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Synthesis of highly dispersed platinum nanoparticles on multiwalled carbon nanotubes and their electrocatalytic activity toward hydrogen peroxide

Jing Zhang, Lian Gao*

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China

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ABSTRACT

Multiwalled carbon nanotubes were successfully coated with Pt nanoparticles through NH_3 gas pretreatment. Pt with particle size distribution of 1–4 nm was highly dispersed on carbon nanotubes. Cyclic voltammetry of ferrocyanide system was used to characterize the real electroactive surface area of platinum nanoparticle–multiwalled carbon nanotube (PtNP–MWCNT) coated glassy carbon electrode, and cyclic voltammetry for the PtNP–MWCNT coated electrode toward detecting H_2O_2 was measured to characterize the electrocatalytic property of the composite. Our results showed that the electroactive surface area of PtNP–MWCNT was higher than those of pristine multiwalled carbon nanotubes and Pt nanoparticles, and the composite exhibited the best electrocatalytic property for H_2O_2.

1. Introduction

Carbon nanotubes (CNTs) exhibit unique mechanical, electrical and electrochemical properties, which have gained great interest for the application of CNTs in biosensors. Due to their good electronic conductivity and biocompatibility, CNTs have been applied in many amperometric enzyme biosensors, such as glucose [1], cholesterol [2], and myoglobin [3] biosensors. In addition, owing to their fast electron-transfer ability, CNTs demonstrate electrocatalytic activities toward many molecules like H_2O_2 [4], β-nicotinamide adenine dinucleotide [5], and dopamine [6]. The good electrocatalytic properties of CNTs and their good biocompatibility provide great potential for fabricating excellent amperometric biosensors.

On the other hand, transition metal nanoparticles like gold [7], platinum [8], palladium [9], copper [10], nickel [11] and their binary [12–18] or ternary metals [14,19–21] are widely used to enhance the performances of electrodes because of their high catalytic activity. Particularly, Pt nanoparticles (PtNPs) are demonstrated to lower the H_2O_2 oxidation/reduction overvoltage efficiently [22–25], which is very important for biosensors to avoid interference from other co-oxidable substances like ascorbic acid and acetaminophen. However, aggregation of PtNPs often makes such electrodes prone to poisoning or corrosion, and prohibits their applications [26].

Therefore, compositing CNTs and PtNPs have gained growing interest for utilization in amperometric enzyme biosensors, because H_2O_2 is released during the oxidase-based enzyme reaction [27]. CNTs, not only act as a support material to avoid the aggregation of PtNPs, but also combine both of their advantages to possess special properties (huge surface area, enhanced catalytic activity, and good biocompatibility) [28]. As a result, the platinum nanoparticle–carbon nanotube (PtNP–CNT) composite modified electrodes are usually used to fabricate amperometric enzyme biosensors.

According to previous literatures, some researchers fabricate PtNP–CNT composite modified electrodes via physisorbing presynthesized PtNPs on CNTs [29], or via electrodeposition of PtNPs from Pt salt solution on CNTs [27,28]. However, physisorbed PtNPs are easily removed by agitating the composite in liquid and then formed Pt agglomeration [30–32], and electrodeposition of PtNPs is possibly concurrent reduction of H^+ [33]. More researchers prone to synthesize PtNP–CNT composite via chemical reduction, and then modify the electrode to investigate their biosensing properties [2,34,35]. Acid treatment is a common pretreating method to generate acid groups on CNTs so that PtNPs are easy to be linked onto CNTs. For example, Shi et al. [2] prepared PtNP–CNT by pretreating CNTs in HNO_3 and applied the composite in cholesterol biosensors. Xie et al. [35] synthesized PtNP–CNT by pretreating CNTs in the mixture of nitric acid and sulfuric and applied in an amperometric glucose biosensor. However, it is found to be difficult to control the particle size and dispersion of PtNPs on CNTs surface by acid pretreatment [36]. Besides, acid treatment usually leads to structural damage of CNTs and loss of electron conductivity [37]. Yang et al. [38] demonstrated a new method (ultrasonic oxi-

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[*] Corresponding author. Tel.: +86 21 52412718; fax: +86 21 52413122.
E-mail address: liangao@mail.sic.ac.cn (L. Gao).

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dation) to pretreat CNTs, however, ultrasonic can make MWCNTs short out, which may influence the electrocatalytic properties of the composite. Other approaches like functionalizing CNTs with surfactants [39] or polymers, dispersing CNTs in dimethylformamide [40], and depositing Pt using water-in-supercritical CO_2 microemulsion [41] are also reported. However, preparing well-dispersed PtNPs on CNTs is still a challenge. Therefore, it is necessary to explore new ways for pretreating CNTs so that PtNPs coat CNTs with uniform size and good dispersion.

In our previous work, the titania-carbon nanotube [42] and gold-carbon nanotube composites were successfully fabricated through pretreating CNTs in NH_3 gas. Compared with wet chemical treatments to CNTs, NH_3 treatment may be more convenient and introduce no impurities [43]. In this paper, we report a successful method for fabricating the Pt nanoparticle–multiwalled carbon nanotube (PtNP–MWCNT) composite through pretreating MWCNTs in NH_3 gas, and modify the composite on the glassy carbon (GC) electrode to detect H_2O_2.

2. Experimental

2.1. Chemicals

MWCNTs, prepared by chemical vapor deposition (CVD), were obtained from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). Hexachloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$), sodium citrate ($Na_3C_6H_5O_7·2H_2O$), potassium hexacyanoferrate (II) trihydrate ($K_4[Fe(CN)_6]·3H_2O$) and potassium chloride (KCl) with analytical grade were used. A phosphate buffer (0.1 M, pH 7.0) was made by mixing $K_2HPO_4·3H_2O$ and KH_2PO_4 aqueous solution in an appropriate proportion.

2.2. Preparation of PtNP–MWCNT and the modified electrodes

NH_3 gas pretreated MWCNTs (denoted as NH_3-MWCNTs) were obtained by heating pristine MWCNTs at 600 °C for 3 h under NH_3 atmosphere (>99%, 1 l/min). Then 0.01 g NH_3-MWCNTs was immersed into 100 ml of 0.6 mM sodium citrate aqueous solution by ultrasonication. After filtration and drying, MWCNTs coated with sodium citrate were obtained. Ten milliliters of 2 mM H_2PtCl_6, 90 ml of CH_3OH, and the sodium citrate-coated MWCNTs were refluxed in an oil bath at 80 °C for 90 min to get the PtNP–MWCNT composite. PtNPs were also synthesized by refluxing the mixture of 100 ml of 0.6 mM sodium citrate aqueous solution, 10 ml of 2 mM H_2PtCl_6 and 90 ml of CH_3OH in an oil bath at 80 °C for 90 min.

For preparing modified electrodes, a 0.5 wt.% Nafion solution was firstly prepared by diluting the 5 wt.% Nafion solution with phosphate buffer (0.1 M, pH 7.0). Then, 2 mg of PtNP–MWCNT, pristine MWCNTs and PtNPs were dispersed in 1 ml of 0.5 wt.% Nafion solutions by ultrasonication for 4 h. Finally, a 20 μL aliquot of the above solution was dropped onto the GC electrode, and allowed to dry at room temperature.

2.3. Characterization

The morphology of MWCNTs, PtNPs, and PtNP–MWCNT was characterized by the transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan). The size distribution of PtNPs on MWCNTs was obtained by measuring about 300 nanoparticles. The Pt content in the composite was determined by energy dispersive spectrometer (EDS, INCA Energy, Oxford Instruments, UK) and electron probe X-ray microanalyser (EPMA-8705QH_2, Shimadzu, Japan). Images of the PtNP–MWCNT composite were taken on a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan). The electrochemical experiments were conducted using the advanced electrochemical system (PARSTAT 2273, Princeton Applied Research Co., Ltd., USA). A three electrode configuration was employed with a cell volume of 15 ml, PtNP–MWCNT, pristine MWCNTs or PtNPs modified GC electrode (3 mm diameter, CHI104) as a working electrode, an Ag/AgCl reference electrode (CHI111), and a platinum wire counter electrode (CHI115). The GC electrode was polished with 1, 0.3, and 0.05 μm alumina polishing slurry each time before use.

3. Results and discussion

Fig. 1(A) shows the TEM image of pristine MWCNTs. As claimed by the producer, MWCNTs have lengths of 5–15 μm, diameters of 20–40 nm, and a purity of more than 95%. The TEM image of the synthesized PtNPs is shown in Fig. 1(B), and it is observed that every small Pt nanoparticle is highly crystalline. However, the lattice fringes of all the PtNPs are random, and the dispersibility of PtNPs is not good.

Fig. 2(A) and (B) displays the TEM images of PtNP–MWCNT. PtNPs coat MWCNTs uniformly, and almost no Pt agglomerates are observed. From EDS measurement (not shown), the Pt content of the PtNP–MWCNT is about 26 wt.%, which approximately agrees with the composition in the starting mixture (28 wt.%). It means that almost all the PtNPs deposit on MWCNTs. TEM images in high resolution (Fig. 2(C) and (D)) reveal that every small Pt nanoparticle coating on MWCNTs is highly crystalline and the lattice fringes of all the PtNPs are also random. However, the aggregation of PtNPs is avoided because MWCNTs act as a support material. Fig. 2(E) shows that the PtNP–MWCNT has narrow PtNPs size distributions with average diameter of about 1.9 nm. Most of the PtNPs are in the range of 1–3 nm, with a few particles larger than 4 nm. To verify the uniformity of PtNPs deposited on MWCNTs, SEM images of PtNP–MWCNT are provided in Fig. 3. It is observed that almost all MWCNTs are coated with small PtNPs, and the dispersion of PtNPs on each MWCNT is uniform.

Such small PtNPs and good dispersion on MWCNTs are attributed to the following. Firstly, sodium citrate acts as a stabilizer to prevent PtNPs from aggregating, according to Lin et al. [44]. Negatively charged citrate ions adsorb onto Pt via electrostatic interaction, resulting in the electrostatic repulsion between Pt particles [44]. Secondly, according to many fundamental researches on the surface chemistry of activated carbon [45,46] and our previous studies [42,43], NH_3 treatment is able to remove part of the negatively charged acid oxygen-containing functional groups,

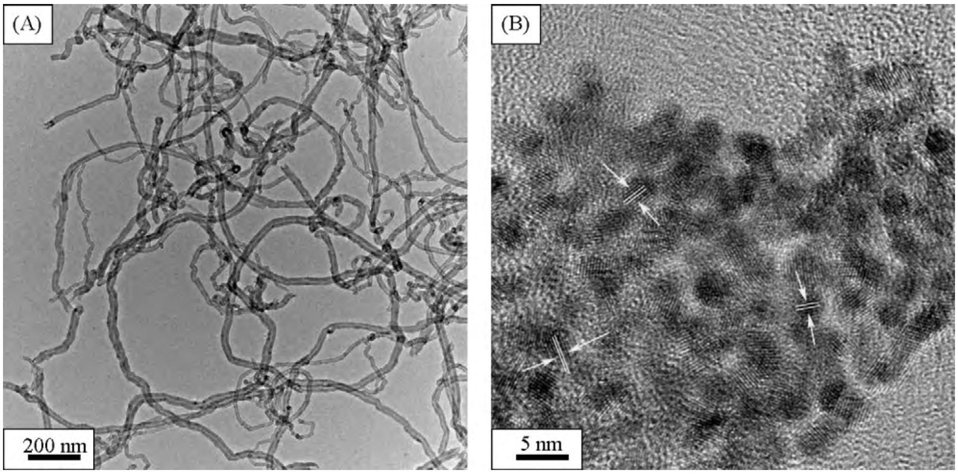

Fig. 1. TEM images of (A) pristine MWCNTs and (B) PtNPs.

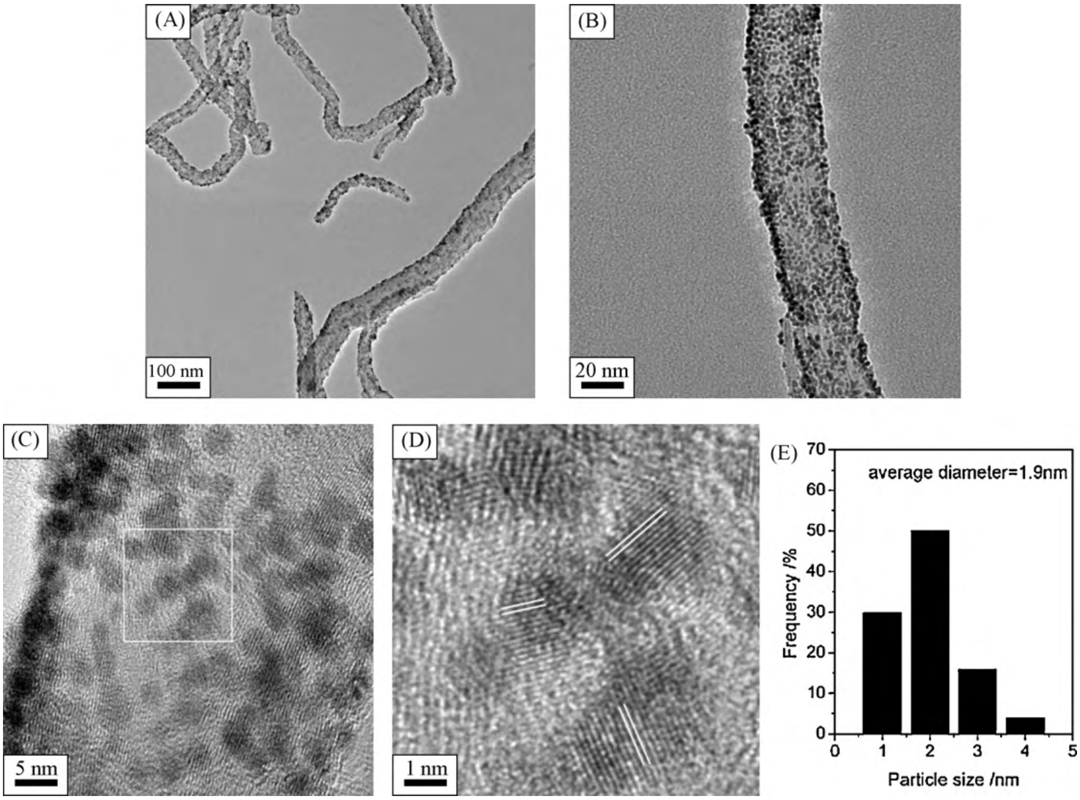

Fig. 2. (A and B) TEM images of PtNP–MWCNT, (C) high resolution TEM image of PtNP–MWCNT, (D) magnification of the square area in (C), and (E) PtNPs size distribution of PtNP–MWCNT.

and introduce positively charged nitrogen-containing groups onto MWCNTs. When sodium citrate is mixed with NH_3-MWCNTs, the negatively charged citrate ions firstly adsorb onto the positively charged nitrogen-containing groups on NH_3-MWCNTs by electrostatic attraction [43]. Then H_2PtCl_6 and CH_3OH react with citrate-coated MWCNTs. Since NH_3 pretreatment makes most part of NH_3-MWCNTs have positively charged groups, negatively charged citrate which acts as a stabilizer is easy to coat on the sidewall of MWCNTs uniformly. As a result, PtNPs with small sizes are uniformly reduced by CH_3OH onto the sidewall of MWCNTs. For MWCNTs pretreated by acid method, there are lots of negatively charged oxygen-containing groups, which are easily repulsed with negatively charged citrate ions. Thus, the citrate coatings on MWCNTs are not as uniform as those on NH_3-MWCNTs. As a result, the PtNPs are easily aggregated on the side wall of MWCNTs. Therefore, NH_3 pretreatment to MWCNTs is an effective way for fabricating highly dispersed PtNPs on MWCNTs.

Cyclic voltammetry (CV) of ferrocyanide system is a common method to characterize the real electroactive surface area of the modified electrode [30,31,35]. Fig. 4 shows the steady-state CV (third cycle recorded) in 20 mM $Fe(CN)_6{}^{4-}$ and 0.2 M KCl for PtNP–MWCNT, pristine MWCNTs and PtNPs modified electrodes at 20 mV s^{-1}. The well-defined oxidation and reduction peaks are due to the Fe^{3+}/Fe^{2+} redox couple. The electroactive surface area can be estimated according to the Randles-Sevcik equation [47].

$$I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} \gamma^{1/2} C$$

In our case, D (the diffusion coefficient of the molecule in solution), n (the number of electrons participating in the redox reaction), γ (the potential scan rate), C (the concentration of the probe molecule in the bulk solution) are the same. The electroactive surface area A is directly proportional to the peak current value I_p. From Fig. 4, we find that the ratio of the peak current of PtNP–MWCNT and MWCNTs modified electrode is around 2.2, which means 120% more

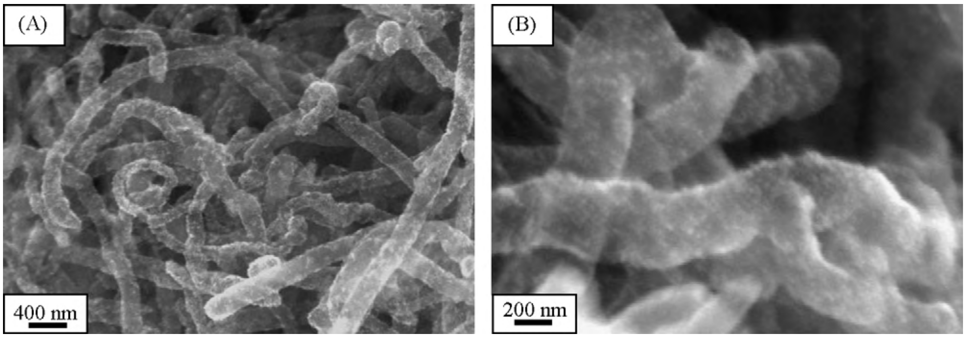

Fig. 3. (A and B) SEM images of PtNP–MWCNT.

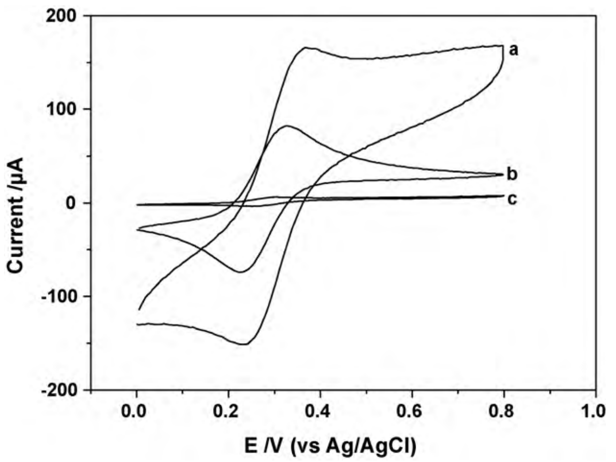

Fig. 4. Cyclic voltammograms (20 mV s^{-1}) in 20 mM $K_4[Fe(CN)_6]$ and 0.2 M KCl at GC electrodes modified with (a) PtNP–MWCNT, (b) pristine MWCNTs, (c) PtNPs dispersed in 0.5 wt.% Nafion solution.

electroactive surface area are achieved after PtNPs decorating on MWCNTs. For PtNPs modified electrode, the electroactive surface area is small, which may be due to the aggregation of PtNPs.

According to Yang et al. [30], excellent electrocatalytic activity of the electrode toward H_2O_2 implies that the electrode is able to provide a good signal transduction in fabricating amperometric enzyme biosensors, because H_2O_2 is the product of oxidase-based enzyme reactions. Therefore, the electrocatalytic activity of PtNP–MWCNT, pristine MWCNTs and PtNPs modified GC electrodes for detecting H_2O_2 is investigated and the CV (third cycle) is shown in Fig. 5. For the pristine MWCNTs and PtNPs modified electrodes, current responses are small with higher oxidation/reduction potentials. For the PtNP–MWCNT composite modified electrode, largely increased current signals with lower oxidation/reduction overvoltage are observed, which means that PtNP–MWCNT exhibits the best electrocatalytic activity toward H_2O_2. The good electrocatalytic property of PtNP–MWCNT is attributed to three reasons. Firstly, the excellent electron-transfer ability of MWCNTs improves the electrocatalytic activity of PtNPs. Secondly, the composite with small PtNPs highly dispersed on MWCNTs avoids the aggregation of PtNPs and furthermore avoids the electrode poisoning. Thirdly, the PtNP–MWCNT modified electrode exhibits the highest electroactive surface area, which is important for the electrocatalytic properties of PtNP–MWCNT toward H_2O_2. Therefore, the PtNP–MWCNT composite displays better electrocatalytic activity toward H_2O_2 than those of pristine MWCNTs and PtNPs.

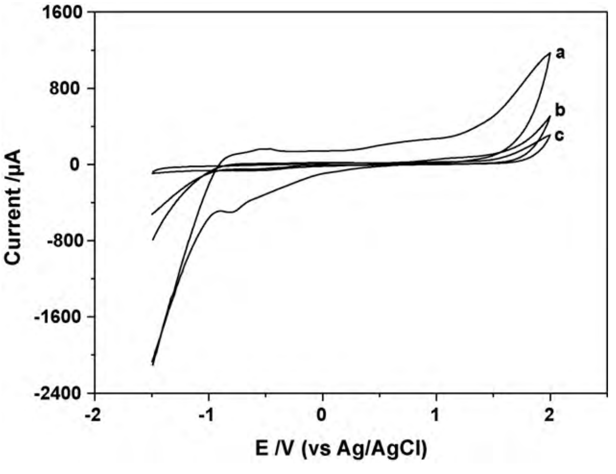

Fig. 5. Cyclic voltammograms (50 mV s^{-1}) for 5 mM H_2O_2 in phosphate buffer (pH 7.0) at GC electrodes modified with (a) PtNP–MWCNT, (b) pristine MWCNTs, (c) PtNPs dispersed in 0.5 wt.% Nafion solution.

4. Conclusions

We have demonstrated an easy strategy to attach PtNPs onto MWCNTs through pretreating MWCNTs in NH_3 gas. Highly dispersed PtNPs on MWCNTs with small particle size (average size is 1.9 nm) and higher electroactive surface area was successfully fabricated. The composite exhibited better electrocatalytic activity toward H_2O_2 than those of pristine MWCNTs and PtNPs. This kind of PtNP–MWCNT composite is potentially useful in amperometric enzyme biosensors.

Acknowledgments

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