

# Supporting Information

## Sulfur and Nitrogen co-doped Carbon Nanotubes for Enhancing Electrochemical Oxygen Reduction Activity in Acidic and Alkaline Media

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## 1. Experimental Section

### 1.1 Preparation of materials

The N-doped carbon nanotubes (N-CNTs) were prepared by thermolysis of aniline using FeMo/Al<sub>2</sub>O<sub>3</sub> as catalyst in NH<sub>3</sub> atmosphere. In a typical experiment, 0.1 g of FeMo/Al<sub>2</sub>O<sub>3</sub> in quartz boat was put in the quartz tube loaded in a tubular furnace with 500 mL/min of NH<sub>3</sub> flow. The aniline (a flow rate of 3 mL/h) was injected in the quartz tube after the temperature of the tubular furnace arrived to 800 °C. The tubular furnace continued to be kept at 800 °C for 10 minutes after the total infusion of aniline (15 mL). After the equipment cooled down to the room temperature, the resulting sample was collected from quartz boat. The as-prepared N-CNTs were treated with 12 mol/L HCl for 2 h to remove metals for subsequent use as a catalyst and a precursor of SN-CNTs catalyst.

A series of SN-CNTs catalysts were prepared by annealing of N-CNTs and different sulfur sources (CS<sub>2</sub>, toluenethiol and sulfur). For CS<sub>2</sub> as a sulfur source, the N-CNTs were dispersed ultrasonically in excessive CS<sub>2</sub> and then dried at room temperature. The result black solid was annealed at 900 °C with at a mixed gas environment of Ar and H<sub>2</sub> (volumetric flow ratio of 10: 1) for 4h, finally, SN-CNTs were collected. When toluenethiol and sulfur were selected as sulfur sources, SN-CNTs catalysts were prepared with the same method described below. N-CNTs and sulfur sources (weight ratio of 1: 2) were mixed in deionized water. The mixture was hydrothermally treated at 180 °C for 5.5 h to ensure a full mixture of sulfur sources and N-CNTs. After the mixture was cooled down to room temperature, the black N-CNTs containing sulfur source was collected by filtration and dried in vacuum at 70 °C for 12 h. Next, the solid mixture was put into a quartz tube which was loaded in a tubular furnace for annealing. The annealing process was taken place at 900 °C with a continuous flowing gas stream composed of Ar and H<sub>2</sub> (volumetric flow ratio of 10: 1) for 4h. Finally, SN-CNTs were collected from the quartz tube.

For comparison, CNTs were prepared by thermolysis of xylene using FeMo/Al<sub>2</sub>O<sub>3</sub> as catalyst in Ar atmosphere at 800 °C. The S-doped CNTs (S-CNTs) were synthesized by the pyrolysis of CNTs with sulfur with the same method described above. All other chemicals were purchased and used without any further purification.

## 1.2 Catalyst characterization

The morphologies of the N-CNTs and SN-CNTs samples were performed by scanning electron microscopy (SEM) (1530VP, LEO Co.) operating at 200 kV and transmission electron microscopy (TEM) (FEI Tecnai G2 F20) with the accelerating voltage of 100 kV. X-ray photoelectron spectroscopic (XPS) measurements were characterized on a VG Scientific ESCALAB 250. BET surface areas were tested by Micromeritics, TriStar II 3020.

## 1.3 Electrode preparation and electrocatalytic performance test

Electrochemical experiments were analyzed using three-electrode cell, which was connected to an electrochemical analyzer (Eco Chemie B. V. Autolab PGSTAT30) and a rotator (pine Instrument Co). The glass carbon electrodes (4.0 mm in diameter for CV test, and 5.0 mm in diameter for LSV test) loaded with N-CNTs and SN-CNTs catalysts were used as the working electrodes. In acidic solution, an Ag/AgCl with saturated KCl was used as reference electrode. In alkaline solution, a saturated calomel electrode (SCE) was used as reference electrode. A carbon electrode was used as counter electrode in acidic solution to eliminate the influence of Pt due to the dissolution of Pt electrode<sup>[S1]</sup>, and it was instead by a Pt wire in alkaline medium. The working electrodes were prepared as follows: the catalysts (1mg) were dispersed in 0.5 ml of solvent mixture of Nafion (5%), deionized water and acetone (V:V:V=15:385:100) by sonication, then the catalysts inks (20  $\mu$ l for N-CNTs and SN-CNTs catalysts, and 10  $\mu$ l for Pt-C catalyst) were dropped onto the GC electrode surface. The electrodes were dried at 60 °C before measurement.

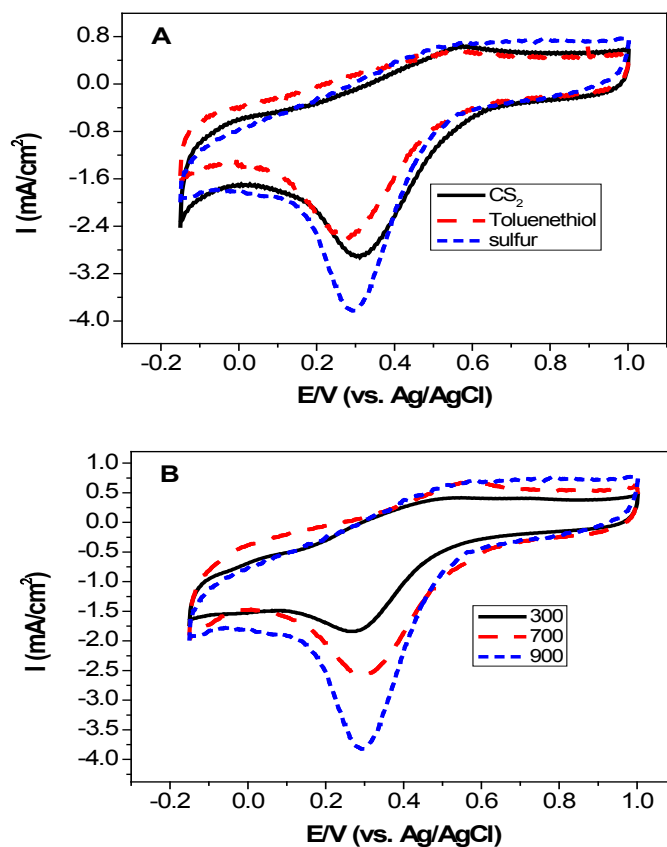
## 1.4 The calculation of electron-transfer numbers

The electron-transfer numbers ( $n$ ) of all the samples at different potentials were calculated according to the Koutecky-Levich equation<sup>[S2]</sup>.

$$I^{-1} = I_k^{-1} + (0.62nFC D^{2/3} \nu^{-1/6} \omega^{1/2})^{-1}$$

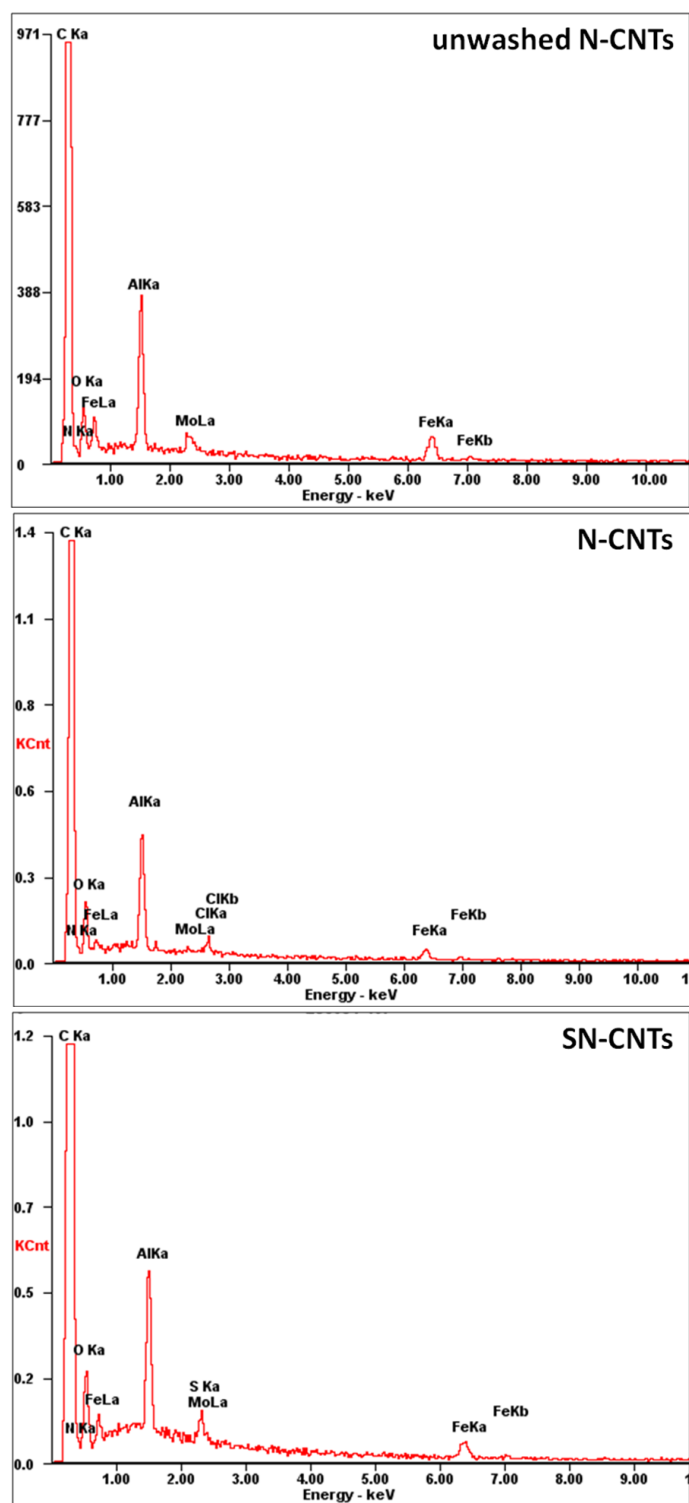
$I$  is the measured current density,  $I_k$  is the kinetic current density of the ORR,  $n$  is the overall number of electrons transferred during the oxygen reduction,  $F$  is the Faraday constant (96500 C/mol),  $C$  is the bulk oxygen concentration,  $D$  is the molecular diffusion coefficient of O<sub>2</sub> in bulk solution,  $\nu$  is the kinematic viscosity of the solution, and  $\omega$  is the angular velocity of the disk ( $\omega = 2\pi N$ ,  $N$  is the linear rotation speed). In acidic media:  $C = 1.6 \times 10^{-3}$  mol/L,  $D = 1.1 \times 10^{-5}$  cm<sup>2</sup>/s,  $\nu = 0.01$  cm<sup>2</sup>/s. In 0.1 M KOH media:  $C = 1.2 \times 10^{-3}$  mol/L,  $D = 1.9 \times 10^{-5}$  cm<sup>2</sup>/s,  $\nu = 0.01$  cm<sup>2</sup>/s.

## 2. Supplementary Figures



**Fig. S1** Typical cyclic voltammograms for the ORR of the SN-CNTs prepared with different sulfur precursor (A) and different annealing temperature (B) in 1 M HClO<sub>4</sub> saturated with oxygen gas (the 150<sup>th</sup> cycle).

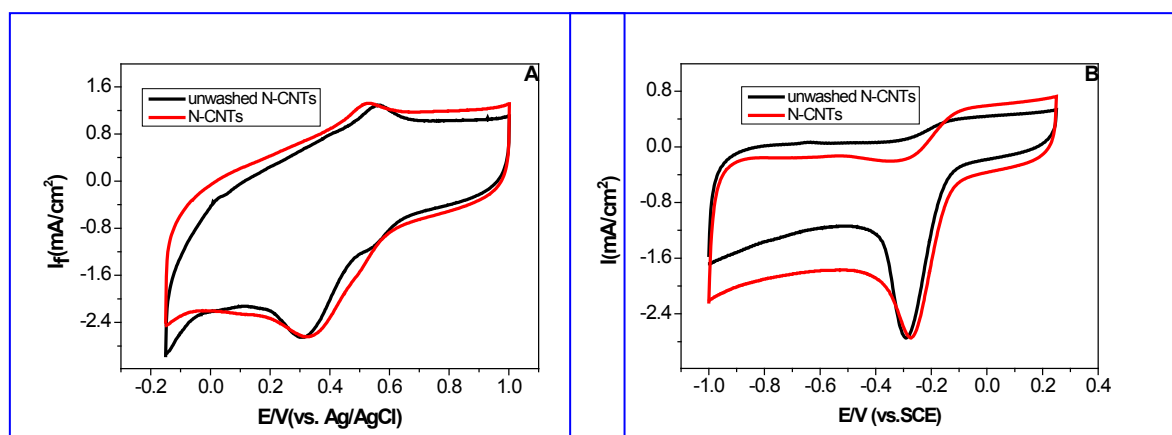
A series of SN-CNTs catalysts were prepared by annealing of N-CNTs and different sulfur sources. The effect of sulfur sources (CS<sub>2</sub>, toluenethiol and sulfur) on electrocatalytic performance of SN-CNTs for ORR has been evaluated. The CV results show that sulfur is the best precursor as it has the highest current density (Fig. S1A), which is proportional to the electro-catalytic performance. The ORR activities of SN-CNTs prepared with sulfur as sulfur source under the different annealing temperatures were tested in the same condition. Fig. S1B shows that the peak current increases as the annealing temperature increasing, considering the limit of reaction condition, the suitable annealing temperature of 900 °C was selected.



**Fig. S2** Typical EPMA spectrum obtained from unwashed N-CNTs, N-CNTs and SN-CNTs.

**Table. S1** The content of residual metal elements of different samples from EPMA test

<i>samples</i>	<i>Element Contents, at%</i>		
	<i>Fe</i>	<i>Mo</i>	<i>Al</i>
<i>Unwashed N-CNTs</i>	1.03	0.15	1.34
<i>N-CNTs</i>	0.40	0.05	1.10
<i>SN-CNTs</i>	0.27	0.05	0.55



**Fig. S3** Typical cyclic voltammograms for the ORR of the unwashed N-CNTs and N-CNTs in 1 M HClO<sub>4</sub> (A) and 0.1 M KOH (B) saturated with oxygen gas (the 150<sup>th</sup> cycle).

The EPMA spectra of unwashed N-CNTs, washed N-CNTs (N-CNTs) and SN-CNTs exhibit that there are still minor content of Fe, Mo and Al after treated with HCl (Table.S1). However, after washing by HCl, the electrochemical activities of N-CNTs did not decrease due to the lower content of metallic residues (**Fig. S3**). Therefore, the residual metals have no dominant impact to the electrocatalysis of prepared N-CNTs. Additionally, the content of metallic residues in SN-CNTs is lower than that of N-CNTs, and the loss of metals may be due to the hydrothermal and annealing process.

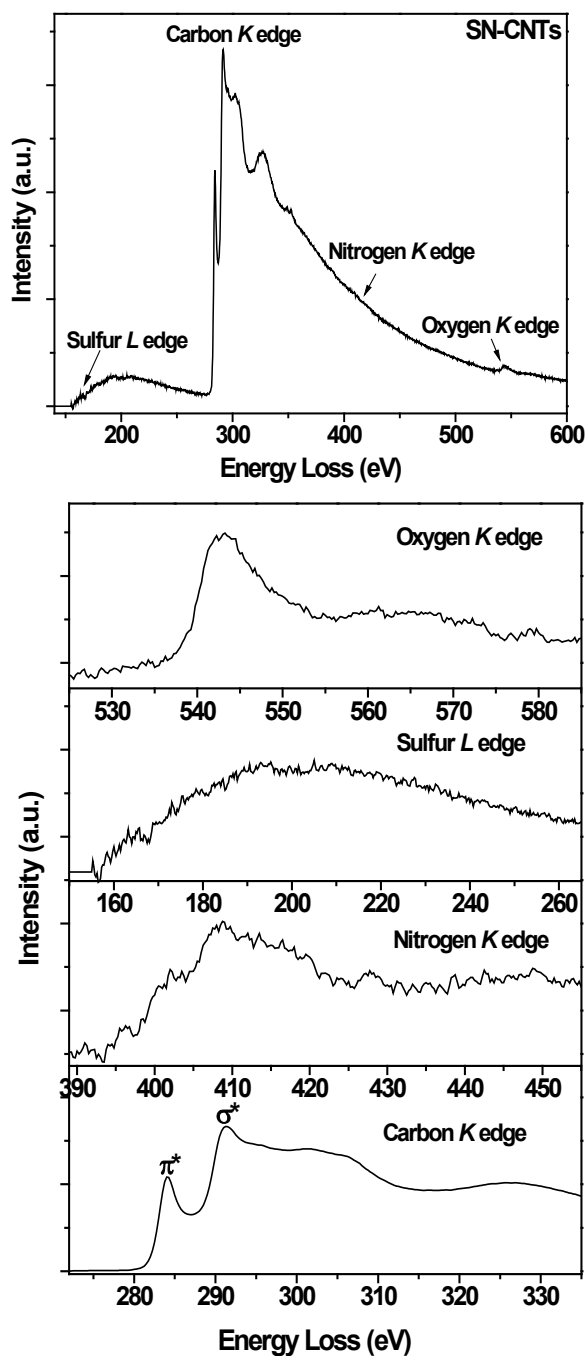
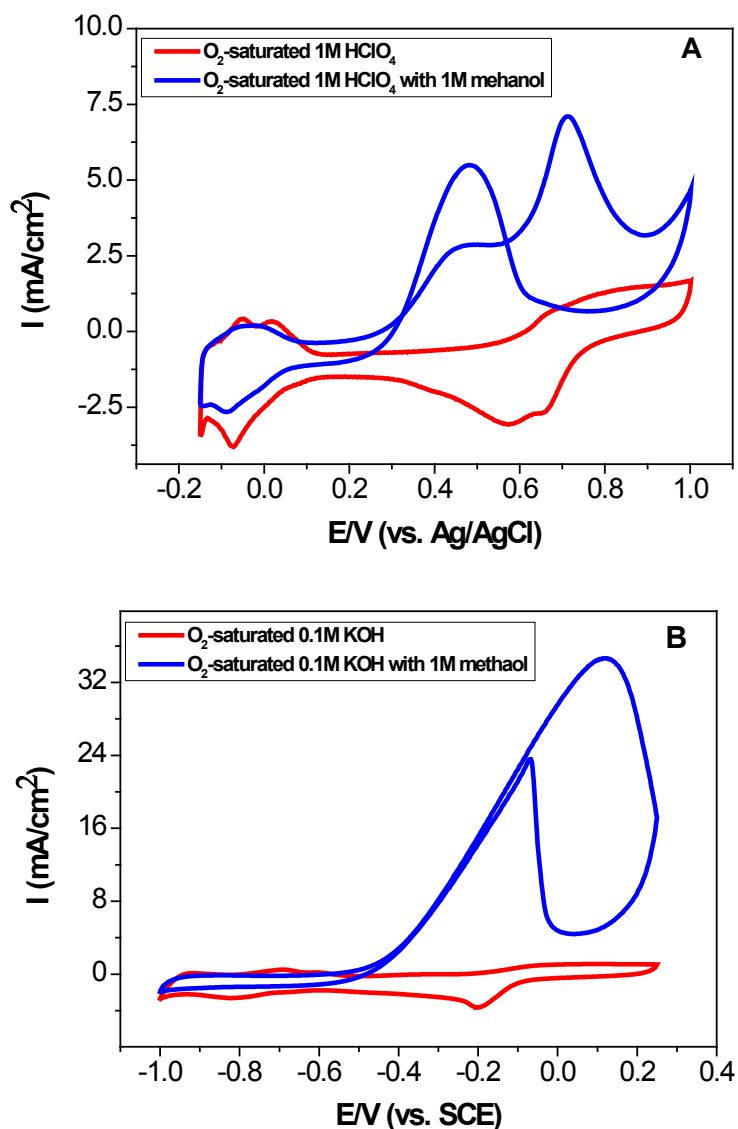


Fig. S4 EELS spectra of SN-CNTs.

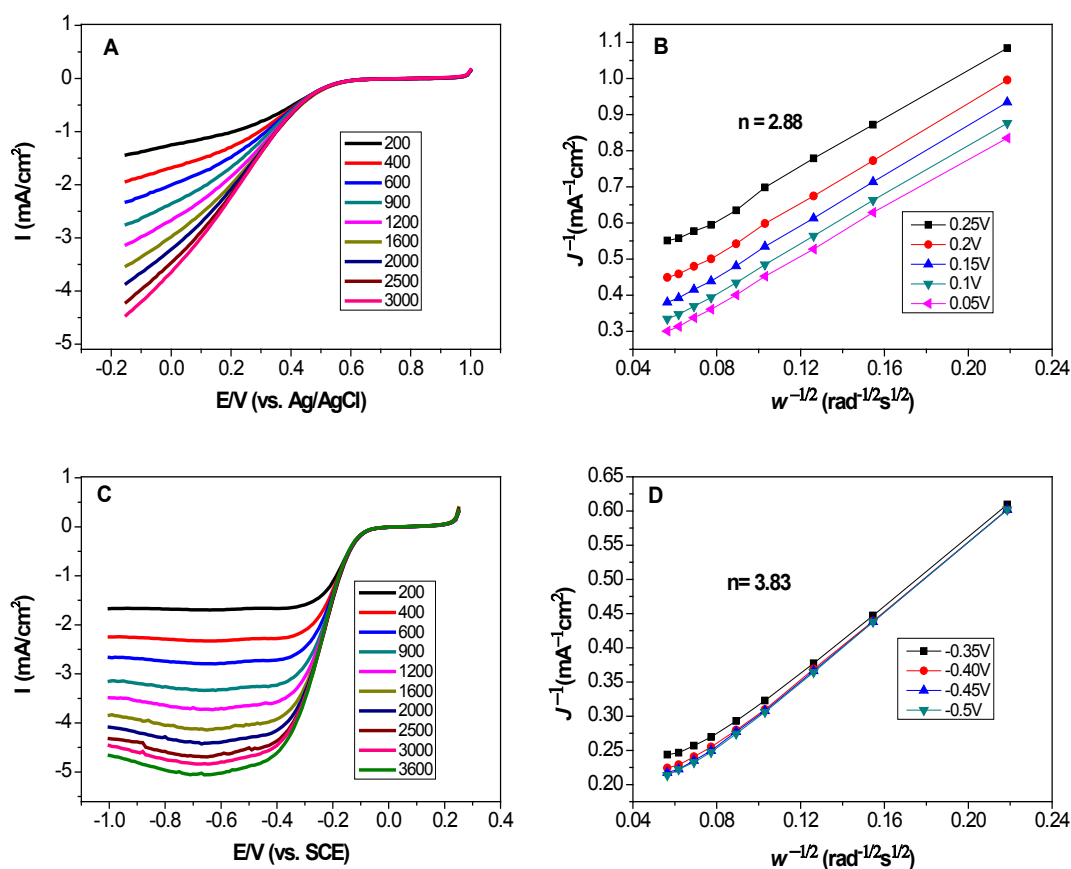
The electron energy loss spectroscopy (EELS) shows four edges which corresponding to the characteristic K-shell ionization edges of C, N and O, and L-shell ionization edges of S, respectively. Detailed features of the O and N K-edges and S L-edge also show the presence of these elements. The distinct  $1s \rightarrow \pi^*$  (284 eV) and  $1s \rightarrow \sigma^*$  (291 eV) peaks of the C K-edge prove that the C element is  $sp^2$ -hybridized.<sup>[S3]</sup>



**Fig. S5** Typical cyclic voltammograms for the ORR of the Pt-C (20 wt. %) catalysts in an aqueous solution of 1 M HClO<sub>4</sub> (A) and 0.1 M KOH (B) saturated with oxygen gas with or without 1M CH<sub>3</sub>OH at room temperature (the 150th cycle).

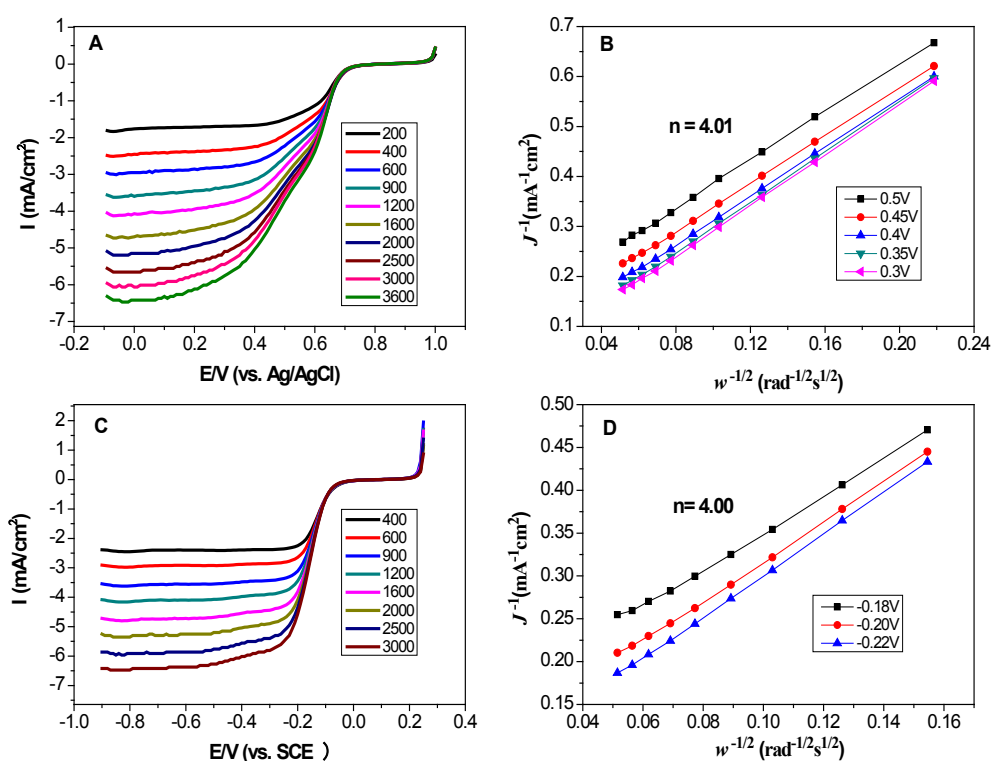
The ORR activity of Pt-C catalyst was tested by CV method in an O<sub>2</sub>-saturated solution with or without 1M methanol (Fig. S5). In 1M HClO<sub>4</sub> solution saturated with O<sub>2</sub>, the result shows a normal ORR peak, but after adding methanol, an obvious methanol oxidation peak appeared with the disappearance of ORR peak. This result is also found in 0.1 KOH solution. These results indicate that Pt-C catalyst exhibits poor tolerance to methanol crossover effects in acidic and alkaline solution.





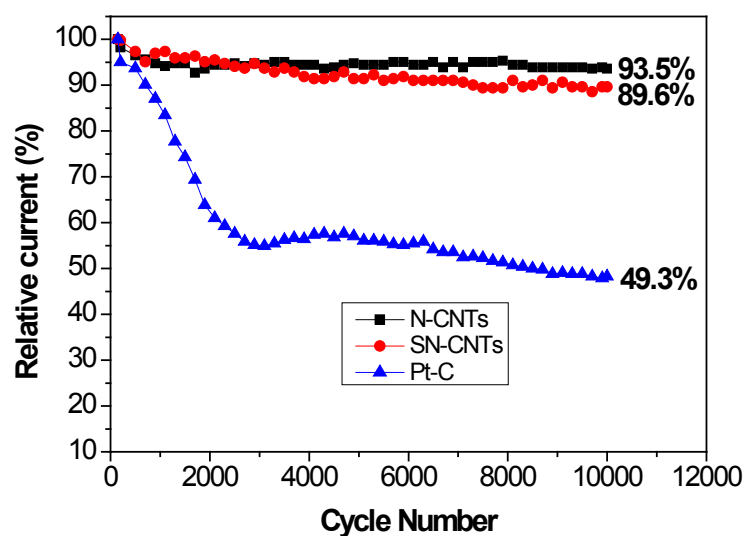
**Fig. S6** RDE voltammograms of N-CNTs catalysts in oxygen-saturated 1 M HClO<sub>4</sub> solution (A) and 0.1M KOH solution (C) at different rotation rates, at a scan rate of 10 mVs<sup>-1</sup>. Koutecky-Levich plot of  $J^{-1}$  versus  $w^{-1/2}$  at different electrode potentials of N-CNTs in oxygen-saturated 1 M HClO<sub>4</sub> solution (B) and 0.1M KOH solution (D).

The oxygen reduction current densities of N-CNTs were tested at different rotating speeds from 200 rpm to 3000 rpm in 1M HClO<sub>4</sub> (Fig. S6-A) and from 200 rpm to 3600 rpm in 0.1M KOH (Fig. S6-C) aqueous solution saturated with O<sub>2</sub>. The corresponding Koutecky-Levich plots ( $j^{-1}$  vs  $w^{-1/2}$ ) displayed good linearity (Fig. S6-B and D). The electron-transfer numbers ( $n$ ) of N-CNTs catalyst at different potentials were calculated according to the Koutecky-Levich equation. The calculated values for N-CNTs at different potentials is 2.88 in acidic medium and 3.83 in alkaline medium (Fig S6B, D), indicating the mixed process of two and four-electron transfers.



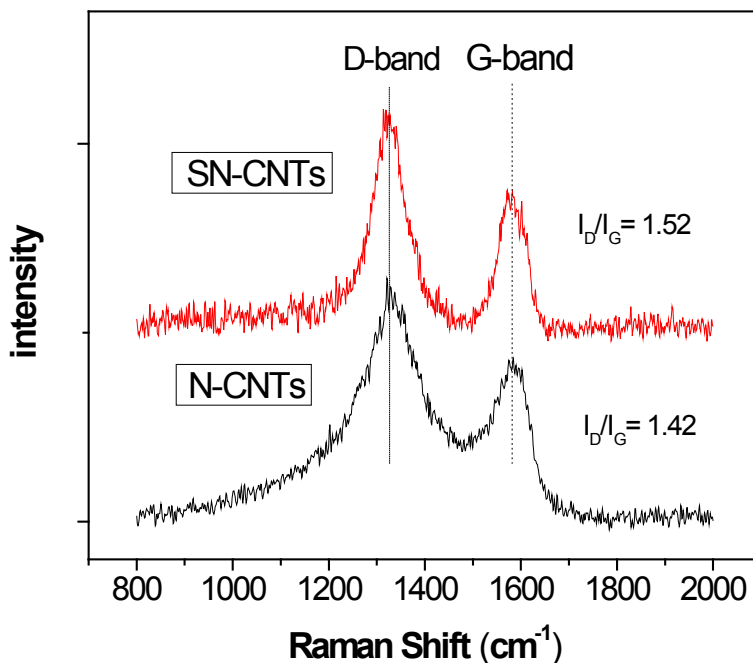
**Fig. S7** RDE voltammograms of Pt-C 20 wt.% catalyst in oxygen-saturated 1 M HClO<sub>4</sub> solution (A) and 0.1M KOH solution (C) at different rotation rates, at a scan rate of 10 mVs<sup>-1</sup>. Koutecky-Levich plot of  $J^{-1}$  versus  $\omega^{-1/2}$  at different electrode potentials of N-CNTs obtained in O<sub>2</sub>-saturated 1 M HClO<sub>4</sub> solution (B) and 0.1M KOH solution (D).

The oxygen reduction current densities of Pt-C 20 wt.% were also tested at different rotating speeds from 200 rpm to 3600 rpm in 1M HClO<sub>4</sub> (Fig. S7-A) and from 400 rpm to 3000 rpm in 0.1M KOH (Fig. S7-C) aqueous solution saturated with O<sub>2</sub>. The calculated values for Pt-C 20 wt.% at different potentials is 4.01 in acidic medium and 4.00 in alkaline medium (Fig. S7-B, D), indicating the standard four-electro process.



**Fig. S8** The maximum oxygen reduction current densities of the N-CNTs (■) SN-CNTs (●) and Pt-C (▲) recorded during repeated cycling in oxygen saturated aqueous solution of 1 M HClO<sub>4</sub>.

Fig. S8 shows the relative current change of N-CNTs, SN-CNTs and Pt-C catalysts. We can see that the stability of SN-CNTs has a slight decrease compared with N-CNTs, while it is still much higher than that of Pt-C, exhibiting high potential to be an alternative ORR catalyst.



**Fig. S9** The D-band and G-band in Raman spectroscopy for the SN-CNTs and N-CNTs catalysts.

Fig. S9 show two conspicuous peaks at 1581 cm<sup>-1</sup> for the G-band and 1326 cm<sup>-1</sup> for the D-band. The intensity ratio ( $I_D/I_G$ ) of D-band ( $I_D$ ) to G-band ( $I_G$ ) in Raman spectra have been used to evaluate the defectiveness of CNTs<sup>[S4]</sup> The value of  $I_D/I_G$  increased from 1.42 for N-CNTs to 1.52 for SN-CNTs, indicating that the surface defects of N-doped carbon nanotubes increased after doping S.

## References

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