Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

# Pd induced Pt(Ⅳ) reduction to form Pd@Pt/CNT core-shell catalyst for a more complete oxygen reduction

## Preparation of SH- functionalized CNT

In a typical routine, the pristine CNT (purchased from Bill Nanotechnology, Inc.) were purified by refluxing in 14 mol $L^{-1}$ $HNO_3$ for 5 h, followed by diluting, filtering, washing and vacuum drying at 80 °C overnight. The carboxylation of the purified CNT was then carried out in $H_2SO_4/H_2O_2$ mixture solution (4:1 by volume) for 3 h, followed by diluting, filtering, washing and vacuum drying at 80 °C overnight. Then the COOH-CNT were reduced to OH-CNT by putting COOH-CNT in excess $LiAlH_4$ dissolved in anhydrous ether in refluxing conditions for 3 h. The above suspension were filtered and washed with excess DI water and dried at 80 °C. The obtained OH-CNT was then substituted with bromide groups by refluxing the suspension in excess phosphorus tribromide dissolved in actone for 3 h at room temperature. After the suspension was filtered and washed with excess actone, the Br-CNTs were transferred into a 0.5 M NaHS solution, which were stirred strongly at room temperature for 3 h. The SH- functionalized CNT was finally obtained by filtration and washing with excess DI water and drying at 180 °C for 3 h to remove the residue $H_2S$.

## Preparation of Pd/CNT Nanostructures

In the first step, we synthesized uniform, nano particle of Pd by reducing $PdCl_2$ with Trisodium citrate in an aqueous solution. A 15 mL sample of $PdCl_2$ solution (25 mM), 160 mg of CNT and Trisodium citrate (153mg) were suspended in 10 mL of $H_2O$, and then the mixture was placed into an ultrasonic bath for 30 min and stirred overnight. After that, the solution pH was adjusted to 9 with NaOH solution (1 M), the reaction was carried out by adding sodium borohydride at the room temperature for 24 h. When the mixture turns into a brown black suspension, the Pd/CNT nanostructures are formed. The Pd nanostructures were obtained by centrifugation, washed sequentially with double-distilled water several times, and dried in air.

## Preparation of Pd@Pt/CNT Nanostructures

The same method was also used for the preparation of Pd/CNT nanostructures. Briefly, 289 μL of $H_2PtCl_6$ solution (40 mg $ml^{-1}$) and 30 mg of Pd/CNT were added into 10 ml $H_2O$ and the suspension was sonicating for 30 min. The pH of the mixture was adjusted to 8, by adding an aqueous solution of NaOH (0.1 mol $L^{-1}$) under stirring. The supernatant solution was stirred at 46 °C for 24 h for the preparation of Pd@Pt/CNT, with nitrogen atmosphere. The obtained carbon nanotubes supported catalysts were collected by centrifugation and dried at 60 °C in vacuum dryer. Then following the same procedure as a forementioned, the Pd-Pt nanostructures with various ratios of Pd to Pt could be synthesized.

## Characterization

Transmission electron microscopy (TEM) images were obtained on a JEOL-2010, working at an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy(HRTEM) and XRD patterns were recorded on a Rigaku Ultima III diffractometer with Cu Kα radiation (λ = 0.154178) at 40 kV and 40 mA. The scanning range (2θ) was from 2° to 80° at a scanning rate of 2° min$^{-1}$. The composition of Pd-Pt bimetallic catalyst was determined by inductively coupled plasma emission spectrometry (ICP-AES, Shimadzu) analysis.

**Electrochemical measurements**

Electrochemical measurements for the synthesized catalysts were performed using Princeton electrochemical workstation in a standard three electrode configuration with a RHE as reference and a platinum foil as counter electrode at room temperature. The catalyst particles were deposited on a glassy carbon (GC) disk electrode (Pine Instruments, Grove City, PA). A leak-free AgCl/Ag/KCl (3M) electrode (Warner Instrument) was used as the reference. All potentials were converted to the values with reference to a reversible hydrogen electrode (RHE). The electrolyte was 0.1 M perchloric acid diluted from 70% (Baker, ACS Reagent grade) using ultrapure water. A platinum flag was used as counter electrode. A glassy carbon (GC) disk electrode with a diameter of 5 mm and a geometric area of 0.1963 cm$^2$ was polished with 0.05 μm alumina before each experiment and used as a working electrode and a substrate. A mixture containing electrocatalyst, Millipore water, and Nafion solution was ultrasonicated for 20 min to obtain a well-dispersed ink. For JM-Pt/C catalyst an aqueous dispersion (1 mg mL$^{-1}$) was prepared and sonicated for 5 min. Preparing an electrode with Pd nanoparticles involved dispersing a certain amount of 20% Pd/CNT in 200 μL ethanol, and sonicating it for 5-10 min to make a uniform suspension. Then, 5 μL of this suspension was placed on a glassy carbon disk electrode and dried in air. After depositing Pt, the electrode was covered by 5 μL of 0.1%Nafion solution (diluted with water from 5% Nafion solution by Aldrich). The catalyst ink was then quantitatively transferred onto the GC electrode surface by using a micropipet and dried in vacuum to obtain a catalyst thin film. The CVs were recorded between potential limits of 0 and 1.28 V (vs RHE) at a sweep rate of 50 mV $s^{-1}$ and under continuous high-purity nitrogen purging. The ORR experiments were carried out using LSV in a potential range between 0.28 and 1.18 V and at a scan rate of 10 mV $s^{-1}$ in the electrolyte saturated with high-purity oxygen and at rotation speeds of 1600rpm using a MSR rotator from PINE instruments.

**RDE measurements** were performed in 0.1 M $HClO_4$ solutions under flow of $O_2$ (Airgas, Research grade) using the glassy carbon at a rotation rate of 1,600rpm and a sweep rate of 10 mV $s^{-1}$. In the ORR polarization curve, current densities were normalized in reference to the geometric area of the glassy carbon RDE (0.196 $cm^2$). For the ORR at a RDE, the Koutecky-Levich equation can be described as follows:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \tag{1}$$

where $i$ is the experimentally measured current, $i_d$ is the diffusion-limiting current, and $i_k$ is the kinetic current. Then, the kinetic current was calculated based on the following equation:

$$i_k = \frac{i \times i_d}{i_d - i} \tag{2}$$

For each catalyst, the kinetic current was normalized to loading amount of metal and ECSA in order to obtain mass and specific activities, respectively.

The CV curves were recorded every 50 cycles to calculate the electrochemical surface area (ECSA) of Pt in the catalysts using the following equation:

$$ECSA = \frac{Q_H}{0.21 \times [Pt]} \tag{3}$$

where $Q_H$ (mC) is the charge due to the hydrogen adsorption/desorption in the hydrogen region (0.05–0.40 V) of the CVs, 0.21 mC $cm^{-2}$ is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and [Pt] is the loading of Pt on the working electrode. All of the electrodes were pretreated by cycling the potential between 0.05 and 1.0 V at a sweep rate of 50 mV $s^{-1}$ for 50 cycles in order to remove any surface contamination prior to ORR activity testing. The ORR polarization curves were conducted in $O_2$-saturated 0.1 M $HClO_4$ solution at a 10 mV $s^{-1}$ scan rate. The rotation speed was controlled at 1,600 rpm.

**RRDE experiments** were conducted using 0.1M $HClO_4$ to prevent Pt/C performance loss caused by bisulfate adsorption. In the RRDE experiments, the ring potential was set to 1.2 V. Before the experiments, the Pt catalyst in the ring was activated throughpotential cycling in 0.5 M $HClO_4$ from 0 to 1.4 V at a scan rate of 50 mV / s for 10 minutes. The four-electron selectivity of catalysts was evaluated based on the $H_2O_2$ yield, which was calculated from the following equation (4):

$$H_2O_2\% = 200\frac{i_{ring}/N}{i_{disk}+i_{ring}/N} \tag{4}$$

Where $i_{disk}$ and $i_{ring}$ are the disk and ring currents, respectively, and N is the ring collection efficiency. The ring collection efficiency was independently determined using 10 mM

$K_3[Fe(CN)_6]$ in 0.1 M $KNO_3$ solution and a NG catalyst on a carbon disk at a "typical" loading of 0.6 mg/cm$^2$. The measured N value was 36.7%, which is similar to the RDE manufacturer's value of 37%.

Table 1S Measured Pt content of different components by ICP

| sample | Pt% (designed) | Pt% (measured) |
|---|---|---|
| $Pd_2$-$Pt_1$/SH- CNTs | 20 | 19 |
| $Pd_4$-$Pt_1$/SH- CNTs | 10 | 9.6 |
| $Pd_8$-$Pt_1$/SH- CNTs | 5 | 4.9 |