

# Electrochemical deposition of platinum nanoparticles in multiwalled carbon nanotube–Nafion composite for methanol electrooxidation

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**Abstract** Platinum nanoparticles were successfully deposited within a multiwalled carbon nanotube (MWCNT)–Nafion matrix by a cyclic voltammetry method. A Pt(IV) complex was reduced to platinum nanoparticles on the surface of MWCNTs. The resulting Pt nanoparticles were characterized by scanning electron microscopy, transmission electron microscopy, and energy-dispersive X-ray spectroscopy. The Pt–MWCNT–Nafion nanocomposite film-modified glassy carbon electrode had a sharp hydrogen desorption peak at about  $-0.2$  V vs. Ag/AgCl (3 M) in a solution of 0.5 M  $\text{H}_2\text{SO}_4$ , which is directly related to the electrochemical activity of the Pt nanoparticles presented on the surface of MWCNTs. The electrocatalytic properties of the Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrode for methanol electrooxidation were investigated by cyclic voltammetry in a 2 M  $\text{CH}_3\text{OH}+1$  M  $\text{H}_2\text{SO}_4$  solution. In comparison with the Pt-coated glassy carbon electrode and the Pt–Nafion modified glassy carbon electrode, the Pt–MWCNT–Nafion-modified electrode had excellent electrocatalytic activity toward methanol electrooxidation. The stability of the Pt–MWCNT–Nafion nanocomposite-modified electrode had also been evaluated.

**Keywords** Multiwalled carbon nanotubes · Nafion · Platinum nanoparticles · Methanol

## Introduction

Methanol electrooxidation has attracted much attention for their potential applications in fuel cells. The advantages of a

direct methanol fuel cell are low operating temperature, the stability of methanol in an acidic medium, and the easy manufacturing of methanol. However, the sluggish kinetics of methanol oxidation at the anode that led to high overpotentials is one of the problems for practical application. Therefore, the use of noble metals to increase the electrocatalytic ability and generation of high-power density seems very attractive [1, 2]. Metal nanoparticles possess a large surface-to-volume ratio and a high catalytic efficiency. In particular, the use of Pt nanoparticles is proven to be very useful for the enhancement of the electrochemical oxidation of methanol. Pt is a well-known catalyst that has a high catalytic activity for methanol electrooxidation in an acid medium [3]. Many factors can affect the electrocatalytic activity of platinum particles toward electrochemical oxidation of methanol, for example, particles size and distribution [4, 5] and preparation methods [6, 7]. Several methods have been developed to prepare Pt nanoparticles. The strategies of synthesis can be roughly classified as electrochemical deposition [8] or solution-phase reduction [9]. The electrochemical synthesis of Pt nanoparticles on the surface of carbon nanotubes (CNTs) has been reported [10]. The complexes of Pt(IV), precursors of Pt nanoparticles, were converted to Pt nanoparticles by a potentiostatic method in sulfuric acid aqueous solutions.

CNTs have attracted much attention because of their unique chemical, electronic, and mechanical properties. The deposition of Pt nanoparticles within a CNT–Nafion composite for a wide range of sensing applications has been reported in the literature [11–18]. Recently, CNTs have been considered as a promising material for catalyst support in electrocatalysis and fuel cells because of their high chemical stability, good electrical conductivity, and tubular structure [19, 20]. The applications of CNTs in fuel cells as a catalyst support and electrode materials have been reported [21–23]. The Pt nanoparticles can be decorated on

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the surface of CNTs by the ways of chemical reduction [24, 25], supercritical carbon dioxide [26], pyrolysis process [27], and electrochemical reduction [28, 29]. Among these methodologies, the one-step electrochemical method is considered as an effective procedure for the preparation of Pt nanoparticles on the surface of CNTs when compared with others that are time consuming and where the impurity might be involved during the process [3]. The electrodeposition of Pt nanoparticles on CNTs offers a high purity of deposits and a simple procedure for deposition [30].

The aim of this work is to investigate the electrodeposition of Pt nanoparticles within multiwalled CNT (MWCNT)–Nafion nanocomposite film to improve the electrocatalytic ability toward the electrochemical oxidation of methanol. MWCNTs act as efficient conduits for electrons. Nafion, a perfluorinated sulfonated cation exchanger, is a polymeric binder and acts as the backbone. Pt nanoparticles act as the catalyst to facilitate the methanol electrooxidation. The preparation of the Pt–MWCNT–Nafion nanocomposite and the electrocatalytic activity of the Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrode for the electrochemical oxidation of methanol are presented and discussed.

## Materials and methods

### Reagents

Potassium hexachloroplatinate (IV) was obtained from Arcos. Nafion (5 wt% in lower aliphatic alcohol) was purchased from Aldrich. Methanol was purchased from Sigma. Sulfuric acid was obtained from Tedia. The MWCNTs (TECO Nanotech, Taiwan) used in this study was of ~99% purity and synthesized by an electric arc discharge method. The reagents were obtained in the purest commercially available grade and used without further pretreatment. In this study, all solutions were prepared with deionized water of resistivity not less than 18 M $\Omega$  cm taken from a Milli-Q water purification system (Milli-Q, USA).

### Apparatus

Electrochemical experiments were performed with an Autolab PGSTA30 Electrochemical Analyzer (Eco Chemie, The Netherlands). A conventional three-electrode electrochemical system consisted of a glassy carbon working electrode (3 mm diameter), a platinum wire counterelectrode, and an Ag/AgCl (3 M KCl) reference electrode (all Metrohm, Switzerland). Field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDS) were performed using a JSM-6700F (JEOL, Japan).

Transmission electron microscopy (TEM) images were obtained using a JEM-1200CXII (JEOL, Japan).

### Preparation of Pt–MWCNT–Nafion nanocomposite film-modified glassy carbon electrode

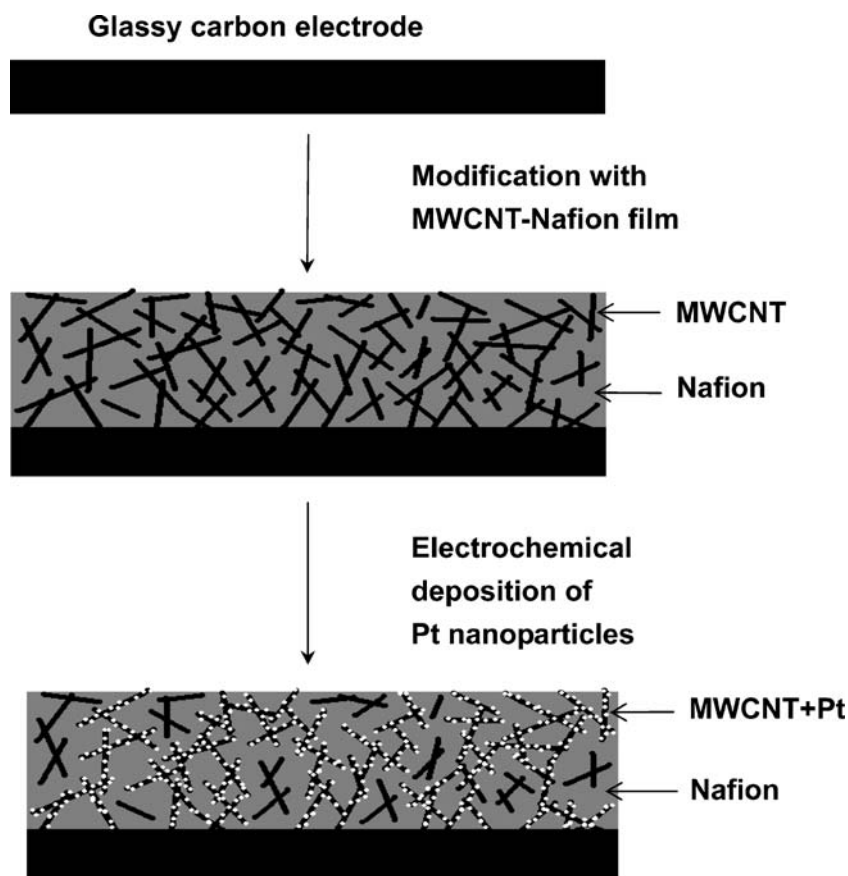
The optimum composition of MWCNTs/Nafion for electroanalytical applications has been reported in our previous study [31]. A 0.5-wt% Nafion solution was prepared by diluting the 5-wt% Nafion solution with 0.1 M phosphate buffer solution (pH 7), and then 10 mg MWCNTs were added in a 1-mL 0.5 wt% Nafion solution, and ultrasound agitation was performed for 1 h to form a homogeneous solution. Before the preparation, the 3-mm glassy carbon electrode was polished with 0.3- and 0.05- $\mu$ m alumina slurry and cleaned with deionized water in an ultrasound bath for several minutes. The MWCNT–Nafion film was prepared by casting a 6  $\mu$ L of 10 mg mL<sup>-1</sup> MWCNT–Nafion solution on the surface of the glassy carbon electrode. The solvent was allowed to evaporate at room temperature in the air for 1 h. The prepared electrode was immersed in a 0.1-M phosphate buffer solution (pH 7) containing 1 mM K<sub>2</sub>PtCl<sub>6</sub> for 1 h. The nanostructured Pt was electrochemically deposited within the MWCNT–Nafion matrix by cyclic voltammetry in a 0.1-M phosphate buffer solution (pH 7) containing 1 mM K<sub>2</sub>PtCl<sub>6</sub>. The potential was scanned between –1.0 to 0 V versus Ag/AgCl at a scan rate of 50 mV s<sup>-1</sup>.

## Results and discussion

### Pt–MWCNT–Nafion nanocomposite characterization by FESEM, TEM, and EDS

Figure 1 shows the schematic drawing of the preparation of Pt–MWCNT–Nafion nanocomposite film. The Pt nanoparticles were electrodeposited on the surface of MWCNTs, which were connected to the electrode. On the contrary, there were no Pt nanoparticles that could be seen on the disconnected MWCNTs. The electrochemical deposition of Pt nanoparticles within the MWCNT–Nafion nanocomposite was achieved by cyclic voltammetry. Repetitive cycling leads to the formation of the Pt–MWCNT–Nafion nanocomposite. Figure 2 shows the FESEM images of the MWCNT–Nafion nanocomposite before and after electrodeposition of Pt nanoparticles at cyclic numbers of 1 and 7. Platinum nanoparticles were deposited to the surface of CNTs, which could form a passageway for electrons to carry out the reaction of electrodeposition. The Pt nanoparticles are in electrical contact with the electrode throughout the MWCNT–Nafion nanocomposite. Further information of the electrodeposition of Pt nanoparticles

**Fig. 1** Schematic drawing of the preparation of the Pt–MWCNT–Nafion nanocomposite film



onto the surface of MWCNTs was investigated by TEM. Figure 3 shows the TEM images of the MWCNT–Nafion nanocomposite before and after electroreduction of Pt nanoparticles. It is clear from Fig. 3b that the Pt nanoparticles are grown on the MWCNTs with a diameter of about 20–50 nm after electrodeposition. The Pt nanoparticles decorated the external walls of the MWCNTs. The formation of Pt nanoparticles within the MWCNT–Nafion nanocomposite is supported by EDS observation. Figure 4 shows the EDS patterns of the MWCNT–Nafion nanocomposite before and after electroreduction of Pt nanoparticles. It can be seen from Fig. 4a that C and F are the major elements before electrodeposition of Pt. C comes from MWCNTs and Nafion and F is derived from Nafion. In Fig. 4b, the appearance of the Pt element after the electroreduction demonstrated that the nanoparticles within the MWCNT–Nafion are Pt.

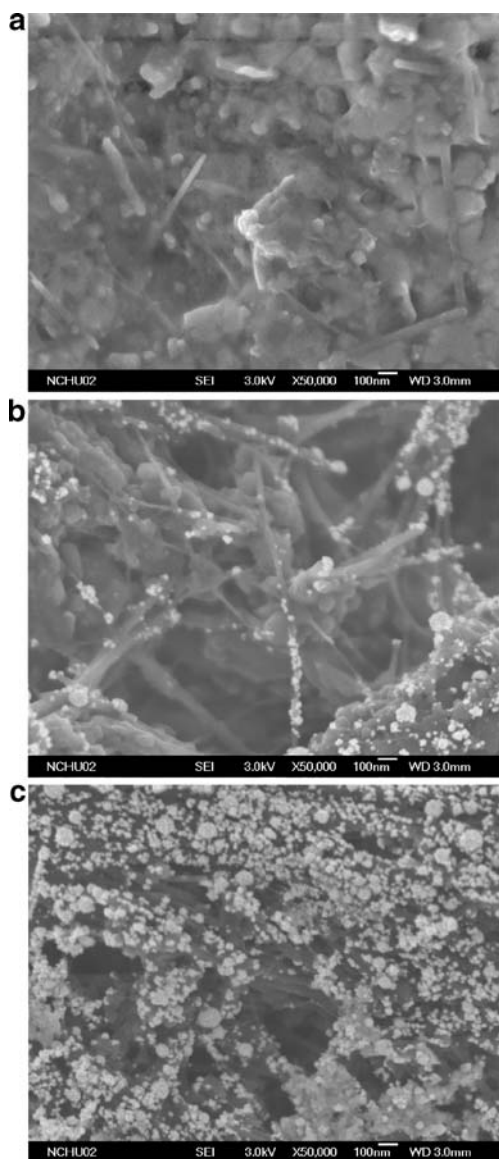
#### Electrochemical characterization of Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrode

To investigate the electrochemical properties of the Pt–MWCNT–Nafion nanocomposite, cyclic voltammetry in sulfuric acid was performed. Figure 5 shows the current–potential profiles of the MWCNT–Nafion nanocomposite-

modified glassy carbon electrode before and after deposition of Pt nanoparticles in a solution of 0.5 M  $\text{H}_2\text{SO}_4$  saturated by nitrogen. No hydrogen adsorption and desorption peaks are observed at the MWCNT–Nafion film-modified glassy carbon electrode (Fig. 5a). On the contrary, the hydrogen adsorption and desorption peaks can be seen at the Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrode (Fig. 5b). The sharp anodic peak at around  $-0.2$  V versus Ag/AgCl after incorporation of Pt nanoparticles within the MWCNT–Nafion matrix is attributed to the hydrogen desorption on the crystalline plane Pt(110) in the Pt nanoparticles decorated on the surface of MWCNTs. These data are in agreement with the results reported in the literature [32–34].

#### Electrocatalytic activity for methanol electrooxidation at the Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrode

Cyclic voltammetry in 2 M  $\text{CH}_3\text{OH}+1$  M  $\text{H}_2\text{SO}_4$  solution were conducted to investigate the electrocatalytic ability toward the electrochemical oxidation of methanol at the Pt–MWCNT–Nafion-modified glassy carbon electrode. For comparison, two control experiments at the Pt-coated glassy carbon electrode and Pt–Nafion-modified glassy

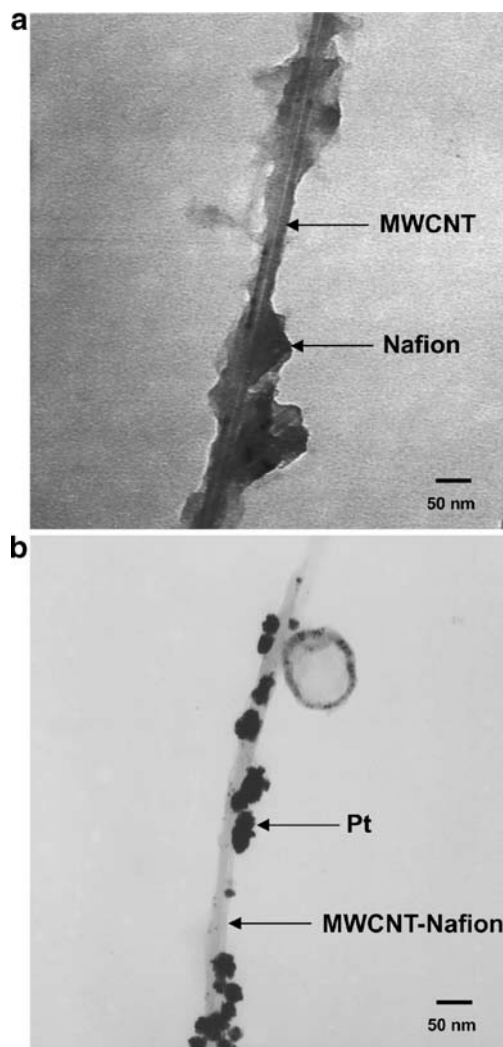


**Fig. 2** FESEM images of MWCNT–Nafion (a) and Pt–MWCNT–Nafion prepared at cyclic numbers of 1 (b) and 7 (c)

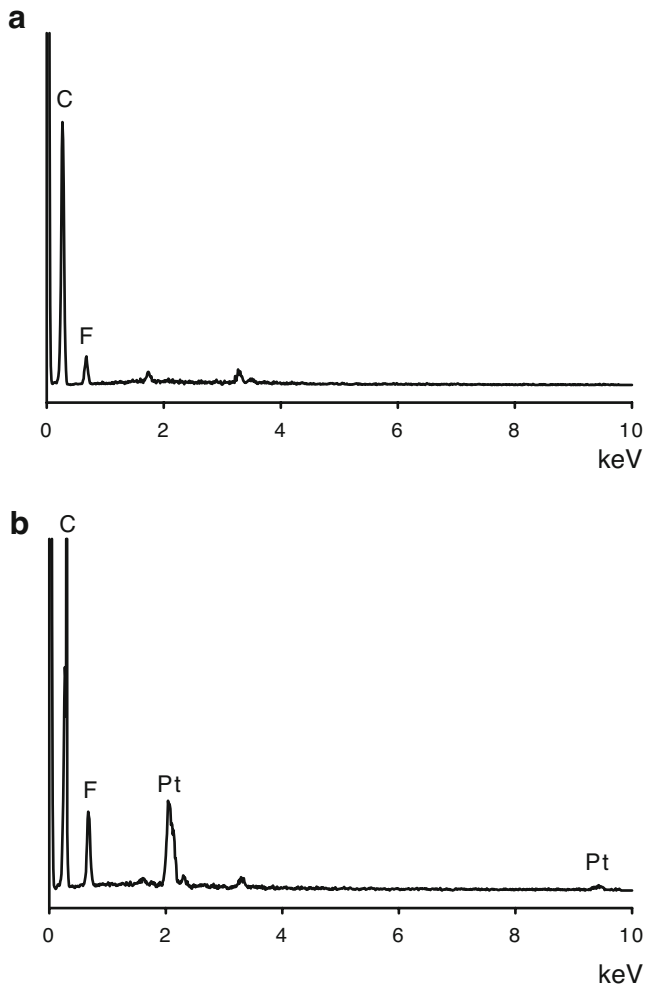
carbon electrode under the same condition as in the preparation of Pt–MWCNT–Nafion nanocomposite modified were performed. Figure 6 shows the cyclic voltammograms recorded in the 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> solution at the Pt- (Fig. 6a), Pt–Nafion- (Fig. 6b), and Pt–MWCNT–Nafion- (Fig. 6c) modified glassy carbon electrodes in the potential range from 0 to 1.0 V at a scan rate of 50 mV s<sup>-1</sup>. The 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> solution was purged with N<sub>2</sub> for 30 min to eliminate oxygen before methanol oxidation. From Fig. 6c, two peaks of methanol oxidation could be observed, and the peak potentials ( $E_p$ ) were 0.65 and 0.46 V for the forward and backward scans, respectively. The forward anodic peak represented that the methanol was oxidized to carbon dioxide; the reverse anodic peak might result from the accumulation of carbonaceous species [35].

The shape of the cyclic voltammogram and the  $E_p$  were in agreement with other works [3, 29]. The peak current densities ( $i_p$ ) at  $E_p=0.65$  V are 3.30 and 0.28 mA cm<sup>-2</sup> for the Pt–MWCNT–Nafion-modified glassy carbon electrode and the Pt-coated glassy carbon electrodes, respectively. A signal with almost tenfold more sensitivity is obtained after electroreduction of Pt within the MWCNT–Nafion composite. The result implied that the three-dimensional nanostructure of the MWCNT–Nafion composite is a suitable matrix for platinum nanoparticle loading.

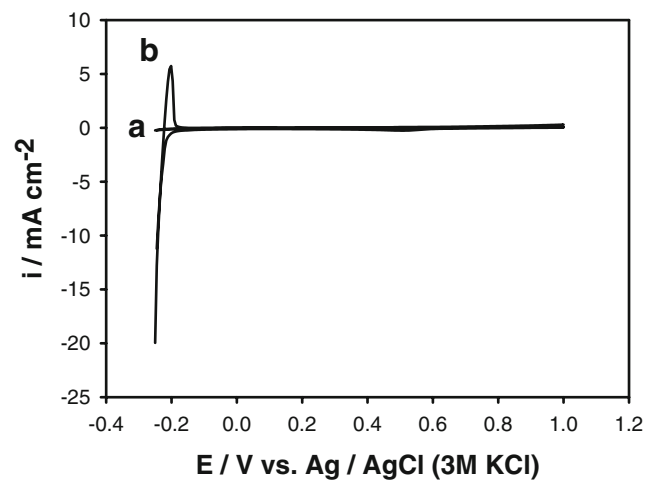
Figure 7 shows the cyclic voltammograms obtained with different scan rates in the 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> solution at the Pt–MWCNT–Nafion-nanocomposite modified electrode. The increase in potential scan rate promoted an increase in anodic currents. The  $E_p$  for the forward scan shifted from 0.63 to 0.72 V when the scan rate increased from 10 to 100 mV s<sup>-1</sup>. The inset of Fig. 7 shows the relationship between the peak currents and scan rates. The



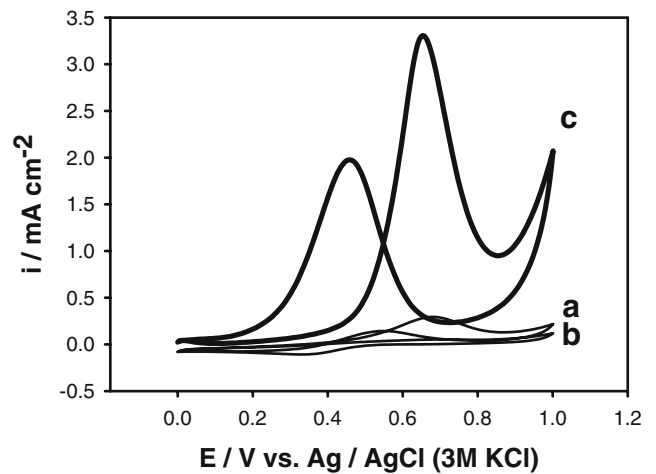
**Fig. 3** TEM images of MWCNT–Nafion (a) and Pt–MWCNT–Nafion (deposition charge 0.27 C cm<sup>-2</sup>; b)



**Fig. 4** EDS patterns of MWCNT-Nafion (a) and Pt-MWCNT-Nafion (deposition charge  $0.27 \text{ C cm}^{-2}$ ; b)

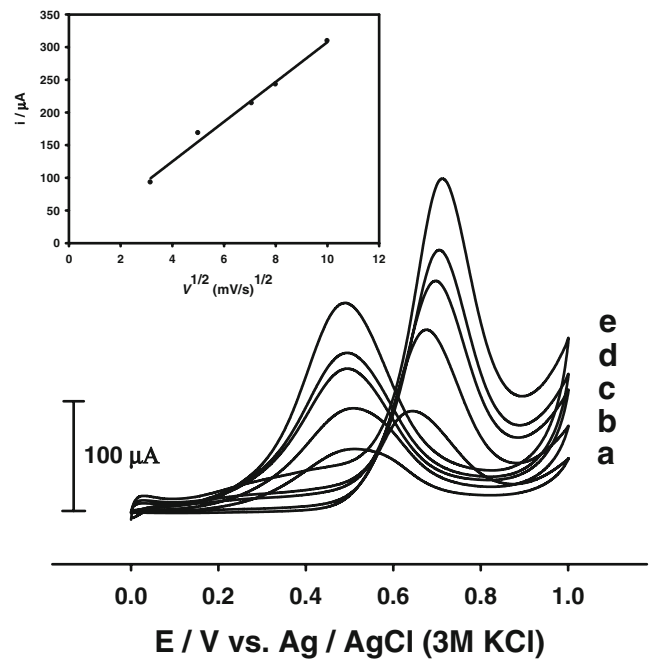


**Fig. 5** Cyclic voltammograms of MWCNT-Nafion (a) and Pt-MWCNT-Nafion (deposition charge  $0.27 \text{ C cm}^{-2}$ ; b) in  $0.5 \text{ M H}_2\text{SO}_4$  solution with a scan rate of  $30 \text{ mV s}^{-1}$



**Fig. 6** Cyclic voltammograms recorded in  $2 \text{ M CH}_3\text{OH} + 1 \text{ M H}_2\text{SO}_4$  solution at Pt- (a), Pt-Nafion- (b), and Pt-MWCNT-Nafion- (c) modified glassy carbon electrodes in the potential range from 0 to 1.0 V at a scan rate of  $50 \text{ mV s}^{-1}$

peak currents vary approximately linearly with the square root of the scan rate in the range of  $10$  to  $100 \text{ mV s}^{-1}$  with a correlation factor of 0.995; however, a correlation factor of 0.979 was obtained when the plot of peak currents versus scan rates was made. The results suggest that the electrochemical process is diffusion controlled. A similar



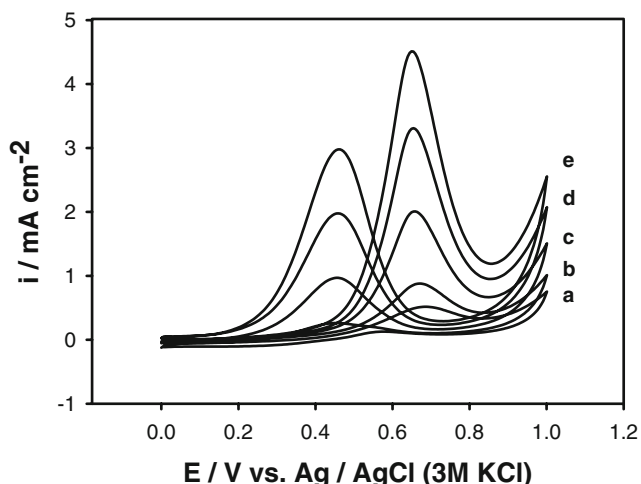
**Fig. 7** Cyclic voltammograms of the Pt-MWCNT-Nafion-modified glassy carbon electrode in  $2 \text{ M CH}_3\text{OH} + 1 \text{ M H}_2\text{SO}_4$  solution with scan rates of  $10$  (a),  $25$  (b),  $50$  (c),  $65$  (d), and  $100 \text{ mV s}^{-1}$  (e). The inset shows the anodic peak current for the forward scan as a function of the square root of the scan rate obtained at a Pt-MWCNT-Nafion-modified glassy carbon electrode in  $2 \text{ M CH}_3\text{OH} + 1 \text{ M H}_2\text{SO}_4$  solution

behavior has been reported using Pt-modified single-walled CNTs [29].

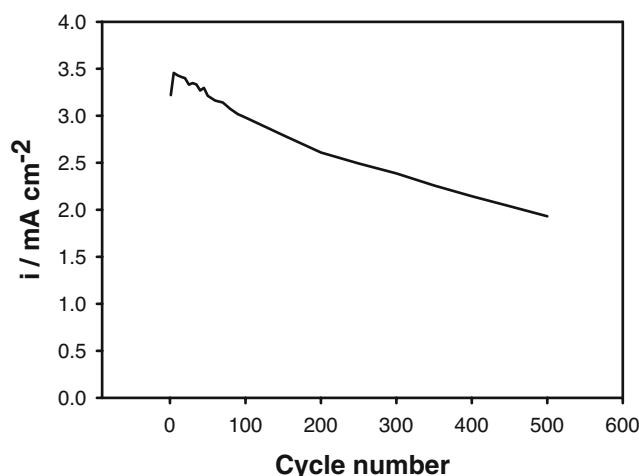
To evaluate the effect of Pt loading toward the electrooxidation of methanol, cyclic voltammetry was performed to investigate the performance of the Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrodes prepared at different cyclic numbers. Figure 8 shows the cyclic voltammograms of 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> at the Pt–MWCNT–Nafion nanocomposite-modified electrode prepared with different cyclic numbers. The peak current density increased with the increase in the cyclic number during the preparation of the Pt–MWCNT–Nafion nanocomposite. This is attributed to the high amount of Pt loading in the MWCNT–Nafion matrix at high cyclic numbers.

#### Stability of the Pt–MWCNT–Nafion nanocomposite-modified electrode

The stability of the Pt–MWCNT–Nafion nanocomposite-modified electrode was also investigated by cyclic voltammetry in the 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mV s<sup>-1</sup>. Figure 9 shows the change of the anodic peak current density obtained from the forward scan with the successive scans. It could be observed that the peak current density decreased gradually with the increase in scan numbers. It maintained about 60% of its initial peak current after 500 scans. The stability after 500 scans in this study is comparable to Pt–CNTs [3] but is less than the Pt-sulfonated-CNTs [24] and Pt-single-walled CNT [28]. Future work needs to improve the long-term stability for practical applications. The loss of the peak current at the Pt–MWCNT–Nafion nanocomposite-modified electrode toward the methanol electrooxidation might result from the



**Fig. 8** Cyclic voltammograms of 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> at the Pt–MWCNT–Nafion-modified glassy carbon electrode prepared at cyclic numbers of: 1 (a), 3 (b), 5 (c), 7 (d), and 9 (e)



**Fig. 9** The change in anodic peak current density for the forward scan of the Pt–MWCNT–Nafion (deposition charge 0.27 C cm<sup>-2</sup>) nanocomposite-modified glassy carbon electrode in 2 M CH<sub>3</sub>OH+1 M H<sub>2</sub>SO<sub>4</sub> solution for 500 scans. Scan rate=50 mV s<sup>-1</sup>

consumption of methanol, the accumulation of poisonous species on the surface of platinum nanoparticles [36], and the structural change of Pt nanoparticles during the cyclic voltammetry scan.

#### Conclusions

We have successfully demonstrated that the Pt nanoparticles can be electrochemically deposited in the MWCNT–Nafion three-dimensional matrix by the cyclic voltammetry method. Pt nanoparticles are in electrical contact with the glassy carbon electrode throughout the MWCNT–Nafion film. The electrocatalytic ability toward the methanol electrooxidation at the Pt–MWCNT–Nafion-modified glassy carbon electrode in the acidic solution is investigated. The Pt–MWCNT–Nafion nanocomposite-modified glassy carbon electrode has higher electrocatalytic ability for electrooxidation of methanol than the Pt-coated glassy carbon electrode and the Pt–Nafion-modified electrode. It indicates that MWCNTs are good candidates for catalyst support because of their high chemical stability and surface-to-volume ratio. The Pt nanoparticles can be fabricated rapidly and controlled easily and uniformly by electrochemical synthesis, which is contrasted with chemical synthesis. This methodology has a promising potential application to synthesize other metals or alloys of Pt nanoparticles such as Ru or Pt–Ru for direct methanol fuel cells [20].

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