



Fabrication of carbon nanotube-nickel nanoparticle hybrid paste electrodes for electrochemical sensing of carbohydrates



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ARTICLE INFO

Article history:

Received 1 August 2013

Received in revised form 4 November 2013

Accepted 7 November 2013

Available online 15 November 2013

Keywords:

Carbon nanotube

Nickel nanoparticle

Hybrid

Amperometric detection

Capillary electrophoresis

ABSTRACT

Carbon nanotube-nickel nanoparticle (CNT-NiNP) hybrid was prepared by the chemical reduction of a mixture containing nickel sulfate and CNTs using hydrazine. The structure of the material was characterized by scanning electron microscopy, energy dispersive spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and vibrating sample magnetometry. A mixture of the CNT-NiNP hybrid and paraffin oil was packed into fused capillaries to fabricate paste electrodes for electrochemical sensing. The performance of the fabricated electrodes was demonstrated by measuring four carbohydrates in combination with cyclic voltammetry and capillary electrophoresis. The advantages of the electrodes include higher sensitivity, satisfactory stability, surface renewability, and low expense of fabrication. They may find wide applications in microchip capillary electrophoresis, flowing-injection analysis, and other microfluidic analysis systems.

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1. Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure in which carbon atoms are combined in a hexagonal pattern. Since Iijima et al. reported the existence of CNTs in 1991, they have attracted tremendous attention because of their unique structure, high electrical conductivity, excellent mechanical performance, and satisfactory chemical stability [1–5]. CNTs are ideal materials for the fabrication of electrochemical sensors and biosensors [6–9]. It has been demonstrated that CNTs exhibited strong electrocatalytic activity and excellent anti-passivation ability when they were employed to improve the electrochemical response of some bioactive substances [10–14]. A series of CNT-based electrodes have been fabricated for electrochemical sensing, including CNT modified carbon electrode [15], CNT screen-printed electrode [16], CNT-Teflon composite electrode [17], CNT-epoxy composite electrode [18], CNT-copper hybrid electrode [19], CNT-Fe₃O₄ hybrid electrode [20], CNT-cellulose composite electrode [21], CNT-polysulfone composite electrode [22–24], etc.

To date, a variety of approaches have been developed for the fabrication of CNT-based electrodes, including surface coating, screen-printing, magnetic loading, in situ polymerization, etc. Among them, surface modification is the most commonly used approach. CNT-dispersed solvents [25,26] or polymer solutions

[27,28] were coated on glassy carbon electrodes to fabricate CNT modified electrode. In addition, electrochemical deposition [29] and electrochemical polymerization [30,31] were also employed to prepare CNT-polymer composite coatings on electrodes. Recently, a method based on in situ polymerization was developed for the fabrication of CNT-polymer composite electrodes as the end-column amperometric detectors of capillary electrophoresis (CE) [14,32]. The mixtures of CNTs and prepolymers were filled into the inner bores of fused silica capillaries. After the CNT-containing mixtures solidified, CNT-polymer composite electrodes could be obtained.

As the products of photosynthesis, carbohydrates are the most abundant class of organic compounds found in living organisms. A variety of approaches based on liquid chromatography [33], CE [34], and microchip CE [35] have been developed for their analysis. Prior to ultraviolet or fluorescence detection, carbohydrates need to be derivatized because they have neither chromophore nor fluorophore. In addition, underivatized carbohydrates can be directly detected at platinum or gold electrodes using pulsed amperometric detection [36,37]. The applied potentials must be continuously pulsed to reduce the passivation of the electrodes. To solve the problem, copper and nickel electrodes are employed in the amperometric detection (AD) of carbohydrates in strongly alkaline mediums to minimize electrode fouling [38,39].

Recently, some nanomaterials have been applied in the electrochemical sensing of carbohydrates to improve the sensitivity and anti-fouling capability of the electrodes. Escarpa et al. prepared nickel and nickel-copper nanowires by electrodeposition in the porous anodic aluminum oxide templates [40,41]. The

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magnetic nanowires were loaded on screen-printed carbon electrodes with the aid of magnets for carbohydrate sensing. Moreover, NiO nanoparticles [42] and CuO nanorod bundles [43] were also employed to prepare electrodes for sensing carbohydrates. These nanomaterials showed strong electrocatalytic activity toward the oxidation of carbohydrates. Because CNTs own large specific surface area and high electrical conductivity, it is interesting to deposit nickel nanoparticles (NiNPs) on them for the sensitive detection of carbohydrates.

CNT-NiNP hybrids were mainly prepared by mechanical grinding [44], chemical vapor deposition [45], electrochemical deposition [46–48], gas-phase reduction [49–51], and e-beam evaporation [52]. In this work, CNT-NiNP hybrid was prepared by the chemical reduction of a mixture containing nickel sulfate and CNTs using hydrazine. It was mixed with paraffin oil and packed into the ends of fused silica capillaries to form paste electrodes. The preparation details and characterization of the CNT-NiNP hybrid as well as the feasibility and performance of the hybrid paste electrodes are reported in the following sections in combination with the measurement of carbohydrates by cyclic voltammetry (CV) and CE.

2. Experimental

2.1. Reagent and solutions

Multiwall carbon nanotubes (MWCNTs, 40–60 nm diameter, 5–15 mm long) were provided by Shenzhen Nanoport Company (Shenzhen, China). Prior to use, they were treated with concentrated nitric acid at 60 °C for 12 h. Mannitol, sucrose, glucose, fructose, nickel (II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), paraffin oil, and sodium hydroxide were purchased from SinoPharm (Shanghai, China). They were all analytical grade. The separation medium for CE was 75 mM NaOH aqueous solution. The stock solutions (100 mM) of the four carbohydrates were prepared in doubly distilled water.

2.2. Preparation of NiNP and CNT-NiNP hybrid

To prepare CNT-NiNP hybrid, 300 mg CNT powder was dispersed in 20 mL of 0.5 M NiSO_4 aqueous solution with the aid of sonication. And then, 4 mL of hydrazine hydrate (85%, w/w) was mixed with 25 mL of 1.0 M NaOH aqueous solution and added to the CNT-containing NiSO_4 solution. After the mixture solution was stirred at room temperature for 30 min, it was heated in an 80 °C water bath for 30 min. The obtained black CNT-NiNP hybrid could be easily isolated from the solution by vacuum filtration and was purified by washing with copious amounts of doubly distilled water. Finally, it was washed with absolute ethanol and dried in vacuum. The content of CNTs in the hybrid was determined to be 32.6% (w/w) by dissolving NiNPs with diluted hydrochloric acid. For comparison, NiNPs were prepared by mixing 20 mL of 0.5 M NiSO_4 aqueous solution with the mixture solution of 4 mL of hydrazine hydrate (85%, w/w) and 25 mL of 1 M NaOH aqueous solution. The obtained mixture was heated in an 80 °C water bath for 30 min. The prepared NiNPs could be easily separated from the solution by using an NdFeB magnet (~3000 Gs).

2.3. Electrode fabrication

The fabrication process of the paste electrodes was illustrated in Fig. A-1 (the details see Appendices). CNT-NiNP hybrid powder was mixed with paraffin oil at a weight ratio of 3:1 on a glass plate. And then, a piece of copper wire (15 cm long and 150 μm diameter) was inserted into a 4.5 cm long fused silica capillary (320 μm I.D., 450 μm O.D., Hebei Yongnian Ruipu Chromatogram Equipment Co.,

Ltd., Hebei, China) and a ~3 mm long opening was left for filling the paste. Hot melt adhesive was applied to the other end of the capillary to glue the copper wire in place. The mixture was then packed into the empty end of the capillary to a depth of ~5 mm. The paste should touch the end of the copper wire in the capillary for electrical contact. Finally, the paste electrode was smoothed on a piece of weighing paper to get a flat surface. For comparison, NiNPs, CNTs, and the mixture of CNTs and NiNPs were also employed to fabricate paste electrodes following the same procedures. The content of the paraffin oil in all pastes was 25% (w/w). The mixture of CNTs and NiNPs was prepared by mixing CNTs and NiNPs at a weight ratio of 1:2.

2.4. Apparatus

The CE-AD system used in this work has been described in our previous reports [14,26]. A ± 30 kV high-voltage dc power supply (Shanghai Institute of Nuclear Research, China) provided a separation voltage between the two ends of the capillary. The inlet of the capillary was held at a positive potential while the outlet of capillary was maintained at ground. The separations were carried out in a piece of 50 cm long fused silica capillary (25 μm I.D., 360 μm O.D., Polymicro Technologies, USA).

As illustrated in Fig. A-2 (the details see Appendices), the three-electrode electrochemical cell used in this work consisted of a working electrode, a platinum auxiliary electrode, and an Ag/AgCl wire served as pseudo reference electrode. It was used in combination with a BAS LC-4C amperometric detector (Bioanalytical Systems Inc., West Lafayette, IN, USA) for the amperometric detection in CE. The working electrode was positioned carefully opposite to the outlet of the capillary with the aid of a 3-D amperometric detection setup and arranged in a wall-jet configuration [14]. The gap between the end of the capillary and the surface of the working electrode was ~50 μm . The schematics and operation procedures of the 3-D adjustable alignment device can be found in the appendices.

The surface morphologies and the energy dispersive spectroscopy (EDS) spectra of the prepared materials were measured by using a scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands). A FT-IR spectrometer (NEXUS470, NICOLET) was used to measure the Fourier transform infrared (FT-IR) spectra of NiNPs, CNTs, and CNT-NiNP hybrid. The X-ray diffraction (XRD) measurements were carried out using a Rigaku D/max-rB diffractometer (Rigaku, Tokyo, Japan) with $\text{CuK}\alpha$ radiation (40 kV, 60 mA). A vibrating-sample magnetometer (Model 155, EG&G Princeton Applied Research, USA) was employed to study the magnetic properties of NiNPs and CNT-NiNP hybrid at room temperature.

2.5. CV measurements

CV was performed using a CHI 660D electrochemical analyzer (CH Instruments, Austin, USA) in combination with the three-electrode electrochemical cell mentioned above. The working electrode was a CNT-NiNP hybrid paste electrode, a NiNP paste electrode, a CNT paste electrode, or a CNT-NiNP mixture paste electrode. Prior to electrochemical sensing, the electrodes were pretreated by cyclic voltammetric scanning over the potential range of 0 to +0.80 V (vs. Ag/AgCl electrode) at a scan rate of 100 mV/s.

2.6. Sample preparation

Three samples of *Radix Puerariae Thomsoni* purchased from local drug stores were dried at 60 °C for 30 min and then were pulverized. Prior to extraction, 1.0 g of each sample was dispersed in 50 mL of doubly distilled water in a 100 mL flask. After the

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