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Amperometric biosensor based on carbon nanotubes coated with polyaniline/dendrimer-encapsulated Pt nanoparticles for glucose detection

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ABSTRACT

A novel amperometric glucose biosensor based on the nanocomposites of multi-wall carbon nanotubes (CNT) coated with polyaniline (PANI) and dendrimer-encapsulated Pt nanoparticles (Pt-DENs) is prepared. CNT coated with protonated PANI is in situ synthesized and Pt-DENs is absorbed on PANI/CNT composite surface by self-assembly method. Then Glucose oxidase (GOx) is crosslink-immobilizated onto Pt-DENs/PANI/CNT composite film. The results show that the fabricated GOx/Pt-DENs/PANI/CNT electrode exhibits excellent response performance to glucose, such as low detection limit (0.5 μM), wide linear range (1 μM–12 mM), short response time (about 5 s), high sensitivity (42.0 μA mM^{-1} cm^{-2}) and stability (83% remains after 3 weeks).

1. Introduction

Carbon nanotubes (CNT), as a new class of nanomaterials, have been drawn to considerable attention owing to their unique structure, high chemical stability and high surface-to-volume ratio. The ability of CNT to promote the electron-transfer reactions of important biomolecules, such as cytochrome C [1], β-nicotinamide adenine dinucleotide (NADH) [2], ascorbic acid [3] and H_2O_2 [4–6], has been illustrated at carbon nanotubes modified electrodes, which suggests great promise for dehydrogenase and oxidase based amperometric biosensors [7–9]. In addition, nanoparticulate hybrid materials from CNT and metal have been applied in advanced catalytic and sensory materials. Noble metals such as Pt [10], Au [11], Rh [12] or semiconducting CdSe nanoparticles [13] immobilized on CNT surfaces by different methods, have been proven to be effective towards oxidation/reduction reactions. The report shows that the uniform dispersion of metallic nanoparticles on CNT surfaces can yield ideal nanocatalysts for various reactions [14]. However, there are difficulties in dispersing metal nanoparticles on the CNT surfaces. In order to obtain a good dispersity of metal nanoparticles, the surface of CNT must be modified via a proper functionalization.

Conducting polymers have been proven to be suitable host matrices for dispersing metallic particles on the surface of CNT [15]. In addition, the composites of conducting polymers with metal nanoparticles permit a facile flow of electronic charges across the polymer matrix during electrochemical processes. Among various conducting polymers, polyaniline (PANI) become attractive owing to its high conductivity, ease of preparation, good environmental stability, which can provide a suitable environment for the immobilization of biomolecules and improve impressive signal amplification [16–18]. On the other hand, based on its excellent conductivity and electroactivity, PANI can act as a mediator for enzyme electrodes which couples electrons directly from the enzyme active site to the electrode surface. Liu et al. [19] have constructed PANI/CNT multilayer films for detection of NADH, and it was found that CNT inside the multilayer film could improve the electroactivity of PANI. Moreover, the obtained multilayer films were very stable and showed high electrocatalytic ability. Santhosh et al. [20] fabricated CNT grafted with PANI for the detection of hydrogen peroxide, and the prepared biosensor exhibited good performance.

As all we know, platinum nanoparticles are very effective as a matrix of enzyme sensors by taking advantage of the biocompatibility and huge surface of Pt nanoparticles and good electrocatalytic activity to hydrogen peroxide. As CNT, PANI and Pt nanoparticles are excellent materials for the construction of electrochemical sensors and biosensors, through a suitable combination of these materials, novel modified surfaces could be generated with higher surface area and enhanced catalytical/electrocatalytical activities, which is also expected to be an excellent platform for electrochemical sensing applications [21].

Our previous works had reported two kinds of glucose biosensors based on self-assembling glucose oxidase (GOx) and dendrimer-encapsulated Pt nanoparticles (Pt-DENs) on supports of CNT [22] and PANI [23], respectively. The biosensor based on CNT support had slightly narrow linear range of 5 μM to 0.65 mM, and PANI support biosensor had slightly high applied potential of 0.6 V. In order to obtain wider linear range and decrease applied potential, in this paper, an amperometric glucose biosensor based on the nanocomposites of CNT coated with PANI and Pt-DENs was prepared. CNT coated with

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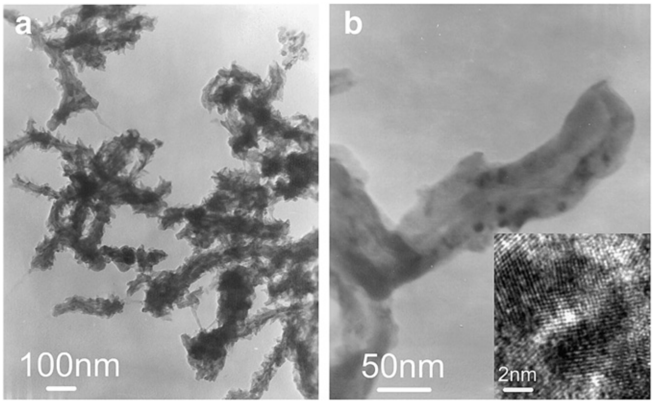

Fig. 1. TEM images of (a) PANI/CNT and (b) Pt-DENs/PANI/CNT composite and HRTEM image of Pt-DENs (inset in Fig. 1 b).

PANI was synthesized by in situ polymerization. Although PANI/CNT nanocomposites are well documented, Pt-DENs/PANI/CNT composite have been rarely reported, especially in the field of biosensor. As-prepared Pt-DENs/PANI/CNT composite are expected to possess the properties of the individual components with a synergistic or complementary effect.

2. Experimental and methods

2.1. Materials

Aniline was from Shanghai Chemical Reagent and distilled under vacuum prior to use. Multiwalled carbon nanotubes (diameter 10–20 nm, length 5–15 μm) were from Shenzhen Nanotech Port Co. and the as-received CNTs were treated via sonication in 1:3 concentrated nitric-sulfuric acid for 6 h. Glucose oxidase (GOx, EC.1.1.3.4, TYPEVII, 150 U/mg), glucose and poly(sodium 4-styrenesulfonate) (PSS, MW ~70,000) were purchased from Sigma-Aldrich. Fourth-generation poly (amidoamine) dendrimers having amine terminal groups were synthesized according to the previous literature [24,25]. The other chemicals were of analytical grade. Doubly distilled and deionized water were used throughout the experiment. A 0.05 M phosphate buffer solution (PBS, pH 6.0) purchased from Shanghai Chemical Reagent Co. was used in this paper unless indicated otherwise.

2.2. Measurements

The transmission electron microscopic (TEM) images were recorded on JEOL, JEM-100CX at 100 kV and high-resolution transmission electron microscopy (HRTEM) was on JEM-2100F that was used to examine particle size and shape and the effectiveness of the coating procedure. Fourier transform infrared spectra (FT-IR) were recorded as a KBr pellet on Nicolet 5700 spectrometer.

Electrochemical measurements were performed on an electrochemical analyzer CHI 660C (Shanghai Chenhua Instrument Co., China) connected to a personal computer. All electrochemical experiments were carried out in a 10 ml cell containing 8.0 ml of 0.05 M PBS at room temperature (25 °C) and using GOx/Pt-DENs/PANI/CNT modified platinum disk electrode (2 mm diameter) as a working electrode, a platinum wire as counter electrode, and Ag/AgCl (3 M KCl) as reference against which all potentials were measured. The influence of applied potential and the solution pH on the response of the biosensor were studied by changing the potential on cell and using the buffer solution with different pH value, respectively. The amperometric experiments were performed by adding various volume of different concentration of glucose or interferences on a stirred cell.

2.3. Preparation of GOx/Pt-DENs/PANI/CNT composite-modified electrode

Pt-DENs were synthesized according to our previous literature [26]. Briefly, to 10 ml of water was added 1.0 ml of 1 mM poly (amidoamine) dendrimer aqueous solution and, subsequently, 0.25 ml of 0.1 M K_2PtCl_4 aqueous solution. After the mixture was adjusted pH to 4.5 with HCl and NH_4OH and then stirred for 48 h, 1.67 ml of a 0.3 M $NaBH_4$ aqueous solution was added. The resulting dark brown solution was purified by dialysis against water for 24 h to obtain Pt-DENs.

CNT were coated with protonated PANI in situ during the oxidative polymerization of aniline according to the method reported previously [27]. Typically, 0.7 g of aniline monomer in 100 ml of 0.1 M HCl solution was added to 150 ml of 0.1 M HCl solution containing CNT (0.2 g). And 0.8 g ammonium persulfate was slowly added dropwise into the above solution with stirring at the room temperature 24 h. The resultant products were filtered and rinsed with distilled water several times until neutrality.

50 ml PSS (3 mg/ml, 0.5 M NaCl) was added to as-prepared 0.5 g PANI/CNT composites stirring 2 h to introduce well-dispersive negatively charged PANI/CNT aqueous solution. 20 ml the above prepared positive Pt-DENs were added to negatively charged PANI/CNT solution adsorbed 10 h and formed the Pt-DENs/PANI/CNT composite. After each adsorption step, the excess supernatant was removed by centrifuged and washed.

10 μl of the Pt-DENs/PANI/CNT composite aqueous solution (10 mg/ml) was dripped on the cleaned Pt disk electrode and the coating was dried at room temperature. The modified electrode was dipped in 5 mg/ml GOx solution (in pH 6.0 PBS) containing 1 mg/ml bovine serum albumin (BSA) and 5% glutaraldehyde for 2 h. Then, the GOx/Pt-DENs/PANI/CNT electrode was rinsed with doubly distilled water and dried in nitrogen.

3. Results and discussion

3.1. Morphology and characterization of Pt-DENs/PANI/CNT and PANI/CNT composite

Fig. 1 shows the TEM images for PANI/CNT and Pt-DENs/PANI/CNT composites. The formation of PANI/CNT composites is shown in Fig. 1a. The hollow structure between the two sides of the walls indicates the present of CNT with the diameter of 10–20 nm, and the surface of the CNT becomes very rough indicating the CNT coating with PANI and the coating takes place only at the outer surface of CNT. Platinum nanoparticles (the dark spots in image) are anchored or decorated on

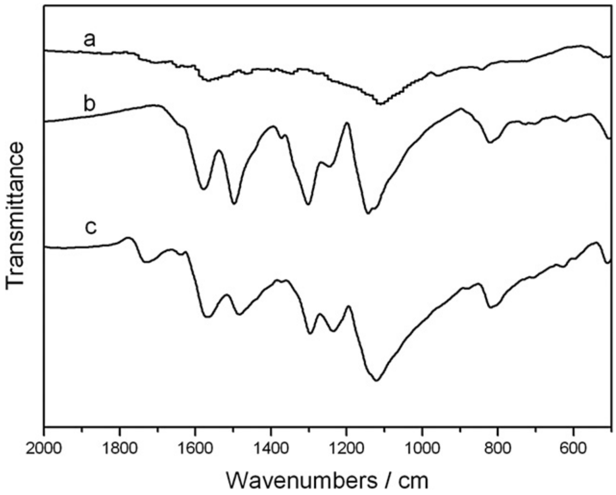

Fig. 2. FT-IR spectra of (a) CNT, (b) PANI and (c) PANI/CNT.