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Platinum Nanoparticles Supported on Nitrobenzene-Functionalized Multiwalled Carbon Nanotube as Efficient Electrocatalysts for Methanol Oxidation Reaction

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ABSTRACT

A novel method of molecular covalently functionalized multiwalled carbon nanotube using nitrobenzene group is prepared and used as a promising support material of Pt-based electrocatalysts (denoted as Pt-NB-MWCNT) for methanol oxidation reaction. The physical and chemical characteristics are performed by X-ray powder diffraction, transmission electron microscopy, Raman spectroscopy, thermogravimetric and X-ray photoelectron spectroscopy. The electrocatalytic are evaluated by cyclic voltammetry and chronoamperometry techniques. Compared with the un-functionalized Pt-MWCNT catalyst, Pt-NB-MWCNTs show more uniform particle dispersion, smaller particle size, improved activity and durability for methanol oxidation reaction. The nitrobenzene group is demonstrated to promote the electrocatalytic activity of Pt-MWCNT for methanol oxidation significantly. The results represent a novel approach to functionalize MWCNT in a simple and economic way to prepare efficient electrocatalysts for methanol oxidation.

1. Introduction

Direct methanol fuel cell (DMFC), a type of polymer electrolyte fuel cell (PEFC), as alternative green and sustainable power sources, has been shown potential applications in portable, stationary power sources, and has aroused tremendous research interest in academic and engineering circles [1]. Platinum-based electrocatalysts have been extensively developed as efficient catalysts for both the anode and cathode of a DMFC [2,3]. However, Pt is a costly and of limited resource, posing problems for DMFCs commercialization. Thus, the strategy to improve electrocatalytic activity with minimum loading of Pt, while maximizing the utilization efficiency of the loaded Pt, is the vital for popularization of DMFCs [4]. The approaches developed so far to improve the Pt performance include alloying with other un-precious metals and efficiently supporting on carbon materials. It should be pointed out that the interaction between Pt and the carbon support could significantly affect its electrochemical performance in fuel cells in terms of activity and durability [5].

To date, carbon black, Vulcan XC-72, was most commonly used as the supporting materials of nanosized Pt particles due to their high surface area and low electrical resistance. But the problems demanding prompt solution of low Pt utilization and poor electrochemical stability remain unresolved for Pt/C composite electrocatalysts [6]. Multiwalled carbon nanotubes (MWCNT) with many beneficial properties such as high electrical conductivity, high chemical stability, as well as extremely high mechanical strength and modulus, providing overwhelming advantages over carbon black when being employed as an electrocatalyst support, have been extensively studied to solve these problems [7–9]. Previously, several methods have been reported to prepare MWCNT-supported Pt catalysts with enhanced electrochemical performance [10–13]. However, due to its highly inert surface because of high graphitization degree, it is very difficult for Pt nanoparticles to directly and evenly be deposited onto MWCNT surfaces without active functional groups [14–16]. The main strategy to modify MWCNT is mostly through harsh oxidative treatment, such as refluxing in HNO_3 followed by metal deposition on activated MWCNT walls [17–21]. Such method introduces an avenue for metal precursors to interact with MWCNT, but it would damage the integrity and seriously decrease the electrical conductivity of the carbon nanotubes. Other approaches, such as physical evaporation, electroless deposition, and electrodeposition

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have been reported [22–25]. For those methods, the size and dispersion of the Pt particle on the MWCNT is difficult to control. Previously, we have developed non-covalent strategies to functionalize carbon nanotubes to support Pt or PtRu nanoparticles as efficient electrocatalysts for methanol oxidation [26,27]. In these techniques, carbon nanotubes were functionalized by adsorbing polyelectrolyte or pyrene-based molecules *via* π-π interaction. However, this non-covalent method is difficult to control the amount of the functionalization species [28,29].

In this work, a new concept of molecular doping of MWCNT as an efficient support material for Pt nanoparticles is presented. As a strong electron-acceptor, nitrobenzene could bond MWCNT through covalent linking of carbon atom. Nitrobenzene group with a strong electron-accepting ability would withdraw electrons from carbon atoms in MWCNT, which would lead to modified electronic properties of carbon nanotubes and thus tune the electrocatalytic activity of the supported Pt nanoparticles. At the same time, nitrobenzene group as a surface oxygen groups would increase the wettability of MWCNT, which would facilitate the aqueous solution of the metal precursor to the internal pore structure during the impregnation stage [30–32]. As a comparison, Pt supported on un-functionalized MWCNT (denoted as Pt-MWCNT) was synthesized with the same method in the absence of nitrobenzene. The morphology, structure, and electrocatalytic activity of two catalysts were systematically characterized and evaluated. The as-prepared Pt-NB-MWCNT catalysts show significantly improved electrocatalytic activity for methanol oxidation reaction, as well as enhanced stability, compared with Pt-MWCNT catalysts without nitrobenzene functionalization. The improved electrochemical performance of Pt-NB-MWCNT was attributed to the homogeneous Pt dispersion, the modified electronic properties, as well as the strengthened interaction between Pt and MWCNT by nitrobenzene covalent functionalization.

2. Experimental

2.1. Synthesis of NB-MWCNT

50 mg of multi-wall carbon nanotube (MWCNT) was immersed in aqueous solution under constant stirring at 35 °C, and then 5 mg of 4-NBD was dissolved by slowly dropping into the above MWCNT dispersion. After reaction for 16 h, NB-MWCNT samples were washed in the sequence of ultrapure water (18.2 MΩ), acetonitrile and ethanol and finally dried in a vacuum oven at 65 °C over night.

2.2. Synthesis of Pt-NB-MWCNT and Pt-MWCNT

NB-MWCNT, $H_2PtCl_6 \bullet 6H_2O$ (10 mg ml^{-1}) aqueous solution and ethylene glycol were mixed and subsequently subjected to sonication for 1 h to obtain a highly dispersed solution. The pH of the solution was next adjusted to 11 with addition of 3 ml of 1 M NaOH solution, and the solution was refluxed at 130 °C for 12 h. Then the solution was naturally cooled to room temperature and the final product was fully washed with ultrapure water and ethanol to remove any impurities, and the sample was dried in a vacuum oven to obtain Pt-NB-MWCNT product. For the synthesis of Pt-MWCNT (without functionalized nitrobenzene), the similar procedure was followed with the pristine MWCNT.

2.3. Characterization

X-ray powder diffraction (XRD) characterization was carried out on a Siemens D500 diffractometer with a Cu Kα source (1.54056 Å). Diffraction data were collected for 2 θ angles from 10° to 90°. The thermogravimetric analysis was carried out by a STA449C instrument with a heating rate of 10 °C in Ar. The morphology and microstructure of the Pt nanoparticles on graphene were investigated transmission electron microscopy

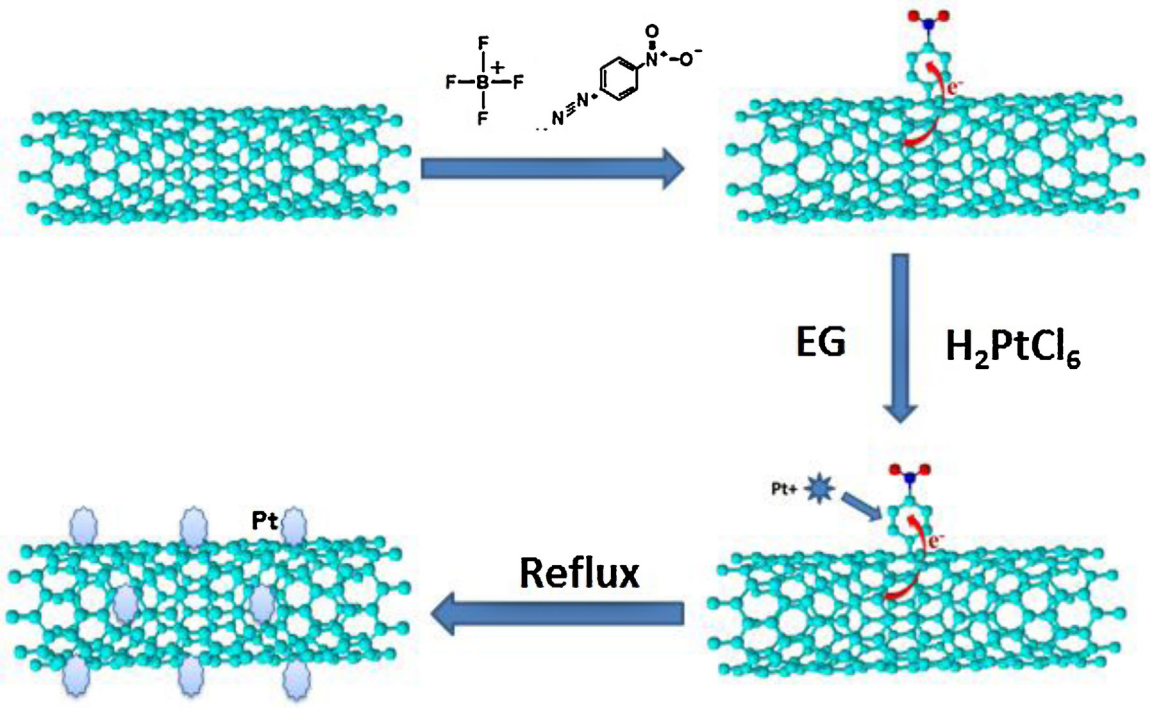

Fig. 1. Schematic diagram of the synthesis of Pt electrocatalysts on nitrobenzene -functionalized MWCNTs.