Front. Chem. China 2008, 3(2): 213–217
DOI 10.1007/s11458-008-0041-0

RESEARCH ARTICLE

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Preparation of glass carbon electrode modified with nanocrystalline nickel-decorated carbon nanotubes and electrocatalytic oxidation of methanol in alkaline solution

Abstract Nanocrystalline nickel with an average diameter of about 16 nm and a face-centered cubic (fcc) structure was uniformly attached to the surface of carbon nanotubes (CNT) by wet chemistry. The sample was characterized by X-ray powder diffraction and transmission electron microscopy (TEM). A glass carbon electrode modified with nickel-modified multi-wall carbon nanotubes (MWCNTs-Ni/GCE) was prepared. The electrochemical behavior of the MWCNTs-Ni/GCE and the electrocatalytic oxidation of methanol at the MWCNTs-Ni/GCE were investigated by cyclic voltammetry in 1.0 mol/L NaOH solution. The cyclic voltammograms showed that the electron transfer between β-$Ni(OH)_2$ and β-NiOOH is mainly a diffusion-controlled quasi-reversible process, and that the electrode has high catalytic activity for the electrooxidation of methanol in alkaline medium, revealing its potential application in alkaline rechargeable batteries and fuel cells.

Keywords carbon nanotube, Ni nanoparticles, electrocatalytic oxidation, methanol

1 Introduction

In recent years, the preparation of new catalysts with high electrocatalytic activity using Pt nanoparticles supported on carbon nanotubes has been a new topic [1,2]. Various literatures have reported the electrocatalytic oxidation of methanol at various Ni electrodes in alkaline medium [3,4]. The metallic Ni is oxidized to $Ni(OH)_2$ or NiO at negative potentials, then they are oxidized to the oxide or hydroxide of nickel with higher valence at positive potentials. The oxidization of some carbohydrates involved the formation of low valence $Ni(OH)_2$ from the reduction of NiOOH [5]. Abdel Rahim et al. [6] found that only Ni dispersed on graphite shows a catalytic activity towards methanol oxidation but massive Ni does not. Successful attachment of Ni-based catalysts on the surface of carbon nanotubes is achieved by various approaches such as electrochemical deposition [7], electroless plating [8] and wet chemistry [9]. However, studies on the electrocatalytic oxidation of methanol at a MWCNTs-Ni/GCE in alkaline solutions are not available. In this paper, we successfully prepared MWCNTs-Ni/GCE and analyzed their crystal structure and morphology by XRD and TEM. The electrochemical behavior and electrocatalytic oxidation of methanol at MWCNTs-Ni/GCE in alkaline solutions were studied by cyclic voltammetry at positive potentials.

2 Experimental

2.1 Instruments and reagents

Cyclic voltammetry was performed with a CHI 660A electrochemical workstation (Shanghai Chenhua Company) using a conventional three-electrode electrochemical cell. X-ray powder diffraction (XRD) was carried out on an XRD-6000 (Japan) X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154060$ nm) at a scanning rate of 0.06°/s in the 2θ range of 20° to 95°. Transmission electron microscopy (TEM) micrographs were taken using a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV. A pHs-3 Acidity Meter was used to monitor pH.

The multi-walled carbon nanotubes (MWNTs) produced by the thermal catalytic decomposition of hydrocarbons have an inner diameter of 3–10 nm and an outer diameter of 20–50 nm (with lengths of up to a few microns). All chemical reagents used were analytical-grade. The water used was triple distilled water.

Translated from *Chinese Journal of Applied Chemistry*, 2007, 24(5): 503–506 [译自: 应用化学]

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2.2 Preparation of MWCNTs-Ni

A suitable amount of MWCNTs was treated with boiling HNO_3 (68%) for 6 h then washed with distilled water and, finally, fully dispersed in an ultrasonic bath. A suitable amount of $Ni(NO_3)_2 \cdot 6H_2O$ was uniformly dispersed in the above solution followed by stirring at room temperature and then vigorous stirring at 100°C until the solvent evaporated completely. The sample was calcined under argon atmosphere followed by heat-treatment at 450°C under H_2 to reduce the metal oxide. After cooling the solution to room temperature, nanocrystalline nickel-modified carbon nanotubes (MWCNTs-Ni) electrode were obtained.

2.3 Preparation of MWCNTs-Ni/GCE

The working electrode was prepared as follows: Prior to modification, the GCE (3 mm diameter) was cleaned by polishing it with 0.01 μm α-Al_2O_3 powder. The electrode was then sonicated for about 5 min with distilled water and then acetone. One milligram of MWCNTs-Ni and 5 mL acetone were mixed ultrasonically. Fifty μL of this slurry was dropped onto the freshly polished GCE via a syringe. After the acetone evaporated completely, the prepared electrode (MWCNTs-Ni/GCE) was used as the working electrode. The MWCNTs/GCE was prepared using the same process for comparison with the MWCNTs-Ni/GCE.

2.4 Cyclic voltammetry

Cyclic voltammetry was performed with a CHI 660A electrochemical workstation (USA) using conventional three-electrode electrochemical cell with the MWCNTs-Ni/GCE as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Experiments were conducted in 1.0 mol/L NaOH with methanol. When a steady-state response was attained, the *E-I* curve was obtained and the apparent current density (the ratio of actual current to apparent electrode area) calculated. All potentials reported are relative to the SCE.

3 Results and discussion

3.1 XRD and TEM characterization of MWCNTs-Ni

Figure 1 shows the XRD pattern of the MWCNTs-Ni. The peaks, corresponding to the crystal planes of (111), (200) (220), and (311) of crystalline face-centered-cubic (fcc) Ni alloys (JCPDS 04-0850), are observed at 2θ values of 44.40°, 51.75°, 76.32°, 92.91°, respectively. Obviously, the X-ray diffraction peak at 25.94° is attributed to the carbon nanotubes (002). The lattice constant, a is calculated to be 0.3529 nm which is consistent with the reported value of 0.3523 nm (JCPDS 04-0850). The average size of the Ni alloy nanoparticles attached on CNT which was calculated using the Debye-Scherrer formula based on the full width at half-maximum (FWHM) of the (111) diffraction peak was 15.0 nm.

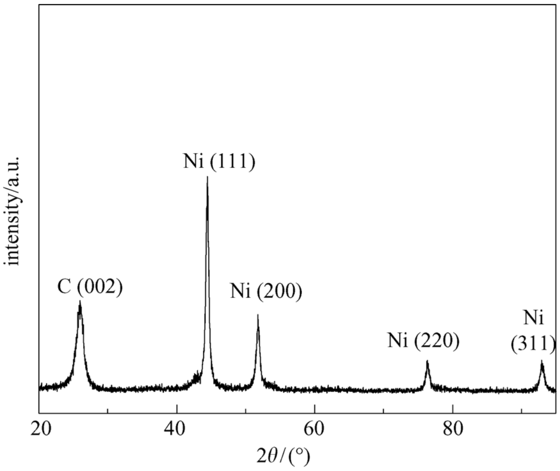

Fig. 1 X-ray diffraction pattern of the MWCNTs-Ni nanocomposite

The TEM image of MWCNTs-Ni nanocomposites is shown in Fig. 2. It can be seen that Ni alloy nanoparticles are highly dispersed on the outer surface of MWCNTs. The average size of the Ni alloy nanoparticles attached on the CNT measured from TEM image was at about 16 nm which is consistent with the result calculated using the XRD pattern. The highly dispersed Ni alloy nanoparticles have large specific surface areas.

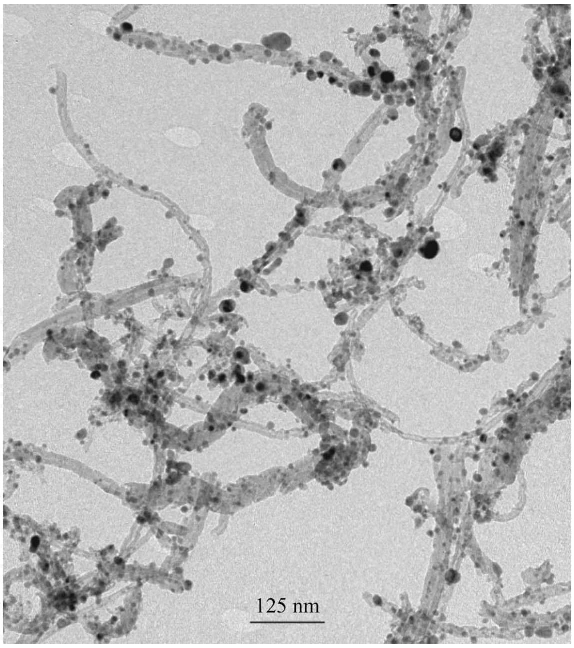

Fig. 2 TEM image of Ni nanoparticles on carbon nanotubes

3.2 Electrochemical behavior of MWCNTs-Ni/GCE in alkaline medium

Figure 3 shows the reproducible cyclic voltammetric response obtained at the MWCNTs/GCE and MWCNTs-Ni/GCE in 1.0 mol/L NaOH solution, where the steady-state response was obtained. It can be seen that, for MWCNTs/GCE, the voltammograms show no obvious anodic peak or cathodic peak. For MWCNTs-Ni/GCE, the voltammograms show a pair of well-defined anodic and cathodic peaks. These peaks appeared due to the transformation between β-Ni(OH)$_2$ and β-NiOOH [10–12]. The anodic and cathodic peak potentials were at about 0.640 and 0.566 V versus SCE. The difference in anodic and cathodic peak potential (ΔE_p) was 0.074 V, which is smaller than the ΔE_p (0.104 V) of Ni nanowire electrode and the ΔE_p (0.111 V) of bulk Ni electrode in 1.0 mol/L KOH solution [5], indicating that the transformation between β-Ni(OH)$_2$ and β-NiOOH has better reversibility.

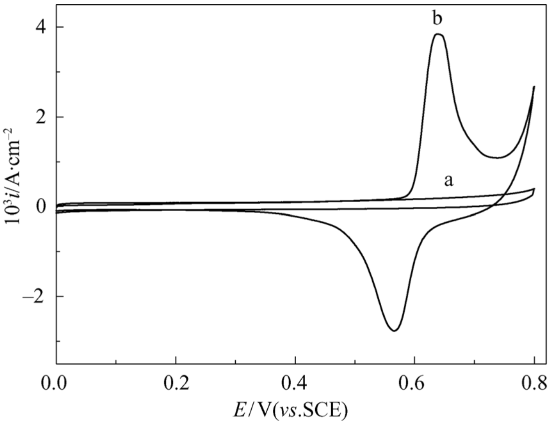

Fig. 3 Reproducible voltammograms obtained at various electrodes in 1.0 mol/L NaOH solution Scan rate: 50 mV/s; a) MWCNTs/GCE; b) MWCNTs-Ni/GCE

Reproducible cyclic voltammograms of MWCNTs-Ni/GCE at various scan rates are shown in Fig. 4. As shown in Fig. 4, with increasing scan rate, the peak current and ΔE_p increased, and the anodic and cathodic peak potential shifted a little. The anodic peak currents (i_pa) and cathodic peak currents (i_pc) are shown as a linear dependence on square-root of scan rate ($v^{1/2}$) in the inset, indicating that the reaction is a diffusion-controlled quasi-reversible process. The diffusion coefficient (D) was calculated using the formula: $i_\mathrm{p} = 2.69 \times 10^5 \times n_\mathrm{e} \times (Dv)^{1/2} \times C$. The calculated D is 1.57×10^{-9} cm^2/s, which has the same magnitude as the proton diffusion coefficient of Ni nanowire [3]. The transformation between β-Ni(OH)$_2$ and β-NiOOH dispersed on carbon nanotubes has a large proton diffusion coefficient in alkaline solution, suggesting that they may be considered as material for alkaline batteries.

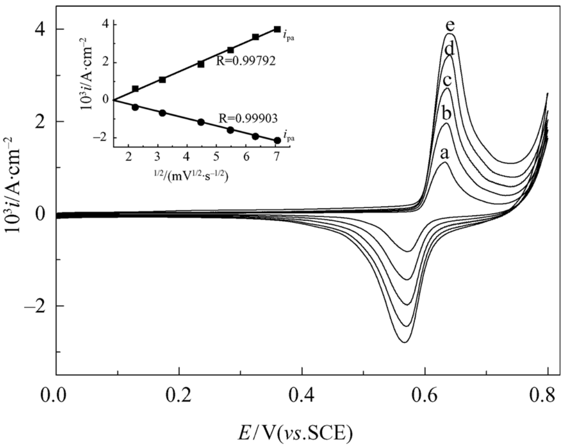

Fig. 4 Reproducible cyclic voltammograms of a MWCNTs-Ni/GCE at different scan rates in 1.0 mol/L NaOH.
Inset: the dependence of anodic peak currents (i_pa) and cathodic peak currents (i_pc) on square-root of scan rate ($v^{1/2}$) E/(mV·s^{-1}): a) 10; b) 20; c) 30; d) 40; e) 50

3.3 Electrocatalytic oxidation of methanol at MWCNTs-Ni/GCE

Figure 5 exhibits the cyclic voltammetric response obtained using MWCNTs/GCE and MWCNTs-Ni/GCE in 1.0 mol/L NaOH with and without 0.08 mol/L CH$_3$OH at a fixed scan rate of 50 mV/s. As shown in Fig. 5, the voltammogram of MWCNTs-Ni/GCE in 1.0 mol/L NaOH in the presence of CH$_3$OH has no obvious anodic peak or cathodic peak, indicating that MWCNTs/GCE is not oxidized electrocatalytically in alkaline solution. Curve b is the voltammogram of MWCNTs-Ni/GCE in 1.0 mol/L NaOH in the absence of CH$_3$OH. Two peaks (p$_2$ and p$_1$) caused by the redox between β-Ni(OH)$_2$ and β-NiOOH can be seen. Curve c is the voltammogram of MWCNTs-Ni/GCE in 1.0 mol/L NaOH in the presence of CH$_3$OH. Comparing Curves b and c, we can see that the current density of the anodic peak (p$_2$) increases and the current density of the cathodic peak (p$_1$) decreases slightly which is consistent with the reported result [6]. These experimental results may result from β-NiOOH acting as an oxidizing agent in the electrooxidation of CH$_3$OH giving rise to β-Ni(OH)$_2$ and consuming β-NiOOH. The increase in the β-Ni(OH)$_2$ concentration caused the increase of the current density of the anodic peak (p$_2$) and the decrease of β-NiOOH concentration caused the decrease of the current density of the cathodic peak (p$_1$). The results demonstrate that Ni(III) seems to act as a strong oxidizing agent for CH$_3$OH in alkaline solution. In addition, a new anodic peak (p$_3$) appears at *ca.* 0.77 V. Obviously, an anodic peak (p$_4$) appears at the same potential in the negative sweep. As reported in the literature [13], the new anodic peaks p$_3$ and p$_4$ are the anodic peaks of CH$_3$OH.

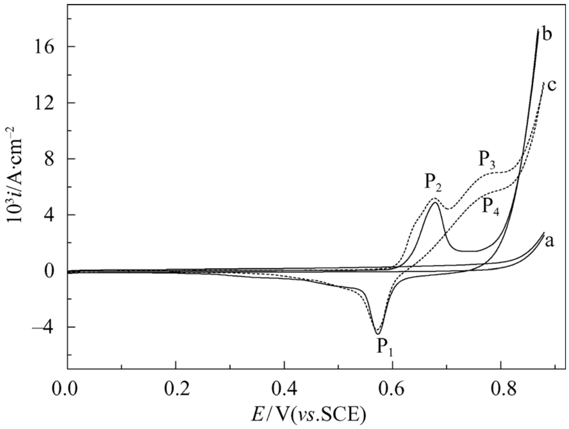

Fig. 5 Cyclic voltammograms of MWCNTs/GCE and MWCNTs-Ni/GCE in 1.0 mol/L NaOH in the absence and the presence of 0.08 mol/L CH_3OH
Scan rate: 50 mV/s; a) MWCNTs/GCE, 1.0 mol/L NaOH + 0.08 mol/L CH_3OH; b) MWCNTs-Ni/GCE, 1.0 mol/L NaOH; c) MWCNTs-Ni/GCE, 1.0 mol/L NaOH + 0.08 mol/L CH_3OH

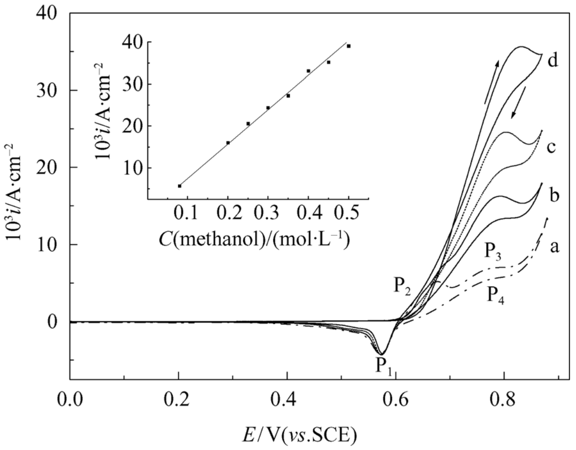

Fig. 6 Cyclic voltammograms of a MWCNTs-Ni/GCE in 1.0 mol/L NaOH solution with methanol present.
Scan rate: 50 mV/s; Insert: variation of the methanol oxidation peak current at MWCNTs-Ni/GCE with its concentration; c (CH_3OH)/(mol·L^{-1}): a) 0.08; b) 0.2; c) 0.3; d) 0.45

Our results demonstrate that MWCNTs-Ni/GCE has high catalytic activity for the electro-oxidation of methanol in alkaline medium. It can be seen that, as the CH_3OH concentration increased, the current density of the cathodic peak of β-NiOOH decreased and the current density of the anodic peak of β-Ni$(OH)_2$ increased. The peak corresponding to the redox reaction between β-Ni$(OH)_2$ and β-NiOOH became less defined and the anodic peaks p_3 and p_4 shifted towards more positive potentials When the CH_3OH concentration was 0.45 mol/L, there was a cross point on curve c, which is similar to that mentioned in the literature [13]. El-Shafei observed an analogous phenomenon, when he used the glass carbon electrode modified with $Ni(OH)_2$ to electrocatalytically oxidize methanol in alkaline solution. El-Shafei suggested that the transformation between β-Ni$(OH)_2$ and β-NiOOH was fast, while the electrocatalytic oxidation of methanol by β-NiOOH was slow. When the CH_3OH concentration was high or the scan rate was small in the electrode surface wings, the intermediate of CH_3OH oxidation was not oxidized completely and its concentration was high, causing the cross on Curve c. The inset in Fig. 6 shows the dependence of the current density of the anodic peak on CH_3OH concentration. It is clear that the current density of the anodic peak (p_3) has good linear dependence on CH_3OH concentration in the concentration range shown indicating that the material can be considered as a sensor for CH_3OH and can be used for the measurement of CH_3OH concentration.

4 Conclusions

Nickel nanoparticles were successfully attached to the surface of CNTs by wet chemistry. The nanocrystalline nickel with an average diameter of about 16 nm had a face-centered cubic (fcc) structure. The electrochemical behavior of the MWCNTs-Ni/GCE and the electrocatalytic oxidation of methanol at the electrode were investigated by cyclic voltammetry in 1.0 mol/L NaOH solution. The results show that the electron transfer between β-Ni$(OH)_2$ and β-NiOOH is mainly a diffusion-controlled quasi-reversible process and that the modified electrode, the MWCNTs-Ni/GCE, has high catalytic activity in the electrooxidation of methanol in alkaline medium.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 20271002).

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