Morphological and compositional engineering of Ni/carbon nanotube composite film via a novel cyclic voltammetric route

YU JUN YANG

School of Chemistry and Chemical Engineering, Xuchang University, Xuchang, China

Abstract. Ni/multi-walled carbon nanotubes (MWCNTs) composite films were deposited on the glassy carbon electrode (GCE) by a Ni plating bath containing homogeneously dispersed MWCNTs using polyvinylpyrrolidone (PVP) as dispersion additive. Incorporation of MWCNTs into Ni matrix was greatly enhanced by the application of cyclic voltammetric (CV) deposition technique. The structure and nature of the Ni/MWCNT were characterized by field emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD). The results show that the content of MWCNT and the morphology of the deposited Ni/MWCNT composite film can be controlled by selecting the appropriate electroplating conditions. Further study indicates that the obtained Ni/MWCNT showed excellent electro-catalytic activity for the oxidation of ethanol in alkaline solution.

Keywords. Carbon nanotubes; cyclic voltammetry; electrodeposition; nickle; composite.

1. Introduction

Nickel is an effective and cheap catalyst for oxidation of small organic compounds including glucose (Huang 2009), carbohydrates (Ojani *et al* 2004, 2008), especially, methanol (El-Shafei 1999; Golikand *et al* 2006; Jin *et al* 2009) and ethanol (Weng *et al* 2004; Basu *et al* 2008; Singh *et al* 2009). For example, nickel redox centres, Ni(OH)$_2$/NiOOH, formed on the nickel surface show high catalytic activity towards the oxidation of ethanol in alkaline media which possibly undergo competition between two electrons to the aldehyde and four electrons to carboxylic acid (Weng *et al* 2004; Basu *et al* 2008; Singh *et al* 2009). On the other hand, MWCNT is an outstanding catalyst support due to its excellent mechanical characteristics, nanometer size and high surface area (Rao *et al* 2003; Ajayan and Tour 2007). Thus, a MWCNT and Ni composite (Ni/MWCNT) are expected to be a promising new catalyst material. The Ni/MWCNT can be produced by electrodeposition (Arai *et al* 2004), electroless deposition (Wang *et al* 2005) or pyrolysis (Kichambare *et al* 2002). Among these, electro-synthesis could be a better method due to its convenience and economy.

While many studies have focused on the improvement of the uniform Ni/MWCNT composite film, the ability to synthesize Ni/MWCNT composite film with predictable morphology and composition remains a challenge. The control of surface morphology of the composite film, in addition to the sizes of the nickel crystals in the composite and nickel-to-MWCNT ratio, provides one more key factor to manipulate the properties of thin composite film. For future applications of the Ni/MWCNT nanocomposite film, it is foreseen that the control of the morphology as well as the composition will become an important issue.

The present study has tried to develop a novel cyclic voltammetric procedure for an ideal electrodeposition of Ni/MWCNT composite film on GCE. The focus of this experiment is to make the engineering of the surface morphology of the Ni/MWCNT composite and adjustment of the content of carbon nanotubes in the composites possibly by varying the experimental conditions. Firstly, we employed PVP as the dispersing agent to prevent the aggregation of carbon nanotubes in the aqueous electrolyte. Subsequently, we designed a cyclic voltammetric (CV) process to prepare the Ni/MWCNT composites. Compared to that prepared with the direct current (DC) technique (Arai *et al* 2004), Ni/MWCNT formed with CV technique is more uniform and compact in appearance due to much smaller particle size.

2. Experimental

MWCNTs were typically 30–50 nm in diameter. MWCNTs were synthesized by a chemical vapour deposition method and purified by refluxing in 2·6 mol/L HNO$_3$ for 48 h before use to remove the trace amount of impurities. As-prepared MWCNTs products were purified by immersing them into concentrated nitric acid and hydrofluoric acid in turn, then filtered and washed with deionized water and dried at 120°C. Prepared 100 mL electrolyte containing 0·07 M NiSO$_4$ and 0·1 M NaCl which was adjusted to pH 3·0. 2·5 mg purified MWCNTs and 0·2555 g PVP were added into 5 mL electrolyte and dispersed under sonication. A three-electrode electrolytic cell was employed for electrodeposition and electrochemical tests. A GCE (3 mm diameter) was used as

(yangyujun@yahoo.com)

the cathode. A platinum wire was used as a counter electrode. The saturated calomel electrode (SCE) was used as a reference electrode. Ni/MWCNT composite deposition was carried out by potential scanning from 0 V to −1·5 V (vs SCE) in a deaerated electrolyte. The scan rates were 5, 10, 15 mV/s, respectively.

Powder X-ray diffraction (XRD) data were collected using a Siemens X-ray diffractometer at a scanning rate of 4°/min (step size is 0·02° and count time/step is 0·3 s) in the 2θ range from 10°–80°, with graphite monochromatized Cu Kα radiation ($\lambda = 1\cdot54056$ Å). Morphology study of the films on the GCE surface was carried out with a Quanta 200 scanning electron microscope (SEM; FEI Company, Holland). The electrochemical tests were carried out with a CHI 830 potentiostat (Chen Hua Company, China).

3. Results and discussion

Electrochemical and electrophoretic methods have been used in the polarization, orientation and deposition of MWC-NTs (Kamat *et al* 2004; Samant *et al* 2007). In this experiment, the oxidatively shortened and –COOH functionalized multiwalled carbon nanotubes were prepared by refluxing MWCNT in nitric acid. In the solution, Ni^{2+} reacted with MWCNT–(COO$^-$)$_n$ to form positively charged Ni-MWCNTs, which migrated towards the GCE cathode and deposited on the cathode surface under d.c. electric field while the Ni^{2+} cations on the MWCNT surface and in the vicinity of cathode were reduced due to good conductivity of MWCNTs.

To synthesize the metal/carbon nanotube composites by electrodeposition, it would be indispensable to uniformly disperse carbon nanotubes in the aqueous electrolyte, thus achieve the incorporation of carbon nanotubes into the composites. However, carbon nanotubes have a propensity to aggregate into packed ropes or entangled networks due to strong inter-tubes van der Waals attraction. Thus, selecting an appropriate dispersing additive is crucial for deposition of Ni/MWCNT composite. Our study has discovered that PVP is more effective for MWCNT dispersion than tetraoctyl ammomium bromide (TOAB) (Kamat *et al* 2004), hexadecyltrimethylammonium bromide (CTAB) (Jiang *et al* 2008), sodium dodecyl sulfate (SDS) (Islam *et al* 2003) and hydroxypropylcellulose (HPC) (Yang *et al* 2008). The electrolyte containing PVP is highly stable and no precipitate is observed even after one month.

It was found that carbon nanotubes can be easily solubilized in water by non-covalently wrapping them with a variety of linear polymers such as PVP and polystyrene sulfonate (PSS) (O'Connell *et al* 2001). The surface pKa value of PVP was detected from the derivative of the curves of the contact angle ($d\theta/d$pH) vs pH. The pKa value of the pyridyl groups on PVP chains was found to be 7·5 (Demirci *et al* 2009). In this experiment, the MWCNTs were modified with PVP and the pyridyl groups on the PVP chains were protonated and positively charged subsequently in pH 3 aqueous

solution. Thus, the PVP-wrapped MWCNTs (PVP–MWCNT) were positively charged colloids (Bocharova *et al* 2006). The feasible PVP–MWCNTs dispersion in aqueous solution and the improved stability of their suspension were attributed to the strong electrostatic repulsion between the protonated PVP–MWCNTs.

Electrodeposition behaviour of Ni/MWCNT composites were examined with variations of experimental parameters such as scan rates, number of scan cycles, the concentration of MWCNTs and the application of electrolyte stirring. Figure 1 shows SEM photographs of electrodeposits formed at different scan rates without stirring. Scan range was from 0 to −1·5 V. The number of scan cycles is 5, 10 and 15 for experiments carried out at 5, 10 and 15 mVs^{-1}, respectively to maintain a constant deposition time. At 5 mVs^{-1}, irregularly shaped nickel crystal aggregates together and the carbon nanotubes distributed sparsely in the composite film (figure 1(a)). As shown in figure 1(b), at 10 mVs^{-1}, the spherical Ni crystals with a diameter of about 200 nm assembled separately along the carbon nanotubes. Similar phenomenon has been observed by Arai *et al* (2004). It is probably more preferable for the Ni nanoparticles to form at the local defects and end of MWCNT as a lot of irregular or spherical aggregate islands. Compared to the Ni/MWCNT composite obtained at 10 mVs^{-1}, aggregation of the Ni crystals in figure 1(c) is much more serious although the average diameter of the Ni crystals obtained at 15 mVs^{-1} is only 74 nm.

Figure 2 illustrates surface morphologies of the Ni/MWCNT composites electrodeposited at different concentrations of MWCNT in the electrolytic cell without stirring.
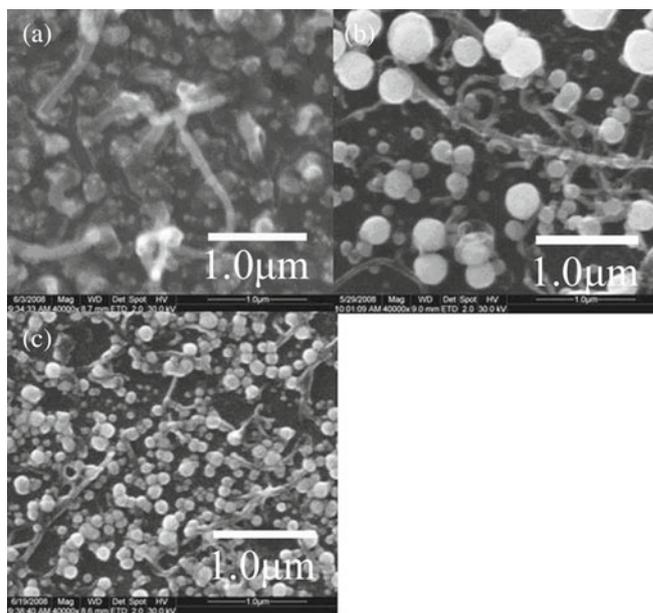
Figure 1. Morphology of composite film obtained in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·5 mg/mL MWCNT and 0·0511 g/mL PVP) by cycling from 0 to −1·5 V at scan rates of 5 (a), 10 (b), and 15 mVs^{-1} (c) for 5, 10 and 15 cycles without stirring.
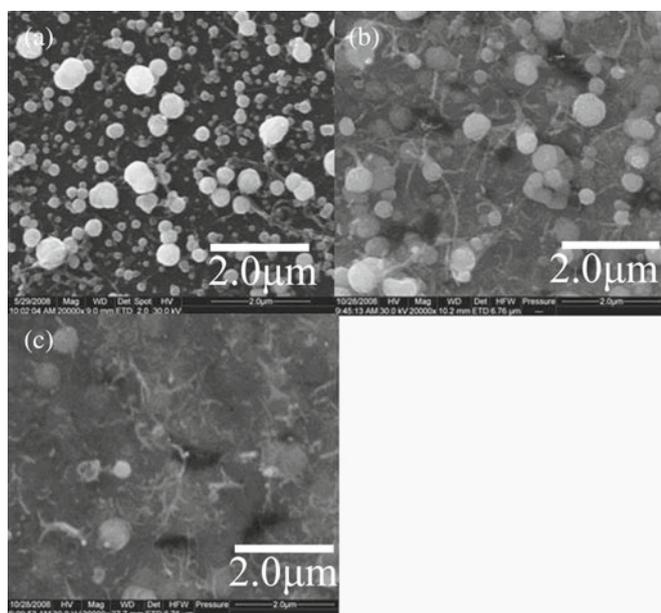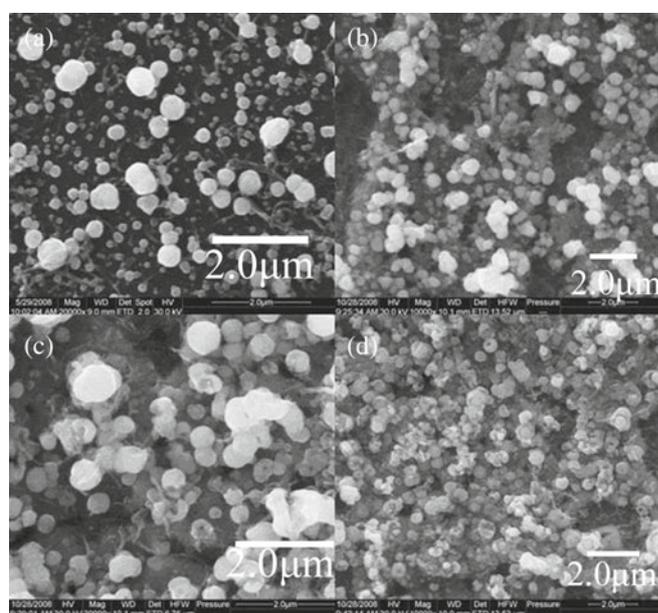
Figure 2. Morphology of composite film obtained in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·5 (a), 0·8 (b) and 1·4 mg/mL (c) MWCNT and 0·0511 g/mL PVP) by cycling from 0 to −1·5 V at a scan rate of 10 mVs^{-1} for 10 cycles without stirring.

Figure 3. Morphology of composite film obtained in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·5 mg/mL MWCNT and 0·0511 g/mL PVP) by cycling from 0 to −1·5 V at a scan rate of 10 mVs^{-1} for 10 (a), 15 (b), 20 (c) and 30 (d) cycles without stirring.

As shown in figures 2(a), (b) and (c), amount of MWCNTs in the composite film deposited on GCE cathode apparently increased with increasing concentration of MWCNT from 0·5–0·8 and 1·4 mg/mL in the electrolytic cell. From the results mentioned above it can be recognized that the concentration of MWCNTs plays an important role in the preparation of composite of Ni and MWCNTs by electrodeposition. With the increase of concentration of MWCNTs, more MWCNTs can be deposited on the surface of the cathode and their coverage on the cathode also increases. When the concentration of MWCNTs was increased to cover the whole surface of the cathode, the current can be distributed more uniformly, and thus Ni can be more uniformly deposited on the surface of MWCNTs to form the composite. However, MWCNTs are easy to agglomerate in aqueous solution. Higher MWCNTs concentration will enhance the agglomeration of MWCNTs in the electrolytic cell, which results in difficulty of deposition and coverage of MWCNTs on the cathode. Hence there should be an excess amount of PVP dispersing additive in the electrolyte to prevent the aggregation of MWCNTs.

Figure 3 shows SEM photographs of electrodeposits formed at different scan cycles without stirring, in other words, different deposition times while other experimental conditions remain constant. The density of Ni nanocrystals increases as the number of scan cycles is increased from 10 (a) to 15 (b), 20 (c) and 30 (d) cycles.

The effect of stirring was also investigated. Figure 4 shows SEM photographs of electrodeposits formed at different scan rates under stirring. After comparing figure 2 with figure 4, the result clearly indicates that the employment of stirring significantly enhances the incorporation of carbon nanotubes
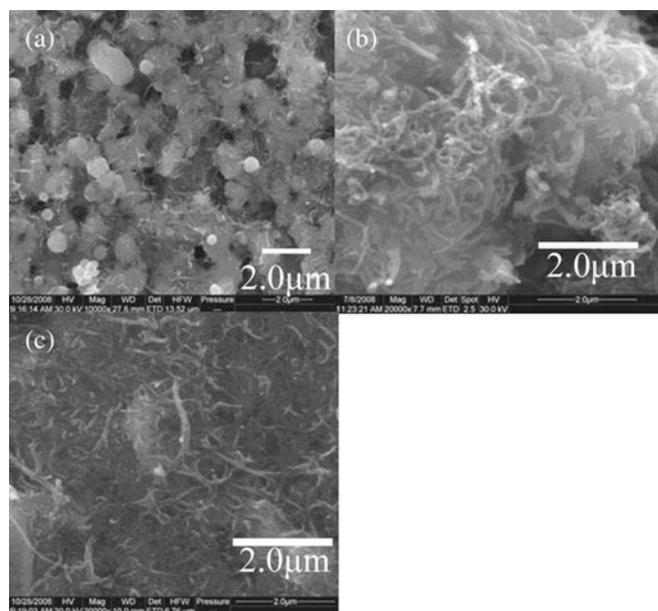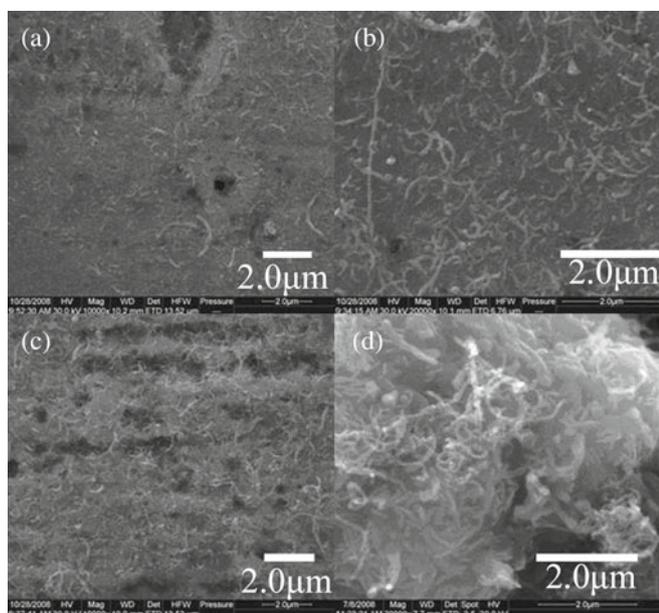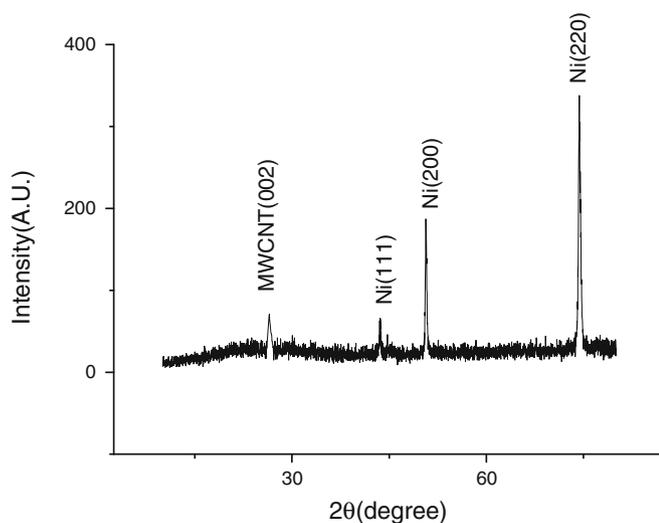

Figure 4. Morphology of the composite film obtained in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·5 mg/mL MWCNT and 0·0511 g/mL PVP) by cycling from 0 to −1·5 V at scan rate of 5(a), 10(b) and 15 mVs^{-1}(c) for 5, 10 and 15 cycles under stirring.

into the composite films. As shown in figure 4, it is very obvious that a more homogeneous coating was formed when the scan rate was raised from 5 mVs^{-1} to 15 mVs^{-1}.

Figure 5 shows SEM photographs of electrodeposits formed at different concentrations of MWCNT in the
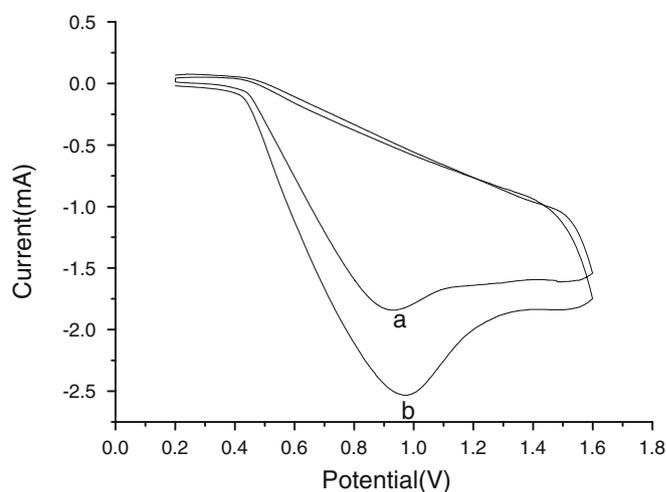
Figure 5. Morphology of composite film obtained in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·1 (a), 0.2 (b), 0.3 (c), and 0·5 mg/mL (d) MWCNT and 0·0511 g/mL PVP) by cycling from 0 to −1·5 V at a scan rate of 10 mVs^{-1} for 10 cycles under stirring.

Figure 6. XRD pattern of Ni/MWCNT composite with cyclic voltammetric deposition in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·5 mg/mL MWCNT and 0·0511 g/mL PVP) by cycling from 0 to −1·5 V at a scan rate of 10 mVs^{-1} for 10 cycles under stirring.

electrolytic cell under stirring. Without stirring, the density of MWCNTs increased apparently with the increasing concentration of MWCNT in the electrolyte (figure 2). However, no obvious change of density of MWCNTs in the composite film is observed when stirring was applied (figure 4). A homogeneous coating was formed in the cell with lower MWCNTs concentration, but the surface became coarser when MWCNTs concentration was raised. This may

Figure 7. CVs of 0·03 M C$_2$H$_5$OH in 0·1 M NaOH at Ni/ MWCNT obtained in 5 mL deposition bath (pH 3, 0·1 M NaCl, 0·07 M NiSO$_4$, 0·5 mg/mL MWCNT and 0·0511 g/mL PVP) by cycling from 0 to 1·5 V at scan rate of 10 mVs^{-1} for 10 cycles without stirring (a) or under stirring (b) (scan: 100 mVs^{-1}).

be due to the agglomerative effect of MWCNTs in the coatings since MWCNTs content in the co-deposited coatings increased with the increase of MWCNTs concentration in the electrolytic cell.

Figure 6 shows X-ray diffraction patterns taken from the Ni/MWCNT composites deposited on glassy carbon substrates. It can be seen that a diffraction peak from the (002) plane of carbon nanotubes is observed at $2\theta = 26\cdot4°$ together with three peaks at $2\theta = 44\cdot5°$, $51\cdot8°$ and $74\cdot7°$, which can be assigned to (111), (200) and (220) (2θ) reflection of face-centred cubic Ni crystals. This result confirms co-existence of carbon nanotubes and Ni, being in good agreement with SEM results. As can be seen from figure 4(b), the fibre shaped products formed on the cathode consists of Ni and MWCNTs. Therefore, it can be deduced that Ni deposit layer has been formed on the surface of MWCNTs. The fibre shaped products comprise of a Ni outer layer and an inner MWCNTs covered with Ni layer, viz. a composite of MWCNTs coated with Ni.

Figure 7 shows CVs of 0·03 M C$_2$H$_5$OH at Ni/MWCNT in 0·1 M NaOH. It can be readily seen that the Ni/MWCNT shows an excellent electrocatalytic oxidation of C$_2$H$_5$OH with a sharply increasing peak current and negative potential. The oxidation of ethanol undergoes two processes, one corresponds to the formation of Ni(III) species with a reversible transformation of Ni(OH)$_2$/NiOOH. The other is only Ni(III) species (NiOOH) produced at the electrode surface, and a new anodic peak with a large peak current formed in the presence of ethanol. This suggests that ethanol is oxidized and accompanied by the transformation of NiOOH to Ni(OH)$_2$ (Weng *et al* 2004; Basu *et al* 2008; Singh *et al* 2009). Therefore, NiOOH probably acts as an electrocatalyst (Basu *et al* 2008). Figure 7 also indicates that the Ni/MWCNTs obtained under different experimental conditions show different catalytic effects upon

oxidation of ethanol. In figure 1(b), content of MWCNT in the composite is low and Ni nanoparticles form at defects and ends of MWCNT resulting in a gathering effect. However, figure 4(b) shows that the external walls of MWCNT were homogeneously coated by Ni thin film and no aggregate of Ni crystals can be observed. Comparing figure 1(b) and 4(b) indicates that, under stirring, content of MWCNTs in the composite film is much higher and the formation of Ni on MWCNTs is more homogeneous than those without stirring. Thus, it is not surprising to find out that the Ni/MWCNT obtained under stirring shows better catalytic effect (figure 7b) than that obtained without stirring (figure 7a) towards the electro-oxidation of ethanol.

4. Conclusions

A novel cyclic voltammetric method for preparing Ni/MWCNT composite film is proposed. FE–SEM reveals that the composition and morphology of the composite film can be readily adjusted by varying the experimental parameters such as scan rate, potential scan cycles, concentration of MWCNT and application of stirring. Preliminary tests indicated that the Ni/MWCNT composite exhibits a high catalytic activity for the electro-oxidation of ethanol. This simple deposition technique is not limited to Ni but may be used to prepare a variety of metal/MWCNT composite with various metal-to-MWCNT ratios and morphology through similar routines for application as catalysts in fuel cells.

Acknowledgement

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