Supporting Information

Strong-Coupled Co-g-C_3N_4/SWCNTs Composites as High-Performance Electrocatalysts for Oxygen Reduction Reaction

Qiangmin Yu, [a,b,c] Jiaoxing Xu,[a,b] Chuxin Wu,[a,b] and Lunhui Guan* [a,b]

Experimental

Materials

Melamine, Cobalt (Ⅱ) acetate tetrahydrate, NaOH, HCl solution, isopropyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Commercial Pt/C (20 wt% Pt on Vulcan XC-72) was purchased from Alfa Aesar. Purified SWCNTs was produced by arc-discharged method by using Y/Ni as catalyst and then purified by the previously reported method.[1]

Synthesis of Co-g-C_3N_4/SWCNTs composites

The Co-g-C_3N_4/SWCNTs were synthesized by a typical pyrolysis process.[2] 50 mg purified SWCNTs, 50 mg melamine and 10 mg Cobalt (Ⅱ) acetate tetrahydrate (denoted as Sample 50-10) were added to an agate mortar, and then grinded for half an hour until the mixture mixed fully. The mixture was loaded into a quartz boat, and then the boat transferred to tube furnace. The furnace was heated to 600 °C for 1 h, kept at 600 °C for 3 h under flowing N_2. The final sample was grinded again and collected for further characterizations. Similarly, g-C_3N_4, Co-g-C_3N_4, g-C_3N_4-SWCNTs and the different proportions of the Co-g-C_3N_4/SWCNTs samples (150 mg melamine, 50 mg SWCNTs and 30 mg Cobalt (Ⅱ) acetate tetrahydrate, denoted as Sample 150-30; 20 mg melamine, 50 mg SWCNTs and 4 mg Cobalt (Ⅱ) acetate tetrahydrate, denoted as Sample 20-4) were synthesized under the same conditions.

Preparation of the electrode

5 mg of catalysts and 100 μL of Nafion solution (DuPont Corp., 5 wt %) were dispersed in 1.9 mL of isopropanol alcohol and mixed solvent to form a homogeneous ink by an ultrasonic bath. Then, 30 μL of the catalysts ink were loaded onto a clean glass carbon electrode (GCE) surface with a diameter of 5 mm. Commercial Pt/C catalysts were also fabricated using the same procedure.

Characterizations

The morphology and elemental mapping of Co-g-C_3N_4/SWCNTs were observed by using field-emission transmission electron microscopy (TEM, FEI, JEM-2010). BET test was conducted on Autosorb-iQ2-XR (Quantachrome Instruments). XPS measurements were performed on a VG Scientific ESCALAB MK II using AlKa radiation (1486.71 eV) and the C1s peak at 284.5 eV as internal standard. Raman measurements were carried out on LabRAM HR. X-ray diffraction (XRD) measurements were performed on MiniFlex Ⅱ diffractometer. Electrochemical characterizations were performed on a CHI 760D electrochemical analyzer (CH Instruments, Inc., Shanghai, China), coupled with a RDE system (from Taizhou Keruite Analysis Instruments Co. Ltd.). A conventional three-electrode cell was used with a gas flow system. A GCE was used as the working electrode, an Ag/AgCl electrode (saturated KCl-filled) as the reference electrode, and a Pt wire as the counter electrode. All the experiments were carried out at ambient temperature. The electrochemical performance of the catalysts was explored by cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) measurements in an aqueous solution of 0.1 M NaOH. CV curves were obtained at a scan rate of 50 mV s^{-1}. LSV was performed at rotating rates of 500, 900, 1200, 1600, 2000, and 2500 rpm with a sweeping rate of 10 mV s^{-1}. The NaOH solution was bubbled with pure N_2 (99.999%) or O_2 (99.999%) both before (at least 30 min) and during the electrochemical measurements. Chronoamperometric tests were performed at -0.30 V for 12 h with a speed of 1600 rpm.

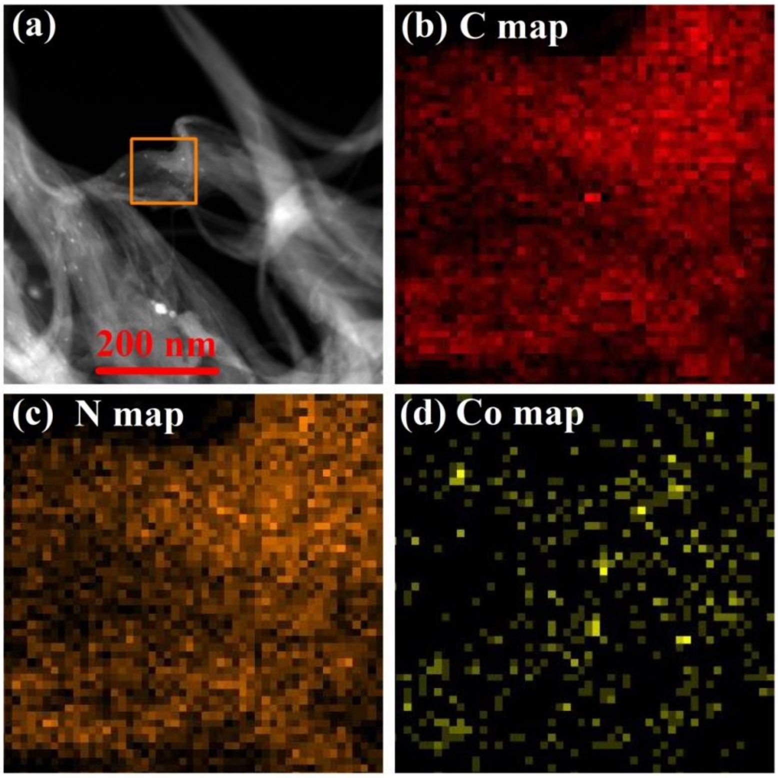

Fig. S1 (a) Scanning transmission electron microscopy (STEM) image of Co-g-C_3N_4 on SWCNTs. The corresponding element mapping images of (b) carbon, (c) nitrogen and (d) cobalt of the Co-g-C_3N_4/SWCNTs composite, indicating the homogeneous distribution of Co-g-C_3N_4 on SWCNTs.

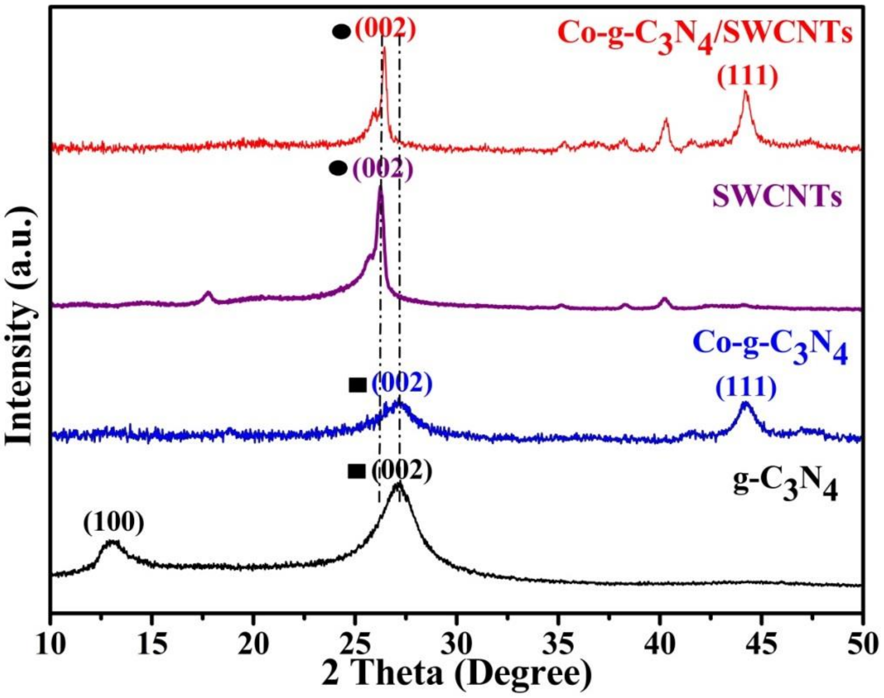

Fig. S2 The XRD patterns of Co-g-C_3N_4/SWCNTs in comparison to g-C_3N_4, Co-g-C_3N_4, and SWCNTs.

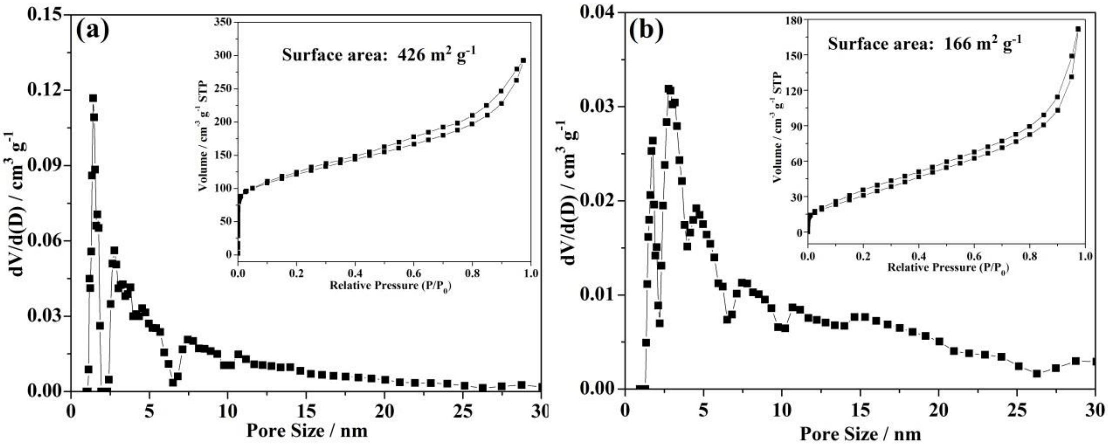

Fig. S3 The pore-size distribution curve: (a) Co-g-C_3N_4 /SWCNTs. Inset: the nitrogen adsorption isotherm of Co-g-C_3N_4 /SWCNTs; (b) Pure-SWCNTs. Inset: the nitrogen adsorption isotherm of Pure-SWCNTs.

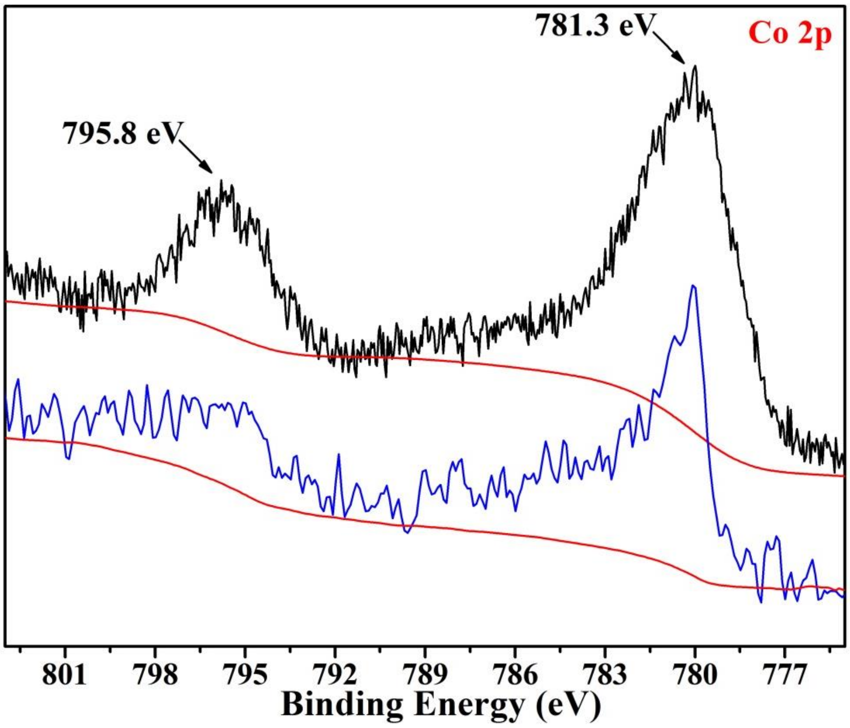

Fig. S4 The XPS survey spectra of Co 2p spectrum: Co-g-C_3N_4/SWCNTs (**black curves**) and the Co-g-C_3N_4/SWCNTs composites washed by excess HCl solution (**blue curves**).

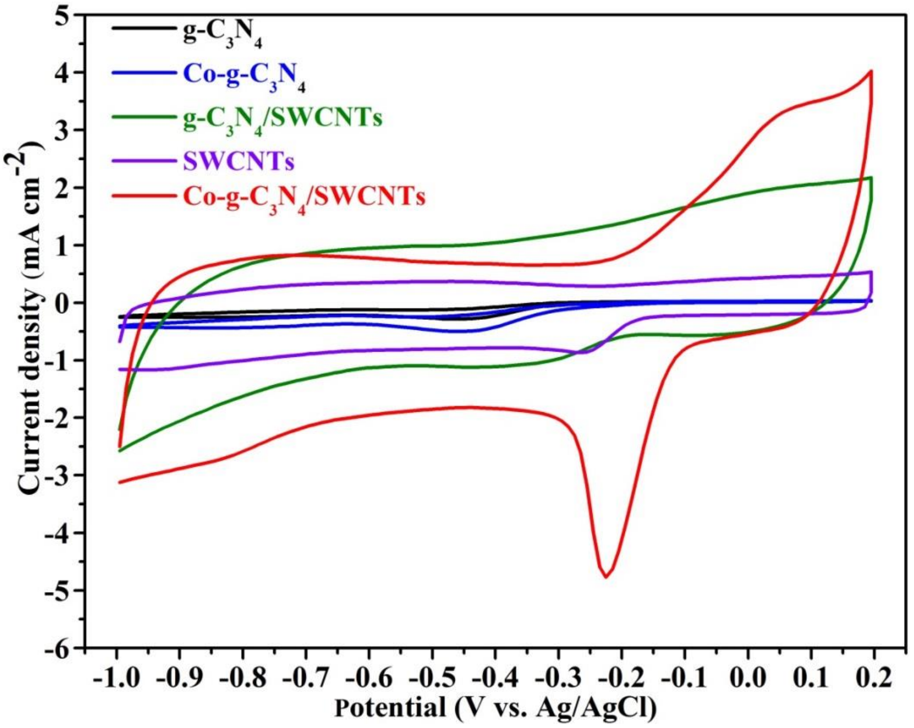

Fig. S5 Cyclic voltammograms of g-C_3N_4, Co-g-C_3N_4, SWCNTs, g-C_3N_4/SWCNTs, and Co-g-C_3N_4/SWCNTs with s scan rate of 50 mV s^{-1} in an O_2-saturated 0.1 M NaOH solution.

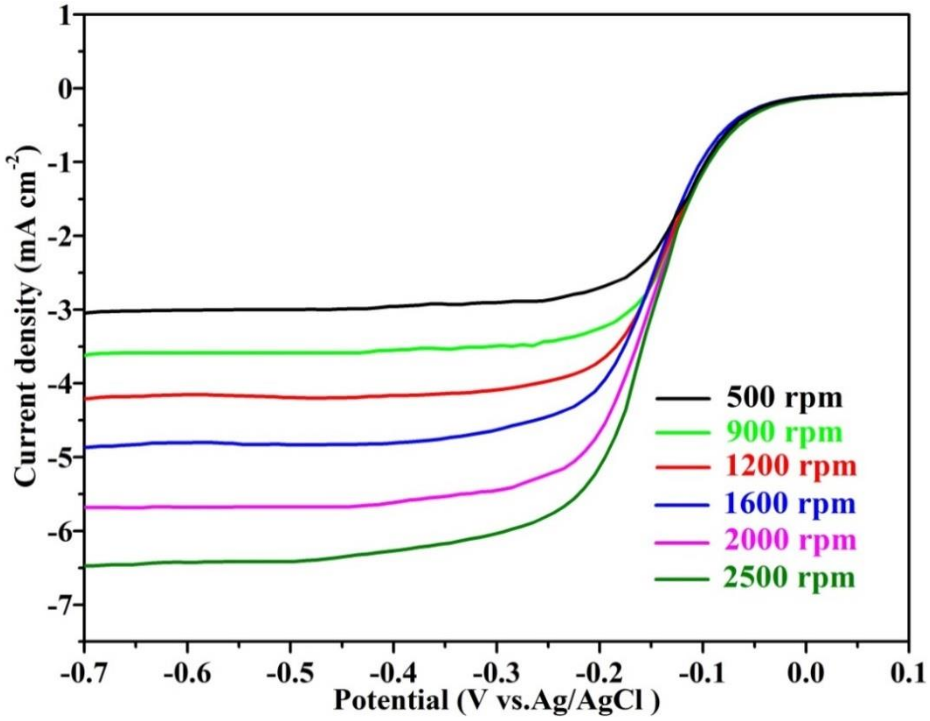

Fig. S6 Linear sweep voltammetry curves of the commercial Pt/C in an O_2-saturated 0.1 M NaOH solution at a sweep rate of 10 mV s^{-1} under various rotation rates.

Table S1. The ORR performance of different catalysts in alkaline media

Sample	Onset potential (V)[a]	Half wave potential (V)[a]	Diffusion-limiting current (mA/cm^2)	Electron transfer number at -0.35V[a]
Co-g-C_3N_4	-0.27	-0.38	3.42	2.58
g-C_3N_4/SWCNTs	-0.18	-0.35	4.71	3.03
Co- g-C_3N_4/SWCNTs	-0.03	-0.15	5.70	3.97
Pt/C	-0.01	-0.14	5.05	3.91

[a] V vs. Ag/AgCl

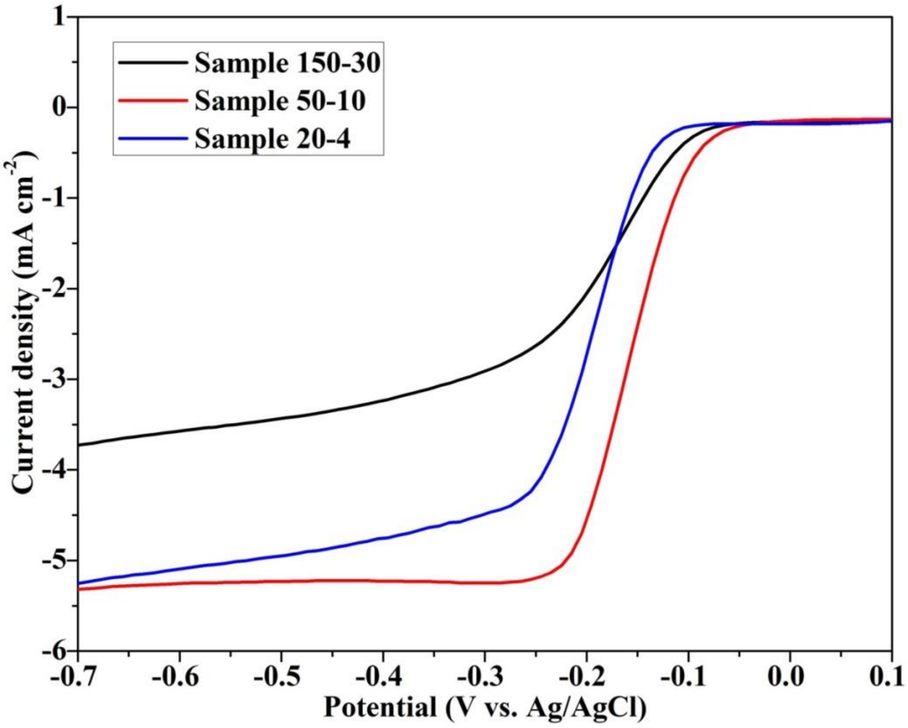

Fig. S7 LSV curves of Co-g-C_3N_4/SWCNTs with varying proportions in an O_2-saturated 0.1 M NaOH solution at a sweep rate of 10 mV s^{-1} and 1600 rpm.

The different proportions of samples toward ORR catalytic performance were also investigated. As shown in Figure S7, by comparison of their LSV measurements, sample 50-10 (See synthesis of Co-g-C_3N_4/SWCNTs composites for detailed information) has the best activity with regard to the current density, onset potential and half-wave potential. Sample 150-30 reveals lower current density result from the high ratio of mal-conductivity Co-g-C_3N_4 samples. Sample 20-4 has a more negative potential root in a few of Co-g-C_3N_4 derived active sites. The results turned out that Co-g-C_3N_4 derived active sites and and SWCNTs with a high conductivity.

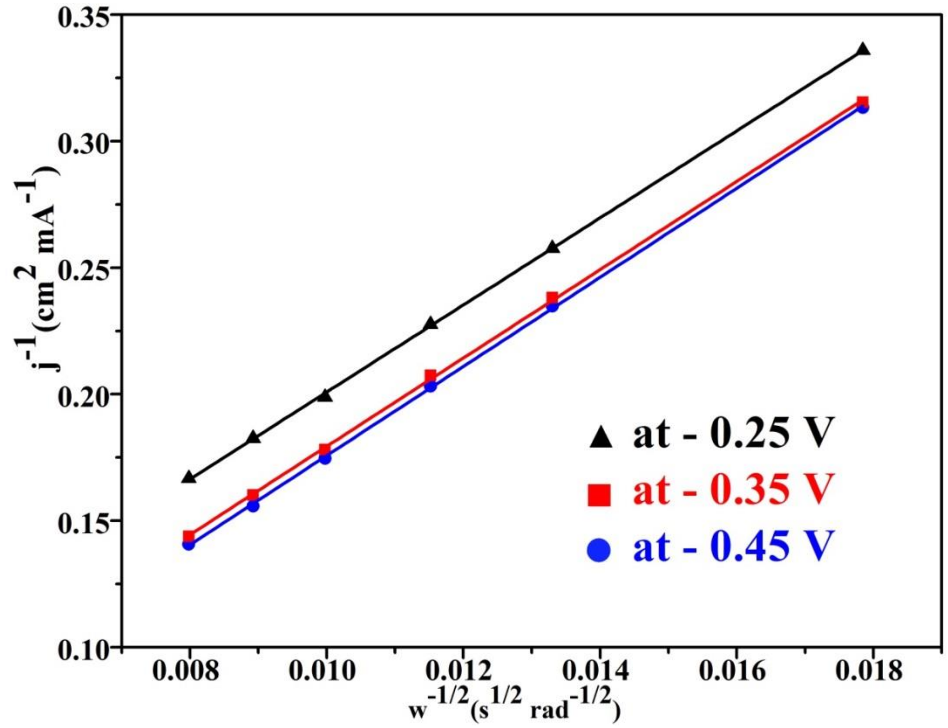

Fig. S8 Koutecky-Levich plots at different potentials for ORR in an O_2-saturated 0.1 M NaOH solution for Co-g-C_3N_4/SWCNTs.

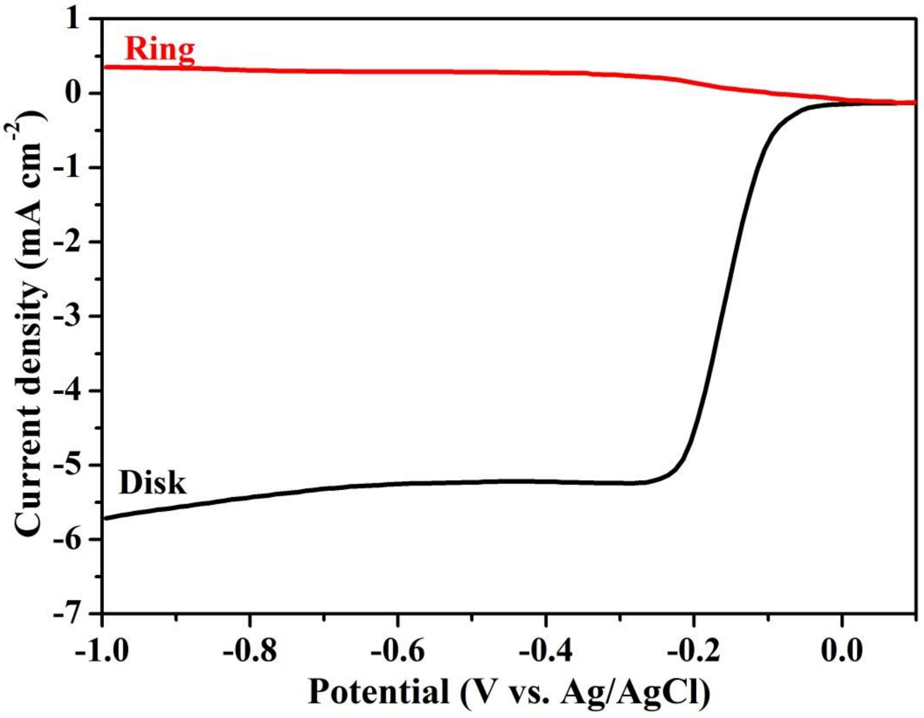

Fig.S9 RRDE voltammogram curves of Co-g-C_3N_4/SWCNTs catalyst at the rotation speed of 1600 rpm.

As shown in Fig.S9, for the Co-g-C_3N_4/SWCNTs, the number of electron transfer (n, eq. S1) was calculated to be 3.61~3.75 at the potential ranging from -0.2 to -0.4 V, with a low H_2O_2 yield of 7.8~16.9%

over the measured potential range (eq. S2). It suggesting that the Co-g-C_3N_4/SWCNTs favored a nearly 4e ORR process.

$$\mathrm{n} = \frac{4I_{Disk}}{I_{Disk}+\frac{I_{Ring}}{N}} \qquad \text{(eq. S1)}$$

$$H_2O_2\% = \frac{200I_{Ring}/N}{I_{Disk}+\frac{I_{Ring}}{N}} \qquad \text{(eq. S2)}$$

where N is the collection efficiency (37%), I_{Disk} and I_{Ring} are the voltammetric currents at the disk and ring electrodes, respectively.

1. C. X. Wu, J. X. Li, G. F. Dong and L. H. Guan, *Journal of Physical Chemistry C*, 2009, **113**, 3612-3616.
2. Y. H. Zhang, Q. W. Pan, G. Q. Chai, M. R. Liang, G. P. Dong, Q. Y. Zhang and J. R. Qiu, *Scientific Reports*, 2013, **3**.