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Synthesis and characterization of carbon nanotubes synthesized over NiO/Na-montmorillonite catalyst and application to a hydrogen peroxide sensor

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ABSTRACT

In this study, we demonstrate the synthesis of carbon nanotubes (CNTs) on clay mineral layers, and the preparation of hydrogen peroxide (H_2O_2) sensor based on CNT/Nafion/Na-montmorillonite (Clay) composite film for the detection of H_2O_2. The nickel oxide metallic catalyst (NiO) has been prepared by the polyol method and then dispersed onto the clay mineral layers. The CNTs were successfully synthesized over the NiO/Clay catalyst onto clay layers to form a three-dimensional CNT/Clay network by thermal chemical vapor deposition method. From field-emission scanning electron microscope images, the results of X-ray diffraction and Fourier transfer infrared spectra; the layered clay platelets are apparently delaminated and exfoliated after the growth of CNTs onto the surface of clay minerals. The mixed hybrid film of Nafion and CNT/Clay is coated on the glassy carbon electrode to detect hydrogen peroxide (H_2O_2). This composite film performs a detection limit of 1.0×10^{-4} M for H_2O_2 and the current is linear for H_2O_2 concentrations from 0.1 to 12.8 mM. Furthermore, the sensitivity of the GCE modified with the CNT/Clay/Nafion hybrid film to H_2O_2 was calculated to be 1.71×10^5 μA M^{-1} cm^{-2}. Consequently, the CNT/Clay/Nafion medium can probably be a useful electrode for the development of sensors due to its high sensitivity and applicability.

1. Introduction

Sodium montmorillonite (Clay) is a layered aluminosilicate clay mineral with a layer thickness of 1 nm, and exhibits excellent intercalation properties for swelling, strong adsorption and ion exchange. Clay minerals have been extensively used as the reinforcement material for composites [1–3] and polymers [4–7]. In addition, carbon nanotubes (CNTs), which are the graphite sheet rolled-over into the cylinder tube material, have become an attractive material for its specific mechanical, physical, chemical, electro-conductive, and field emission properties [8–11]. The single-walled and multi-walled CNTs are synthesized by thermal chemical vapor deposition (CVD) over the effective catalysts such as cobalt or iron nanoparticles supported on metal oxides [12–14]. Furthermore, an iron cation intercalated clay catalyst has been studied for the growth of CNTs on clay minerals [15,16], and clay platelets are used as the support for the formation of iron nanoparticles. Zhang et al. have reported that the CNT/Clay/Nylon-6 hybrid composite possesses a better mechanical tensile module and strength, and higher electron transfer ability than Nylon-6 itself. This three-dimensional (3D) nanostructure material consists of the two-dimensional (2D) nano-clay platelet and one-dimensional (1D) CNTs. Polyol method [17–22] with a liquid EG medium at a low temperature is one of chemical methods to prepare nano-scale metals or metallic alloy catalysts. Suitable metallic precursors are well dissolved and dispersed in liquid polyol solution, which plays the role of the reducing medium, and heated with an increasing temperature to maintain the hydrolysis reduction. The nickel oxide (NiO) catalyst was chosen and prepared by using the polyol method and then dispersed on the surface of clay minerals to form the NiO/Clay catalyst for the growth of CNTs in this study.

Glassy carbon electrodes (GCEs) modified with various materials, such as CNTs, metallic nanoparticles and Nafion, have been investigated for the detection of hydrogen peroxide (H_2O_2) [23,24], and applied in monitoring the blood glucose [25–27]. Yao et al. have reported that an amperometric sensor for the determination of H_2O_2 was prepared based on the GCE modified with MnO_2/Na-montmorillonite. They improved the sensitivity of detecting H_2O_2 sufficiently, and applied to measure its concentration in samples of hair dye successfully. Simple Nafion modified electrodes have

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been widely used and the combination of Nafion with CNT/Clay material into an electrode may have further applications. In this research, clay platelets are used for the support of NiO particles to form the NiO/Clay catalyst. The CNTs synthesized onto the surface of the clay mineral platelets over the NiO/Clay catalyst by thermal CVD has been investigated for the formation of CNT/Clay nanostructure. The GCE modified with the major CNT/Clay/Nafion composite films has been used to detect H_2O_2. It appears that the formation of CNTs over the NiO/Clay catalyst exfoliates the layered clay structure. The detection sensitivity of the modified GCE is strongly dependent on the formation of CNTs. Compared with other studies in monitoring H_2O_2 [23], the GCE modified with the CNT/Clay/Nafion composite film performs a better sensitivity for determination of H_2O_2. The CNT/Clay/Nafion medium system can be a useful electrode composite film for the development of sensors because of its high sensitivity and applicability. Consequently, the CNT/Clay/Nafion hybrid composite film can be applied to the enzyme-based biosensors.

2. Experimental

2.1. Preparation of the NiO/Clay catalyst and the growth of CNTs on clay by thermal CVD

The nickel oxide (NiO) powder was prepared by the polyol method. The starting precursor of 0.04 mol of 99% nickel acetate tetrahydrate ($Ni(CH_3COO)_2{\cdot}4H_2O$, 99%, Showa) was dissolved in 150 ml ethylene glycol (EG, Tedia). EG is used as a weak reduction reagent to form various molar compositions of metallic alloy catalysts. A 10.0-g poly(*N*-vinyl-2-pyrrolidone (PVP), MW = 10,000) was also dissolved in another 150 ml of EG. Then two solutions were mixed and stirred with agitation of 400 rpm at 190 °C for 30 min. 0.01 g of 99% silver nitrate ($AgNO_3$, Showa) was further added at 180 °C and refluxed for more 1 h. The product (NiO powder) was washed with 85% ethanol solution and centrifuged at 7000 rpm for several times and dried at 70 °C.

The sodium montmorillonite (Clay) used in this study was purchased from Nanocor with the cation-exchange capacity of 1.20 mequiv. g^{-1}. The clay mineral (2.0 g) was immersed into a 0.014-M cetyltrimethylammonium bromide (CTAB, 99%, Acros) aqueous solution, which was used as a cationic surfactant to increase the distance between layers of clay, and stirred for 12 h to form the surfactant intercalated clay (CTA^+/Clay). Then, 50.0 mg of ground NiO powder was dispersed into the CTA^+/Clay solution with the aid of ultrasonic agitation. By this means, NiO powder was physically bound to the surface of CTA^+/Clay. The black-brown dispersion of NiO/Clay was washed with deionized water and separated by centrifugation and dried at 70 °C.

The CNTs were synthesized by thermal CVD with mixed gases containing acetylene (C_2H_2) and argon (Ar) at 650 °C. Typically, a 50.0 mg of NiO/Clay catalyst was sprayed on a quartz boat and then placed the boat in a horizontal tube furnace. The quartz tube was first evacuated and flushed with Ar gas to remove the air and pollutants. Then hydrogen gas was introduced into the furnace to reduce the catalyst for 20 min at 650 °C. Finally, H_2 gas was turned off and a mixture gas of C_2H_2/H_2 with total flow rate of 500 sccm (C_2H_2/H_2 = 400/100) was introduced into the furnace and lasted for 15 min. After the growth of CNTs, the resulting sample (CNT/Clay) was slowly cooled down to room temperature by flushing with the Ar gas.

2.2. Preparation of the CNT/Clay modified GCE

Before modification, the bare GCE (0.07 cm^2 area) was polished with 0.05 μm α-Al_2O_3 slurries and rinsed with deionized water for several times. The 0.5 wt.% Nafion solution was diluted from the 5 wt.% Nafion solution (5 wt.% in a mixture of lower aliphatic alcohols and water, Aldrich) with 0.1 M phosphate buffer solution. 8 mg of raw CNT/Clay was added into 1 ml of 0.5 wt.% Nafion solution. And the dispersed solutions were ultrasonicated over 30 min at 4 °C to form homogeneous solutions. After that, 6 μl of as-described Nafion/CNT/Clay or Nafion/Clay dispersed solution was deposited onto the surface of clean GCE immediately, and dried at room temperature for 1 h. Finally, the CNT/Clay modified glassy carbon electrodes for H_2O_2 sensor was obtained after the solvent was evaporated at room temperature. All solutions were prepared with deionized water of a resistivity higher than 18 MΩ cm (Milli-Q, USA). Different concentration of H_2O_2 solutions were prepared in 0.1 M phosphate buffer solution (pH 7.0) consisting of Na_2HPO_4 and NaH_2PO_4.

2.3. Characterizations

Surface morphology of the modified clay and GCE were investigated by field-emission scanning electron microscope (FESEM, JEOL JSM-6700F) operating at 5–30 kV. Transmission electron microscope (TEM) studies were performed by using a JOEL 1200-EXII microscope with an accelerating voltage of 120 kV, and a high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2010, operated at 200 kV) was also employed to monitor the morphology and structural properties of the synthesized samples. X-ray powder diffraction (XRD) data were carried out by using the X-ray diffraction instrument (MAC Science, MO3XHF) with Cu Kα radiation source (λ = 1.54056 Å), and recorded in the 2θ ranging from 2° to 80° with a scanning rate of 2° min^{-1} under the controlling of 40 kV and 30 mA. Fourier transfer infrared (FTIR) spectra were investigated with a PerkinElmer Paragon 500 spectrometer using a KBr pellet from 400 to 4000 cm^{-1} at room temperature.

2.4. Electrochemical apparatus and measurements

Cyclic voltammetry and amperometry experiments were carried out on a CHI 627A Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode setup. Three electrodes were a GC working electrode, a platinum wire counter electrode and an Ag/AgCl (3 M KCl) reference electrode. And the GC working electrodes were modified with the film of Nafion, Nafion/Clay and Nafion/CNT/Clay composite, respectively. Before performing the experiments, the phosphate buffer solution was purged with Ar gas for 1 h. Typically, constant-potential amperometric detections of H_2O_2 (or glucose) was performed in a 20-ml phosphate buffer solution medium with magnetic stirring of 300 rpm at room temperature by applying a holding potential of −0.6 V vs. Ag/AgCl. After the current achieved a steady state in the absence of substrate as H_2O_2 (or glucose), the current–time data were recorded in every 1 min with adding substrate into cell.

3. Results and discussion

Polyol method [17,28], which is a liquid EG medium to reduce desired metals and metallic alloy catalysts at a low temperature, is a useful and beneficial chemical reduction method to prepare nano-scale metals or metallic alloy catalysts. Desired metallic precursors are well dissolved and dispersed in liquid polyol solution and heated with a suitable temperature to maintain the hydrolysis reduction. The NiO metallic catalyst was prepared by using the polyol method and calcined at 600 °C with air in this study, and then physically bound to the surface and layers of CTA^+/Clay.

The CNTs were synthesized by thermal CVD with a total flow rate of 500 sccm (C_2H_2/H_2 = 400/100) at 650 °C for 15 min. Typical FESEM images of NiO/Clay catalyst, the CNTs synthesized over NiO/Clay catalyst, and higher magnification of the inner surface of CNT/Clay composite are shown in Fig. 1. After immersed in CTAB and NiO solution, the NiO/Clay mineral platelets are mainly aggregated with clay layers as shown in Fig. 1(a) due to their high-specific area. The growth of CNTs on the surface of clay was obtained at 650 °C by thermal CVD of acetylene as shown in Fig. 1(b)–(d). Delaminated clay layers and CNTs network are clearly observed and besides, clay layers are apparently entangled with CNTs. Higher magnification images of the inner surface of CNT/Clay composite are shown in Fig. 1(d) and (e). The TEM images of the formation of NiO/Clay catalyst before and after the synthesis of CNTs are also shown in Fig. 1(f) and (g). After the growth of CNTs, NiO particles are smaller than the raw NiO/Clay catalyst. It is probably suggested that aggregated clay layers were split by the growth of long CNTs to form the exfoliated clay platelets. Because of the diffusion limitation of carbon source, in addition, shorter warm-like CNTs are also grown randomly and observed on the surface of clay platelet [15]. Consequently, the CNT/Clay composite is conductible because of the synthesized CNTs network in the clay mineral layers. Furthermore, the residual NiO metallic catalyst or Ni element is not obtained from the data of X-ray energy dispersive spectrometer (not shown here). Consequently, the electric-conductivity results of H_2O_2 sensor mentioned below are not resulted from the contribution of the residual NiO metallic particles but the synthesized CNTs network.

The powder XRD patterns of the clay and CNT/Clay hybrid composite are shown in Fig. 2. The characteristic peaks appearing at 2θ = 27.5°, 34.9°, and 61.9° are of the clay mineral, and the peaks appearing at 26.4° and 44.3° are characteristic of the presence of the CNTs [28]. Besides, the basal spacing (d_{001}) reflection of the