

# Highly dispersed Pt nanoparticles immobilised on 3-amino-silane-modified MWNT materials for methanol oxidation

Dao-Jun Guo · Shu-Kun Cui

Received: 25 September 2007 / Revised: 20 October 2007 / Accepted: 30 October 2007 / Published online: 30 November 2007  
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**Abstract** We demonstrate the use of molecular monolayers to enhance the nucleation of electrocatalytically active platinum nanocrystals onto carbon nanotubes. The multi-walled carbon nanotube (MWNT) is embedded within the polysiloxane shell with large amounts of hydrophilic amino groups outside after the siloxane is polymerized on the nanotube surfaces. Subsequent deposition of platinum nanoparticles led to high densities of 2- to 5-nm diameter Pt nanocrystals uniformly deposited along the length of the carbon nanotubes. The structure and nature of the resulting Pt/Si-MWNT composites were characterized by transmission electron microscopy and X-ray diffraction. Electrochemical measurements show that the molecular monolayers do not impede redox behavior of the electrode, and measurements of the electrocatalytic oxidation of methanol show very high catalytic efficiency.

**Keywords** Si-MWNTs · Platinum nanoparticle · Methanol oxidation · Electrocatalyst

## Introduction

Direct methanol fuel cells (DMFC) have been paid much attention for their potential as clean and mobile power sources for the future [1–3]. The operating principle for

DMFC involves the oxidation of methanol on precious platinum particles dispersed over a carbon support. The price of Pt metal is high and its resource is limited; it is a high barrier to the commercialization of DMFC, which makes it essential for lowering the loading of Pt metal in DMFC. It is known that the electrocatalytic activity depends on the metal distribution and particle size on supporting materials. Therefore, an alternative method to achieve a high Pt utilization is increasing the specific surface area by highly dispersing it on a high surface area support.

Recently, carbon nanotubes (CNTs) have been used as templates or scaffolds for the hybrid assembly of nanoparticles [4–10]. Because of their great hardness and toughness, CNTs keep their morphology and structure even at high nanoparticle loadings. Several methods have been developed to prepare CNTs-supported metal nanoparticles including electrochemical [11–13], microwave irradiation [14], and wet chemical [15–17] methods. A review concerning the use of different methods (electrochemical, chemical, and physical methods) as well as some applications (catalysis, hydrogen storage, sensing, optical, electronic, and energy storage applications) of metal nanoparticles and related materials supported on carbon nanotubes has been recently published [18].

In this work, we report on a hybrid system of monodisperse phase-pure Pt nanoparticles with a narrow size distribution on functional multiwalled carbon nanotube (MWNT) scaffolds synthesized via a very simple and straightforward process. This involves the coating of siloxane by hydrophobic interaction on MWNT surface. Then, siloxane micelles were cross-linked with Si–O–Si framework by addition of hydrochloric acid to obtain siloxane-modified MWNTs, analogous to the procedure employed to disperse Au particles on MWNTs in the literature [19]. Such a structure probably originates from

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D.-J. Guo (✉)  
College of Chemistry Science, Qufu Normal University,  
West Jingxuan Road No. 57,  
Qufu, Shandong 273165, People's Republic of China  
e-mail: guodaojun03@163.com

S.-K. Cui  
Qufu Normal School,  
Qufu, Shandong 273100, People's Republic of China

the formation of the micelle in which ammonium groups extrude outside; the amine groups on MWNT surfaces provide a uniform functional surface, which can effectively prevent the preferred nucleation process on the MWNT surface and can offer convenient ways for further functionalization of carbon nanotubes. The benefit of the ammonium-modified MWNTs has also been described in our other work [20]. Finally, MWNTs were dispersed in distilled water and mixed with the ascorbic acid– $\text{H}_2\text{PtCl}_6$  solution for about 20 min to prepare Pt nanoparticles on the polysiloxane-embedded MWNT (Si–MWNT) surface. Wang et al. [19] first used this method to coat CNTs with Au nanoparticles. Considering that the method to prepare Au nanoparticles on the functional MWNT by their method seemed to be usually aggregated and not uniformly dispersed on the MWNT surface, the procedure is complex and time-consuming. This procedure is simple, time-saving, and easy to control, allowing for deposition of finely dispersed Pt nanoparticles while avoiding admetal aggregation. The prepared catalyst exhibits a remarkable enhancement of catalytic activity for methanol oxidation as compared to that of the commercially available Pt catalyst. It may have potential application in commercialization for preparing anodic material of DMFC and proton exchange membrane fuel cell.

## Experimental

### Non-covalent functionalization of MWNTs with polysiloxane

MWNTs were purchased from Shenzhen Nanotech Port (Shenzhen, China) and further purified before use by stirring in concentrated nitric acid for 12 h. Our strategy for embedding MWNTs within polysiloxane shells is similar to disperse Au particles on MWNTs in the literature [19]. In a typical process, 20.00 mg of MWNTs were added to 40.00 ml of distilled water and could not be well dispersed by ultrasonication in a laboratory ultrasonic bath. Then, with the addition of 3 ml 3-aminopropyl triethoxysilane (3-APTES; purchased from Aldrich) and ultrasonication for 5 min, a homogeneous well-dispersed suspension could be easily prepared. Next, the siloxane micelles were cross-linked with Si–O–Si framework by addition of 1.5 ml of hydrochloric acid (0.1 M; Sigma). After the cross-linking of siloxane, excess reagents were removed by dialysis of the suspension against distilled water. The Si–MWNTs were purified from the suspension by several cycles of centrifuging the suspension and discarding the supernatant. The Si–MWNTs were dried in a vacuum oven at 50 °C for about 2 h for further use. The dispersibility of carbon nanotubes in water can be attributed to the presence of a large number of amino groups on the surfaces of the carbon nanotubes.

### Preparation of Pt/Si–MWNT catalysts

Ten milligrams of purified Si–MWNTs was dispersed in 20.00 ml of distilled water and mixed with the ascorbic acid– $\text{H}_2\text{PtCl}_6$  solution prepared by mixing 1 ml water with 50  $\mu\text{l}$  0.2 M ascorbic acid (Sigma) and 0.4 ml of  $\text{H}_2\text{PtCl}_6$  (77.8 mM; Sigma) aqueous solution for about 50 min to prepare Pt nanoparticles on the Si–MWNT surface with stirring. After centrifugation, the black solids left at the bottom of the container were extensively washed with distilled water. For comparison, the Pt/MWNT nanoparticles with the same Pt contents compared with Pt/Si–MWNT in the samples were prepared according to the above method.

### Measurements

Electrochemical reactivity of the catalysts was measured by cyclic voltammetry (CV) using a three-electrode cell at the PARSTAT 2273 potentiostat controlled by PowerSuite® software (Princeton Applied Research). The working electrode was a gold plate covered with a thin layer of Nafion-impregnated catalyst. As a typical process, about 1 mg catalyst sample was ultrasonically mixed with 25  $\mu\text{l}$  Nafion and ethanol glycol solution (the volume ratio of Nafion and ethanol glycol is 1:4) to form a homogeneous ink which was cast on the gold plate. Pt gauze and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in this report are quoted vs SCE. CV test was conducted at 50  $\text{mV s}^{-1}$  in a solution of 1 M  $\text{HClO}_4$  with 1 M  $\text{CH}_3\text{OH}$ , potential ranging from –0.2 to 1.0 V. The electrochemical measurements were conducted under 25 °C.

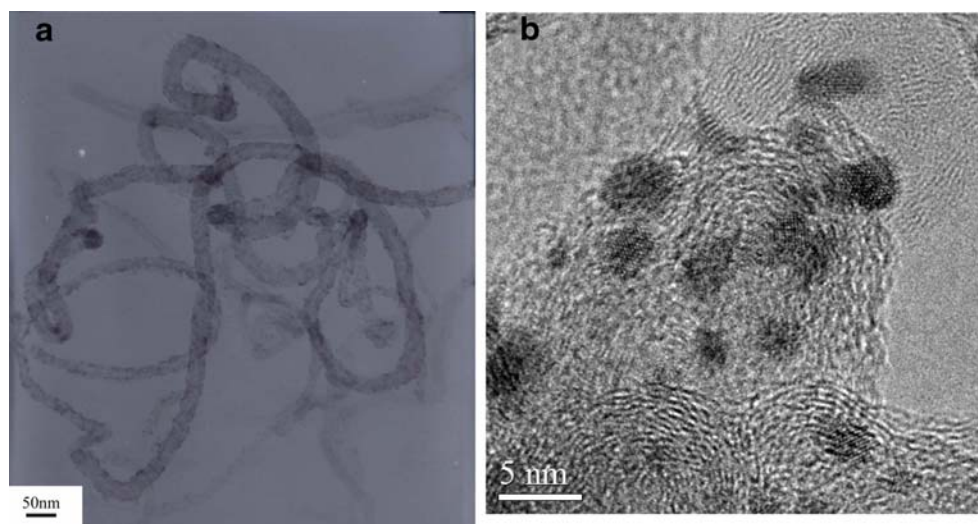
The morphology of Pt/Si–MWNT composites was investigated using a Hitachi600 transmission electron microscopy (TEM). The X-ray diffraction (XRD) analysis was performed using the Rigaku X-ray diffractometer with  $\text{CuK}_\alpha$  radiation source.

## Results and discussion

### TEM analysis of the Pt/Si–MWNT composites

Figure 1 shows transmission electron micrographs (a) and high-magnification view (b) of platinum nanoparticles decorated on polysiloxane-coated carbon nanotubes. The carbon nanotubes exhibit a multiwalled microstructure with an average diameter of about 40 nm. More importantly, however, very high particle densities for platinum were found at all CNT surfaces in the image. Consequently, the polysiloxane-embedded MWNT applied for the dispersion of the CNTs combined with the chosen deposition method appears to be a very powerful and effective technique.

**Fig. 1** TEM image of Pt/Si–MWNT composites



The hollow structure of the CNTs is not clearly visible, probably due to the polysiloxane coating. The average platinum particle size was determined from the HRTEM images to be about 2–5 nm (Fig. 1b). Despite the small size of the platinum particles, particle agglomeration is very rare, probably because of the large number of nucleation centers available on the surface of the polysiloxane-coated CNTs. This unique structure appears to provide a suitable support for many uniform platinum particles, thereby favoring the high performance of methanol oxidation, as discussed below.

#### XRD analysis of Pt/Si–MWNT composites

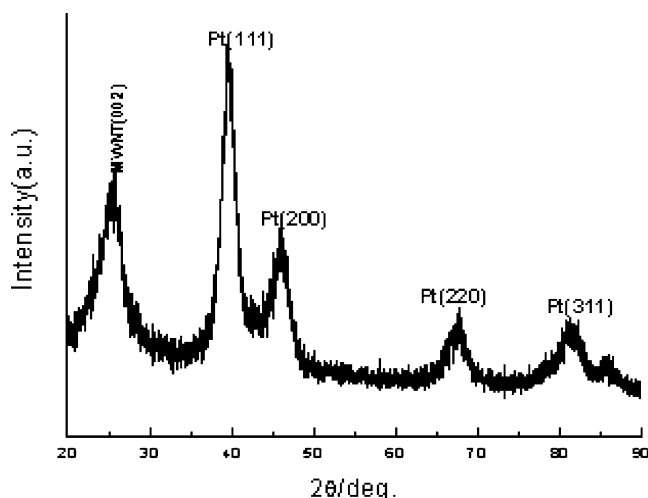
The XRD pattern of the finely ground Pt/Si–MWNT shows the characteristic peaks of MWNTs (about  $26.5^\circ$  and  $54.3^\circ$ ) and wide maxima corresponding to Pt (about  $40^\circ$ ,  $46.5^\circ$ ,  $67.5^\circ$ , and  $82^\circ$ ) with a face-centered cubic structure shown in Fig. 2. The average particle size of Pt nanoparticles calculated from the broadening of the (220) diffraction peak using Scherrer's equation is about 3.6 nm, in good agreement with the mean particle size observed in the TEM micrograph.

#### Electrochemical properties of Pt/Si–MWNT composites

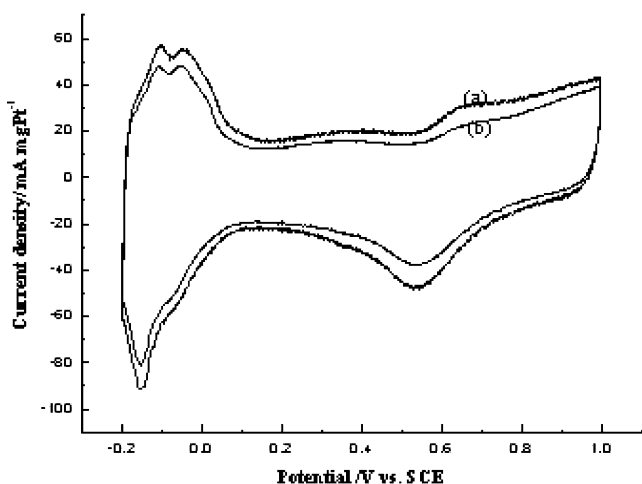
In general, the real surface area of Pt particles is one of the important parameters to determine the catalytic properties of electrocatalysts for methanol electrooxidation, as this reaction is surface-sensitive. The active specific surface area of Pt particles for Pt-based catalysts could be estimated from the hydrogen adsorption curves [21]. Figure 3 shows the cyclic voltammograms of Pt/Si–MWNT and Pt/MWNT catalysts in 1.0 M HClO<sub>4</sub> as an electrolytic solution at a scan rate of 50 mVs<sup>-1</sup> with N<sub>2</sub> purging. For the Pt/Si–MWNT, well-defined hydrogen adsorption/desorption peaks with a larger area compared to Pt/MWNT catalyst are

observed in the potential region  $-0.2$  to  $0.1$  V, demonstrating the higher surface area of the catalyst. The high surface area may be owing to the disentanglement of the MWNT ropes when treated with 3-APTES solution. On the other hand, the presence of functional groups, such as  $-\text{NH}_2$ , on the surface of the Si–MWNTs is advantageous for Pt nanoparticles to deposit on the surface of the MWNTs. The average size of platinum particle, H adsorption charges, and specific surface area for Pt/Si–MWNTs and Pt/MWNTs were listed in Table 1.

The electrocatalytic activity of the Pt/Si–MWNTs toward the oxidation of methanol was tested, and the results were compared with Pt/MWNT catalysts. The measurements were carried out in a 1 M HClO<sub>4</sub> aqueous solution containing 1.0 M methanol. Figure 4 shows the voltammetry curves of samples in 1 M HClO<sub>4</sub> containing 1 M CH<sub>3</sub>OH. Although all samples show catalytic activities toward methanol oxidation, the peak currents' density catalyzed by the Pt/Si–MWNTs are much larger than those



**Fig. 2** Powder XRD pattern of Pt/Si–MWNT composites



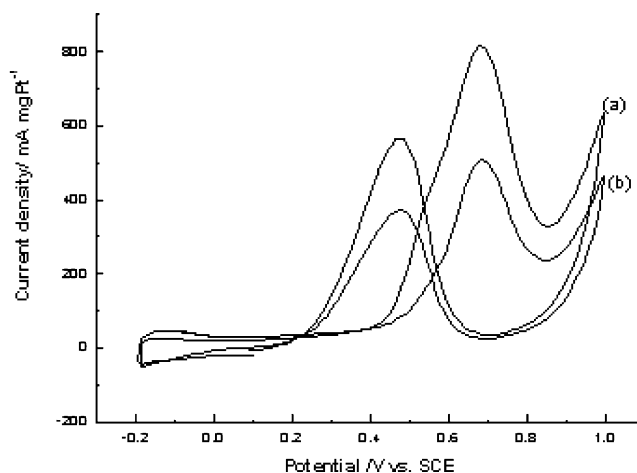
**Fig. 3** Cyclic voltammetry curves of (a) Pt/Si-MWNT and (b) Pt/MWNT catalysts in 1 M HClO<sub>4</sub> solution, 50 mV s<sup>-1</sup>

for Pt catalyst. The appearance of a prominent symmetric anodic peak around 0.76 V in the forward scan ( $I_f$ ) resembles the methanol electro-oxidation. In the reverse scan, the removal of the incompletely oxidized carbonaceous species formed in the forward scan promotes the appearance of an asymmetric anodic peak ( $I_b$ ) at 0.62 V. The ratio of the forward anodic peak current density to the reverse of the anodic peak current density ( $I_f/I_b$ ) has been used to describe the catalyst tolerance to carbonaceous species accumulation [22]. In our experiments, the ratio of peak current density ( $I_f/I_b$ ) was estimated to be about 1.8 for the Pt/Si-MWNT catalyst, even higher than the value of 1.1 for the Pt/MWNT catalysts, implying that the Pt/Si-MWNT catalyst had the least carbonaceous accumulation and, hence, more “tolerant” toward CO poisoning. This can be attributed to the high dispersion of platinum catalysts and effective functionalization of MWNTs.

The above results demonstrate several important points. Firstly, they demonstrate that the use of a molecular functionalization layer can greatly enhance the nucleation of nanocrystalline metals onto carbon nanotubes by providing large numbers of ammonium groups on the surface. Secondly, they show that the molecular layers do not necessarily act as blocking layers for electron transport, with the result that electron-transfer reactions to redox species in solution and the adsorbed nanoparticles are facile. Finally, they demonstrate that nanocrystalline metals

**Table 1** Comparison of the as-prepared Pt/Si-MWNT and Pt/MWNT catalysts in terms of the average particle size, H adsorption charges, and specific surface area

Catalyst	Weight percent Pt (mg)	$d$ (nm)	$Q_H$ (mC/mg)	$S_s$ (cm <sup>2</sup> /mg)
Pt/Si-MWNT	19.8	3.2	116.0	551
Pt/MWNT	20.1	4.8	109.4	514



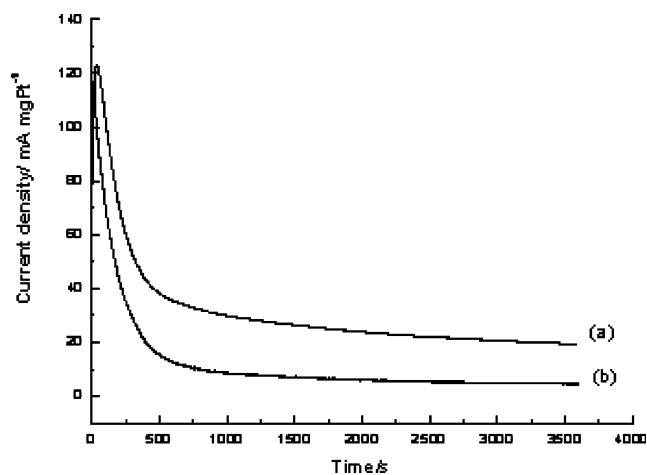
**Fig. 4** Cyclic voltammetry curves of (a) Pt/Si-MWNT and Pt/MWNT catalysts in 1 M HClO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution, 50 mV s<sup>-1</sup>

deposited onto the molecular layers exhibit excellent electrocatalytic activity, as evidenced by their ability to facilitate the methanol oxidation reaction.

To test the stability of the as-prepared catalysts, the chronoamperometry curves were recorded at the oxidation potential of 0.45 V for 3,600 s as shown in Fig. 5. The decay of current is in the similar model for two catalysts during the process going; however, the methanol oxidation current at the electrode of Pt/Si-MWNT is found to be kept to the highest in the whole process. The result shows that Pt/Si-MWNT is much more efficient than pure Pt/MWNT [23], which is consistent with the CV results.

## Conclusion

We developed a novel approach to synthesize Pt/Si-MWNT composite by nocovalent Si-MWNT surface within



**Fig. 5** Plot of specific current vs. time of the as-prepared catalysts (a) Pt/Si-MWNT and Pt/MWNT (b), recorded at the oxidation potential of 0.45 V in 1 M HClO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution

polysiloxane with amino group outside. TEM studies show that well-dispersed spherical particles were anchored onto the external walls of Si–MWNTs, and the size range of these particles was about 2–5 nm. Functionalization of multiwalled carbon nanotubes with molecules that expose ammonium groups greatly enhances the nucleation of electrocatalytically active Pt nanoparticles to the MWNT surfaces. The ability to enhance the nucleation of Pt nanoparticles without inhibiting the electrocatalytic activity is significant because it suggests that this approach may be applicable to a wide range of electrocatalytic problems. The ability to use molecular monolayers to tune the chemical properties of the carbon nanotubes without impeding the electron-transport properties opens a range of opportunities for formation of new types of catalytically active hybrid nanostructures.

**Acknowledgment** This project was supported by Qufu Normal University.

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