Supporting information

Construction of Porous Nitrogen-doped Carbon Nanotube with Open-ended Channels to Effectively Utilize the Active Sites for Excellent Oxygen Reduction Reaction Activity

Yao Wang‡, Wei Chen‡, Yao Nie, Lishan Peng, Wei Ding, Siguo Chen, Li Li*, Zidong Wei*

Experiment:

Preparation of manganese Oxide nanotubes

0.658g of $KMnO_4$ and 1.5 ml dense HCl were firstly dissolved in 75 ml of distilled water. After 30min vigorous stirring, the solution was transferred into a 100ml Teflon-lined autoclave. And Then the autoclave was sealed and heated in an oven at 150 ^{o}C for 6 h. After that, the solid products were filtered, washed with DI water and dried in an oven at 60 ^{o}C for 12h.

Fabrication of PANI nanotubes:

In a typical synthesis of PANI nanotubes, the as-prepared 0.264 g MnO_2 nanotubes were firstly dispersed in 180 ml DI water by using ultrasonification. The solution containing 576 μL aniline monomer, 16.8 ml sulfuric acid and 103.2 ml DI water was then mixed with the MnO_2 suspension. The reaction was carried out for 7h at 60 ^{o}C. The resulting green solid product was filtered and washed with DI water and ethanol thoroughly to remove the excess ions and monomers. And finally, the product was freeze-dried.

Preparation of O-NCNTs catalysts

The PANI nanotubes coupled with $FeCl_3$ (mass ratio between PANI and $FeCl_3$ of 1:0.5, 1:1, 1:1.5 and 1:2, respectively) were firstly encapsulated at NaCl solid via salt recrystallization. 60 mg of PANI and 60 mg of $FeCl_3$ were mixed in 1.5 ml of deionized water with magnetic stirring for one day. After that, saturated NaCl solution was continually added to the suspension 60^{o}C to evaporate off water until the NaCl crystallized, encasing the PANI. The composite was the dried under vacuum at 60 ℃ for 24 h. Then, the composite was heated at 800^{o}C, 850^{o}C, 900^{o}C and 950^{o}C, respectively for 2 h under the protection of N_2. After thermal treatment, the NaCl crystal and iron species in the sample were finally washed off in 0.5 M H_2SO_4 solution at 80^{o}C for 24 h. Finally, a second carbonization process was adopted at 900^{o}C to get the O-NCNTs catalysts.

Preparation of NC-H_2O_2 catalysts

The H_2O_2 was selected to replace MnO_2 as the initiator of oxidative polymerization of PANI. And other treatments are same with those of the O-NCNTs catalysts.

Preparation of NC-without NaCl catalysts

The method is almost same with the preparation of O-NCNTs catalysts except of encapsulation of NaCl.

Characterization of catalysts

The morphology and structure of all the catalysts were observed under field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) and transmission electron microscopy (TEM, Zeiss LIBRA 200 FETEM). XPS was acquired by a Kratos XSAM800 spectrometer equipped with a monochromatic Al X-ray source (Al KR, 1.4866 keV). Raman spectrum was carried out using LabRam HR evolution, excited by a 532nm laser. N_2 adsorption–desorption isotherm was obtained on Micromeritics Tristar 3000 at -196 °C.

1.3. Electrochemical activity tests

Electrochemical measurements: All electrochemical experiments were performed in a standard three-electrode cell at room temperature on a Parstat 2273 potentiostat/galvanostat workstation assembled with a model 636 rotational system (AMETEK) at room temperature. The cell is consisting of a glassy carbon working electrode, an Ag/AgCl (saturated KCl) reference electrode in acid solution and an Hg/HgO (1M NaOH) reference electrode in alkaline solution, and a platinum wire counter electrode. The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and ultrasonicated for 15 minutes to form a uniform catalyst ink. Well-dispersed catalyst ink was applied onto a pre-polished GC disk. After drying at room temperature, a drop of 0.05 wt. % Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film.

The catalysts were characterized by a cyclic voltammetry (CV) test at room temperature in 0.1 M aqueous KOH at a scan rate of 50 mV s^{-1}. The linear sweep voltammetry (LSV) was obtained in an O_2-saturated 0.1 M KOH electrolyte at a scan rate of 10 mV s^{-1} in 0.1 M aqueous KOH. The currents for all catalysts were corrected by deducting the background current measured in N_2-saturated 0.1M KOH.

The kinetic parameters can be analyzed based on Koutecky-Levich (K-T) equation:

$1/J=1/J_k+1/(B\omega^2)$; where $B=0.62nFv^{-1/6}\,C_o\,D_o^{2/3}$

where J is the measured current density, J_k is the kinetic current density, ω is the angular velocity, n is the number of electrons transferred, F is the Faraday constant, v is the kinematic viscosity, C_o is the bulk concentration of O_2, and D_o is the diffusion coefficient of O_2.

The RRDE experiments was also performed in oxygen-saturated solution at a standard three-electrode cell at room temperature. In general, the as-prepared catalysts were decorated on the disk electrode. LSV was employed on the disk electrode with the sweep rate of 10 mV/s in the range of 0-1.2V (vs.RHE) at 1600 rpm. The ring electrode was held at 1.2 V (vs RHE) during the ORR measurements.

The collection efficiencies of the ring electrodes were 0.44

The percentage of H_2O_2 and the electron transfer number was calculated by

$$\%H_2O_2 = 100\frac{2 * I_R/N}{I_D + I_R/N}$$

$$n = \frac{4 * I_D}{I_D + I_R/N}$$

where N is the collection efficiency, I_R is the current on ring electrode. I_D is the current on disk electrode.

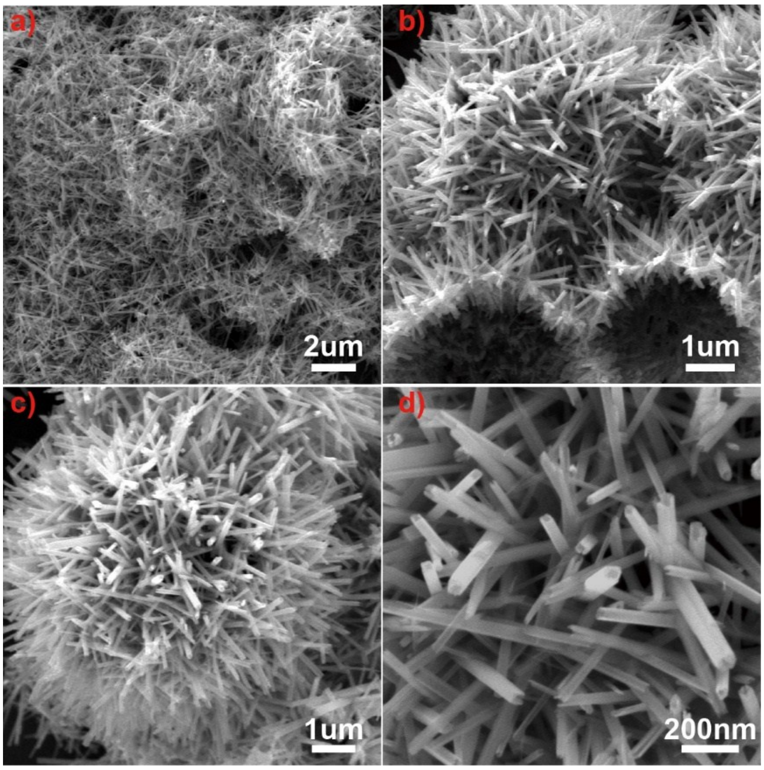

Fig. S1 The SEM images of MnO_2 nanotubes.

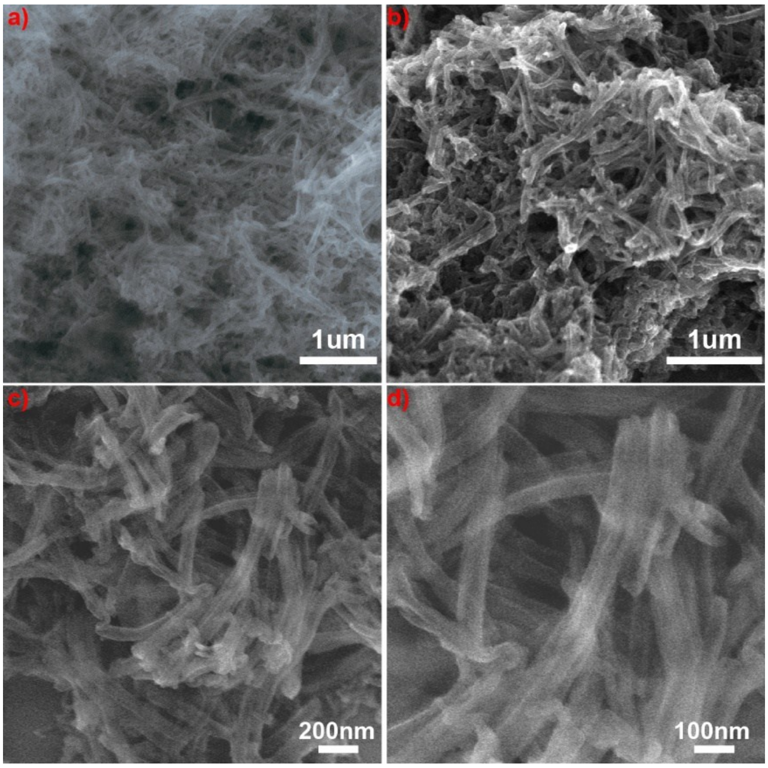

Fig. S2 The SEM images of PANI nanotubes.

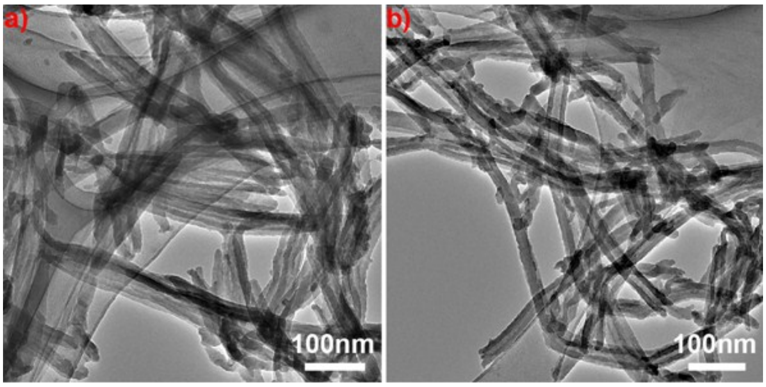

Fig. S3 The TEM images of PANI nanotubes.

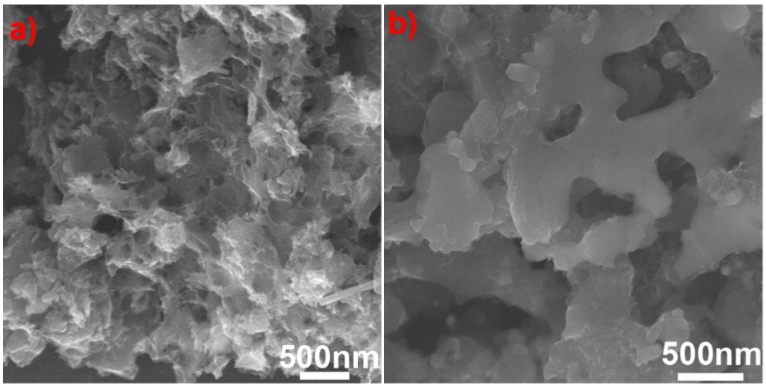

Fig. S4 The SEM images of a) NC-without NaCl, b) NC-H_2O_2.

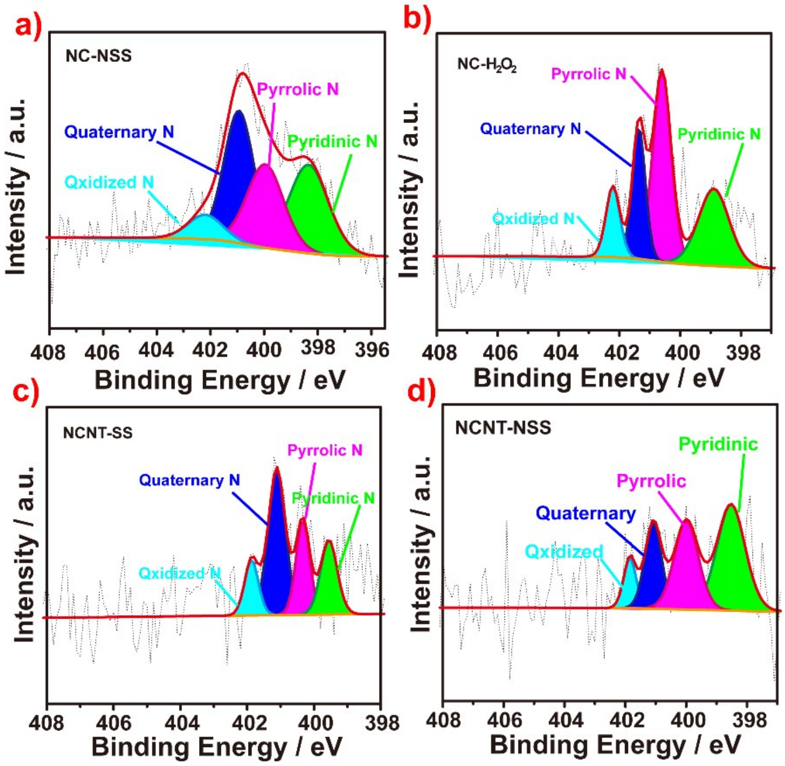

Fig. S5 N1s spectra of as-prepared catalysts

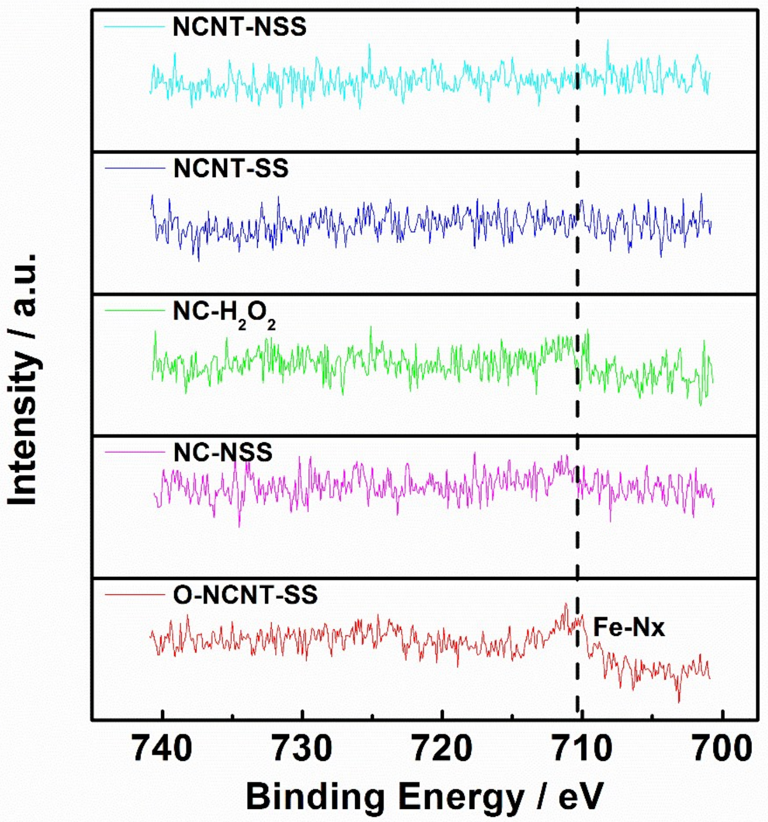

Fig. S6 Fe 2p spectra of as-prepared catalysts

Table S1 The surface content of each element.

catalysts	**Nitrogen content / at. %**	**BET surface area**
N-NCNT-SS	2.17 at. %	1103.9 cm^3 / g
NC-NSS	1.43 at. %	1018.7 cm^3 / g
NC-H2O2	0.85 at. %	887.3 cm^3 / g
NCNT-SS	0.39 at. %	\
NCNT-NSS	0.5 at. %	\

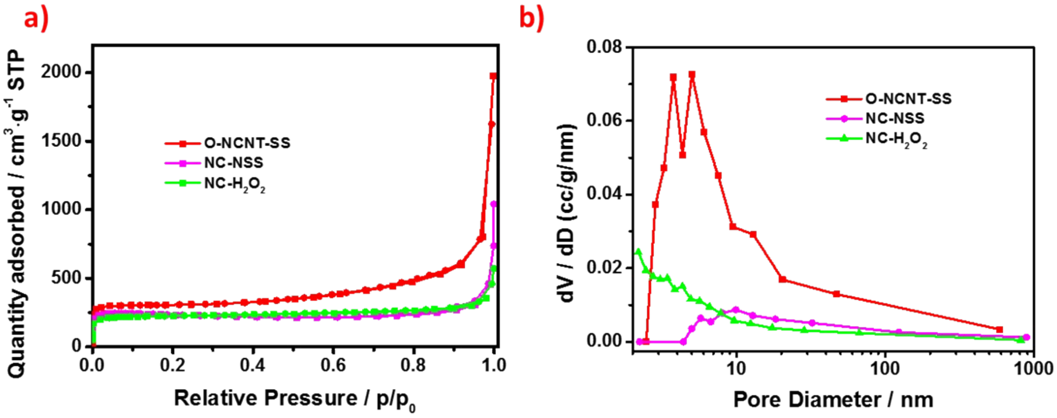

Fig. S7 a) N_2 sorption isotherms the (b) corresponding pore-size distribution (in the mesoporous region) of as-prepared catalyst.

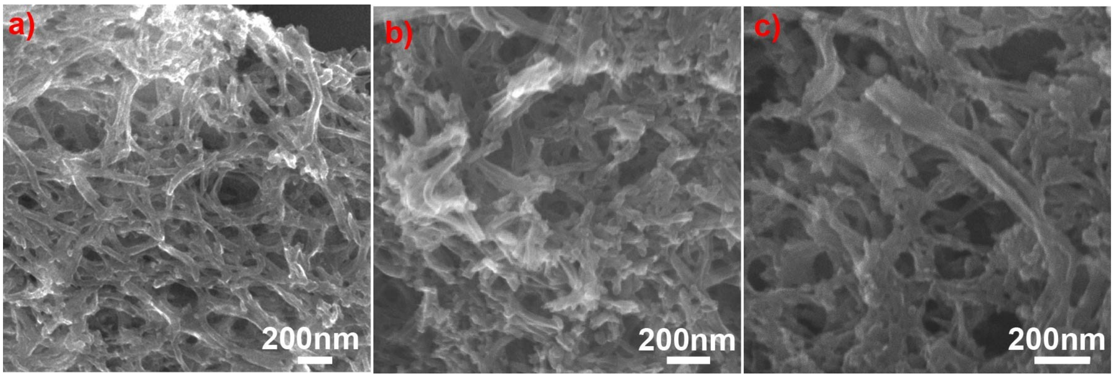

Fig. S8 The SEM images of a) O-NCNT-0.5-900; b) O-NCNT-1.5-900; O-NCNT-2-900.

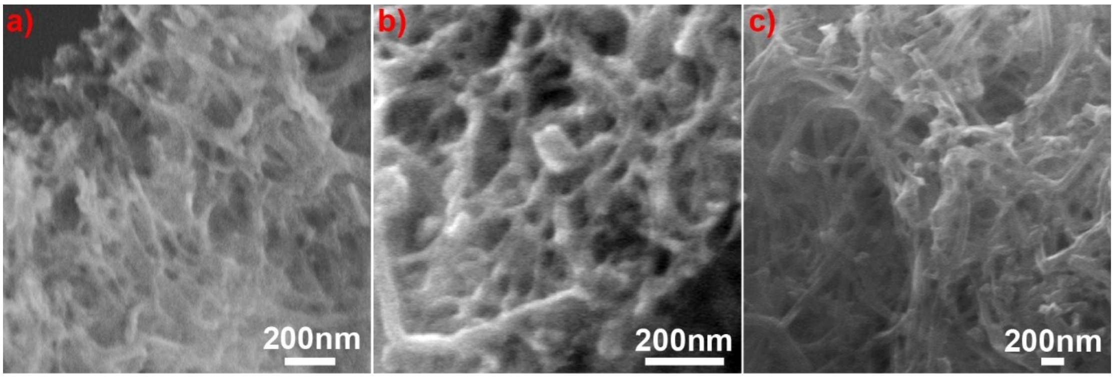

Fig. S9 The SEM images of a) O-NCNT-1-800; b) O-NCNT-1-850; O-NCNT-1-950.

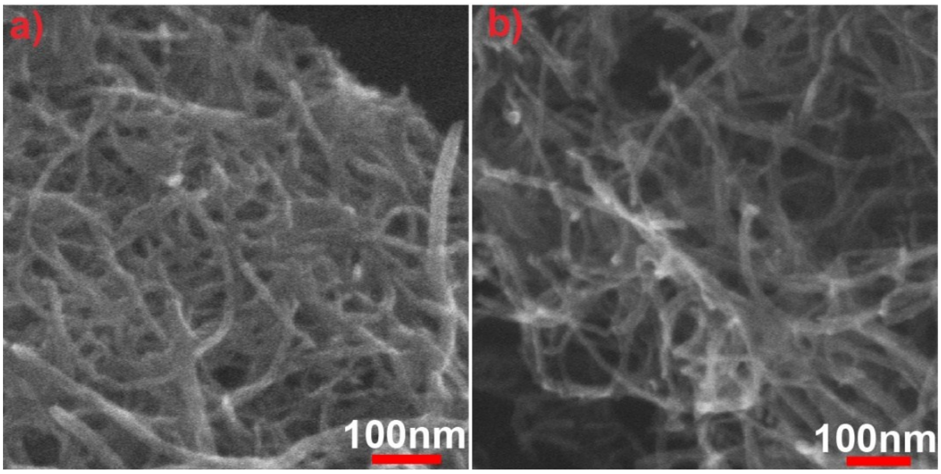

Fig. 10 The SEM images of NCNT-SS (a) and NCNT-NSS (b).

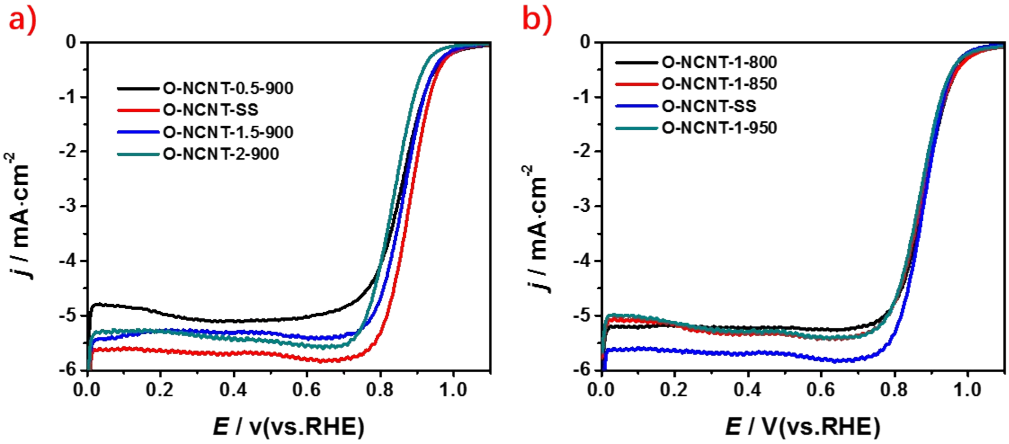

Fig. S11 Other mass ratios between PANI nanotubes and Fe (1:0.5, 1:1.5 and 1:2; noted as O-NCNT-0.5-900, O-NCNT-1.5-900 and O-NCNT-2-900, respectively.) and temperatures (800°C, 850°C, 950°C; noted as O-NCNT-1-800, O-NCNT-1-850, O-NCNT-1-950) were employed to obtain the O-NCNTs in order to optimize the ORR activity of the O-NCNTs. LSV curves of all the as-prepared catalysts (0.6 mg cm^{-2}) in O_2-saturated 0.1 m KOH at a rotation speed of 1600 rpm with a sweep rate of 10 mV s^{-1}. The currents for all catalysts were corrected by deducting the background current measured in N_2-saturated 0.1 m KOH. a) for different ratio between PANI and $FeCl_3$; b) for different temperature.

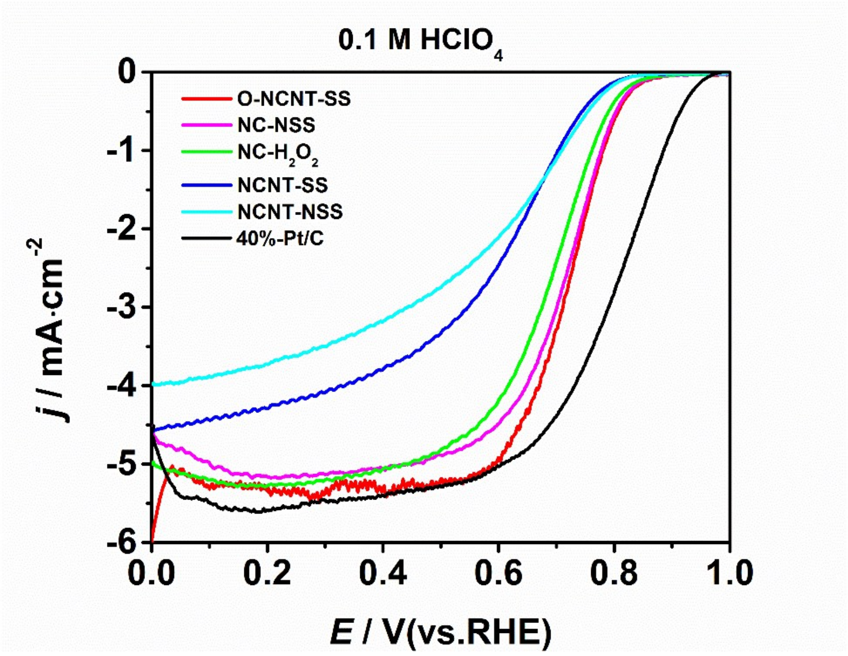

Fig. S12 LSV curves of all the as-prepared carbon catalysts (0.6 mg cm^{-2}) and Pt/C (25ugPt cm^{-2}) in O_2-saturated 0.1 m KOH at a rotation speed of 1600 rpm with a sweep rate of 10 mV s^{-1}.

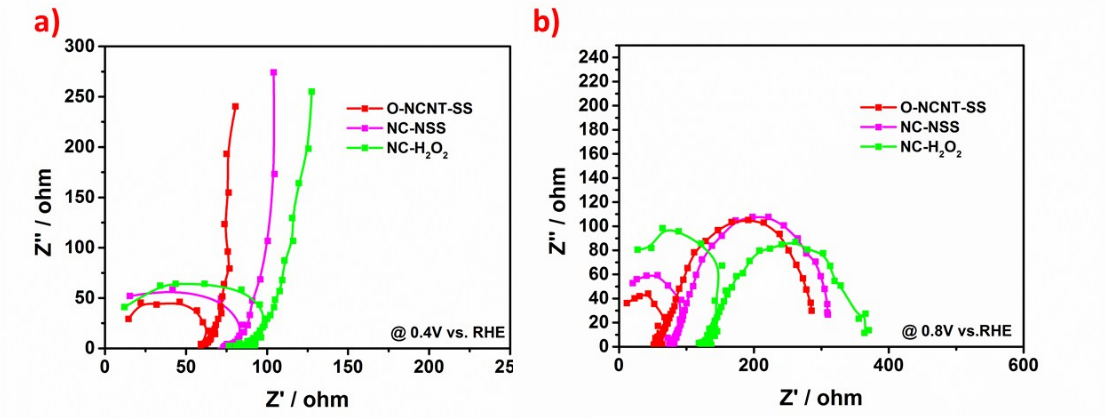

Fig. S13 Nyquist plots under the influence of an amplitude of 10mV with a frequency range from 0.05 Hz to 1MHz (a), and with a frequency range from 0.01 Hz to 1MHz.

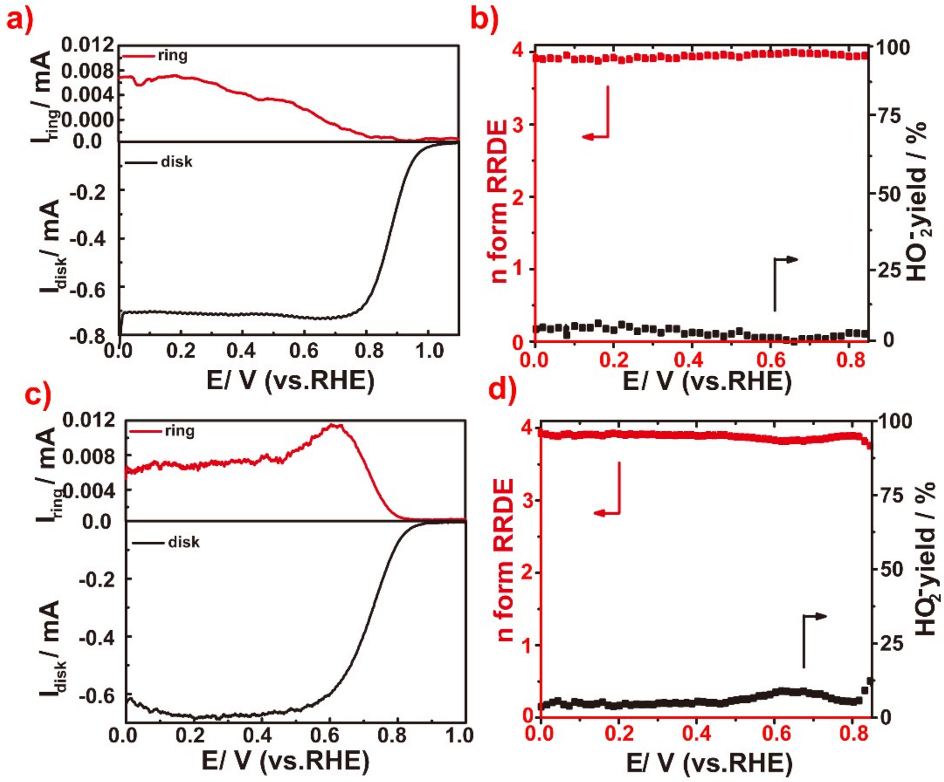

Fig. S14 a) rotating ring-disk electrode (RRDE) voltammograms of N-NCNT-SS at 1600 rpm in 0.1M KOH; b) electron transfer number (n) and HO_2^- yield derived from the (a); c) rotating ring-disk electrode (RRDE) voltammograms of N-NCNT-SS at 1600 rpm in 0.1M $HClO_4$; b) electron transfer number (n) and H_2O_2 yield derived from the (c)