Supplementary Information

Free-Standing Nitrogen-Doped Carbon Nanofibers Films as Highly Efficient Electrocatalyst for Oxygen Reduction

Dong Liu,[a,b] Xueping Zhang,[a,b] Zaicheng Sun[c] and Tianyan You*[a]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China. E-mail: youty@ciac.jl.cn

[b] University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China.

[c] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 East Nanhu Road, Changchun, Jilin 130033, China.

1. Experimental and characterization details

1.1 Materials. Polyacrylonitrile (PAN, M_W=150,000) and nafion®117 solution (5 wt %) were obtained from Sigma-Aldrich. Dimethylformamide (DMF), potassium hydroxide (KOH) and methanol were purchased from Beijing Chemical Co. (China). Platinum on carbon (20 wt. % Pt/C, Johnson Matthey) was purchased from Alfa Aesar. All other reagents were of analytical grade and used without further purification. The double distilled water was used for solution preparation.

1.2 Preparation of free-standing NCNFs films. The free-standing NCNFs films were prepared via the carbonization of electrospun PAN nanofibers films. Typically, 0.5229 g PAN was completely dissolved in 5 ml DMF as the electrospun solution, and the electrospinning process was performed in the electric fields generated by an 18 kV voltage applied to a 14 cm gap between the spinneret and the collector. A syringe pump was employed to control the flow rate of the electrospun solution at 1.0 mL/h. Stabilization and carbonization was performed in a high-temperature furnace by the following steps: (1) stabilized at 300 ℃ in N_2 for 60 min, (2) heat up to 900 ℃ to carbonize the PAN nanofibers for 60 min, (3) cooled down to room temperature. All the thermal treatment process was carried out in nitrogen atmosphere with a heating-up rate of 10 ℃/min. In particular, an enclosed device comprised by two combustion boats was used as the reactor for PAN nanofibers to increase the resident time of tail gas in it during the high-temperature process. The pristine CNFs were prepared via the same procedure except stabilized in the air or carbonized in one combustion boat. The details were shown in Table S1, and the as-prepared carbon nanomaterials were noted as CNFs-A, CNFs-B and NCNFs, respectively.

Table S1. The experiment parameters for the preparation of CNFs and NCNFs

	Stabilization (at 300℃)	Carbonization (at 900℃)	Carbonized in one (A) or two (B) combustion boats
CNFs-A	60 min in air	60 min in N_2	A
CNFs-B	60 min in N_2		A
NCNFs			B

1.3 Characterization. The scanning electron microscopy (SEM) experiment was carried out using a PHILIPS XL-30 ESEM at an accelerating voltage of 20 kV. The TEM images were acquired with a TECNAI G2 with the accelerating voltage of 200 kV. Raman spectra were obtained on Renishaw RM-1000 equipped with a laser excitation of 514.5 nm. X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250 instrument equipped with Al Kα radiation. The water contact angle of all the samples was measured using Krüss DSA100 instrument at room temperature.

1.4 Electrochemical Measurements. *1.4.1 Cyclic Voltammetry (CVs).* Glassy carbon electrode (GCE) with the diameter 5 mm was polished carefully using Al_2O_3 powder. After rinsed and sonicated with double distilled water, the electrode was used for the further experiments. The NCNFs films can be The NCNFs films was cut to the disk-shaped with the diameter of 5 mm, and directly and stably adhered to the surface of GCE by 5 μL of nafion solution (0.5 wt. %). The as-prepared electrode was used for electrochemical experiment. For comparisons, commercial Pt/C catalyst and CNFs suspension was prepared by dispersing a predetermined amount in ethanol solvent with the content of 4 mg/ml, respectively. Then, 5 μL of the suspension was loaded on the surface of working electrode, and 5 μL of nafion solution (0.5 wt. %) was dropped on the electrode. Cyclic voltammetry was performed on a CHI 832C electrochemical workstation (Shanghai, China) with a conventional three-electrode system using the sample modified glassy carbon electrode as the working electrode, a Pt plate as the counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. The electrolyte saturated with O_2 or N_2 was bubbled for 0.5 h before experiments.

1.4.2 Rotating Disk Electrode (RDE) and Rotating Ring−Disk Electrode (RRDE) Measurements. RDE and RRDE measurements were performed using a GCE disk electrode (Pine Instruments) and a GCE disk/platinum ring electrode (Pine Instruments) as working electrode, respectively. The sample-modified working electrode was prepared by the same method as for CVs.

2. Figure S1. SEM, contact angles of CNFs-A, CNFs-B and NCNFs

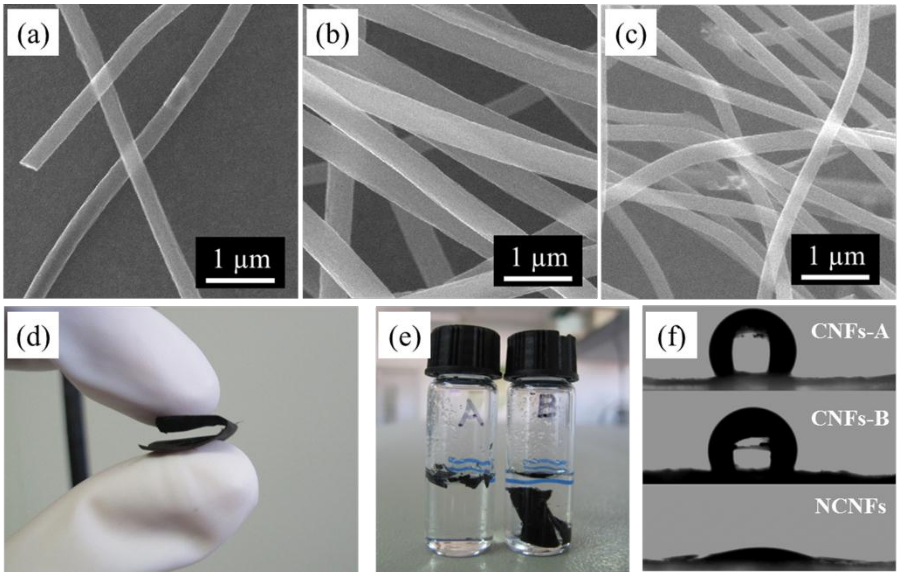

Figure S1. SEM images of a) CNFs-A, b) CNFs-B and c) NCNFs. d) Photograph of free-standing NCNFs films. e) Photograph of CNFs films (noted as A) and NCNFs films (noted as B) in water. (f) Contact angles of CNFs-A, CNFs-B and NCNFs.

3. Figure S2. Rotating disk electrode voltammograms and Koutecky–Levich plots of CNFs-A and CNFs-B

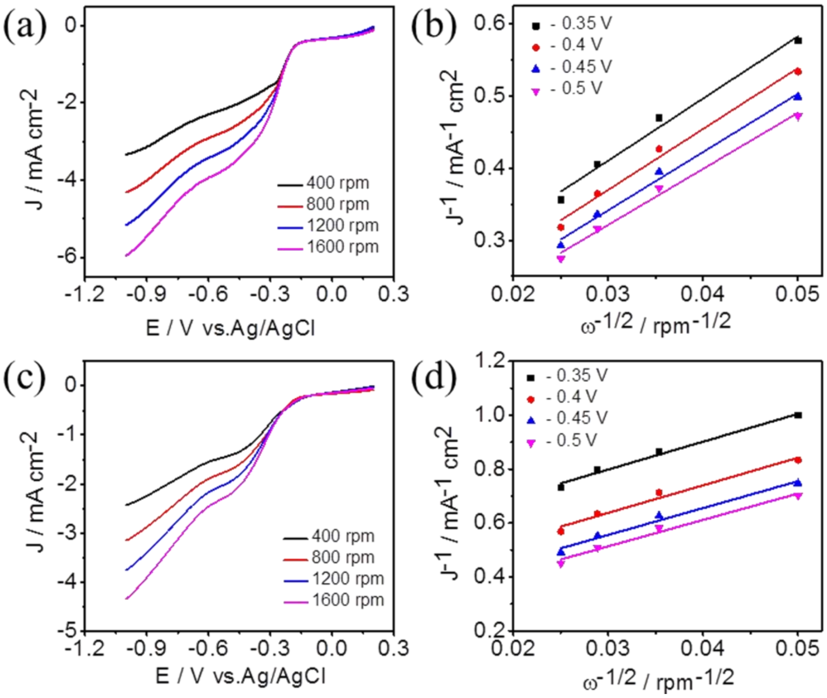

Figure S2. Rotating disk electrode voltammograms recorded for a) CNFs-A and c) CNFs-B in O_2-saturated 0.1 M solution of KOH at different rotation rates with scan rate of 10 mV/s, and the corresponding Koutecky–Levich plot of J^{-1} versus $w^{-1/2}$ at different electrode potentials for b) CNFs-A and d) CNFs-B, respectively.

4. Figure S3. Rotating ring-disk electrode voltammograms of NCNFs and Pt/C

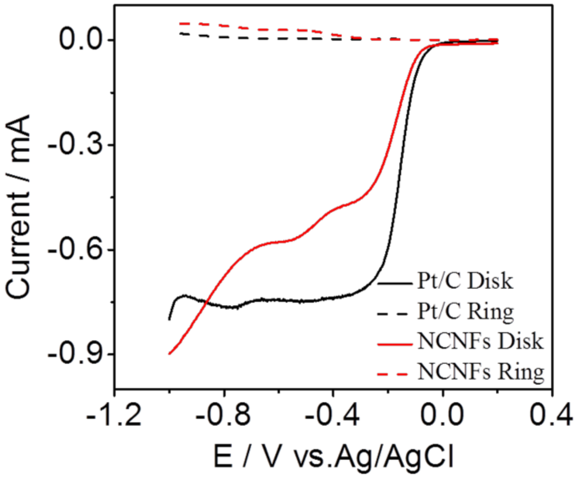

Figure S3. RRDE test of the ORR on NCNFs and Pt/C in O_2-saturated 0.1 M solution of KOH at a scan rate of 10 mV/s with the rotation rate of 1600 rpm.

5. Figure S4. The electrocatalytic selectivity of the NCNFs and Pt/C

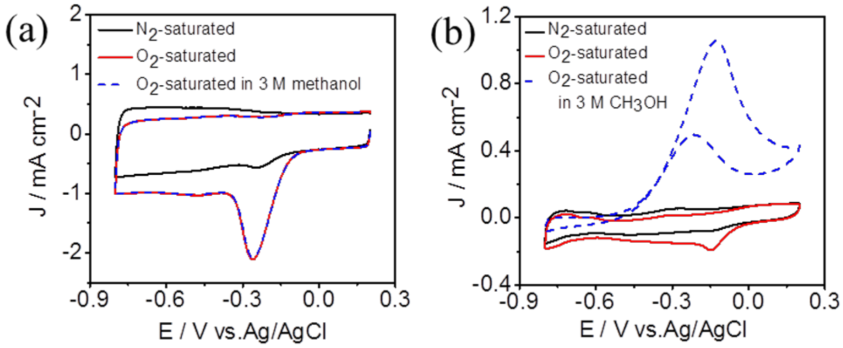

Figure S4. CVs of a) NCNFs and b) Pt/C in N_2- and O_2-saturated 0.1 M solution of KOH, in O_2-saturated 0.1 M solution of KOH upon the addition of CH_3OH (3 M) at a scan rate of 50 mV/s