Ultrafine Pt nanoparticles supported on N,S-codoped porous carbon nanofibers as efficient multifunctional materials for noticeable oxygen reduction reaction and water splitting performance

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# **Part 1: Experiments**

## **1.1 Materials**

Polyvinylpyrrolidone (PVP; Mw = 40000) and polyacrylonitrile (PAN; Mw = 1500000) were bought from J&K scientific Chemical Co., Ltd. Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O) was gotten from Shanghai Titanchem Co., Ltd. Potassium hydroxide (KOH), urea and thiourea were obtained from Sinopharm Chemical Reagent CO.,Ltd. (China). Other chemicals such as ethanol and

dimethylformamide (DMF) were purchased from Shanghai Lingfeng Chemical Reagent CO. Ltd., and were all analytical grade and used as received. Nafion® solution (5 wt.%) was obtained from E. I. DuPont Company (USA). All solutions used in the electrochemical experiments were freshly prepared with Millipore water (resistivity ~ 18.2 M $\Omega$ ).

### **1.2 Apparatus**

The morphology of pCNFs, N-pCNFs, N,S-pCNFs and Pt-N,S-pCNFs was characterized by transmission electron microscopy (TEM, JEM-2010HT) and scanning electron microscopy (SEM, JEOL2100F) from Electron Optics Laboratory Co., Ltd., Japan. Powder X-ray diffraction (XRD) analyses were performed on a diffractometer (Bruker, German, APLX-DUO) with Cu Ka radiation. Raman spectra were recorded using a Thermo Fisher H31XYZE-US with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS,  $K\alpha$ ) analyses were carried out on an AXIS UltraDLD X-ray photoelectron spectrometer system equipped with Al radiation as a probe. Brunauer-Emmett-Teller (BET) tests were performed on ASAP 2460, Micromeritics Instrument Corp. All electrochemical measurements were performed on an Autolab PGSTAT302N (Metrohm, Switzerland) and CHI 660D (Chenhua, China) electrochemical test system. Cyclic voltammograms were collected in a three-electrode system (glass carbon electrode (GCE) or modified GCE as the working electrode, a Pt wire as counter electrode, and a reversible hydrogen electrode (RHE) as the reference) at room temperature. For Rotating disk electrode (RDE) measurements, a glassy carbon rotating disk electrode was used as the working

electrode. Linear sweep voltammetry was performed at the GC disk electrode. In all of the electrochemical measurements, 0.1 M KOH aqueous solution saturated with nitrogen or oxygen was used as the electrolyte. Hydrogen storage properties were tested by a full-automatic PCI monitor apparatus (Suzuki, Japan, Shokan Co., Ltd.)

### 1.3 Synthetic procedures

# 1.3.1 Preparation of porous carbon nanofibers (pCNFs), N-pCNFs, N,S-pCNFs Pt-N-pCNFs and Pt- N,S-pCNFs

PAN (5 wt%) and PVP (5 wt%) were successively dissolved in DMF. The mixture was electrospun in the electric fields of 1000 V cm<sup>-1</sup>. Afterwards, 0.8 g fabricated PAN/PVP nanofibers were transferred into a 100 mL Teflon stainless steel autoclave, with deionized water being added. The hydrothermal treatment was conducted at 110 °C for 24 h to remove PVP. Porous PAN nanofibers were obtained after drying at 80 °C in oven. Stabilization and carbonization of the above porous PAN nanofibers were completed in a high-temperature furnace, which were placed in the center of a quartz tube under Ar flow. After an argon flow for 25 min, the porous PAN nanofibers were heated to 900 °C and annealed for 2 h, then cooled to room temperature to yield the final pCNFs.

The doping of pCNFs were performed by adding urea (52.7 mg), thiourea (66.7 mg), the mixture of urea (52.7 mg) and H<sub>2</sub>PtCl<sub>6</sub> (12.72 mL, 1 g/100mL) solution and the mixture of thiourea (66.7 mg) and H<sub>2</sub>PtCl<sub>6</sub> (12.72 mL, 1 g/100mL) solution before hydrothermal treatment. The following procedures were same as before, and the final products were N-pCNFs, N,S-pCNFs, Pt-N-pCNFs and Pt-N,S-pCNFs separately..

### 1.4 Cyclic voltammograms (CV) measurements

A conventional cell with a three-electrode configuration was applied throughout this work. CV measurement was conducted at 25 °C using an Autolab PGSTAT302 (Metrohm) electrochemical test system using RHE as the reference electrode, a Pt wire as the counter electrode and the sample modified GCE as the working electrode.  $4 \ \mu L \text{ of } 1 \ \text{mg mL}^{-1}$  ink (1 mg sample, 0.2 mL ethanol and 0.8 mL Millipore water) was loaded on a glassy carbon RDE ( $\varphi = 3 \ \text{mm}$ ). 0.1 M KOH aqueous solution was used as the electrolyte, which was saturated with O<sub>2</sub> by bubbling it prior to the start of each experiment. A flow of O<sub>2</sub> was maintained over the electrolyte during the recording of CVs in order to ensure continuous O<sub>2</sub> saturation. In control experiments, CV measurements were performed under N<sub>2</sub> atmosphere. 0.1 M KOH aqueous solution saturated with nitrogen or oxygen was used as the electrolyte in all electrochemical measurements,

#### 1.5 RDE and linear sweep voltammetry (LSV) measurements

For the RDE measurement, catalyst inks were prepared by the same method as that of CV analysis described above. The working electrode serving as RDE was cathodically scanned at a rate of 10 mV s<sup>-1</sup> with varying rotating speed from 400 to 2000 rpm. The ORR current was determined by subtracting the N<sub>2</sub> current from the O<sub>2</sub> current. Koutecky-Levich (K-L) plots were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (*n*) on the basis of the K-L equation:

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_{\rm K}}$$

$$B = 0.62 n FC_0 (D_0)^{2/3} v^{-1/6} J_k = n FkC_0$$

where *J* is the measured current density,  $J_{\rm K}$  and  $J_{\rm L}$  are the kinetic and diffusion limiting current densities,  $\omega$  is the angular velocity, *n* is transferred electron number, F is the Faraday constant (96485 C mol<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-3</sup> mol cm<sup>-3</sup>),  $D_0$  is the diffusion coefficient of O<sub>2</sub> (1.9×10<sup>-5</sup>), *v* is the kinematic viscosity of the electrolyte (0.01 m<sup>2</sup> s<sup>-1</sup>), and k is the electron-transfer rate constant. LSV measurement was carried out in an O<sub>2</sub>-saturated 0.1 M KOH electrolyte with a scan rate of 10 mV s<sup>-1</sup>. Stable voltammogram curves were recorded after scanning for 6 cycles in LSV experiment.

## 1.6 Water splitting performance measurements

The electrochemical tests were performed using the CHI 660D electrochemical testing system and a PINE instrument (America, AFCPRBE). 4 mg Pt-N,S-pCNFs and 100 µL Nafion solution (5.0%) were added into the mixture of water and ethanol (volume ratio = 1:1) (0.9 mL), and treated with ultrasonication for 0.5 h to form a ink. The as-prepared ink was added dropwise on a carbon fiber paper with a mass loading of 1 mg cm<sup>-2</sup>. The polarization curves (10 mV s<sup>-1</sup>) were obtained in 1 M KOH solution. The stability measurements were conducted by CV scanning for 1000 cycles at a scan rate of 100 mV s<sup>-1</sup>. The water-splitting test of Pt-N,S-pCNFs was conducted in 1 M KOH solution using a two-electrode configuration. Two pieces of graphite paper were used as the electrode (mass loading of about 1 mg cm<sup>-2</sup>). Unless stated otherwise, all polarization curves obtained in a three-electrode configuration are iR-corrected.

## 1.7 Hydrogen storage capabilities measurements

Hydrogen adsorption of samples (150 mg) was measured using a conventional Sieverts-type apparatus (Suzuki, PCT-1SPWIN, Japan) at 20 °C and pressure of 10 MPa. Before the measurements, the samples were degassed under vacuum state at 300 °C for at least 12 h.



**Fig. S1.** The SEM images of (a) porous-PAN, (b) pCNFs, (c) porous urea-PAN, (d) N-pCNFs, (e) porous thiourea-PAN, (f) N,S-pCNFs, and (g) H<sub>2</sub>PtCl<sub>6</sub>-thiourea-porous PAN nanofibers.



Fig. S2. (a) CV curves in N<sub>2</sub>- (dot line) and O<sub>2</sub>-(solid line) saturated electrolyte with the scan rate at 10 mV s<sup>-1</sup>, (b) LSV curves at different rotation rates (in rpm), (c) The corresponding K-L plot obtained from those RDE curves at  $0.2 \sim 0.6$  V with n, and (d) Chronoamperometric responses of Pt-N-pCNFs at 0.62 V and 1600 rpm. The electrolyte solution is 0.1 M KOH solution.



**Fig. S3.** (a) LSV curves of pCNFs in O<sub>2</sub>-saturated electrolytes with a scan rate of 10 mV s<sup>-1</sup> at different rotation rates (in rpm). (b) The corresponding Koutecky–Levich (K-L) plot of pCNFs derived from the RDE curves at 0.2~0.6 V with the electron transport number (n).



**Fig. S4.** (a) LSV curves of N-pCNFs in O<sub>2</sub>-saturated electrolytes with a scan rate of 10 mV s<sup>-1</sup> at different rotation rates (in rpm). (b) The corresponding K-L plot of N-pCNFs derived from the RDE curves at  $0.2\sim0.6$  V with *n*.



**Fig. S5.** (a) LSV curves of N,S-pCNFs in O<sub>2</sub>-saturated electrolytes with a scan rate of 10 mV s<sup>-1</sup> at different rotation rates (in rpm). (b) The corresponding K-L plot of N,S-pCNFs derived from the RDE curves at  $0.2\sim0.6$  V with *n*.



Fig. S6 Electrochemical impedance spectra of Pt-N-pCNFs and Pt-N,S-pCNFs.



Fig. S7 (a) CV curves of the Pt-N,S-pCNFs on glassy carbon electrodes in N<sub>2</sub>- (dot line) and O<sub>2</sub>-(solid line) saturated acidic electrolyte with the scan rate at 10 mV s<sup>-1</sup>. (b) LSV curves of Pt-N,S-pCNFs at different rotation rates (in rpm). (c) The corresponding Koutecky-Levich (K-L) plot of Pt-N,S-pCNFs obtained from those RDE curves at  $0.2 \sim 0.6$  V with n.



Fig. S8 HER LSV curves recorded for Pt-N-pCNFs before and after 1000 cycles.



Fig. S9 HER LSV curves recorded for IrO<sub>2</sub> before and after 1000 cycles.



Fig. S10 OER Tafel plots of the Pt-N,S-pCNFs, Pt-N,S-pCNFs and IrO<sub>2</sub> electrodes.



Fig. S11 HER Tafel plots of the Pt-N,S-pCNFs, Pt-N,S-pCNFs and IrO<sub>2</sub> electrodes.