Oxidized Carbon Nanotubes as Efficient Metal-free Electrocatalyst for Oxygen Reduction Reaction

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Supplementary Information

Experimental Details

CNT (diameter < 8 nm SSA > 350 m^2g^{-1}) was purchased from Shenzhen Nanotech Port Co., Ltd. H_2SO_4 （98%） and HNO_3 (68%) were purchased from a commercial company. All the chemical reagents were used without further purification.

Preparation of H_2SO_4 treated oxidized CNTs (ST-CNT): 200 mg MWCNT was added into 80 mL H_2SO_4. The mixture was then gently stirred at 70 °C in an oil bath for 2 h. After that, the obtained mixture was diluted with a large amount of DI water. Acid treated MWCNTs were collected by filtration and washed with DI water until the PH was nearly 7. The final product was obtained after dried under vacuum at 70 °C overnight.

Preparation of both HNO_3 and H_2SO_4 treated oxidized CNTs (NST-CNT): The experimental procedures were the same as ST-CNT preparation with just a little change that is different volumes of HNO3 were introduced into the acid hybrid. HNO_3/H_2SO_4 (v:v=1:3, 1:1, 3:1) and only HNO_3 were denoted as NST-CNT(1:3), as NST-CNT(1:1), as NST-CNT(3:1) and NT-CNT, respectively.

Catalyst preparation: At first, 4 mg as-prepared samples were added into 2 ml ethanol to get a well dispersed suspension (2 mg / ml) under sonication. Then, 100 μl Nafion solution (5 wt%) as a binder was added into the catalyst suspension. To prepare the electrode, 5 μl catalyst suspension was dropped onto the surface of a pre-polished glassy carbon electrode (GCE). After fully dried at room temperature, the catalyst casted GCE was used as the working electrode to measure its ORR activity.

Electrochemical measurements: All the electrochemical measurements including CV and LSV were carried out using an electrochemical workstation (CHI 760E, CH Instrument, USA) with a typical three-electrode system. A platinum mesh was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. For the measurement of linear sweep voltammetry (LSV), rotating disk electrode (RDE) was employed at a rotation rate of 1600 rpm in 0.1 M KOH solution saturated with O_2. All the measurements were conducted at room temperature (25±1 °C).

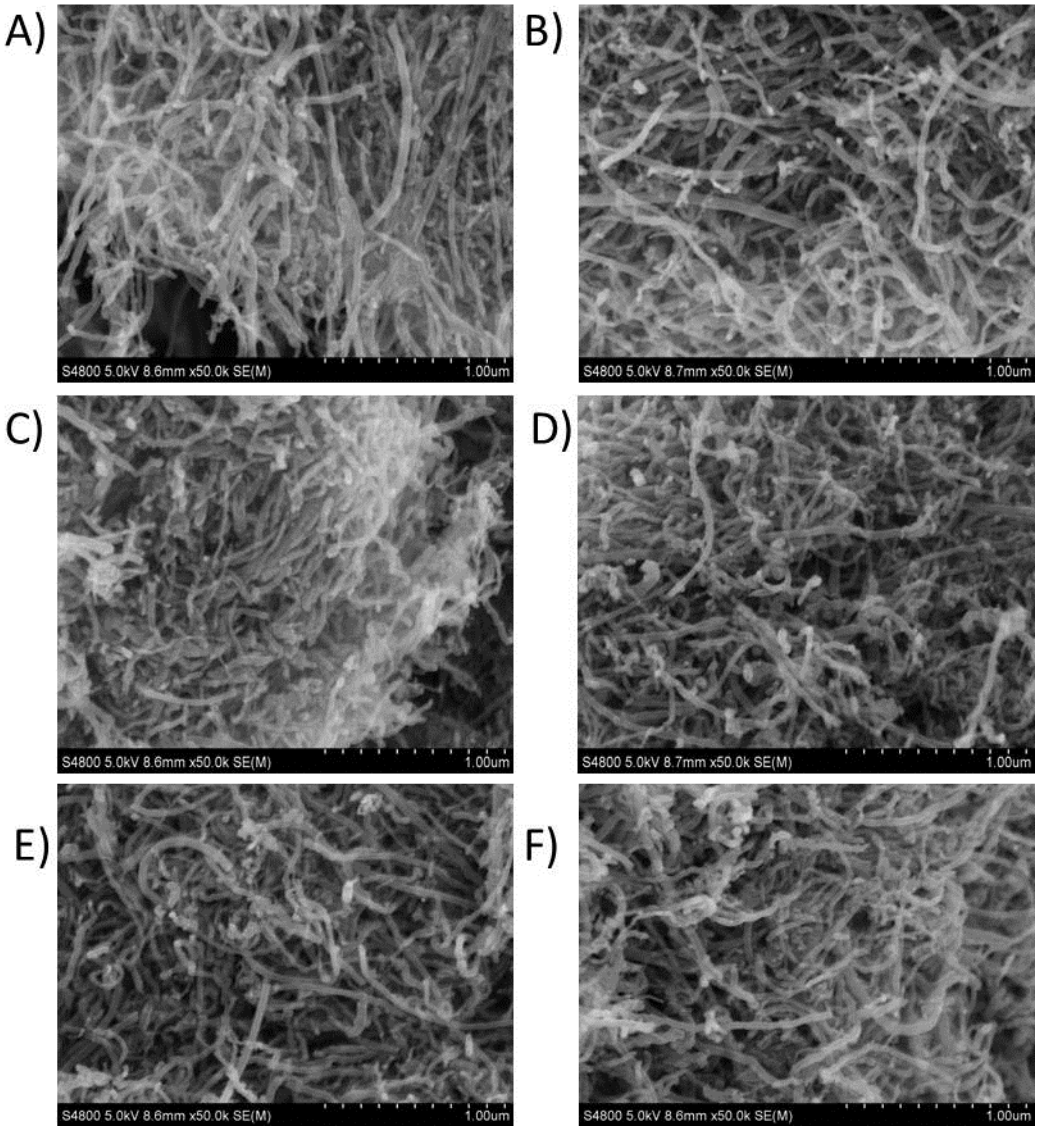

Figure S1. SEM of Pristine CNT (A), NT-CNT (B), NST-CNT(1:3) (C), NST-CNT(1:1) (D), NST-CNT(3:1) (E), Pristine CNT (F).

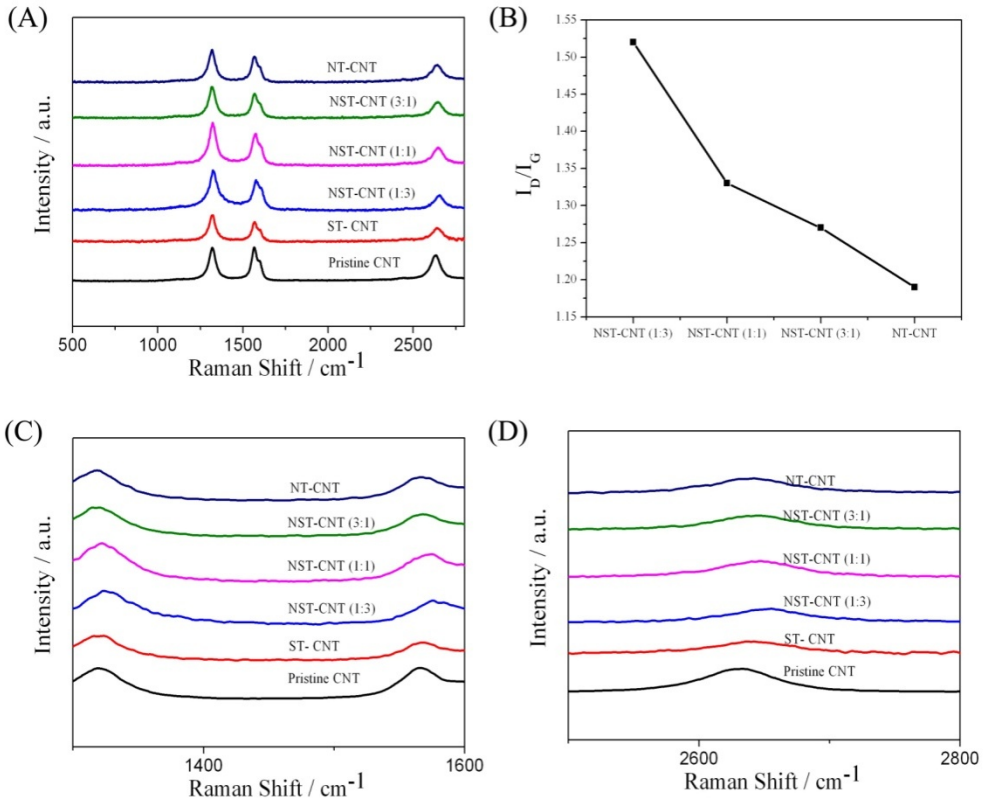

Figure S2. Raman spectra of acid treated samples (A); ID/IG ratio of NT-CNT NST-CNT(1:3) NST-CNT(1:1) NST-CNT(3:1) (B); D and G peaks shift observation of different samples (C); 2D peak shift observation (D).

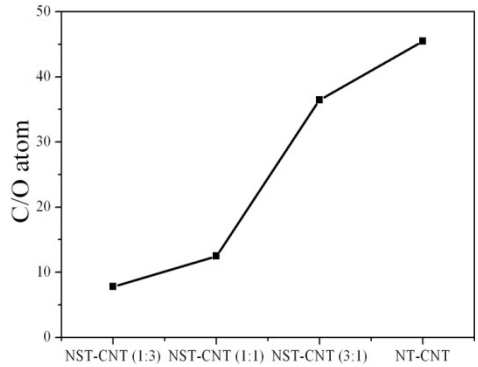

Figure S3. The value of C/O atom for NST-CNT (1:3), NST-CNT (1:1), NST-CNT (3:1) and NT-CNT.

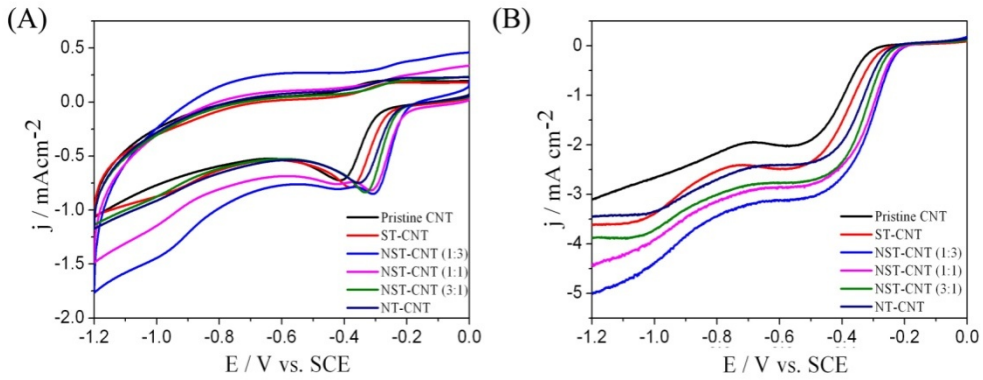

Figure S4. The cyclic voltammetry curves of oxygen reduction reactions on Pristine CNT, ST-CNT, NST-CNT (1:3), NST-CNT (1:1) NST-CNT (3:1) and NT-CNT in oxygen saturated 0.1 M KOH solution with a scan rate of 10 mV s^{-1} (A); Linear-sweep voltammetry (LSV) of P Pristine CNT, ST-CNT, NST-CNT (1:3), NST-CNT (1:1) NST-CNT (3:1) and NT-CNT in oxygen saturated 0.1 M KOH solution with a scan rate of 10 mV s^{-1} at 1600 rpm (B).

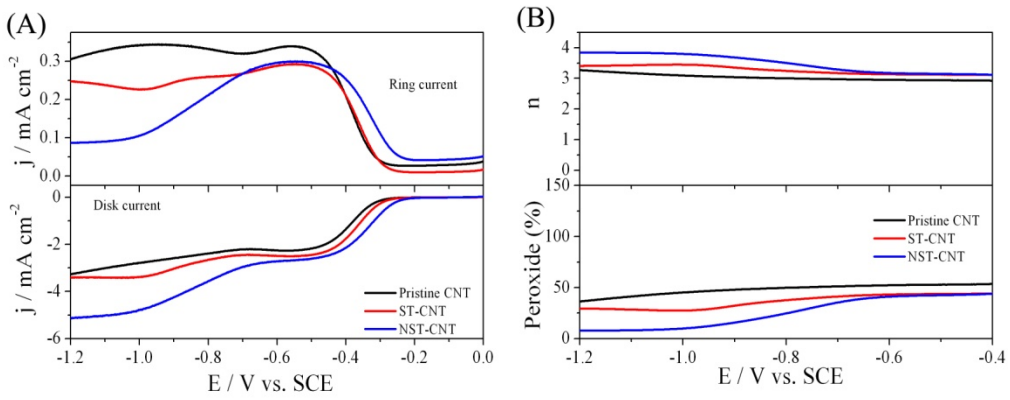

Figure S5. RRDE tests of different samples for ORR in oxygen saturated 0.1 M KOH at 1600 rpm with a scan rate of 10 mV s-1 (A); The calculated electron transfer number and peroxide production percentage during the ORR process (B).

Electron transfer number calculation (1):

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$

where j_k is the kinetic current and ω is the electrode rotating rate. B could be determined from the slope of K-L plots (Figure 4E) based on Levich equation as follows:

$$B = 0.2nF(D_{O_2})^{2/3}\nu^{-1.6}C_{O_2}$$

where n represents the number of electrons transferred per oxygen molecule, F is the Faraday constant (F = 96485 C mol^{-1}), $\boldsymbol{Do_2}$ is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}), υ is the kinetic viscosity (0.01 cm^2 s^{-1}), and $\boldsymbol{Co_2}$ is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}). The constant 0.2 is adopted when the rotation speed is expressed in rpm

Electron transfer number calculation (2) and peroxide (%) calculation for oxygen reduction reaction:

$$n = 4\frac{I_d}{I_d + I_r/N}$$

$$HO_2^- = 200\frac{I_r/N}{I_d + I_r/N}$$

where Id is disk current, Ir is ring current, and N is current collection efficiency of the Pt ring. N was determined to be 0.42.

Table S1. List of the onset potential values of functionalized carbon materials

Samples	Onset potential	References
Our work	-0.2 V vs. SCE	NA
Polyelectrolyte functionalized CNT	-0.12 V vs. SCE	S1
Sulfur doped graphene	-0.25 V vs. SCE	S2
Nitrobenzene doped graphene	-0.25 V vs. SCE	S3
Nitrogen containing groups functionalized CNT	-0.139 V, -0.181 V, -0.250 V vs. SCE	S4
Nitrogen doped carbon nanotubes	-0.1 V vs. Hg/HgO	S5
Nitrogen doped carbon nanotubes	-0.04 V vs. Ag/AgCl	S6
Sulfur doped graphene	-0.05 V vs. Ag/AgCl	S7

S1 Wang S, Yu D, Dai L. Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction[J]. Journal of the American Chemical Society, 2011, 133(14): 5182-5185.

S2 Ma Z, Dou S, Shen A, et al. Sulfur‐Doped Graphene Derived from Cycled Lithium–Sulfur Batteries as a Metal‐Free Electrocatalyst for the Oxygen Reduction Reaction[J]. Angewandte Chemie, 2014.

S3 Dou S, Shen A, Tao L, et al. Molecular doping of graphene as metal-free electrocatalyst for oxygen reduction reaction[J]. Chemical Communications, 2014, 50(73): 10672-10675.

S4 Tuci G, Zafferoni C, D'Ambrosio P, et al. Tailoring carbon nanotube N-dopants while designing metal-free electrocatalysts for the oxygen reduction reaction in alkaline medium[J]. ACS Catalysis, 2013, 3(9): 2108-2111.

S5 Sharifi T, Hu G, Jia X, et al. Formation of active sites for oxygen reduction reactions by transformation of nitrogen functionalities in nitrogen-doped carbon nanotubes[J]. ACS nano, 2012, 6(10): 8904-8912.

S6 Chen Z, Higgins D, Tao H, et al. Highly active nitrogen-doped carbon nanotubes for oxygen reduction reaction in fuel cell applications[J]. The Journal of Physical Chemistry C, 2009, 113(49): 21008-21013.

S7 Yang Z, Yao Z, Li G, et al. Sulfur-doped graphene as an efficient metal-free cathode catalyst for oxygen reduction[J]. ACS nano, 2011, 6(1): 205-211.