



Decoration of carbon nanotubes with highly dispersed platinum nanoparticles for electrocatalytic application



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ABSTRACT

A novel approach to the synthesis of mono-dispersed platinum nanoparticles (Pt NPs) on multiwalled carbon nanotubes (MWNTs) has been proposed. With this method, we successfully assembled mono-dispersed Pt NPs on MWNTs. The method involved the in situ high-temperature decomposition of the precursor, platinum (II) acetylacetonate (Pt(acac)₂), in liquid polyols. We used X-ray diffraction, scanning electron microscopy, and transmission electron microscopy to characterize the resulting MWNTs covered with Pt NPs (Pt@MWNTs). We found that the size of the Pt NPs and the coverage density on MWNTs could be tuned easily by changing the reaction temperature and the initial mass ratio of Pt(acac)₂ to MWNTs. Electrocatalytic measurements showed that the Pt@MWNTs had excellent catalytic activities in the electrooxidation of methanol and in the oxygen reduction reaction. These Pt@MWNTs have potential applications in fuel cells and biosensors.

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1. Introduction

Direct methanol fuel cells (DMFCs) have recently come to be regarded as one of the most promising power generators for portable electronic devices and electric vehicles because of their high energy conversion efficiency and low pollutant emission [1]. Although platinum (Pt) possesses unique and high electrocatalytic activity for oxygen reduction reaction and methanol oxidation, large-scale commercial applications have been precluded by its high cost and scarcity [2]. Thus, considerable efforts have been devoted to reducing the amount of platinum needed, for example in platinum-based catalysts, by using various Pt-carbon hybrids, such as Pt/porous carbons [3], Pt/graphene [4–6], and Pt/carbon nanotubes (Pt/CNTs) [7–9]. Carbon nanotubes (CNTs) have attracted great scientific and technological attention because of their potential applications in fabricating novel materials and devices [10]. CNTs are considered to be ideal candidates due to their remarkable structure-dependent properties [11–13], including high tensile strength and surface area, together with their high electric and thermal conductivity [14,15]. Moreover, it has been reported that the use of CNTs as supports renders materials that are more resistant against corrosion than for example carbon black, permitting as well as better contact between reactant and

nanoparticles (NPs) surface than porous carbons [16–19]. Thus, the main reason for the high activity of the Pt/CNTs catalyst seems to be that reactant molecules easily arrive at the catalyst and the product molecules readily diffuse away from the Pt NPs when supported on CNTs [20]. The enhanced electrocatalytic properties of CNTs are expected, for example, to reduce the amount of precious metal catalyst increasing the commercial viability of DMFCs [21–24].

Up till now, a number of groups have reported methods for preparing CNTs-supported Pt catalysts [25–29]. Most of these methods involve the reduction of Pt^{II} salts by microemulsion [30], chemical vapor deposition [31,32], or electrochemical deposition [26]. Although CNTs-supported Pt electrocatalysts have been shown to be effective in fuel cell systems, many of the reported methods can only be applied on a laboratory scale, due to the high cost of synthesis. In addition, those methods often require a harsh pretreatment of CNTs substrates prior to metal deposition. Furthermore, it is difficult to estimate the loading mass of the metallic catalyst based on the deposition charge [33]. For example, a common strategy for depositing metal NPs onto CNTs is to first functionalize the external wall with oxidative treatments and then, to deposit the particles [34–36]. This strategy includes the pretreatment of CNTs with acid-oxidation, which typically causes some structural damage to the CNTs and leads to the partial loss of CNTs electrical conductivity [37–40]. Moreover, in the course of electrochemical deposition, a major problem is that H⁺ is reduced during the

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electrodeposition process. Other methods, such as a physical adsorption technique [41], electroless deposition [42], and organic molecule cross-linking have also been reported [43]. All of these protocols loaded Pt NPs successfully. However, how to deposit size- and shape-controlled Pt NPs on CNTs is still under development. Although some progress has been made in this field, it remains a challenge to achieve a highly efficient CNTs-supported metallic catalyst that has non-aggregated, mono-dispersed metal particles deposited on the CNTs.

In this paper, we present a novel, simple method for efficiently decorating multiwalled carbon nanotubes (MWNTs) with mono-dispersed Pt NPs. This method involves in situ high-temperature decomposition of the precursor, platinum (II) acetylacetonate ($\text{Pt}(\text{acac})_2$) in liquid polyols. The prepared MWNTs have high potential for commercial applications, because they can be used directly without any pretreatment procedures. Both the size and coverage density of Pt NPs on the surface of MWNTs can be tuned easily by changing the initial mass ratio of $\text{Pt}(\text{acac})_2$ to MWNTs. Therefore, the in situ strategy is an attractive method for the decoration of CNTs with size- and shape-controlled Pt-based NPs and other nanocatalysts. We used transmission electron microscopy, scanning electron microscopy, X-ray diffraction, and energy dispersive spectrometer to characterize the resulting MWNTs covered with Pt NPs. Electrochemical measurements of the Pt@MWNTs catalysts were performed on an Autolab PGSTAT30 electrochemical workstation. Our results showed that Pt@MWNTs catalysts have significantly high electrocatalytic activities for electrooxidation of methanol and oxygen reduction reaction (ORR).

2. Experimental section

2.1. Materials

MWNTs of >95% purity, 20–40 nm diameter, and 5–15 μm length were provided by Shenzhen Nanotech Port Co. Ltd. The platinum precursor, $\text{Pt}(\text{acac})_2$, 97% purity, was purchased from Aldrich and used as received. Triethylene glycol (TREG, 99%) was purchased from Aldrich. High-purity nitrogen, oxygen gas, and super pure water were used in all experiments. CH_3OH , H_2SO_4 , and other reagents were of analytical grade.

2.2. Synthesis of a Pt@MWNT nanocomposite

10.0 mg of MWNTs were dispersed in 20.0 mL triethylene glycol with ultrasonication for 25 min. Various amounts of $\text{Pt}(\text{acac})_2$ (8.0, 18.0, 28.0, or 38.0 mg) were added to the suspension under ultrasonication within 5 min to ensure the precursor was completely dissolved. The resulting mixture was then heated to 245 $^\circ\text{C}$ at a rate of 2.5 $^\circ\text{C min}^{-1}$ with stirring under the protection of a high-purity nitrogen atmosphere. After refluxing for 30 min, the reaction solution was cooled to room temperature, and 20 mL of absolute ethanol was added to dilute the solution. Then, the product was centrifuged and washed with absolute ethanol several times and dried under reduced pressure at 60 $^\circ\text{C}$ for 15 h.

2.3. Electrode preparation and modification

Glassy carbon electrode (GCE, 3 mm in diameter) was first polished with alumina slurry of 1.0, 0.3, and 0.05 μm , then ultrasonically cleaned with 1:1 nitric acid, ethanol, and super pure water. A 5.0 mg catalyst powder was dispersed ultrasonically in 5.0 mL super pure water to obtain a homogeneous black suspension solution. A 5 μL aliquot of this solution was uniformly dropped on the pretreated GCE surface. The electrode was then air dried and served as the working electrode for all electrochemical studies.

2.4. Characterization

Morphology characterization was performed on a scanning electron microscopy (SEM, FEI QUANTA 200F microscope). Transmission electron microscopic (TEM) images with operating voltage of 200 kV were obtained on a HD-2000 microscope equipped with an energy dispersive spectrometer (EDS). X-ray diffraction (XRD) patterns of the products were obtained on a Rigaku powder diffractometer equipped with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TG/DTA PYRIS DIAMOND) over a temperature range of 25–800 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C min}^{-1}$. Electrochemical measurements were performed on an Autolab PGSTAT30 electrochemical workstation (Eco Chemie). A conventional three-electrode system was used; it included an Ag/AgCl reference electrode, a Pt wire counter-electrode, and the catalyst modified GCE (Section 2.3).

3. Results and discussion

3.1. Characterization of the Pt@MWNTs nanocomposites

Morphologies of the Pt@MWNT nanocomposites formed by decomposing $\text{Pt}(\text{acac})_2$ in polyol were imaged with SEM (Fig. 1a and b). The nanocomposites were formed with an initial 14:5 weight ratio of platinum precursor to MWNTs (0.5 mg mL^{-1} of MWNTs was used throughout). Clearly, an abundance of uniform Pt NPs was attached to the sidewalls of the MWNTs with little or no agglomeration. In addition, the detailed structures of Pt@MWNT nanocomposites were visualized with TEM (Fig. 1c). A large number of Pt NPs with approximately 8 nm diameters were observed on the surface of MWNTs; this indicated the feasibility of our method. An EDS analysis was performed to validate the composition of the Pt@MWNTs (Fig. 1d). We recorded the presence of carbon and Pt, but no other element was detected; this demonstrated that the nanostructures bound on the walls of the MWNTs were Pt NPs.

The temperature-dependency of Pt@MWNTs nanocomposite formation was tested to investigate the underlying mechanism. We started with an initial $\text{Pt}(\text{acac})_2$:MWNT weight ratio of 14:5 (Fig. 2). At the early stage, a treatment of 220 $^\circ\text{C}$ for 30 min caused an abundance of loose, intermediate-sized Pt NP products to form on the side walls of MWNTs (Fig. 2a). However, at this low temperature (220 $^\circ\text{C}$), $\text{Pt}(\text{acac})_2$ did not completely decompose, and TREG only partly reduced it into subparticles. Thus, these intermediate products were difficult to further reduce to smaller subparticles. When the reaction temperature was increased to 245 $^\circ\text{C}$ for 30 min, all the MWNTs became decorated homogeneously with a high-density of Pt NPs. The average particle size was approximately 8 nm (Fig. 2b). When the reaction temperature was heated to 262 $^\circ\text{C}$ for 30 min, the size of Pt NPs increased to relatively large particles, with an average particle size of approximately 16 nm (Fig. 2c). When the reaction temperature was heated to 296 $^\circ\text{C}$ for 30 min, the Pt NPs aggregated, with an average particle size of approximately 25 nm (Fig. 2d). These results suggested that the Pt NPs were formed by the aggregation of very small nanoparticles into larger nanoparticles; moreover, this can be strongly influenced by the reaction temperature and the presence of TREG [44]. Therefore, we proposed a possible mechanism for the formation of Pt@MWNTs. First, $\text{Pt}(\text{acac})_2$ was decomposed and partly reduced by TREG into single Pt particles at an appropriate temperature. These single Pt particles were unstable, and their high surface energy favored some extent of growth or aggregation in order to reduce their surface energy [45]. Once these particles grew to a critical size, they could be stabilized by TREG, and they formed the monodispersed nanoparticles that decorated the

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