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Arrayed CNT–Ni nanocomposites grown directly on Si substrate for amperometric detection of ethanol

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ABSTRACT

A novel amperometric biosensor utilizing carbon nanotube (CNT)–Ni nanoparticle hybrid arrays for ethanol detection has been developed. The sensor was fabricated by e-beam deposition of thin Ni film on arrayed multi-walled carbon nanotubes grown directly on Si substrate. As the Ni film thickness is $\leq$200 nm, high-resolution SEM and TEM images showed well-dispersed and strongly adhered crystalline Ni nanoparticles uniformly populated on the sidewalls of CNTs, and the sensitivity of the resultant CNT–Ni sensor generally increased with increasing nickel thickness. The best sensor showed a wide response range of 50–600 μM, a response time of <10 s, and a sensitivity of 14.81 $\mu A\,\mu M^{-1}\,cm^{-2}$ which is $\sim$380% higher in comparison with the nanostructured Ni/Pt/Ti electrodes.

1. Introduction

Ethanol sensors with high sensitivity, selectivity, and short response time are needed for many applications, such as in medicine, fermentation, and food industry. Accurate and reliable measurement of ethanol is also very important in clinical, agricultural, and environmental analyses. Conventional analytical methods, such as chromatography, spectrometry, and refractometry, often require relative expensive instruments which are laborious, complex, and time-consuming to operate. Thus, much progress has been made in finding a more cost-effective approach of using electrochemical biosensors with enzyme-modified electrodes. The enzymatic biosensors were commonly fabricated by attaching either alcohol oxidase (AOD) (Xie et al., 1992; Vijayakumar et al., 1996) or alcohol dehydrogenase (ADH) (Wang et al., 1992; Katrlik et al., 1998) to suitable solid electrodes, which catalyze the conversion of alcohol to aldehyde. In the case of AOD-based biosensors, the consumption of O_2 or the production of H_2O_2 is measured, while the ADH-based biosensors rely upon the electrocatalytic ability toward the NADH in the presence of coenzyme nicotinamide adenine dinucleotide (NAD^+). However, the enzyme-modified electrodes have several constraints, such as short lifetime, poor stability, and susceptible to temperature change.

To overcome the disadvantages of enzymatic methods mentioned above, electrodes based on pure nickel or nickel-coated substrates have appeared to be promising alternatives for electrochemical ethanol sensing (Liao and Chou, 2000; Pang et al., 2001; Weng et al., 2004). The ethanol detection mechanism of nickel-based electrodes is based on the oxidation of ethanol, at a lower electrocatalyzed potential, by the redox pair of $Ni(OH)_2$/NiOOH on nickel surface in alkaline media (Sattar and Conway, 1969; Carbonio et al., 1982; Lo and Hwang, 1995). However, these two-dimensional plate-type nickel electrodes provide relatively insufficient surface area and thus showed marginal catalytic activity towards the oxidation of ethanol (Liao and Chou, 2000; Pang et al., 2001). Nevertheless, the sensing performance of the Ni-based electrochemical sensors had been considerably improved by increasing surface area of the electrodes by using nanostructured nickel (Weng et al., 2004).

Due to the high surface free energy provided by their enormous surface areas, many kinds of metal nanoparticles exhibit excellent catalytic properties and have been widely used in electrochemical sensors and biosensors (Luo et al., 2006). On the other hand, many studies have revealed that carbon nanotubes (CNTs) is an outstanding catalyst support (Fang et al., 2007) due to its high surface area and excellent electron transfer rate (Nugent et al., 2001). Furthermore, vertically aligned CNTs can act as molecular wires to allow efficient electron transfer between the underlying electrode and the redox centers (Wang, 2005). There are many active efforts to develop a variety of electrochemical sensors with hybrid nanoparticles/CNTs materials. For example, gold (Manso et al., 2007), palladium (Lee et al., 2007; Lim et al., 2005), platinum (Tang et al., 2004), and CdTe (Liu et al., 2007) nanoparticles have been used in conjunction with CNTs for the electrocatalytic sensing of glucose. The as-produced nanocomposites have demonstrated electrochemical and sensing performances superior to their bulk counterparts. Thus, hybrid nanocomposites constructed by modifying the surface of arrayed CNTs with well-dispersed Ni nanoparticles is expected to be a promising catalyst material for

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ethanol detection. The Ni–CNT nanocomposites have been produced by electro deposition (Arai et al., 2004; Jin et al., 2007), electroless deposition (Wang et al., 2005), or impregnation (Kim et al., 2005). However, due to the insolubility of CNTs in all solvents, wet chemical pretreatments and/or metal organic precursors were commonly utilized to obtain dispersed Ni nanoparticles on CNTs in those studies. In this work, we present a simple yet efficient route for the preparation of well-dispersed Ni nanoparticles on vertically aligned CNTs grown directly on Si substrates. It is found that well-dispersed Ni nanoparticles can be formed on the sidewalls of CNTs by e-beam deposition without using any wet chemical pretreatments or metal organic precursors. The resulting CNT–Ni nanocomposite showed a sensitivity of up to 14.81 $\mu A\ \mu M^{-1}\ cm^{-2}$ with a response time of <10 s.

2. Experimental

2.1. Preparation of arrayed CNT–Ni nanocomposites

Prior to CNT growth, chromium (Cr), titanium (Ti), and cobalt (Co) metals with thicknesses of 100, 40, and 8 nm, respectively, were consecutively deposited onto a SiO_2/Si substrate of an area of 2 cm^2 by e-beam evaporation. Then, aligned multi-walled carbon nanotubes were grown by microwave-heated chemical vapor deposition (MH-CVD) (Huang et al., 2005). The MH-CVD growth of CNTs was carried out at a microwave power of 1100 W, a substrate temperature of 680 °C, and a growth time of 15 min. Only CH_4 was fed into the deposition chamber, and the chamber pressure was maintained at 1 atm. The deposited Cr/Ti bilayer was used to improve the adhesion and reduce the contact resistance between the CNTs and the Si substrate. Finally, Ni with thickness of 60–240 nm was deposited on the CNT arrays using e-beam evaporation in a vacuum of $\sim 10^{-7}$ Torr. To ensure the deposited Ni is in the form of nanoclusters, the deposition rate of Ni was kept as slow as 0.1–0.5 Å/s.

2.2. Characterization

The surface morphology of the arrayed CNT–Ni nanocomposites was characterized by field-emission scanning electron microscopy (FESEM). The detailed nanostructure of the hybrid nanocomposites was studied by use of high-resolution transmission electron microscopy (TEM). The electrochemical (EC) behaviors of the CNT–Ni nanocomposites were characterized by cyclic voltammetry and chronoamperometry using an EG&G 273 potentiostat. In addition, high-resolution X-ray photoelectron spectroscopy (HRXPS) was employed to investigate the states of $Ni(OH)_2$/NiOOH before and after the EC sensing of ethanol.

2.3. Sensing system

The sensing system contained a three-electrode cell using the fabricated CNT–Ni hybrid nanocomposites (area of 0.16 cm^2) as the working electrode, platinum wire as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. All operational potential values given below refer to Ag/AgCl. Amperometric measurements were carried out under steady-state conditions in a 0.5 M KOH aqueous solution by applying a desired potential within the limiting current window of the working electrode. When the background current had achieved a steady-state value, 50 μM of ethanol (or other interfering species) was added and the new steady-state current was noted. With each addition, the response current increased and a new steady-state was reached. The differences between these currents and the background current were used to construct a calibration curve for concentration of ethanol versus response current. The sensitivities of the CNT–Ni sensors were calculated using the equation

$$S = \frac{\Delta I}{\Delta C \times A},$$

where S is the sensitivity in $\mu A/(\mu M\,cm^2)$, ΔI is the current response in μA, ΔC is the difference of ethanol concentration in μM, and A is the surface area of the CNT–Ni electrode in cm^2.

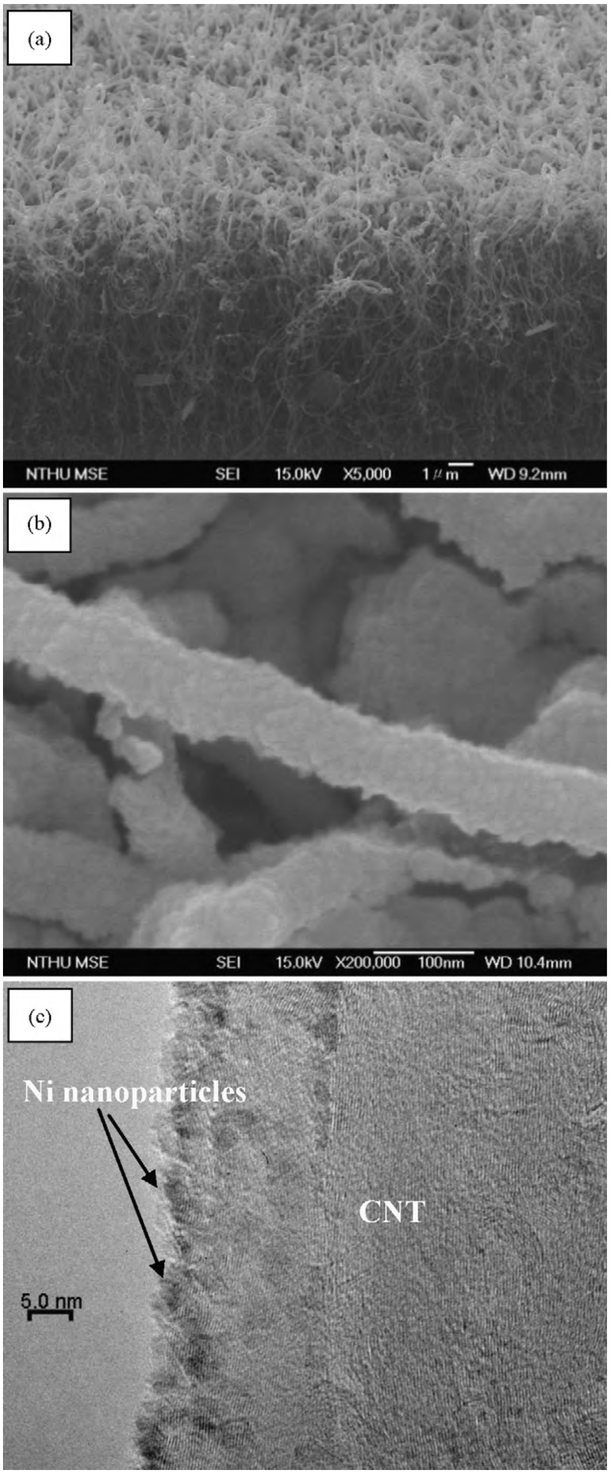

Fig. 1. (a) Low-magnification cross-sectional and (b) high-magnification top-view FESEM micrographs of CNTs with 100 nm Ni coating. (c) High-resolution TEM image showing dispersed nanonickel crystallites.