

# The effect of the Pt deposition method and the support on Pt dispersion on carbon nanotubes

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## Abstract

Carbon nanotube supported platinum (Pt/CNTs) catalysts prepared by different Pt deposition methods and on different CNT supports were studied. Colloidal based methods were demonstrated to be more effective than other wet chemistry deposition methods (e.g., impregnation and precipitation) for the preparation of highly dispersed Pt/CNTs. Pt catalyst supported on CNTs with a dispersion uniformity comparable to that supported on carbon powder was achieved using a zwitterionic surfactant 3-(*N,N*-dimethyldodecylammonio) propanesulfonate (SB12) as stabilizer in a monitored pH environment. It was experimentally observed that oxygen-containing surface functionalities on CNTs can greatly affect the catalyst particle dispersion by manipulating Pt anchoring and/or nucleating sites. Furthermore, it was revealed that the performance of Pt/CNTs based fuel cell is strongly dependent on the electrode fabrication method.

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## 1. Introduction

Carbon nanotubes (CNTs) have been used as a novel catalyst support in both heterogeneous catalysis and electrocatalysis, due to their unique properties such as one-dimensional structure, high external surface area and good mechanical strength [1–3]. Some CNT supported catalysts (e.g., Ru, Pt, Rh and Pd) have shown good activity and/or selectivity in a variety of chemical reactions [4–7], which was generally attributed to the improved metal-support interaction, mass transfer or catalyst chemical state induced by the CNTs. Moreover, CNTs have been efficiently used as a support material of fuel cell catalysts (e.g., Pt and Pt-based alloys [8–18]). A high catalytic performance for the oxygen reduction reaction and the methanol oxidation reaction has been reported. The possible reasons are that the CNT based catalysts could create special metal-support interaction, and have higher conductivity and lower organic impurities than the traditional carbon black based ones. Particularly, the experiments and theoretical calculations carried out by Britto et al.

showed that a large number of defects of CNTs, such as pentagons at the nanotube tip, pentagon-heptagon defect pairs in the lattice and curvature, are beneficial to the oxygen reduction reaction [19].

Among numerous CNT supported catalysts investigated, Pt/CNTs are the ones most widely used, especially for fuel cell applications. Since the dispersion and particle size of Pt on the support material can strongly affect its utilization and catalytic activity [20,21], the synthesis of Pt/CNTs is of fundamental and practical importance [5,8–16,18,22–26]. Several typical methods, well developed for Pt/C, have been employed for the preparation of Pt/CNTs. They mainly include impregnation [8,11,14,26], precipitation [5,10,24], colloidal [9,12,13,16–18,22,23] and ion-exchange [25] methods. Nevertheless, compared to the conventional Pt/C, the dispersion and the size distribution of Pt particles in the Pt/CNTs is far from satisfactory.

Moreover, the external walls of the CNTs are very inert because they are composed of inert graphite layers, and cannot be wetted by liquids with a surface tension higher than 100–200 mN/m [27]. An oxidative HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>–HNO<sub>3</sub> pretreatment [28,29] on CNTs has been recognized to be necessary for good Pt dispersion. However, in the earlier works, a significant difference in Pt dispersion has been observed for

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Pt/CNTs with identical CNT treatment conditions but different Pt deposition methods. Although many efforts have been made to prepare highly dispersed Pt/CNTs catalysts, there is, to the best of our knowledge, little systematic information available on the influence of the Pt deposition method and the support on Pt dispersions on CNTs [10].

In this work, Pt/CNTs catalysts have been prepared by different Pt deposition methods and on different CNT supports. The physicochemical and electrochemical characterizations of the CNT supports and the corresponding Pt/CNTs catalysts were provided. The influence of the Pt deposition method and the CNT properties on the dispersion and size distribution of Pt particles on CNTs were discussed. The Pt/CNTs with a uniform dispersion comparable to Pt/C were achieved. Furthermore, the influence of the electrode fabrication method on the performance of the Pt/CNTs based fuel cell was revealed.

## 2. Experimental

### 2.1. Pretreatment of CNTs

CNTs were produced by a chemical vapor deposition method. An oxidative treatment was given by refluxing raw CNTs (CNTs-r) either with nitric acid (70%) or with a mixture of sulfuric and nitric acids (1:1 v/v, 98% and 70%, respectively) at 90 °C for 5 h. Afterward, they were washed thoroughly with deionized water and then dried under vacuum at 90 °C for 4 h. In the following discussion, the CNTs treated by nitric acid were denoted as CNTs-n; while the ones treated by a mixture of acids were labeled as CNTs-m. For comparison purpose, Vulcan XC-72 carbon black was also used as support material.

### 2.2. Preparation of Pt/CNTs

#### 2.2.1. Impregnation method

CNTs were mixed with 4.1 mL of 10 mM H<sub>2</sub>PtCl<sub>6</sub> (Aldrich) in isopropyl alcohol–water (1:3 v/v) solvent mixture at 50 °C for 6 h under vigorously stirring. The resulting slurry was dried at 100 °C to remove the solvent, and then heat-treated by a 2 h exposure to pure H<sub>2</sub> flow at 500 °C.

#### 2.2.2. Precipitation method

CNTs were vigorously mixed with 4.1 mL of 10 mM H<sub>2</sub>PtCl<sub>6</sub> in isopropyl alcohol–water (1:3 v/v) solvent mixture at 50 °C for 6 h. Then the suspension was heated up to 80 °C, and the pH of suspension was adjusted to 8.5 using 0.5 M Na<sub>2</sub>CO<sub>3</sub> solution. Abundant amount of KBH<sub>4</sub> was added to make a chemical reduction for 2 h. The resultant suspension was filtered, washed and vacuum-dried at 90 °C for 4 h.

#### 2.2.3. Surfactant-stabilized method

CNTs (or carbon black), 4.1 mL of 10 mM H<sub>2</sub>PtCl<sub>6</sub> and surfactant 3-(*N,N*-dimethyldodecylammonio) propanesulfonate (SB12) were mixed in a methanol–water (1:3 v/v) solvent mixture and sonicated to form a uniform suspension. The methanol was used as the reducing agent. Unless otherwise stated, the pH value of the suspension was adjusted to 7.0. The molar ratio of

SB12 to H<sub>2</sub>PtCl<sub>6</sub> is 80. Then, the suspension was pre-heated in a 50 °C water bath for 15 min and transferred to another water bath maintained at 90 °C. The suspension was kept there for 60 min under constant stirring. Afterward, it was cooled in a cold water bath, filtered and finally washed by an abundant amount of ethanol and deionized water to remove the surfactant. The residue was vacuum-dried at 90 °C for 4 h. Unless otherwise stated, Pt/CNTs or Pt/C was prepared with the surfactant-stabilized method.

### 2.3. Physicochemical characterizations

Transition electron microscopy (TEM) was carried out with a JEOL 2010F TEM system. The size distribution of Pt nanoparticles in the catalyst was obtained by measuring about 300 nanoparticles. Scanning electron microscopy (SEM) was performed with a JEOL 6300F scanning microscope. X-ray photoelectron spectroscopy (XPS) (Physical Electronics PHI 5600 multi-technique system) was achieved to analyze the surface concentration of the elements in the catalyst. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin Elmer, Optima 3000XL) was used to analyze Pt bulk concentration in the catalyst. BET surface area was obtained with Coulter SA3100 surface area and pore size analyzer. The pH value was measured with a pH meter (Model 420A, ORION Research Inc.). The solubility properties of CNTs in various solvents were evaluated as the following: 32 mg of CNTs was mixed by sonication in 100 mL of water, methanol or water–methanol (3:1 v/v) solvent mixture for 30 min. The resulting suspension was allowed to settle at room temperature for 6 h. The solubility was qualitatively estimated by the color of supernatant liquid and by the quantity of residue.

### 2.4. Electrochemical measurements

RDE measurements were conducted in a three-electrode cell with an Autolab potentiostat (Eco Chemie). The working electrode was a glassy carbon disk (4 mm diameter) with a CNT ink. The ink was made by ultrasonically mixing 16 mg of CNTs with 0.8 mL of 5 wt.% Nafion, 0.8 mL of deionized H<sub>2</sub>O and 1.6 mL of ethanol. 5 μL of the suspension was pipetted onto the disk electrode. A Pt spiral and Ag/AgCl were the counter and reference electrodes, respectively. All potentials were referenced to the reversible hydrogen electrode (RHE). 0.5 M H<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. Nitrogen was used for the solution deaeration. All experiments were performed at room temperature.

Fuel cell measurements were performed at 70 °C and 3 atm in a fuel cell test station (Hydrogenics Corp.). Both anode and cathode consisted of a diffusion layer and a catalyst layer. The diffusion layer was coated on the water-proof carbon paper (SGL) and was made of Vulcan XC-72 carbon (loading: 2 mg/cm<sup>2</sup>) and polytetrafluorethylene (PTFE, content: 30 wt.%). The cathode catalyst layer was prepared by two different methods: the single-layer method and the double-layer one. For the single-layer method, the catalyst layer was prepared with the slurry composing of Pt/C (or Pt/CNTs-m), PTFE, Nafion solution (Aldrich)

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