Supporting Information

NCNTs Derived from Zn-Fe-ZIF Nanospheres and Their Application as Efficient Oxygen Reduction Electrocatalysts with in-situ Generated Iron Species

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Experimental section

Preparation of Zn-Fe-ZIFs

In a typical experiment, $Zn(NO_3)_2 \cdot 6H_2O$ (1.1175 mmol) and $FeSO_4 \cdot 7H_2O$ (0.2235 mmol) were dissolved in 15 mL DMF solvent and then mixed with DMF solution of 2-methylimidazole (15 mL, 0.08 M) under stirring. The resulting mixture was stirred for another 30 min at room temperature and then transformed into Teflon-lined stainless steel sealed vessel (40 mL) and heated at 140 °C for 48 h. After cooling down to room temperature, the basal precipitate was isolated by centrifugation and washed thoroughly with DMF. The product was denoted as Zn-Fe-ZIFs. The Zn-Fe-ZIFs was dispersed in DMF solution containing proper quantity DCDA (0.125g / mL), and then the DMF solvent was removed at 70 ^{o}C in a low pressure system. The products were denoted as Zn-Fe-ZIFs-x DCDA, where x refers to the mass ratio of DCDA to Zn-Fe-ZIFs.

Synthesis of nitrogen doped carbon nanotubes

The calcination procedures of Zn-Fe-ZIFs were conducted in a flow of ultrapure N_2, and kept for 4 hours under 900 ^{o}C with the heating rate of 5 ^{o}C/min. The pyrolyzed samples were treated with acid (HCl (12 M): HNO_3 (14.5 M) =3:1 volume ratio) for 6 h and then refluxed in HNO_3 solution (14.5 M) for 2 h at 120 ^{o}C. Subsequently, the products were washed with deionized water thoroughly and then dried at 100 ^{o}C for 24 h.

The synthesis procedures for NCNTs-x were similar to NCNTs. Zn-Fe-ZIFs-x DCDA were calcinated in a flow of ultrapure N_2, and keep for 3 hours under 700 ^{o}C with the heating rate of 5 ^{o}C/min. In order to remove a part of metal species formed during carbonization process, 0.2 g product was dispersed in 40 mL aqua regia (HCl (12 M): HNO_3 (14.5 M) =3:1 volume ratio) and stirred at room temperature for 20 min. The other procedures were similar to those for NCNTs and the products were denoted as NCNTs-x, where x refers to the mass ratio of DCDA to Zn-Fe-ZIFs.

Characterization

The scanning electron microscopy (SEM) was performed on JEOL JSM-6360 scanning electron microscope operating at an acceleration voltage of 20 kV. The transmission electron microscopy (TEM) was undertaken using an FEI Tecnai G^2 Spirit at an acceleration voltage of 120 kV. The samples were placed onto an ultrathin carbon film supported on a copper grid. The powder X-ray diffraction data were collected on a Rigaku D/Max2500PC diffractometer with Cu Kα radiation (λ=1.5418 Å) over the 2θ range of 3^{o}-85^{o} with a scan speed of 5 ^{o}/min at room temperature. High resolution transmission electron microscopy (HRTEM) images were recorded on a FEI Tecnai F30 microscope with a point resolution of 0.20 nm operated at 300 kV. The nitrogen sorption experiments were performed at 77 K on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were degassed at 140 °C for 6 h. Elemental analyses were determined on a Vario ELIII Elemental analyzer. The metal content was determined by PLASAM-SPEC-II inductively coupled plasma atomic emission spectrometry (ICP). Visible Raman spectra were recorded at room temperature on a Jobin Yvon LabRAM HR 800 instrument with a 532 nm excitation laser at a power of around 1 mW.

Electrochemical measurements

Electrochemical measurements were performed using a CHI Electrochemical Station (Model 730D) in a three-electrode electrochemical cell at room temperature. Platinum foil and a saturated calomel electrode (SCE) were using as the counter and reference electrode, respectively. The catalyst layer on the glassy carbon electrode (0.1256 cm^2) was prepared as follows. A mixture with 5 mg NCNTs-x catalyst, 1 mL isopropanol and 50 μL Nafion (5 wt %, Du Pont Corp.) was prepared using sonication. A 30 μL ink was dropped onto the glassy carbon disk, which was then left to dry in air at room temperature, to yield a catalyst loading of ca. 570 μg cm^{-2}. For comparison, the loading of commercial Pt/C (20 wt %, Johnson Matthey) catalyst was controlled at 10 μgPt cm^{-2}.

Cyclic voltammetry (CV) experiments were carried out in O_2 or N_2 saturated 0.1 M KOH solution. The potential was varied from -1.0 V to 0.2 V at a scan sweep of 100 mV/s. In the rotating disk electrode (RDE) tests, the linear sweep voltammograms (LSVs) were recorded in O_2 saturated 0.1 M KOH solution and the electrode potential was scanned between -1.0 V and 0.2 V with a scan rate of 10 mV/s at various rotating speeds from 100 to 2500 rpm. The oxygen reduction current was corrected by the background current.

In rotating ring disk electrode (RRDE) tests, the ring potential was set to 0.456 V vs. SCE to oxidize the hydrogen peroxide produced during oxygen reduction on the disk electrode. The transferred electron-transfer number (n) and the hydrogen peroxide yield (% H_2O_2) in the ORR was calculated as follows,

$$\%H_2O_2 = \frac{2I_r}{N|I_d| + I_r} \times 100\%$$

$$\mathrm{n} = 4 - 2 \times \frac{\%H_2O_2}{100}$$

Where Id and Ir is the disk and ring current, respectively, and N is the RRDE collection efficiency, which was determined to be 0.37 herein.

The Koutecky-Levich plots were obtained by linear fitting of the reciprocal rotating speed versus reciprocal current density collected at different potentials from -0.2 V to -0.5 V. The electron transfer numbers were calculated from the slopes of Koutecky-Levich plots using the following equation:

$$-\frac{1}{j} = -\frac{1}{j_k} + \frac{1}{0.62nFD_{O_2}^{2/3}C_{O_2}\upsilon^{-1/6}\omega^{1/2}}$$

where j is the measured current density, j_k is the kinetic current density, F is the Faradaic constant (96,485 C mol^{-1}), D_{O2} is the O_2 diffusion coefficient 0.1 M KOH (1.9×10^{-5} cm^{2}s^{-1}), C_{O2} is the O_2 saturation concentration in 0.1 M KOH (1.2×10^{-3} mol L^{-1}), υ is the kinematic viscosity in 0.1 M KOH (0.1 m^2 s^{-1}) and ω is the rotation rate.

Table S1 The textual parameters and metal content of NCNTs-x purified with aqua regia.

Samples	BET surface area (m^2/g)	Fe content (%)	Zn content (%)	Intensity ratio of G and D bands
NCNTs-2.5	124	12.52	2.88	0.4
NCNTs-5	152	10.38	2.76	0.35
NCNTs-10	139	9.62	4.34	0.45
NCNTs-20	151	12.93	3.80	0.34
NCNTs-20-acid-24h	—	5.23	0.62	—

Table S2 The N content and N dopant state of NCNTs-20-900 and NCNTs-20-acid-24h.

Samples	N content	the relative content of different N species to total N		
	(wt %)	graphitic N	pyrrolic N	pyridinic N
NCNTs-20-900	0.86	0.43	0.29	0.28
NCNTs-20-acid-24h	10.65	0.42	0.56	0.02

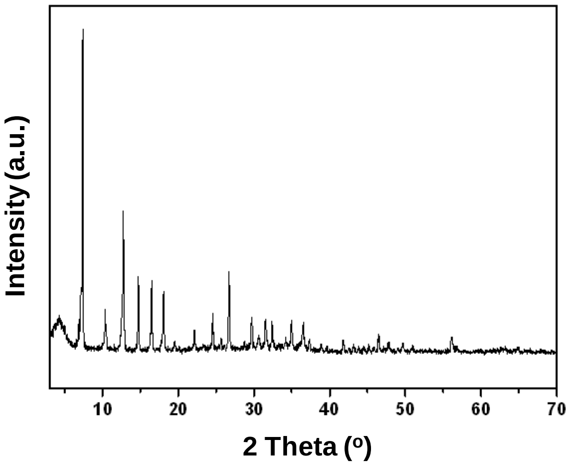

Fig. S1 The XRD pattern of Zn-Fe-ZIFs.

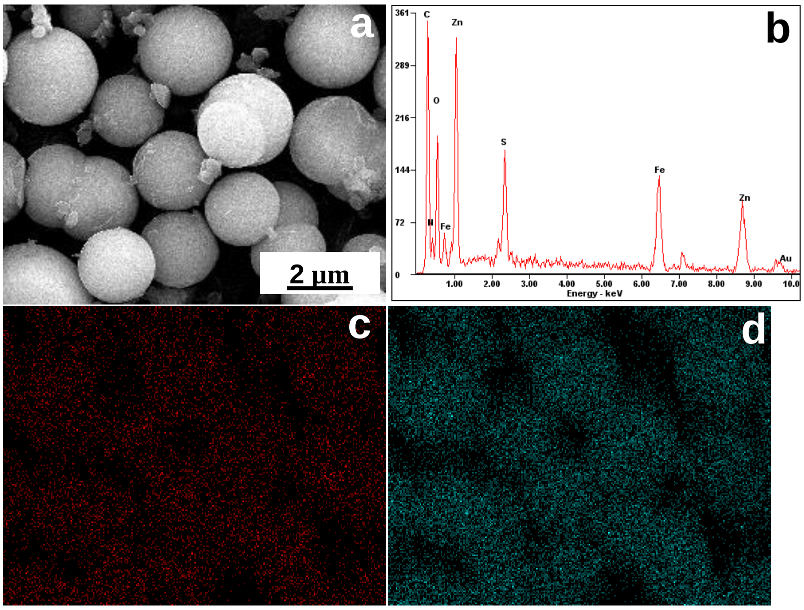

Fig. S2 The SEM image (a), EDX result (b) of Zn-Fe-ZIFs and EDX mapping result of Zn (c) and Fe (d) in Zn-Fe-ZIFs spheres.

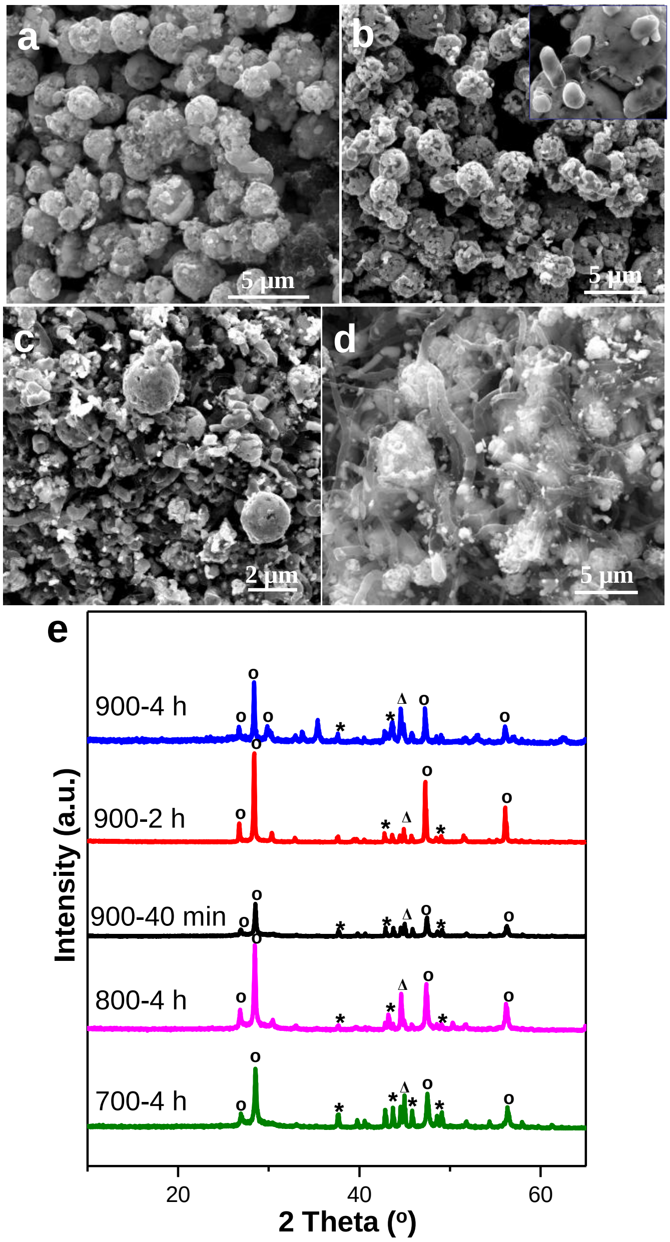

Fig. S3 SEM images (a-d) and XRD patterns (e) of Zn-Fe-ZIFs pyrolyzed under different conditions. SEM images of Zn-Fe-ZIFs pyrolyzed at 900 ^{o}C (a) 40 min, (b) 2 h, (c) 3 h and (d) 4 h; in the XRD patterns, different sign refers to different phase (* Fe_3C, **Δ** Fe, **o** ZnS). For all the carbonized samples, the diffraction peaks of ZnS were observed, probably due to the existence of SO_4^{2-} attached to the samples. During the carbonization step, the SO_4^{2-} may be reduced and then reacted with Zn^{2+} leading to the formation of ZnS.

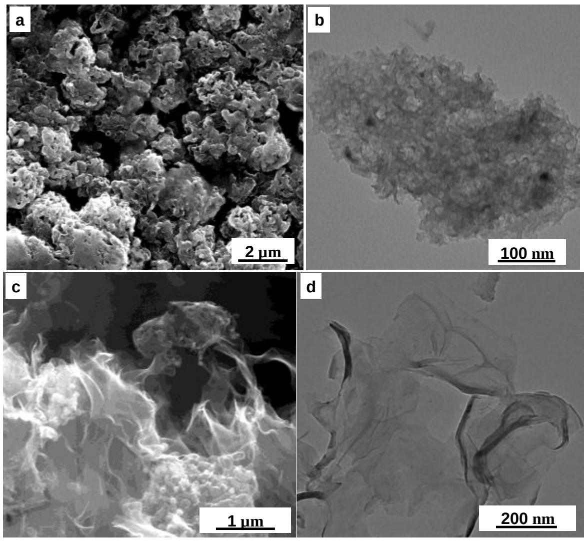

Fig. S4 SEM (a, c) and TEM (b, d) images of the samples (purified with aqua regia and HNO_3) obtained by pyrolysis of Zn-Fe-ZIFs at (a, b) 700 °C and (c, d) 800 °C.

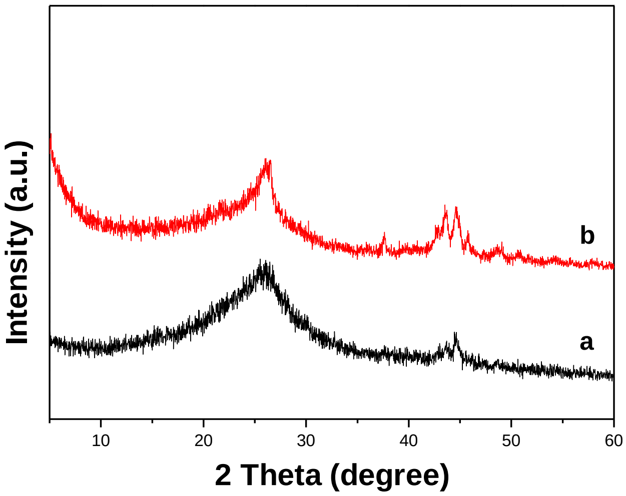

Fig. S5 The XRD patterns of carbon materials (purified with aqua regia and HNO_3) obtained at pyrolyzed temperatures of (a) 700 °C and (b) 800 °C.

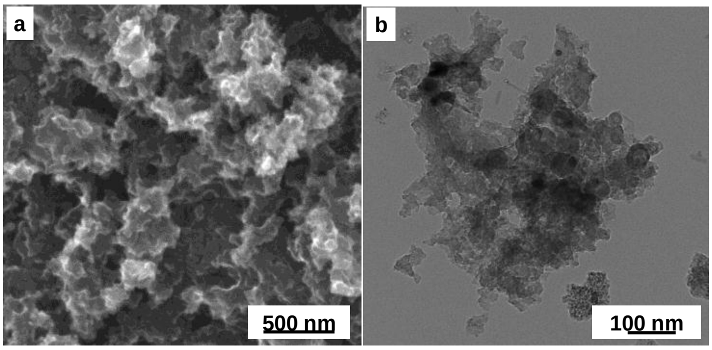

Fig. S6 SEM (a) and TEM (b) images of the samples (purified with aqua regia) obtained by pyrolysis of ZIF-8 impregnated with $FeSO_4$ at 900 °C.

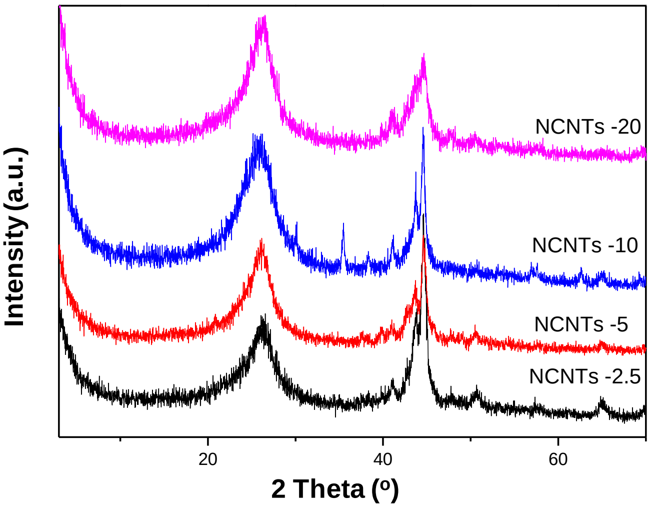

Fig. S7 The XRD patterns of NCNTs-x (x=2.5, 5, 10, 20) purified with aqua regia.

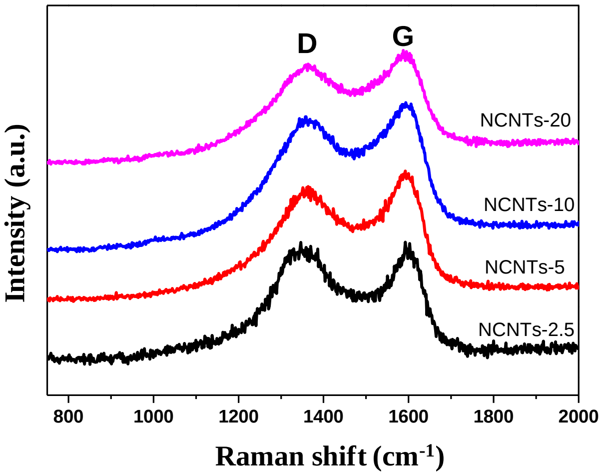

Fig. S8 The Raman spectra of NCNTs-x (x=2.5, 5, 10, 20) purified with aqua regia.

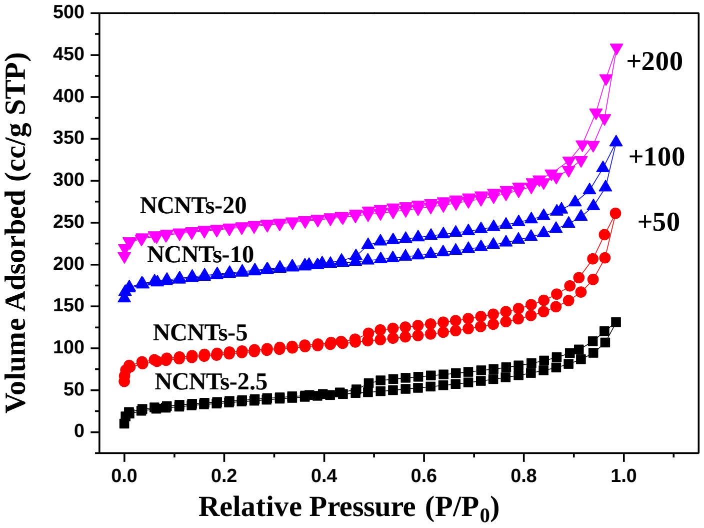

Fig. S9 The nitrogen adsorption-desorption isotherms of NCNTs-x purified with aqua regia.

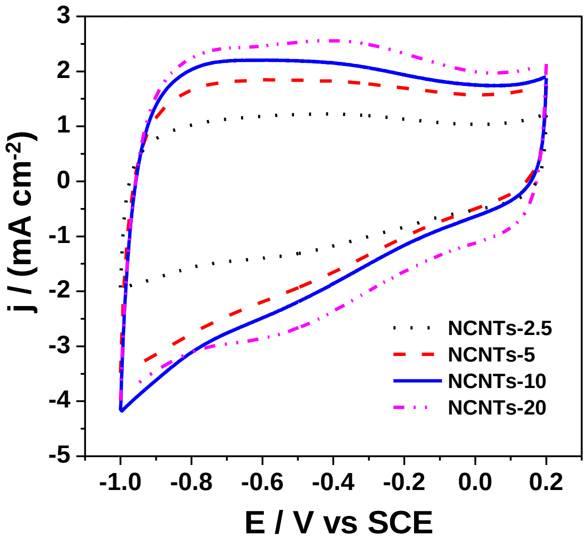

Fig. S10 CV curves for NCNTs-x (purified with aqua regia) and Pt/C (20 wt %, Johnson Matthey) at a scan rate of 100 mV s^{-1} in N_2 saturated 0.1 M KOH solution.

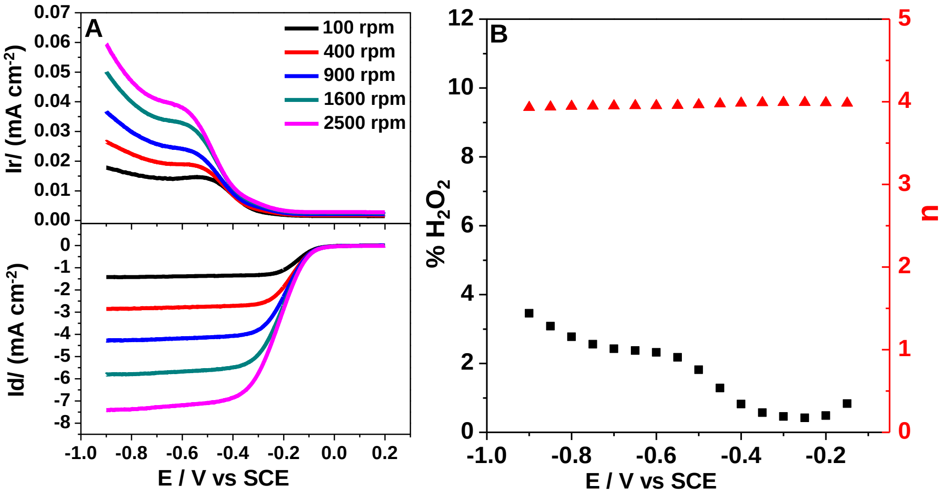

Fig. S11(A) Rotating ring disk electrode measurements for oxygen reduction on purified NCNTs-10 in O_2 saturated 0.1 M KOH with different rotation rates at a scan rate of 10 mV/s and (B) potential–%H_2O_2 curve and potential–n curve for NCNTs-10 catalyst at the rotation rate of 1600 rpm.

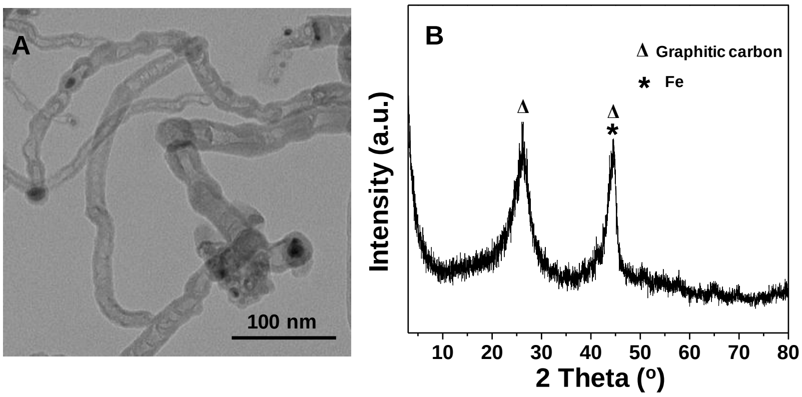

Fig. S12 TEM image (A) and XRD pattern (B) of NCNTs-20-acid-24h.

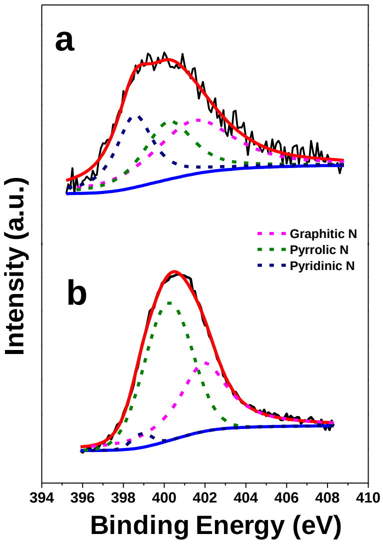

Fig. S13 The N1s XPS spectra of (a) NCNTs-20-900 and (b) NCNTs-20-acid-24h.

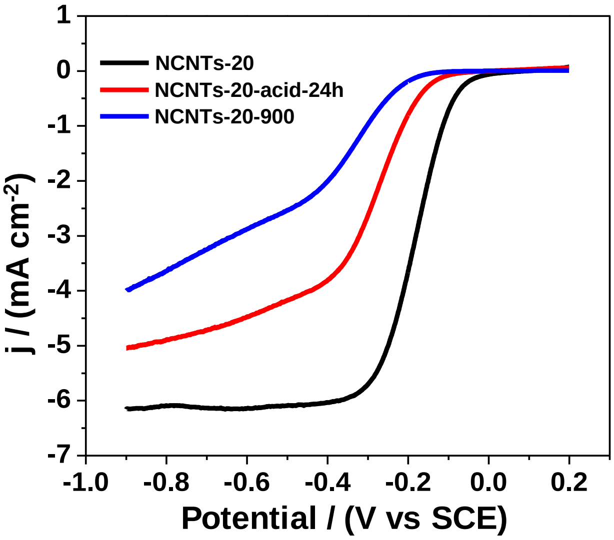

Fig. S14 LSV curves for NCNTs-20, NCNTs-20-acid-24h and NCNTs-20-900 in O_2 saturated 0.1 M KOH at the rotation rate of 1600 rpm.