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An enhanced biosensor for glutamate based on self-assembled carbon nanotubes and dendrimer-encapsulated platinum nanobiocomposites-doped polypyrrole film

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Abstract

An enhanced amperometric biosensor based on incorporating one kind of unique nanobiocomposite as dopant within an electropolymerized polypyrrole film has been investigated. The nanobiocomposite was synthesized by self-assembling glutamate dehydrogenase (GLDH) and poly(amidoamine) dendrimer-encapsulated platinum nanoparticles (Pt-DENs) onto multiwall carbon nanotubes (CNTs). ζ-Potentials and high-resolution transmission electron microscopy (HRTEM) confirmed the uniform growth of the layer-by-layer nanostructures onto the carboxyl-functionalized CNTs. The size of Pt nanoparticles is approximately 3 nm. The $(\mathrm{GLDH/Pt\text{-}DENs})_n$/CNTs/Ppy hybrid film was obtained by electropolymerization of pyrrole onto glassy carbon electrodes and characterized with scanning electron microscopy (SEM), cyclic voltammetry (CV) and other electrochemical measurements. All methods indicated that the $(\mathrm{GLDH/Pt\text{-}DENs})_n$/CNTs nanobiocomposites were entrapped within the porous polypyrrole film and resulted in a hybrid film that showed a high electrocatalytic ability toward the oxidation of glutamate at a potential 0.2 V versus Ag/AgCl. The biosensor shows performance characteristics with high sensitivity (51.48 μA mM^{-1}), rapid response (within 3 s), low detection limit (about 10 nM), low level of interference and excellent reproducibility and stability.
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Keywords: Carbon nanotubes; Dendrimer-encapsulated platinum nanoparticles; Self-assembly; Polypyrrole; Electropolymerization; Biosensor

1. Introduction

Conducting polymers such as polyaniline, polythiophene, polypyrrole have emerged as potential candidates for electrochemical sensors, because of their electrical properties, exclusion of electroactive and surface-active interferences, control of the film thickness, and bio-reagent loading onto tiny electrode surfaces, etc. [1]. Most commonly, conducting polymers which are either doped or modified by biomaterials, exhibit unique catalytic or affinity properties [2,3]. The conductive polymers often used in the design of biosensors. Polypyrrole (Ppy) is one of the conductive polymers mostly used in electrochemical biosensors, since it can be electropolymerized in a neutral pH region and easily entrap various biological compounds [1]. Ramanavicius et al. have reported an interesting overview on the potential use of conducting polypyrrole as electrochemical based affinity biosensors [2].

Recently, nanomaterials for biosensing applications have attracted much interest [3–5]. Carbon nanotubes (CNTs) are promising materials for biosensing applications due to several intriguing properties [6]. Various design methodologies for CNTs-based electrochemical biosensors and their performance characteristics, advantages, and employment for the detection of a number of analytes have been developed [4,5]. In a previous paper, we demonstrated the remarkably improved sensitivity of the amperometric biosensor based on CNTs coated with poly(amidoamine) dendrimer-encapsulated Pt nanoparticles (Pt-DENs) for glucose detection [7]. A biosensor fabrication method based on self-assembling AChE or GOx on the carbon nanotubes (CNTs) surface is created by alternately absorbing the species into poly(diallyldimethylam-monium) chloride polymer (PDDA) as was reported recently [8,9].

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A number of techniques such as physical adsorption, electrochemical entrapment, covalent attachment incorporating nanomaterials and biomolecules into electrode conducting polymeric films, have been adapted to improve the properties of desired biosensors [10,11]. Malinauskas et al. have reviewed the electrochemical aspects of conducting polymer-based nanostructured materials for application to super-capacitors, energy conversion systems, batteries and sensors [12]. Recently, Luo et al. and Frackowiak et al. have fabricated conducting polymer and CNTs composites by chemical or electrochemical method. These composites showed the enhancement of charge density, electrical conductivity, and electrocatalytic ability compared with pure conducting polymer or nanomaterials [13–15].

In this present work, we have investigated combination of electrochemical techniques with some chemical surface modification techniques for development of new nanostructural assemblies based on conducting polymers. Here, an enhanced amperometric enzyme biosensor based on incorporating a nanobiocomposite-dopant based on self-assembling glutamate dehydrogenase (GLDH) and poly(amidoamine) dendrimer-encapsulated platinum nanoparticles (Pt-DENs) on multiwall carbon nanotubes (CNTs) within an electropolymerized polypyrrole film has been developed. Details of the preparation, performance and advantages of the new nanobiocomposites modified biosensor are given in the following section.

2. Experimental

2.1. Chemicals and instrumentation

Glutamate dehydrogenase (EC 1.4.1.3, NAD(P)$^+$-dependent GLDH, MW 300,000, from bovine liver containing in 50% glycerol), glutamate and β-nicotinamide adenine dinucleotide (oxidized form, NAD$^+$) were purchased from Sigma–Aldrich. CNTs are from UNILAB, State Key Laboratory of Chemical Engineering, East China University of Science & Technology. Pt-DENs were synthesized according to the previous literature [17–19]. Stock solution of glutamate dehydrogenase (250 U mL^{-1}) was prepared by phosphate buffer solution (pH 7.4). The other chemicals were of analytical grade. Doubly distilled and deionized water was used through this work.

The high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) images were obtained by using a JEM-3010F and JSM-5600LV, respectively. The electrophoretic mobilities of the adsorbed CNTs suspension were measured using a Malvern Zetasizer 3000HS. Electrochemical measurements were performed by using a CHI 660C (CH Instruments, Chenhua, Shanghai, China) connected to a personal computer. A three-electrode configuration was employed, consisting of a multilayer modified glassy carbon (GC) electrode (3-mm diameter) serving as a working electrode, whereas Ag/AgCl (3 M KCl) and platinum wire served as the reference and counter electrodes, respectively. Batch electrochemical experiments were carried out in a 10 mL voltammetric cell at room temperature (25 °C).

2.2. Preparation of (GLDH/Pt-DENs)$_n$/CNTs bionanocomposites

The multiwall CNTs were first shortened and functionalized by sonicating in a mixture of concentrated HNO_3 and H_2SO_4 (1/3, v/v) for 6 h followed by extensively washing in deionized water several times and finally dried under vacuum and dispersed in double-distilled water at a concentration 5 mg mL^{-1}.

After oxidation, the CNTs are shorter and left with the carboxylic groups that impart a hydrophilic nature and facilitate further functionalization. Then positive, dendrimer encapsulated Pt nanoparticles (Pt-DENs) and negative glutamate dehydrogenase (GLDH) were alternately absorbed onto the carbon nanotubes surface. First, GLDH/Pt-PAMAM/CNTs film was attained by mixing the Pt-PAMAM/CNTs heterostructures with the negatively charged GLDH (0.2 unit mL^{-1}) in a PBS (pH 7.4) for 20 min, centrifuged at 7000 rpm for 10 min, and then washed with distilled water twice to remove the supernatant. Using the same procedure, positively Pt-PAMAM and negatively GLDH were alternately absorbed onto the CNTs until obtained suitable layer. The as-prepared multilayers were denoted as (GLDH/Pt-DENs)$_n$/CNTs. The process was characterized by ζ-potential measurement and the resultant heterostructures were characterized by HRTEM.

2.3. Preparation of the modified electrodes

Glass carbon (GC, 3 mm diameter, Model CHI 104, CH Instruments) electrodes were polished with 1.0, 0.3 and 0.05 μm alumina powder, cleaned in a piranha solution (a 1:3 mixture of 30% H_2O_2 and concentrated H_2SO_4) and finally sonicated thoroughly in double distilled water. Then, 20 μL of the resulting CNTs nanocomposite solution (dispersion by sonicating for 5 min) was dropped onto the clean GC electrode surface with a pipette. The coated electrode was dried at room temperature and then kept under dry conditions at 4 °C before use.

The polypyrrole film was deposited on the surface of the (Pt-DENs/GLDH)$_n$/CNTs-modified electrode by an electrochemical potential cycling process. The electropolymerization of Ppy was performed for five full voltammetric cycles between −0.2 and 1.0 V versus Ag/AgCl at a scan rate of 50 mV s^{-1} in PBS (pH 7.4) containing 0.1 M pyrrole. The resulting electrode was denoted as (Pt-DENs/GLDH)$_n$/CNTs/Ppy/GC electrode. The polymerized electrode was immediately submerged in PBS (pH 7.4) at 4 °C to prevent enzyme denaturation and stored at 4 °C prior to use.

3. Results and discussion

3.1. Multilayers assembling and characterization

Microelectrophoresis measurements were conducted to qualitatively follow adsorption of the layers on the CNTs templates.

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