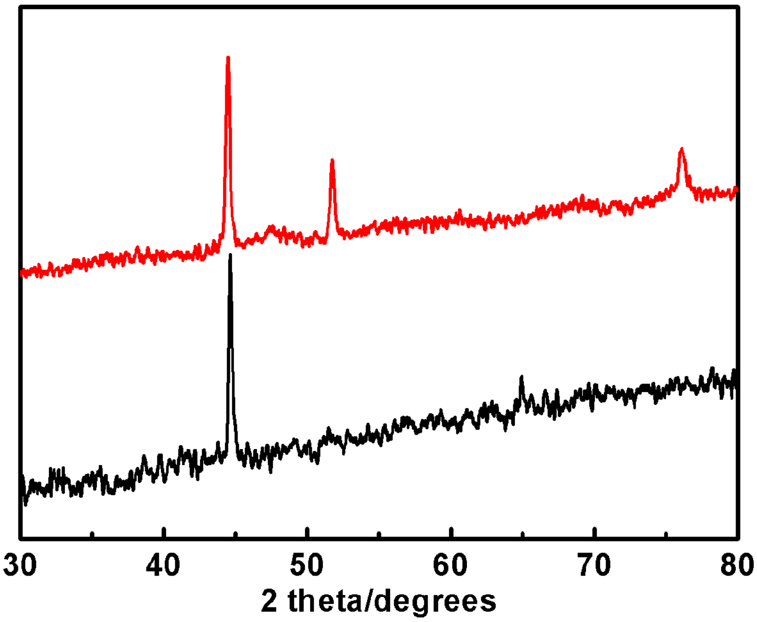

Figure S7. XRD patterns of the products derived from $Fe_3[Fe(CN)_6]_2$ (black) and $Co_3[Co(CN)_6]_2$ (Red) at 700 ^oC for 1 h under Ar atmosphere.

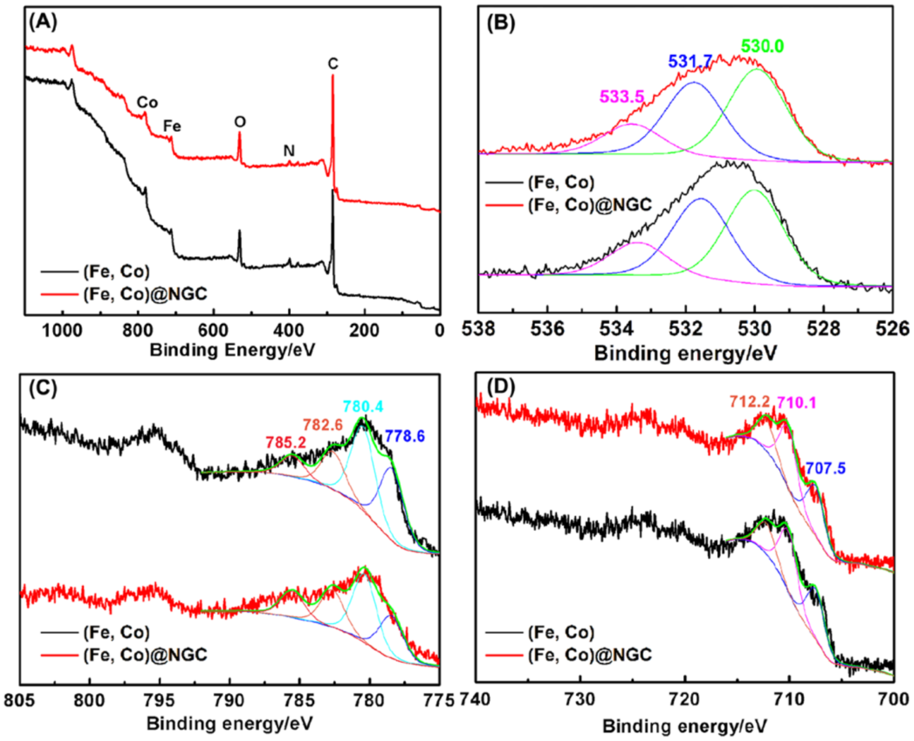

Figure S8. (A) The XPS full spectra, (B) O 1s, (C) Co 2p, and (D) Fe 2p XPS spectra of the (Fe, Co) and (Fe, Co)@NGC NCs.

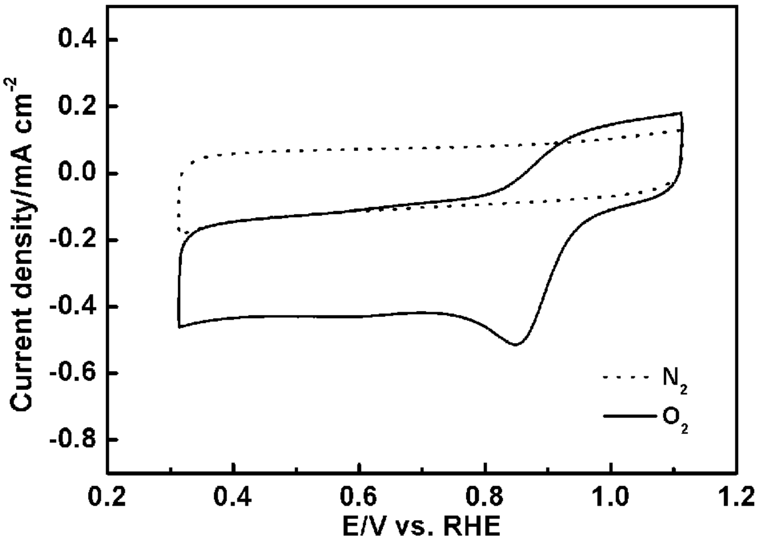

Figure S9. CV curves of the (Fe, Co) NCs in N_2-saturated (dash line) or O_2-saturated (solid line) 0.1 M KOH.

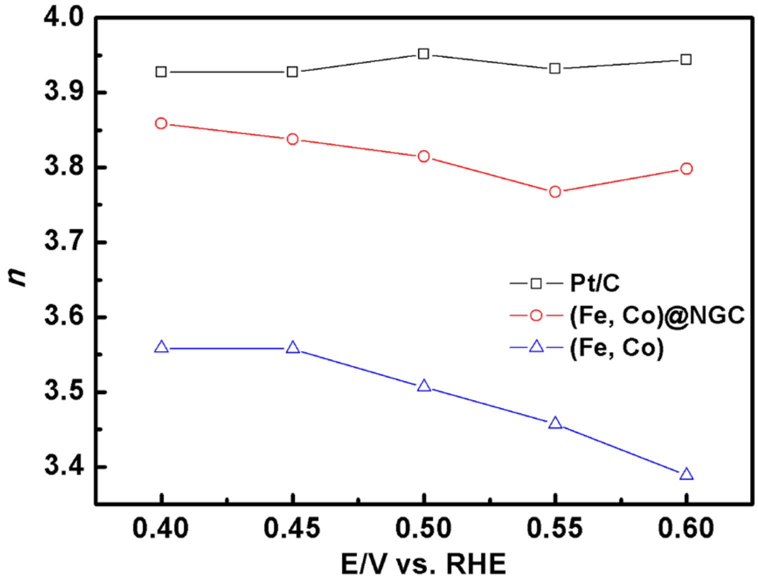

Figure S10. The electron transfer number (*n*) profiles obtained from the Koutecky-Levich plots (J^{-1} versus $\omega^{-0.5}$) in the potential range of 0.60~0.40 V versus RHE.

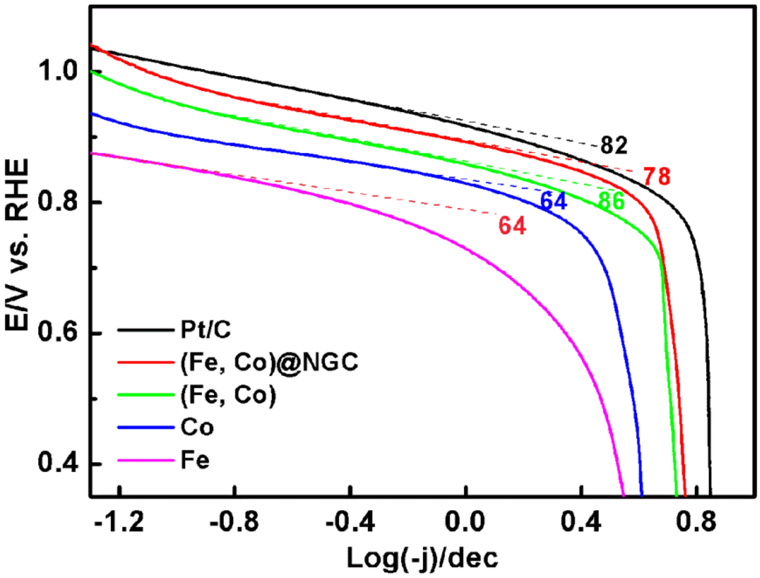

Figure S11. The Tafel plots of the Pt/C, (Fe, Co)@NGC, (Fe, Co), Co, and Fe catalysts measured in O_2-saturated 0.1 M KOH aqueous solution at 2400 rpm.

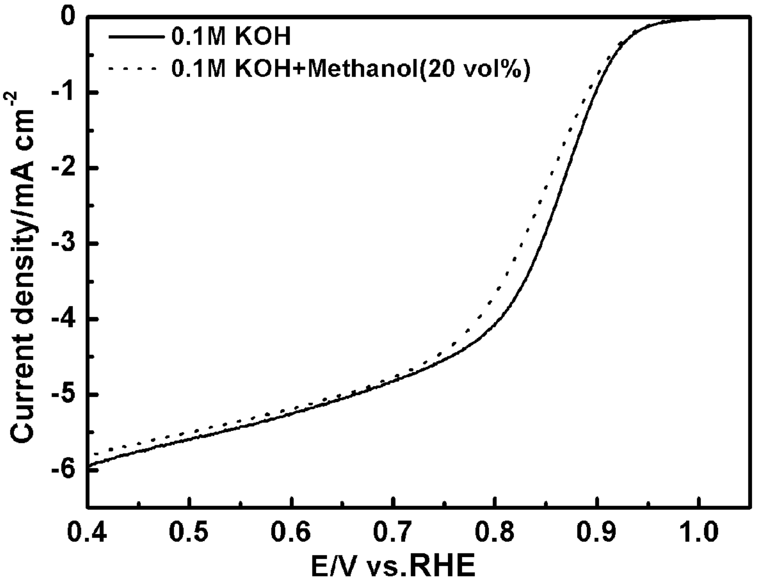

Figure S12. Linear scan voltammograms (LSVs) of the (Fe, Co)@NGC NCs in O_2-saturated 0.1M KOH and 0.1 M KOH (20 vol% of methanol) at a scan rate of 5 mV s^{-1} and a rotating rate of 2400 rpm.

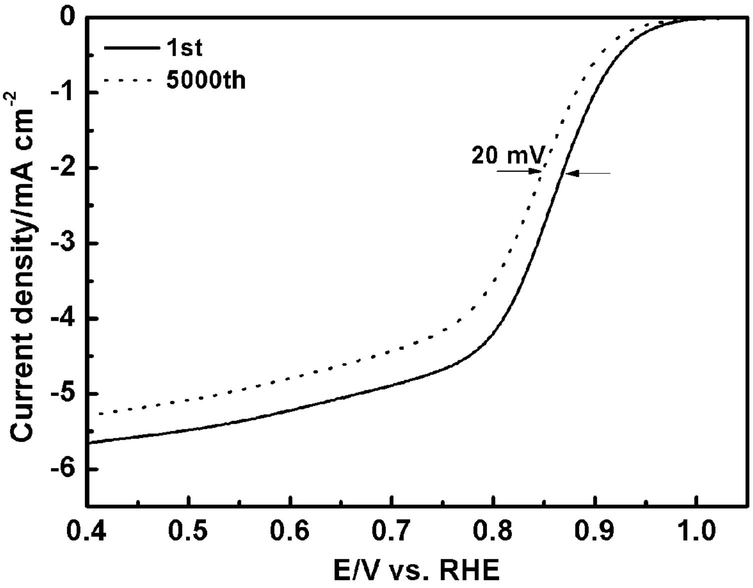

Figure S13. Linear scan voltammograms (LSVs) of the (Fe, Co)@NGC NCs in O_2-saturated 0.1 M KOH at a scan rate of 5 mV s^{-1} and a rotating rate of 2400 rpm.