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Supporting Information for:

One-pot Synthesis of High-performance Co/graphene Electrocatalysts for Glucose Fuel Cells Free of Enzymes and Precious Metals

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Experimental Section

Materials and Methods: A mixture of 2.1 g cyanamide (NH_2CN) and 2.19 g $Co(NO_3)_2 \cdot 6\ H_2O$ was placed in a quartz boat, which was covered with quartz wool and then was transferred to a furnace. The Co/NG was obtained by heating the mixture to 750 ºC at a rate of 1 ºC/min and maintained at 750 ºC for 2 hours under Ar atmosphere. The pure NG was prepared by refluxing the Co/NG in $HNO_3 + H_2SO_4$ solution (1:3) for 2 hours, followed by an extensive washing with deionized water to pH=7, then drying. The rGOs were synthesized by reducing GO with $NaBH_4$ as a reducing agent. Commercial 10% Pt/C was purchased from a fuel cell store (http://www.fuelcellstore.com).

Materials Characterization: The sample morphology and microstructure were characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, Hitachi H 9000 NAR). X-ray diffraction (XRD) data were collected on a Scintag XDS 2000 X-ray diffractometer using Cu-Kα radiation (λ=1.5418 Å). X-ray photoelectron spectroscopy (XPS) was carried out using HP 5950A XPS with an Mg Kα as the source and the C1s peak at 284.6 eV as an internal standard. The surface area and the pore structure were measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption (Shimadzu, Micrometrics ASAP 2010 Instrument).

Electrochemical Measurements

The glassy carbon electrode (GCE, Φ=3 mm) was polished with alumina slurry and then ultrasonically cleaned alternately in ethanol and double-distilled water. A suspension was obtained by dispersing the catalysts (2.5 mg) in a mixture of 0.05 mL Nafion and 0.45 mL distilled water under ultrasonic agitation. Then, 6 μl of the mixture was dropped onto GCE and allowed to dry at room temperature. Cyclic voltammetry (CV) was conducted in a three-electrode electrochemical cell using a Pt wire and an Ag/AgCl electrode as the counter-electrode and the reference electrode, respectively. All the electrochemical measurements were performed in an aqueous solution with an electrolyte of 0.1 M KOH at room temperature. Amperometric detection of glucose was performed by applying an appropriate potential to the working electrode and allowing the transient background current to decay to a steady-state value before the addition of glucose. For ORR tests, Ar or O_2 was used to purge the solution to achieve an O_2-free or O_2-saturated condition. Rotating disk electrode measurements were performed using linear sweep voltammetry in a three-electrode system with a scan rate of 5 mV s^{-1}. The Koutecky–Levich equation was used to determine the number of electrons involved in oxygen reduction reaction at various potentials:

The Koutecky–Levich plot presents the relationship of j_{lim}^{-1} versus $\omega^{-1/2}$ and the Koutecky-Levich equation is shown below:

$$\mathbf{1/J_{lim} = 1/J_{Lev} + 1/J_k} \qquad (1)$$

where $\mathbf{J_{Lev}}$=$0.62nFCD^{2/3}\upsilon^{-1/6}\omega^{1/2}$ [8] (n=number of electrons, F=Faraday=96486.4 Coulombs, C is the saturated concentration of O_2 in 0.1 M PBS (1.26×10^{-3} M) at room temperature, D is the diffusion coefficient of oxygen in water (2.7×10^{-5} cm^2/s), υ is the kinematic viscosity of the solution at room temperature (0.01 cm^2/s), and ω is the angular velocity of the disk (2πN), where N is the linear rotation speed); therefore, the equation (1) can evolve into the equation (2)

$$\mathbf{1/J_{lim} = 1/(0.62nFCD^{2/3}\upsilon^{-1/6}\omega^{1/2}) + 1/J_k} \qquad (2)$$

According to the Koutecky–Levich plot, the slope (**K**) can be used for calculating the electron number occurring in ORR, namely $\mathbf{n}=1/(0.62\mathbf{K}FCD^{2/3}\upsilon^{-1/6})$, and $\mathbf{J_k}$, the kinetic current density, can be evaluated through the interception (**B**) of the plot, namely **B**= **1/J_k,** which determines the rate of the kinetically-limited reaction of ORR.

GFC setup and measurement

The Co/NG was mixed with 5% Nafion solution in an ultrasonic bath, and then deposited on the carbon cloth (0.5 cm × 1 cm) with a loading of ~5 mg cm^{-2}. The same procedure was used to prepare Pt/C electrodes. A batch-type MFC with two chambers was constructed by connecting two glass bottles with an anion-exchange membrane (AEM, Membrane International Inc., Ringwood, NJ, USA) as a separator. Polarization curves were constructed using a potentiostat (Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.5 mV s^{-1}. The cell voltage was recorded by a digital multimeter (Keithley Instruments, Inc., Cleveland, OH, USA). The densities of power and current were calculated based on the surface area of the electrode.

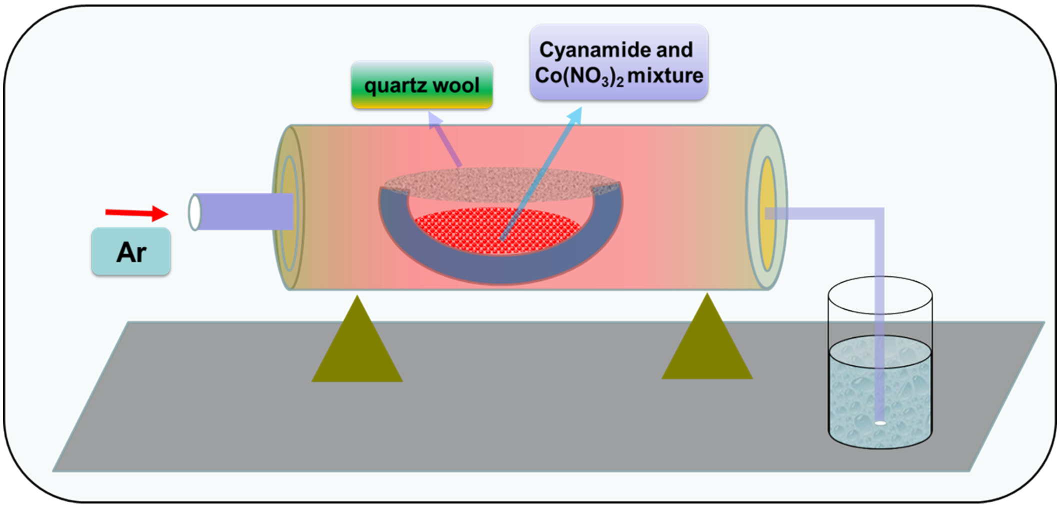

Figure S1. Schematic illustration of the experimental setup for the synthesis of 3D Co/NG nanohybrids.

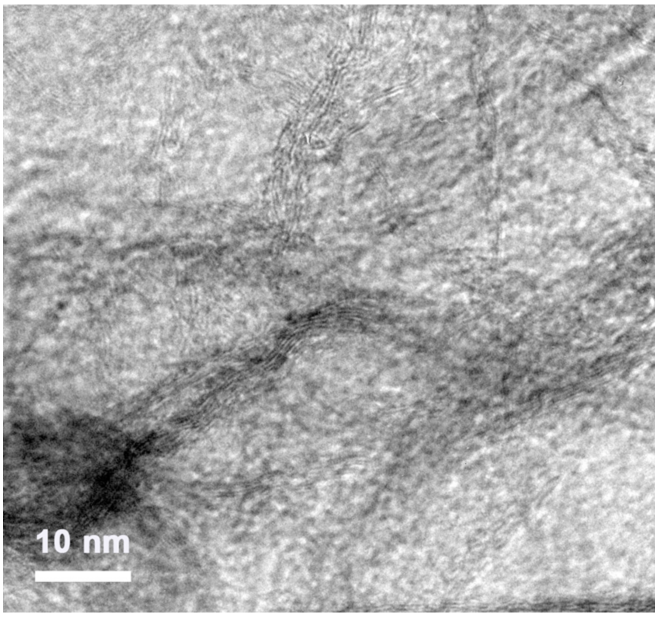

Figure S2. TEM image of the N-doped graphene after removing Co nanoparticles.

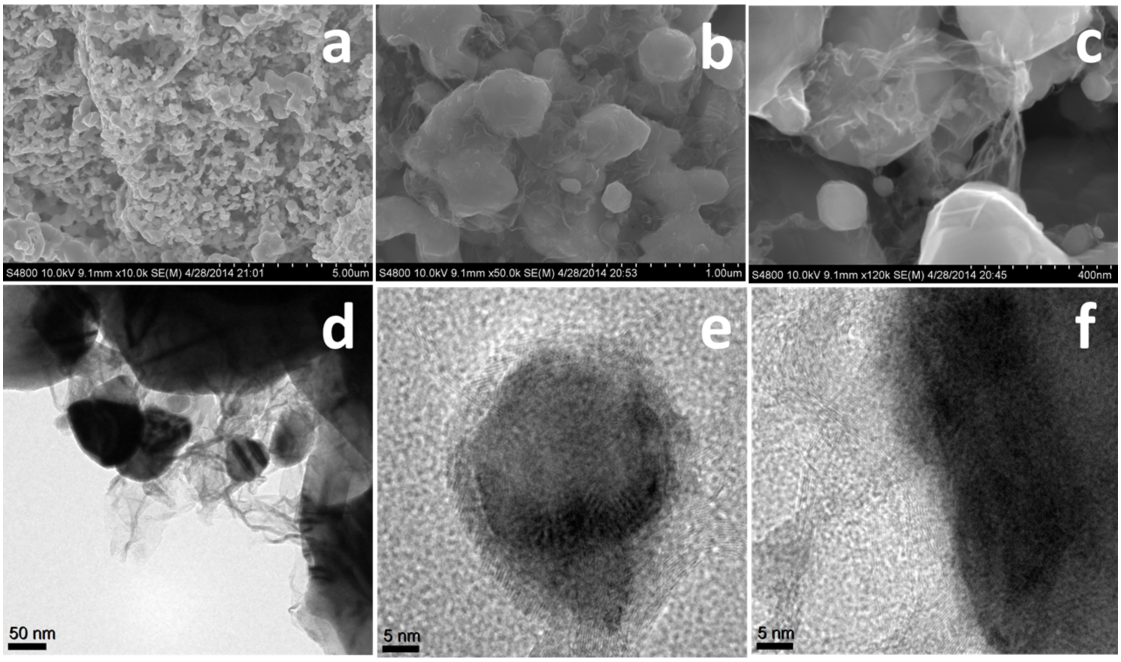

Figure S3. (a-c) SEM images and (d-f) TEM images of the Co/NG nanohybrids.

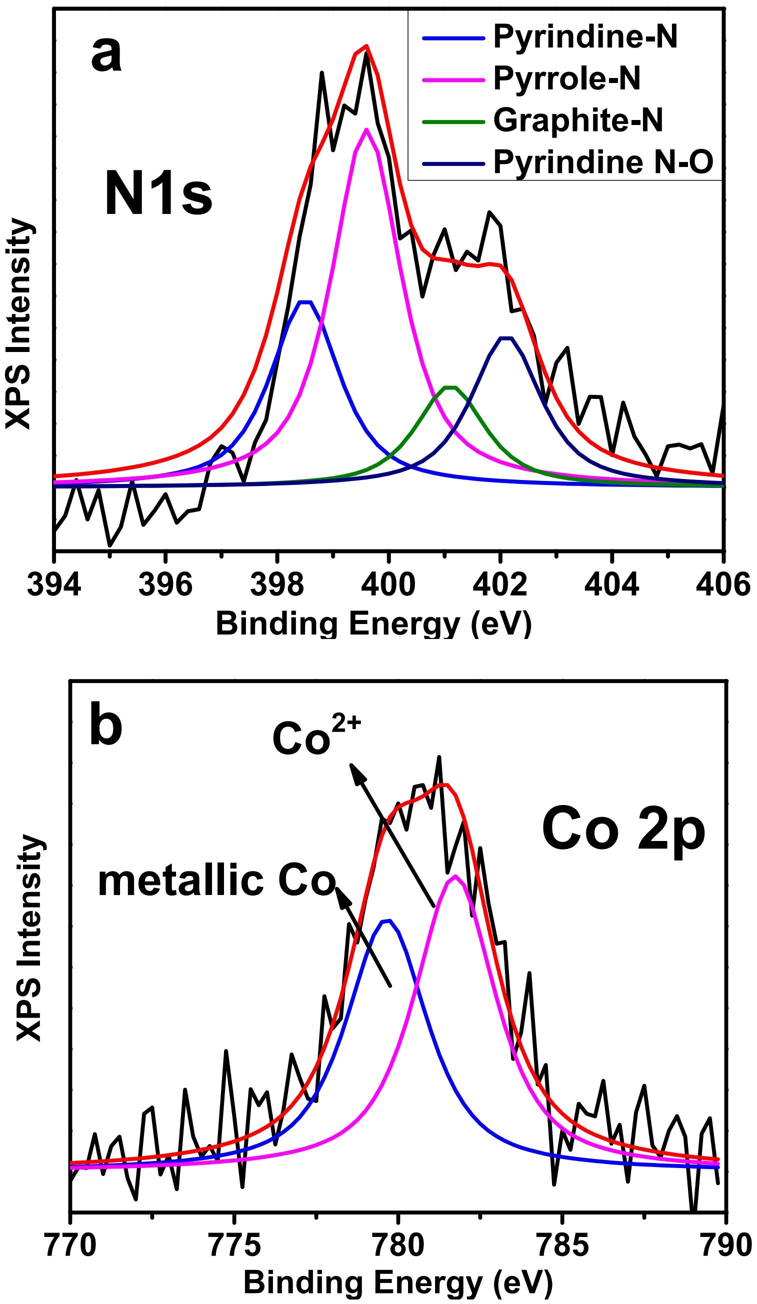

Figure S4. High-resolution XPS spectra of (a) N1s and (b) Co2p for Co/NG hybrids.

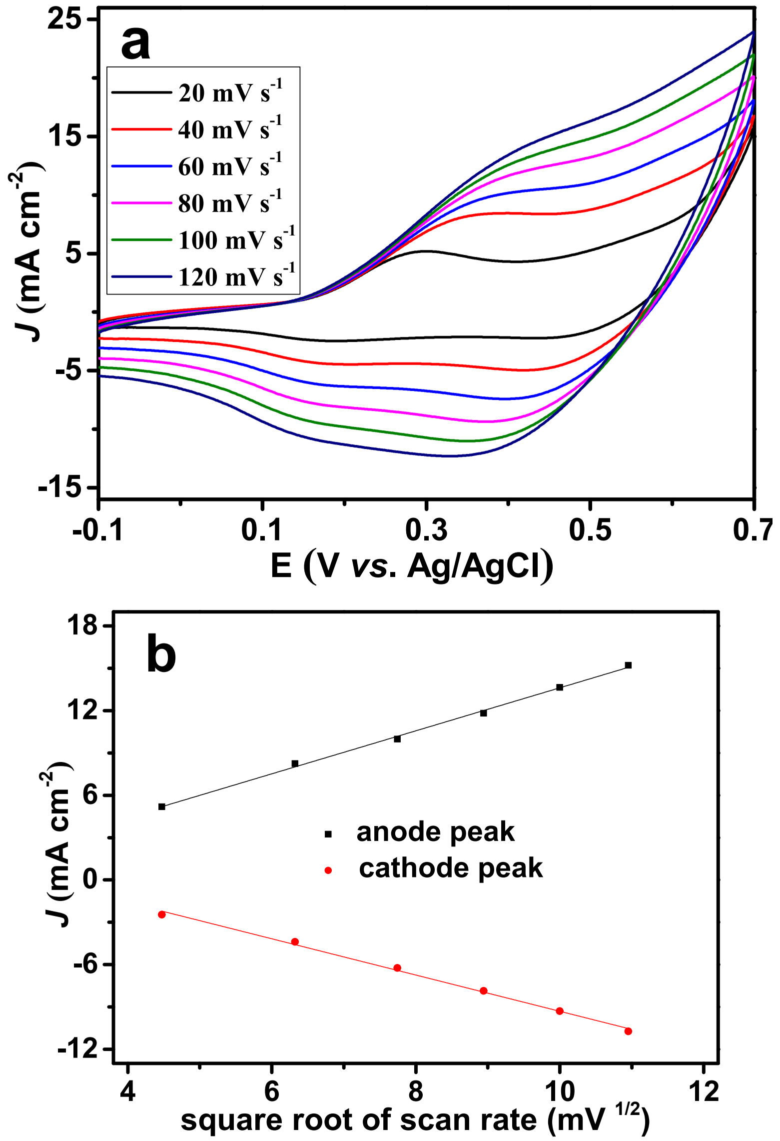

Figure S5. (a) The cyclic voltammetry (CV) curves of the Co/NG in 0.1 M NaOH with different scan rates at the Co/NG hybrid electrode; and (b) the relationship between the anodic/cathodic peak currents and the square root of the scan rate.

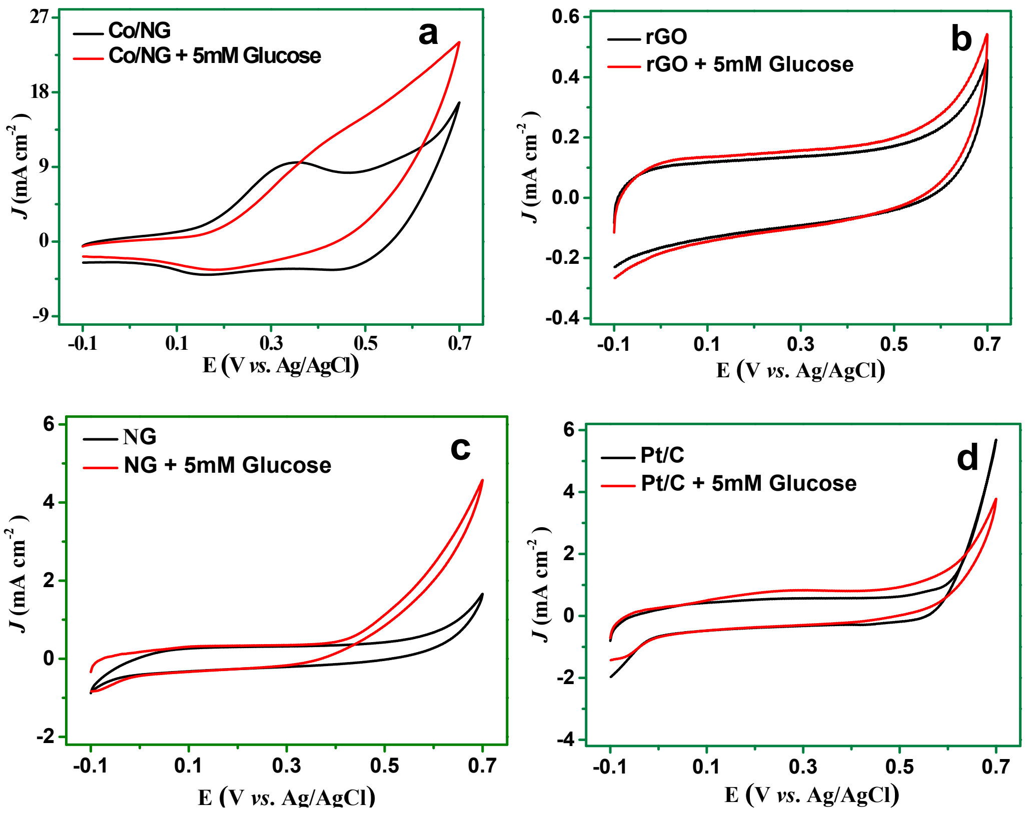

Figure S6. CVs of the (a) Co/NG, (b) rGO, (c) NG and (d) Pt/C in 0.1 M NaOH with the absence (black) of and in the presence (red) of 5 mM glucose.

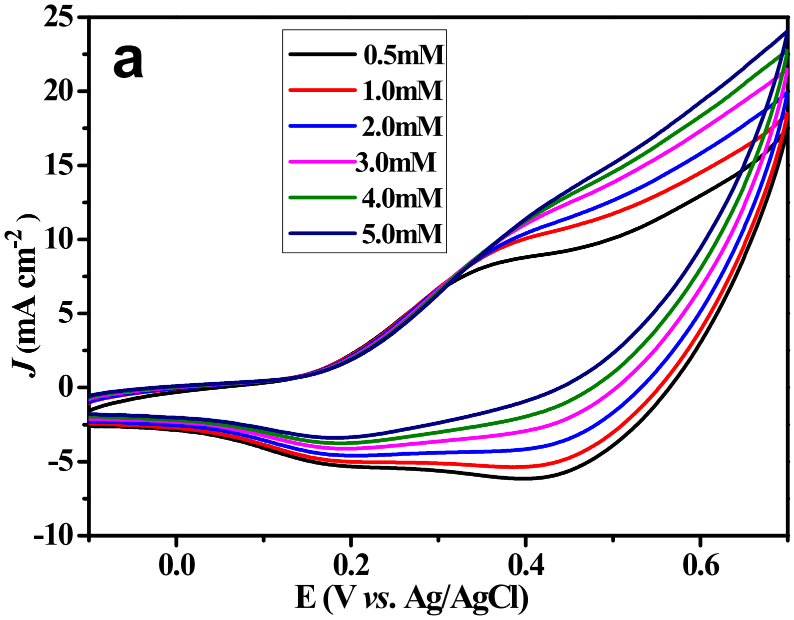

Figure S7. CVs of the Co/NG electrode for various concentrations of glucose with a scan rate of 50 mV s^{-1}.

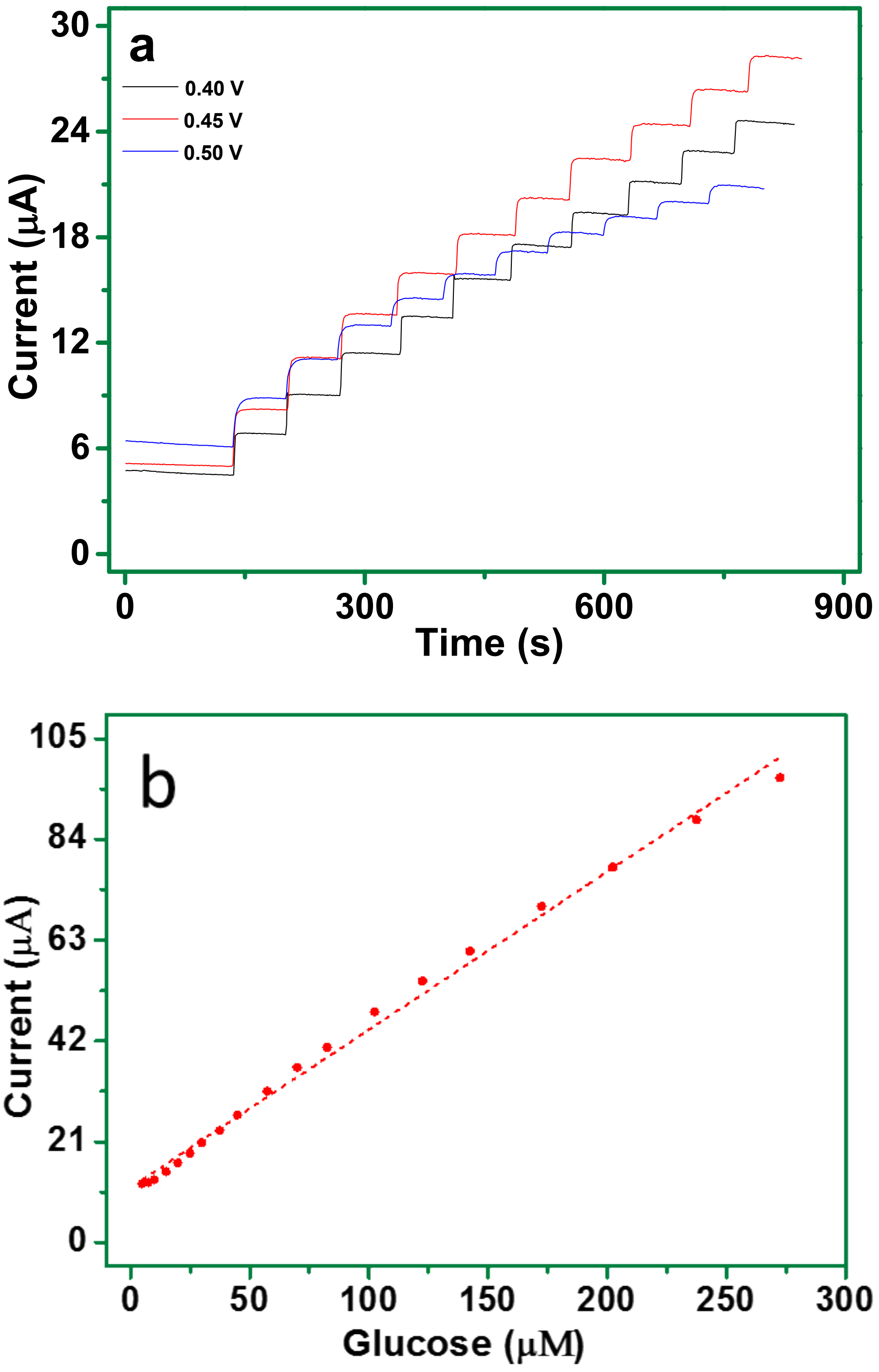

Figure S8. (a) Amperometric responses of CoNG/GCE at different potentials with a drop-wise addition of 10 μM glucose at 100 s intervals, and (b) calibration curve of the current response at 0.45 V *vs.* concentration of glucose.

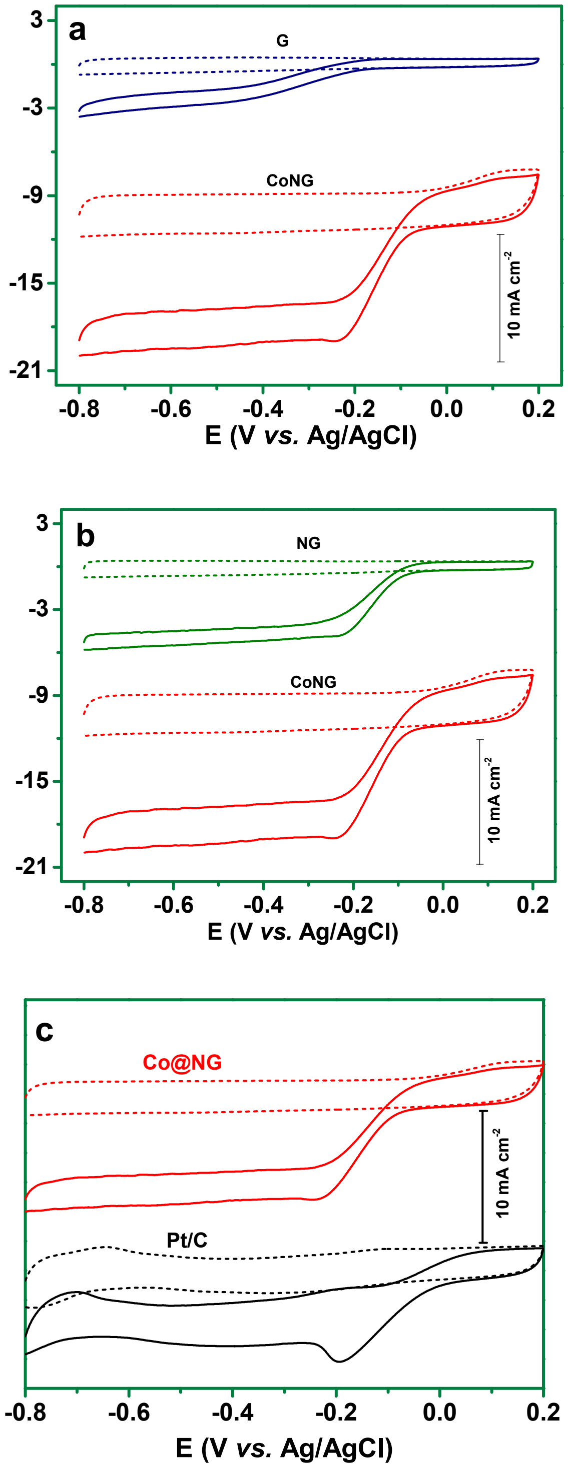

Figure S9. CV curves of Co/NG/GCE (red) compared with (a) rGO/GCE, (b) NG/GCE and (c) Pt/C in Ar-saturated (dash line) and O$_2$-saturated0.1M NaOH (solid line) with a sweep rate of 50 mV s^{-1}.

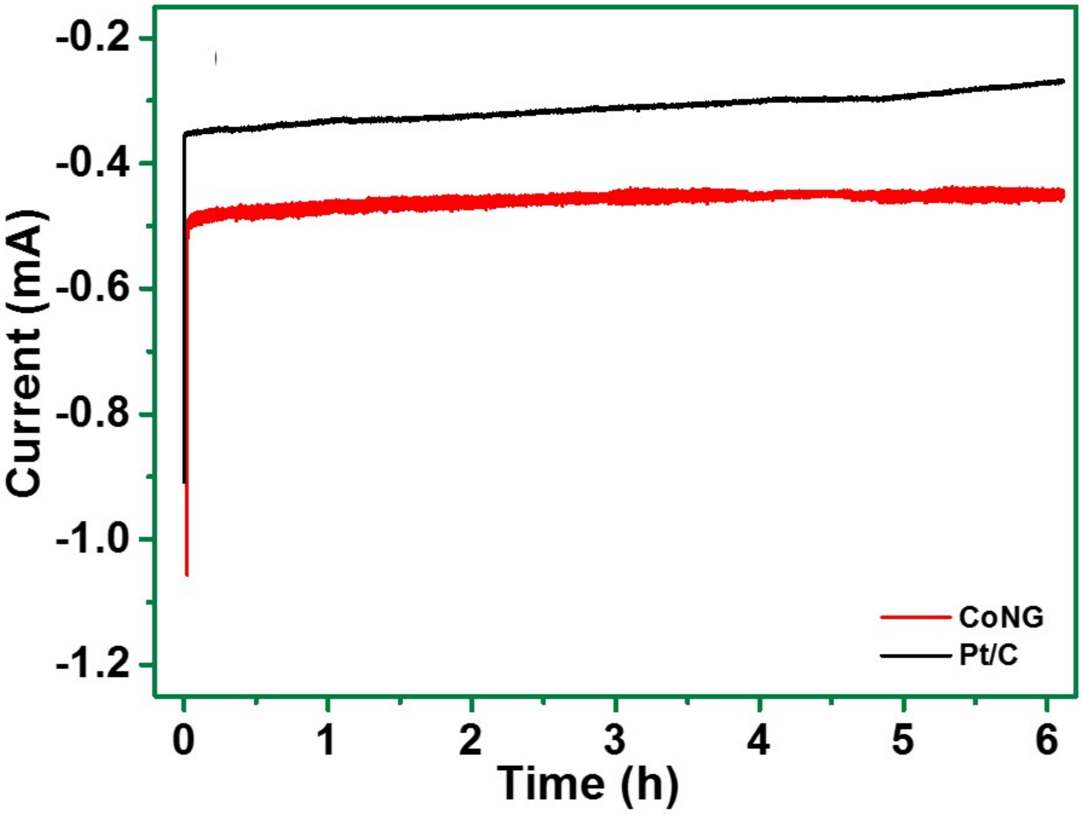

Figure S10, Current-time chronoamperometric response of Co/NG and Pt/C in 0.1 M NaOH solution for about 6 h in O_2-saturated 0.1 M NaOH at -0.30 V *vs.* Ag/AgCl (saturated KCl) with a rotation rate of 1,600 rpm.

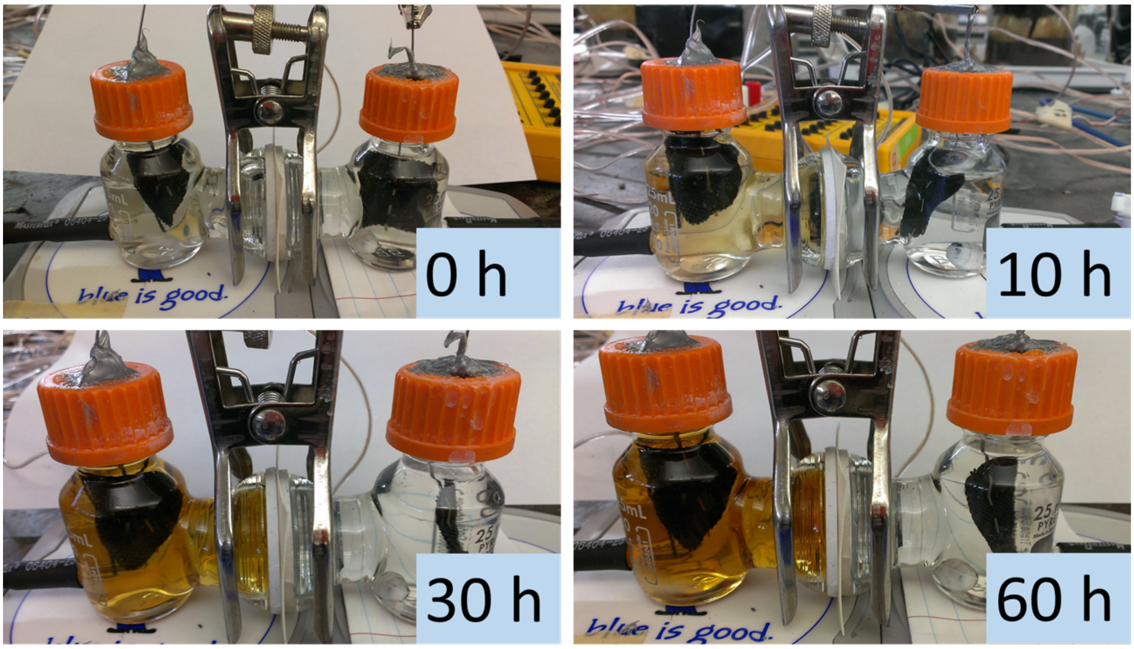

Figure S11. Digital photographs of the $\mathrm{Co/NG}_{(a\|c)}$-GFC taken at different times during operation.

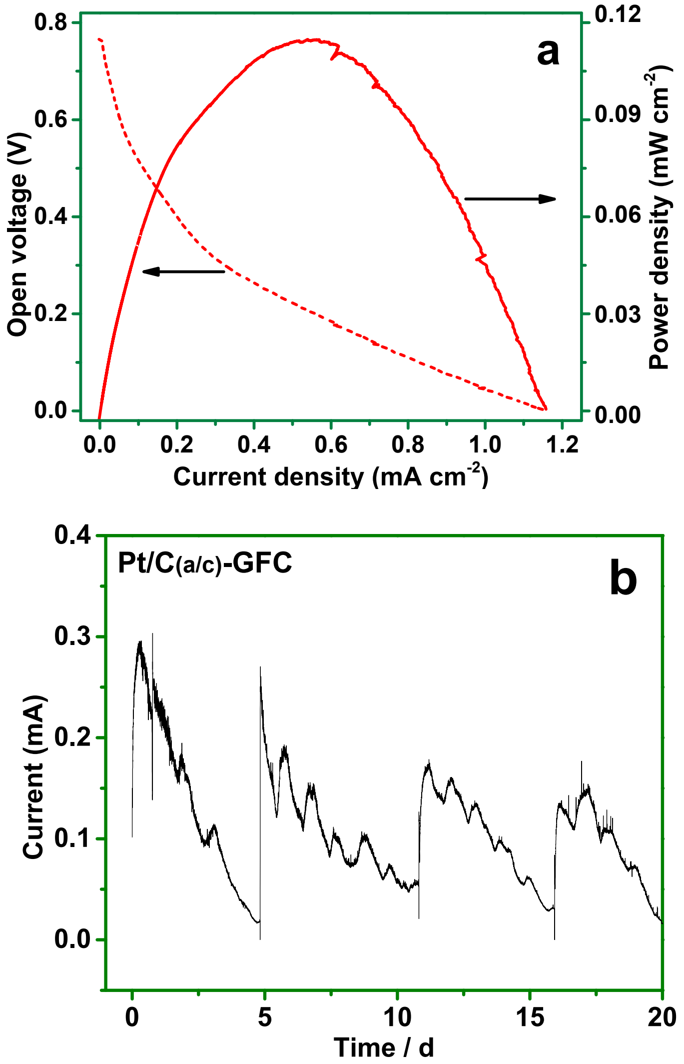

Figure S12. Polarization and power density curves of the Pt/C$_{(a\|c)}$-GFC; (b)The output current vs. time when loading an R$_{ex}$ of 100 Ω in the Co/NG$_{(a\|c)}$-GFC.

Table S1.

Electrocatalysts	E_{peak}^{a} **(V)**	**NPCD**^{a}**(mA cm**$^{-2}$**)**	E_{onset}^{b} **(V)**	$E_{1/2}^{b}$ **(V)**	J^{b}**(mA cm**$^{-2}$**) at -0.8 V**	***Tafel***^{c}***(mV dec***$^{-1}$***)***	n^{d}
Co/NG	-0.23	7.60	-0.01	-0.15	8.49	68.6	3.8
NG	-0.24	3.75	-0.03	-0.17	5.28	76.4	3.7
rGO	-0.48	2.11	-0.15	-0.36	2.99	92.4	2.6
Pt/C	-0.20	6.17	0.06	-0.12	6.39	75.2	3.8

Electrochemical parameters for ORR estimated from CVs and RDE curves in 0.1M NaOH solution.