

Electrodeposited Platinum Nanoparticles on the Multi-Walled Carbon Nanotubes and its Electrocatalytic for Nitric Oxide

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Received: 17 March 2008 / Accepted: 27 March 2008 / Online published: 20 April 2008

The present work describes a new approach to directly electrodeposit platinum nanoparticles on the surface of multi-walled carbon nanotubes (MWNTs) through cyclic potential scanning technique and to prepare a novel carbon nanotubes including platinum nanoparticles modified electrode (noted as Pt/MWNTs). TEM image shows that Pt nanoparticles are attached on the out surface of the MWNTs with average particle size about 20 nm. The electrochemical behaviors of Pt/MWNTs electrode are characterized by cyclic voltammetry (CV) and the CV curves demonstrate the several well-known current features that are the same as that of a Pt film nano-size electrode. At the Pt/MWNTs modified electrode, an obvious electrocatalytic reduction peak of nitric oxide (NO) can be observed, which is at about -0.42V (vs. Ag/AgCl) and the reduction peak current is proportional linearly to the NO concentration. The potential application of the Pt/MWNTs modified electrode as a NO sensor was also investigated in terms of its dose-response curve and stability.

Keywords: Platinum nanoparticles, Multi-walled carbon nanotubes, Electrodeposition, Electrocatalytic reduction, Nitric oxide

1. INTRODUCTION

As known, the physical properties of nanoparticles, which depend strongly on the perturbations of the large fraction of atoms on the particle surface, may differ markedly from that of the bulk solid state [1,2]. Metals with nanostructures, especially noble metal nanoparticles including platinum, palladium, gold and silver etc, are of considerable interest for their applications in catalysis, batteries, fuel cells, capacitors and sensors [3-5]. Recently, they have been used vastly in the fields of electroanalytical chemistry and biosensor [6-8]. However, it is difficult to directly use metal nanoparticle as electrode. So, various approaches including self-assembly [9], grafting reaction [10],

electrophoresis [11] etc, were developed to immobilize metal nanoparticles on the surface of supported electrode. In these immobilization processes, the metal nanoparticles, generally come from a colloidal system, were usually modified or functionalized by organic ligands, which would affect the surface properties of nanoparticle. A significant motivation is the need to directly yield metal nanoparticles on the supported electrode surface.

On the other hand, the previous researches showed that the supported substrates play a significant role because it not only enhances the mechanical and thermal stability of metal nanoparticles but also maintains them in a highly dispersed state [12, 13]. In addition, to meet the requirement of transfer electron for electrochemical application, the idea of supported substrate should be an electrical conductivity.

Due to unique nanostructure, unusual geometry, electrical conductivity, and mechanical and chemical stability, carbon nanotubes had attracted much attention since its discovery in 1991 [14]. Recent studies revealed that carbon nanotubes could act as new supported substrates for metal catalysts and form new reinforced metal/nanotubes composites. Previous approaches to yield metal nanoparticles on carbon nanotubes include physical evaporation [15, 16], solid-state reaction with metal salts at elevated temperature [17], electroless deposition from salt solutions [18, 19]. In this communication, we report a new approach to directly electrodeposit platinum nanoparticles on the surface of multi-walled carbon nanotubes (MWNTs) through cyclic potential scanning technique and to prepare a novel carbon nanotubes including platinum nanoparticles modified electrode (noted as Pt/MWNTs). The Pt/MWNTs electrode shows a strong electrocatalytic activity for the reduction of nitric oxide (NO).

2. EXPERIMENTAL PART

2.1. Apparatus and chemicals

Electrochemical experiments were performed with CHI 660 electrochemical analyzer (CHI, USA) with a conventional three-electrode cell. The working electrode was a nano-Pt/MWNTs modified GC electrode. An Ag/AgCl reference electrode and a platinum electrode were used as the reference and the auxiliary electrode, respectively. The transmission electron microscopy (TEM) micrographs were taken using an H-600 (Hitachi, Japan) transmission electron microscope. The nano-Pt/MWNTs or MWNTs including H_2PtCl_6 (noted as $\text{H}_2\text{PtCl}_6/\text{MWNTs}$) samples were dispersed firstly in an acetone by aids of ultrasonic agitation and then a droplet of sample solution was dropped to a standard Cu grid covered with a carbon film.

The MWNTs were produced by thermal catalytic decomposition of hydrocarbon [20] and the purity is more than 95%. The MWNTs sample was further purified with a mixed acid solution including HClO_4 and HNO_3 ($v/v = 3:7$) before used. Saturated NO solutions were prepared as the previous literature [21]. Aliquots of this saturated solution were used to prepare serial solutions of known NO concentration, using a value of 1.9×10^{-3} mol/l for its concentration at saturation [22]. Other chemicals were of analytical reagent grade. All the solutions were prepared with triply distilled water.

Prior to electrochemical experiments, the solution was deaerated with high purity nitrogen. All experiments were carried out at room temperature.

2.2. Electrodeposition of Pt nanoparticles on MWNTs

4mg MWNTs were evaporated under vacuum conditions prior to use. The evaporated MWNTs were then mixed with 1.5ml H_2PtCl_6 (1.6mg/ml) with the aid of ultrasonic agitation for about 10 min. At last, the dispersed solution was evaporated under the vacuum condition for 20 min. The sample was noted as $\text{H}_2\text{PtCl}_6/\text{MWNTs}$.

2.0 milligrams of $\text{H}_2\text{PtCl}_6/\text{MWNTs}$ were dispersed in 4 ml acetone to give a 0.5 mg/ml black solution. The glassy carbon (GC) electrode (BAS, $\Phi=3\text{mm}$) was firstly polished with an alumina slurry and washed successively with triply distilled water and ethanol in an ultrasonic bath, then 15 cyclic scans were carried out in the potential range of 2.0 to -2.0V (vs. SCE) in the solution of 1.0 mol/l H_2SO_4 . 10 μl suspension of the $\text{H}_2\text{PtCl}_6/\text{MWNTs}$ (0.5 mg/ml) was cast on the surface of the GC electrode and dried in air. Then the electrode was transferred to the electrochemical cell containing NaOH solution (pH 10.0). 55 cyclic scans were carried out in the potential range between 1.1 to -0.5 V (vs. Ag/AgCl) with scan rate 50 mV/s until stable and reproducible voltammogram was obtained. After the end of scanning, the electrode was rinsed with water and acetone, and then dried in air. The sample on the surface of GC electrode can be taken off and characterized by TEM. On the other hand, after the end of scanning, the electrode can be directly used as a modified electrode to investigate its electrocatalytic activity. We noted this electrode as nano-Pt/MWNTs modified electrode.

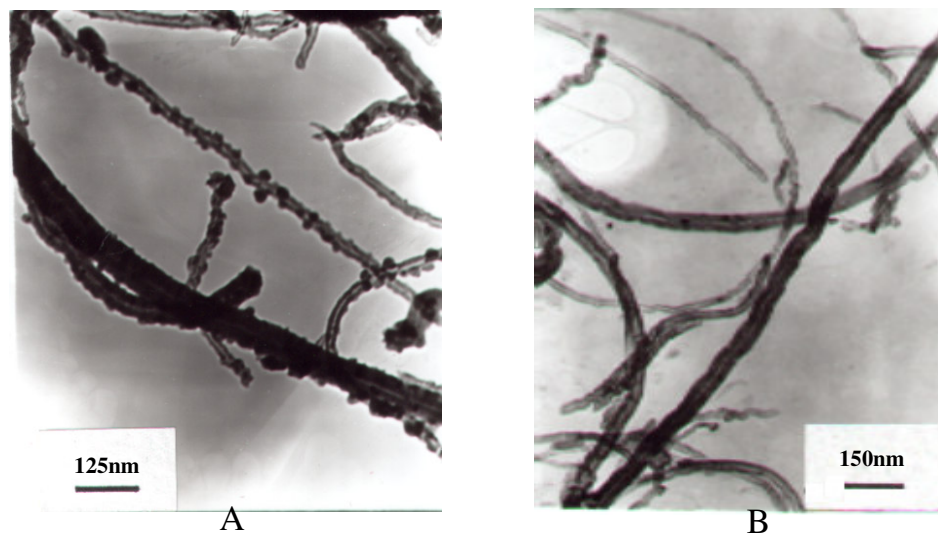


Figure 1. (A) TEM image of Pt nanoparticles adsorbed on the surface of MWNTs through direct electro-reduction. (B) TEM image of H_2PtCl_6 mixed with MWNTs.

3. RESULTS AND DISCUSSION

3.1. TEM characterization of Pt nanoparticle on MWNTs

Fig.1 shows the typical TEM images of nano-Pt/MWNTs and $\text{H}_2\text{PtCl}_6/\text{MWNTs}$. It can be observed from Fig.1A that all of Pt nanoparticles are attached on the out surface of the MWNTs. The average particle size of Pt nanoparticles is evaluated to be about 20 nm. In Fig.1B, no nanoparticles can be observed. Fig.1 suggests that H_2PtCl_6 adsorbed on MWNT surface can accept electron to be reduced into platinum and the platinum can aggregate to form a nanoparticle directly during cyclic potential scanning.

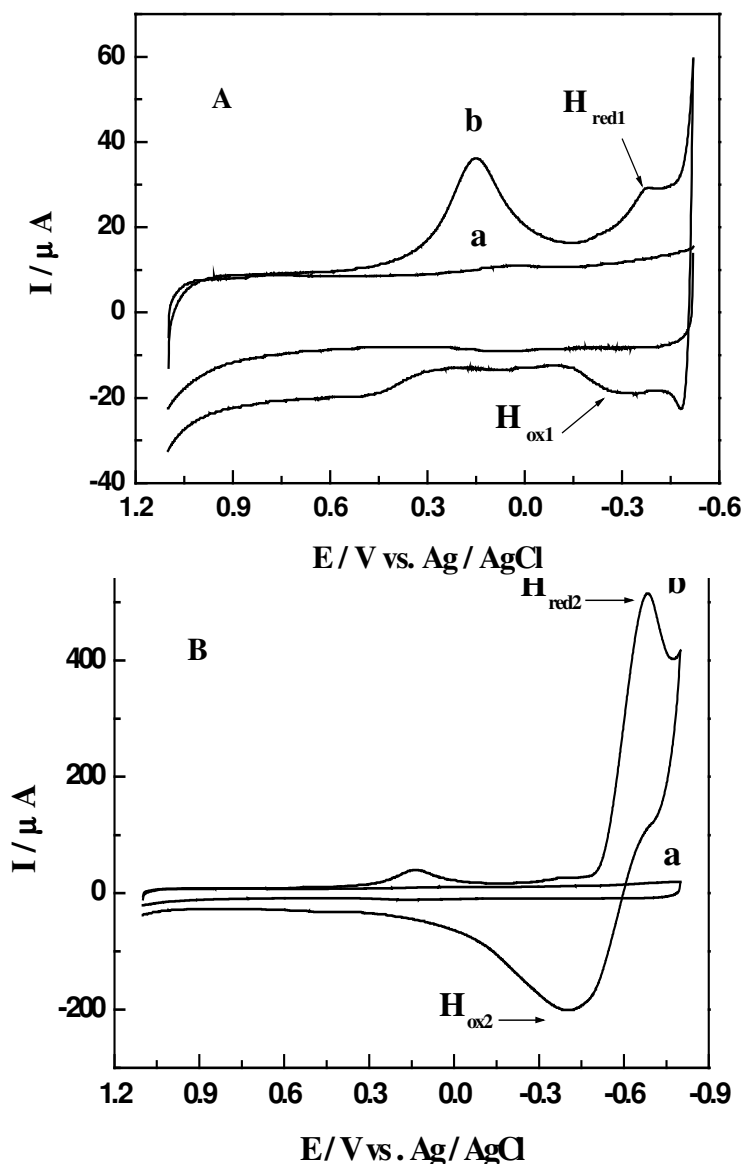


Figure 2. Cyclic voltammograms of a nano-Pt/MWNTs modified electrode (a) and a MWNTs modified electrode in 0.1 phosphate buffer aqueous solution (pH 7.0) with a scan rate of 50 mV/s. (A) potential range: 1.1~-0.5 V; (B) potential range: 1.1~-0.8 V.

3.2. Electrochemical behaviors of the nano-Pt/MWNTs modified electrode

Fig.2 including Fig.2A and Fig.2B shows cyclic voltammograms (CVs) of nano-Pt/MWNTs modified electrode in 0.1M phosphate buffer solution (pH 7.0). The difference between Fig.2A and Fig.2B is that their potential windows are different, while other conditions are the same. As can be seen, no obvious redox peak can be observed for a bare MWNTs modified electrode in whole scanning potential ranges. On the other hand, the CVs of nano-Pt/MWNTs modified electrode show several well-known current features that are the same as that of the nano-size Pt film on the liquid crystalline [3]. Obviously, three distinctive regions, the double layer region, the oxide region and the hydrogen region can be observed in Fig.2A and 2B (curve b). The double layer region lies between the hydrogen and the oxide regions. For the Pt/MWNTs electrode, the double layer region can be observed between -0.15 V and 0.35 V in the anodic scan and between -0.10 V and -0.15 V in the cathodic scan. The oxide region starts at 0.35 V in the anodic scan and finishes in the cathodic scan at -0.10 V. In oxide region, two main features can be observed: an extended oxidation peak in the anodic scan associated with oxygen adsorption above 0.35 V and a sharp reduction peak in the cathodic scan corresponding to oxygen stripping at 0.15 V. The hydrogen region starts at -0.15 V in the cathodic scan and finishes at -0.15 V in the anodic scan. Several features can be observed: firstly, in the cathodic scan, two reduction peaks were observed, the first one is at -0.384 V (H_{red1} in Fig.2A) and the second one is at -0.684 V (H_{red2} in Fig.2B). Secondly, in the anodic scan, two oxidation peaks at -0.290 V (H_{ox1} in Fig. 2A) and -0.400 V (H_{ox2} in Fig. 2B) were observed.

3.3. Electrocatalytic activity of nano-Pt/MWNTs modified electrode for the reduction of nitric oxide

The electrocatalytic activity of nano-Pt/MWNTs modified GC electrode for the reduction of NO in 0.1M phosphate buffer (pH 7.0) solution was investigated with cyclic voltammetry. Fig.3 shows the cyclic voltammograms of NO at the Pt/MWNT modified electrode. Fig.3a (dash line) is the CV curve of the bare MWNTs modified GC electrode in phosphate buffer solution (pH 7.0). Over the potential range from 1.1 to -0.54 V, no obvious redox peak was observed. While NO is added to the buffer solution, there is an obvious anodic peak to be observed at about 0.88 V (vs. Ag/AgCl) (as shown in Fig.3b), which peak corresponds to the electro-oxidation of NO on the surface of MWNT modified electrode [23]. However, no obvious reduction peak could be observed at the bare MWNTs modified electrode. Fig.3c is the CV curve of the nano-Pt/MWNTs electrode in the $40\mu\text{M}$ NO solution. An anodic peak still exists, but its peak potential shifts to positive negative direction about 20 mV, is at about 0.9 V. This peak is still corresponding to the electro-oxidation of NO on MWNTs. On the other hand, at the negative potential direction, a stronger cathodic peak appears at about -0.42 V (vs. Ag/AgCl), its potential is the same as that of the H_{red1} peak of nano-Pt/MWNT in phosphate buffer solution. Fig.4 shows the cyclic voltammograms of nano-Pt/MWNTs modified electrode in phosphate buffer solution containing different NO concentrations. With the addition of NO to electrochemical cell, an obvious increase of the cathodic peak at the location of the H_{red1} peak of nano-Pt/MWNTs and a decrease of the anodic peak at H_{ox1} peak are observed, which is corresponded to the characteristic of a typical electrochemically catalytic reaction [24]. This result suggests that the reduction of NO can be

catalyzed by Pt nanoparticles electrodeposited on the surface of MWNTs. Satsuma et al [25] had reported that NO can be catalytically reduced by hydrogen on the surface of a solid acidic oxide supported Pt catalyst. It is easy to understand why the reduction peak of NO can be observed at the location of H_{red1} . Fig.4b-4e shows that the reduction peak current of NO is proportional to the NO concentration linearly. From Fig.4, the anodic peak current at 0.9V, which corresponds to the oxidation of NO on the surface of MWNTs, is linearly proportional to the NO concentration, too. However, it is obvious that the reduction peak of NO shows a more sensitive response.

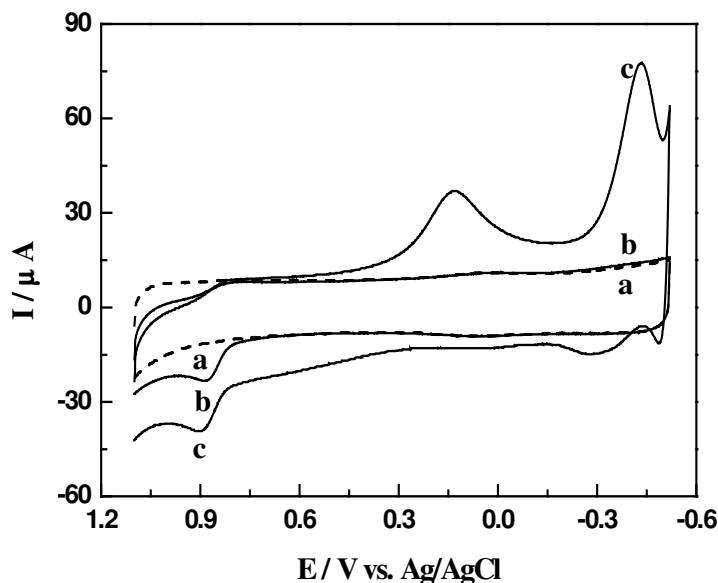


Figure 3. Cyclic voltammograms obtained in 0.1 phosphate buffer solution (pH 7.0) with a scan rate of 50 mV/s. (a) a bare MWNTs modified electrode without NO; (b) a bare MWNTs modified electrode with 40 μM NO; (c) a nano-Pt/MWNT modified electrode with 40 μM NO.

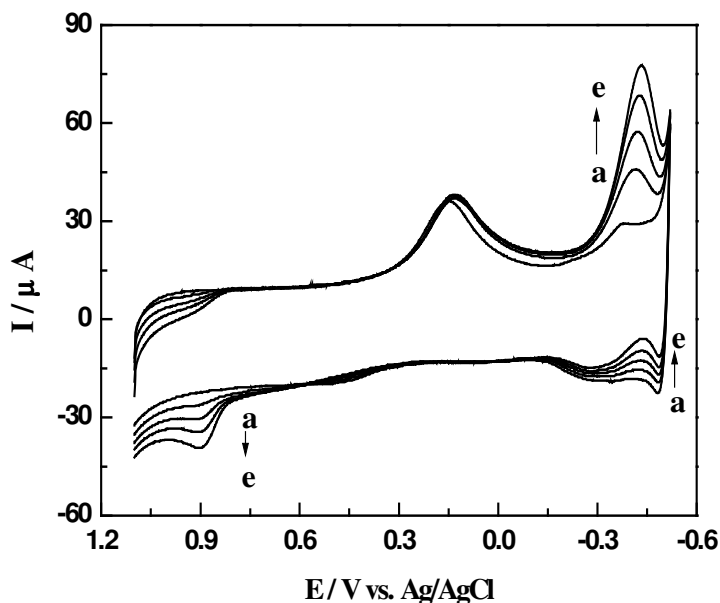


Figure 4. Cyclic voltammograms obtained in 0.1 phosphate buffer solution (pH 7.0) with a scan rate of 50 mV/s at a nano-Pt/MWNTs modified electrode. (a) 0; (b) 10; (c) 20; (d) 30; (e) 40 μM of NO

3.4. Detection of Nitric Oxide

In order to examine the response character of modified electrode to NO, we have undertaken the detection of NO in phosphate buffer solution with a constant potential voltammetry. Figure 5 shows a typical amperogram obtained at the modified electrode, which obviously showed an increase in measured currents with each addition of 4×10^{-7} mol/l of NO solution. According to this experiment, a linear relationship between peak currents and NO concentrations was obtained in a range of $4 \times 10^{-7} \sim 1 \times 10^{-4}$ mol/l with correlation coefficient $r = 0.997$. The response time (time for the signal increase from 10% to 75%) in the amperometric mode was less than 5s. The detection limit has been estimated to be 1×10^{-7} .

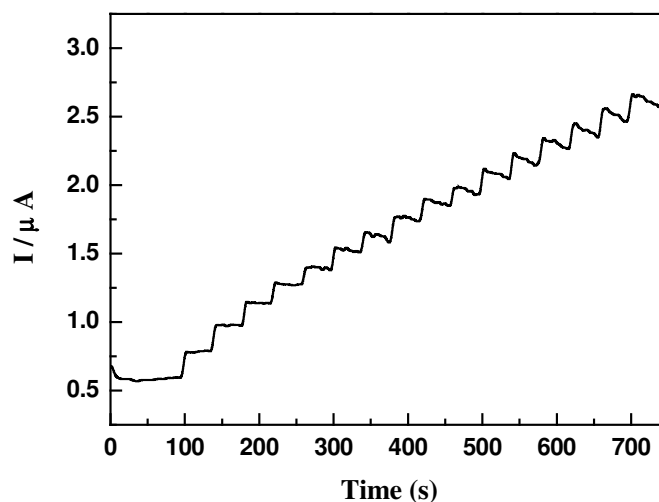


Figure 5. Amperometric detection of NO by modified electrode (alternating current was measured at constant potential of -0.42 V modulated with 50 mV pulse in time intervals of 0.5 s) in 0.1 mol/l phosphate buffer solution (pH 7.0), each addition of 4×10^{-7} mol/l NO.

Table 1. Dependence of the response current of NO reduction on the ratios of H_2PtCl_6 to MWNT

Ratio of H_2PtCl_6 to MWNTs (w/w)	Response Current* (μA)
0.08	10.5
0.1	14.7
0.2	20.5
0.4	30.4
0.6	37.6
0.8	36.9
1	36.5

*The current is obtained by cyclic voltammetry at the nano-Pt/MWNTs modified electrode in 0.1 M phosphate buffer solution (pH 7.0) containing $20 \mu M$ NO at room temperature.

3.5. Effects of the ration of H_2PtCl_6 to MWNTs

The effect of the ratio of H_2PtCl_6 to MWNTs on the reduction peak current of NO is also investigated. The results are listed in Table 1. While the ratio is too small, there is no electrochemical

response to be observed. With the ratio increasing, the catalytic current of NO reduction increases. This phenomenon indicates that H_2PtCl_6 plays a key role in promoting the reduction of NO. When the ratio is over 0.6, the response current trends to a steady value. Thus the ratio of 0.6 was selected for the above experiments.

3.6. Electrode Stability and Reproducibility

The stability of nano-Pt/MWNT modified electrode was also tested by measuring the CV peak currents after continuous scanning in the potential range from -0.54V to 1.1V with a 50 mV/s scan rate. As can be seen in Fig 6, the Pt/MWNTs is very stable after continuous 100 cycles, only 2 % decrease in peak current (curve b) was observed. If the as-prepared nano-Pt/MWNTs modified electrode was stored in 0.1 M phosphate buffer solution for 20 days, only 5% decrease in peak currents was observed (as shown in Fig.6c).

To characterize the reproducibility of the modified electrode, repetitive measurements were carried out in solutions containing $20\text{ }\mu\text{M}$ NO. The results of 10 successive measurements showed a relative standard deviation of 3.5 % for $20\text{ }\mu\text{M}$ NO, indicating that the reproducibility of the modified electrode was excellent.

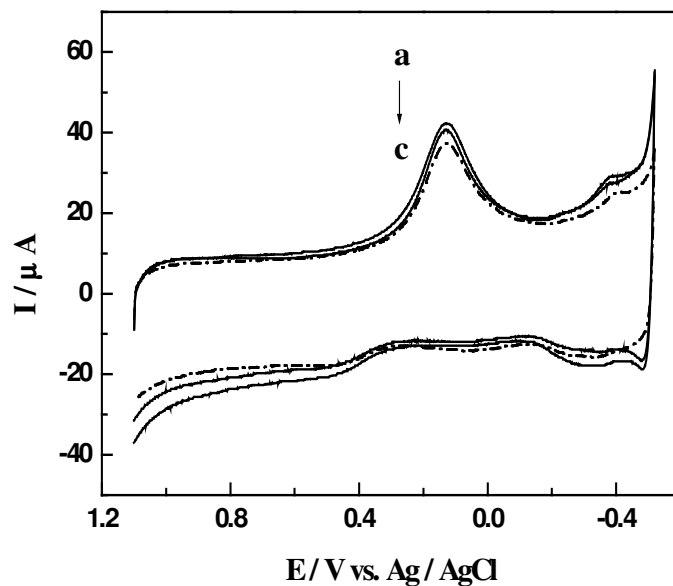


Figure 6. Cyclic voltammograms of a Pt/MWNT modified electrode in 0.1 phosphate buffer solution ($\text{pH } 7.0$) with a scan rate of 50 mV/s . (a) the first scan cycle, (b) after 100 continuous cycles, (c) after 20 days.

4. CONCLUSIONS

Pt nanoparticles can be electrodeposited directly on the surface of MWNTs by using a cyclic potential scanning technique to form a novel nano-Pt/MWNT modified electrode and as-prepared Pt nanoparticle shows a strong electrocatalytic activity for the reduction of nitric oxide. Compared with the bare MWNT modified electrode, Pt/MWNT modified electrode behaves a more sensitive response

for the reduction of NO and it can be developed into a sensor to directly determine the NO concentration in aqueous solution. On the other hand, the experimental results indicate that electrochemical method should be an effective approach to deposit metal nanoparticles on the surface of carbon nanotubes, which may help us to develop a new application for the preparation of carbon nanotubes-metal nanoparticles composite materials in biosensors.

ACKNOWLEDGEMENTS

We thank the National Natural Science Foundation (No. 20475002, No.20701002) and Young Teachers Program of Anhui Education Department (No. 2005jq1047).

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