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High sensitive sensor based on functionalized carbon nanotube/ionic liquid nanocomposite for simultaneous determination of norepinephrine and serotonin

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ABSTRACT

This paper describes the development and utilization of a new nanocomposite consisting of benzofuran derivative-functionalized multiwalled carbon nanotubes and ionic liquid (IL) for glassy carbon electrode modification. A pair of well-defined redox peaks of benzofuran derivative was obtained at the glassy carbon (GC) electrode by direct electron transfer between the benzofuran derivative and the GC electrode. The novel sensor shows excellent electrocatalytic activities toward the oxidation of norepinephrine (NE) and serotonin (5-HT). Furthermore, no obvious interference was found for the detection of NE and 5-HT in the presence of common interferents such as ascorbic acid and uric acid that coexists compounds with NE and 5-HT in biological systems. Differential pulse voltammetry (DPV) exhibited two linear dynamic ranges of 0.1–30.0 μM and 30.0–1000.0 μM for NE and one linear dynamic ranges of 5.0–900.0 μM for 5-HT. The detection limits for NE and 5-HT were found to be 49 nM and 2 μM, respectively. The proposed sensor was successfully applied for the determination of NE and 5-HT in human serum.

1. Introduction

The rapid progress in nanotechnology and nanoscience introduced a scientific momentum that involves the fundamental understanding of the properties of nanostructures, the synthesis of nanoscale materials, the imaging of nanostructures, and the assembly of functional nanoscale devices [1]. The chemical modification and solubilization of carbon nanotubes represent an emerging area in the research on nanotubes-based materials. Surface chemistry of carbon nanotubes is critical to their physical properties and applications. For instance, sidewall functionalization is one of the most important ways to make soluble nanotubes, and is also important for many applications such as nanotubes assembly [2,3] and electrochemical sensing [4–6]. Many methods have been developed to perform sidewall functionalization to carbon nanotubes, such as chemical modification, chemical doping, electrochemical methods and physical treatment [7,8]. Among them, modifying the nanotube surface using aromatic moieties through noncovalent interaction is a very attractive one [9]. Noncovalent functionalization to the CNT not only is a much simpler method compared with covalent functionalization but also has the advantage of preserving nanotube's sp^2 structure, thus the electronic properties [10,11].

Carbon ionic liquid electrode has been reported as a high performance electrode with many good features and provision of high rates of electron transfer [12,13]. The acknowledged advantages of these ILs include good chemical and thermal stability, almost negligible vapor pressure, good ionic conductivity, wide electrochemical windows etc. [14,15]. Since 2003, it is known that imidazolium-type ionic liquids tend to form physical gel when grounded with CNTs [16] by physical cross-linking of the nanotube bundles, mediated by local molecular ordering of ILs. Similar, highly electroconductive material can be formed from polymerizable IL and CNTs [16,17]. IL–CNT gel and analogous material containing carbon microbeads and IL were first recognized by Dong et al. as suitable electrode material [18]. Further studies of these electrodes obtained from variety of hydrophobic or hydrophilic ILs show usefulness of this easy prepared electrode material, which can be deposited in a form of thick film on solid conductive substrate [19].

Norepinephrine (NE) and serotonin (5-hydroxytryptamine, 5-HT) are important catecholamine neurotransmitters in biological systems. NE is a very important catecholamine neurotransmitter in the mammalian central nervous system and is often monitored electrochemically in vivo with microfiber electrodes. The oxidation of this compound is interesting, and this process

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occurs in the human body. 5-HT is an important biomolecule in physiological systems, playing a vital role in the regulation of mood, sleep, emesis, sexuality, and appetite. Low levels of 5-HT are associated with several disorders, including depression, anxiety, and migraines [20]. Extremely high levels of 5-HT can manifest toxicity and potentially fatal effects known as 5-HT syndrome [21]. Catecholamines play an important role in health and disease. Increase in catecholamines is associated with stress, a fall in blood pressure or blood volume, thyroid hormone deficiency, congestive heart failure, and arrhythmias; decreased amounts of catecholamines are seen in idiopathic postural hypotension [22].

Simultaneous determination of NE and 5-HT is important, since both coexist in a biological system. However, the voltammetric determinations of NE and 5-HT are often interfered by some coexisting substances in biological systems, such as ascorbic acid (AA) and uric acid (UA). Thus, the ability to selectively determine NE and 5-HT is significant. Many modified electrodes have been studied and proved to be applicable to the measurement of 5-HT or catecholamines [23–30].

In our previous study, we have reported the modified carbon paste electrode with 7-(1,3-dithiolan-2-yl)-9,10-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one (DC) for catalytic oxidation of hydrazine [31]. To the best of our knowledge, there is no reported to functionalization of CNT/IL bucky gel with DC. Therefore, we used benzofuran derivative functionalized CNTs for the construction of novel nanostructured DC–CNT–IL three-dimensional network film modified GC electrode. The experimental results indicate that modified GC electrode offers several advantages such as high repeatability, good stability and high apparent charge transfer rate constant. To the best of our knowledge, there is no report on the simultaneous determination of NE and 5-HT using biomolecules functionalized carbon nanotubes. Thus, in this paper, we described initially electrocatalytic effect of modified GC electrode (IL–DC–CNT/GC) for the individual and simultaneous determination of NE and 5-HT. Utilizing the developed method, determination of the two compounds has been carried out in water and human blood serum samples.

2. Experimental

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302N, Eco Chemie, Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A three-electrode system was used, where a GCE or a modified GCE served as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl/KCl (3.0 M) electrode as the reference electrode. All potentials reported were versus the Ag/AgCl. A Metrohm 691 pH/Ion Meter was used for pH measurements. Ultraviolet–visible (UV–vis) spectra were obtained by an Optizen 3220 UV–vis spectrophotometer.

All solutions were freshly prepared with double distilled water. Norepinephrine, serotonin and 1-butyl-3-methylimidazolium hexafluorophosphate were reagent-grade from Sigma Aldrich. Phosphate salt, sodium hydroxide, solvents and reagents were of pro-analysis grade from Merck (Darmstadt, Germany). These chemicals were used without further purification. DC was synthesized in laboratory. The multi-wall carbon nanotubes (outer diameter: 5–20 nm; inner diameter: 2–6 nm; length: 1–10 μm and 95% pure) were purchased from Plasma Chem (Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0.

2.2. Synthesis of 7-(1,3-dithiolan-2-yl)-9,10-dihydroxy-6H-benzofuro[3, 2-c]chromen-6-one (DC)

DC was synthesized by electrosynthesis method and the manner described in our previous work [32]. Briefly, 80 mL of 0.15 M phosphate buffer (pH 7.0) in water/acetonitrile (85/15 volume ratio), containing 0.7 mmol of 4-(1,3-dithiolan-2-yl)benzene-1,2-diol and 0.7 mmol 4-hydroxycoumarin was electrolyzed at controlled-potential in a divided cell. The electrolysis was terminated when the current decayed to 5% of its original value. The precipitated solid was collected by filtration and was washed several times with water.

2.3. Preparation of the electrode

The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GC electrode was polished on a polishing cloth with alumina powder. Then the electrode was cleaned by ultrasonication in deionized water, acetone, and ethanol, respectively. To obtain the best conditions in the preparation of the IL–DC–CNT/GC, we optimized the ratio of DC, CNTs and IL. The results of our study showed that the maximum peak current intensity of NE could be obtained at the surface of IL–DC–CNT/GC with optimum ratio of DC, CNTs and IL.

The DC–CNT composites were prepared by mixing 5 mg of DC and 5 mg of CNTs in 8 mL of DMF under stirring for 48 h at room temperature. The resulting suspensions were filtered, and the obtained samples were first thoroughly rinsed with distilled water to ensure removal of the free DC or unadsorption DC from CNTs surface and then dried at 40 °C under vacuum overnight to obtain the DC–CNTs composites.

The DC/GC electrode and DC–CNT/GC modified electrode were prepared by dropping 10 μL of 3 mg/mL DC and 3 mg/mL DC–CNT (dispersed in ethanol) on the surface of GC electrode, respectively. A beaker was covered over the electrodes so that ethanol can evaporate slowly in air and a uniform film electrode can be formed. DC–CNTs mixing with IL (mass ratio 1:4) were ground in a mortar at an ambient temperature for about 15 min, and a black gel was formed. After that, 0.1 mg gel modified glassy carbon electrode (denominated as IL–DC–CNT/GC in this work) was fabricated.

3. Results and discussion

3.1. Characterization of the IL–DC–CNT/GC electrode

In order to understand the performance of the IL–DC–CNT/GC modified electrodes, we investigated various modified electrodes by UV–vis absorption, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), respectively.

Fig. 1 shows the UV–vis absorption spectra of DC in the absence and presence of CNTs. As shows in Fig. 1, curve a, CNTs exhibits a featureless absorption, whereas, in curve b, DC displays strong absorption bands at 285 and 450 nm. After CNTs electrostatically interacted with DC, the absorption bands of DC–CNTs have the similar absorption band at 283 and 443 nm as shown in curve c. There was no obvious change of absorption spectra in DC–CNTs and DC alone, indicating that DC entrapped in DC–CNTs retained its essential conformation, and has been adsorbed successfully on CNTs.

The interfacial characteristic of the different modified electrodes were studied by EIS. Fig. 2 shows the impedance spectra represented as Nyquist plots for bare GC electrode (a), DC/GC (b), DC–CNT/GC (c) and IL–DC–CNT/GC (d) in 1.0 mM $K_4Fe(CN)_6$ and 1.0 mM $K_3Fe(CN)_6$ containing 0.1 M KCl solution. The semicircle