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Electrocatalytic properties of functionalized carbon nanotubes with titanium dioxide and benzofuran derivative/ionic liquid for simultaneous determination of isoproterenol and serotonin

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ABSTRACT

In this paper we report synthesis and application of functionalized multiwalled carbon nanotubes (CNTs) with titanium dioxide nanoparticles (TiO_2), 9-(1,3-dithiolan-2-yl)-6,7-dihydroxy-3,3-dimethyl-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (benzofuran derivative (DDF)) and 1-butyl-3-methylimidazolium tetrafluoroborate (IL) as high sensitive sensors for simultaneous determination of isoproterenol (IP) and serotonin (5-HT) using glassy carbon electrode. The modified electrode was characterized by different methods including a scanning electron microscope (SEM), electrochemical impedance spectroscopy (EIS) and voltammetry. A pair of well-defined redox peaks of DDF was obtained at the modified glassy carbon electrode by direct electron transfer between the DDF and the electrode. Dramatically enhanced electrocatalytic activity was exemplified at the modified electrode, as an electrochemical sensor to study the electro oxidation of IP and 5-HT. The differential pulse voltammetry data showed that the obtained anodic peak currents were linearly dependent on the IP and 5-HT concentrations in the range of 0.1–1300.0 and 1.0–650.0 μM, respectively. The applicability of the modified electrode was demonstrated by simultaneous determination of IP 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 [1,2]. Carbon nanotubes (CNTs) continue to receive considerable attention in electrochemistry [3–5]. CNTs have been the subject of numerous investigations in chemical, physical, and materials areas due to their novel structural, mechanical, electronic, and chemical properties [6].

TiO_2 are widely used in biosensors, solar cells, batteries, additives in toothpaste and white paint, and others. Recently, there is a considerable interest in using TiO_2 nanoparticles as a film-forming material since they have high surface area, optical transparency and good biocompatibility [7–9]. The combination of CNTs and TiO_2 nanoparticles can lead to interesting novel composite materials and devices with relevant properties for a variety of functional and biomedical applications. It has been reported, for example, that the combination of CNTs with TiO_2 can enhance the electrocatalytic effect of TiO_2 and CNTs [10,11]. CNTs are excellent carrier substrates for TiO_2 nanoparticles, due to their high structural integrity and the high surface area they provide due to the possibility of building a mesoporous structure [12]. Multilayer coatings of CNTs and TiO_2 nanoparticles might find also applications in biomedical implant coatings and tissue engineering scaffolds. Other studies have demonstrated that porous structures containing CNTs can be used as scaffolds for tissue engineering [13].

Isoproterenol (IP) and serotonin (5-hydroxytryptamine, 5-HT) are important catecholamine neurotransmitters in biological systems. 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 [14]. IP is widely used in the treatment of allergic emergencies such as styptic, bronchial asthma, status asthmatic, cardiac arrest, glaucoma, ventricular bradycardia also bronchitis, cardiac chock and heart attack [15,16]. IP has positive inotropic and chronotropic effects on the heart. These effects elevate systolic blood pressure, while its vasodilatory effects tend to lower diastolic blood pressure. The

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excess of the drug may cause heart failure and arrhythmias [15]. 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 [17]. Extremely high levels of 5-HT can manifest toxicity and potentially fatal effects known as 5-HT syndrome [18]. Hence, simultaneous determination of IP and 5-HT is important, since both coexist in a biological system.

To the best of our knowledge, no study has been published so far reporting the simultaneous electrocatalytic determination of isoproterenol and serotonin by using any kind of modified electrodes and specially modified electrode with functionalization of CNT/IL bucky gel. Here in continuation of our studies concerning the preparation of modified electrodes [19–23], we used functionalized CNTs with TiO_2 nanoparticles, DDF and IL for the construction of novel nanostructured DDF-CNT-TiO_2/IL film modified GC electrode as a new electrode in the electrocatalysis and simultaneous determination of isoproterenol and serotonin. The experimental results indicate that modified GC electrode offers several advantages such as high repeatability, good stability and high apparent charge transfer rate constant. 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-302 N, 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.

All solutions were freshly prepared with double distilled water. Isoproterenol, serotonin and 1-butyl-3-methylimidazolium tetrafluoroborate 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. DDF 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).

2.2. Synthesis of 9-(1,3-dithiolan-2-yl)-6,7-dihydroxy-3,3-dimethyl-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (DDF)

DDF was synthesized by electrosynthesis method and the manner described in our previous work [24]. 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 dimedone was electrolyzed at controlled-potential (0.35 vs. SCE) 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. Synthesis of TiO_2–CNT composites

The TiO_2–CNT composites were prepared according to the procedures described in the literature [25]. In a typical experiment to prepare composites, titanium isopropoxide (TIP) and MWCNTs (mass ratio of 5:1) were dissolved and ultrasonically dispersed in 8 mL of ethanol, respectively. Then the suspension was loaded in a stainless autoclave of 20 mL. The autoclave was sealed and moved to an oven of 270 °C and maintained at this temperature for 2 h, and then cooled to room temperature naturally. Subsequently, the dark precipitate was separated from the solution by centrifugation and washed with absolute ethanol and distilled water repeatedly. The produced sample was vacuum-dried at 60 °C for 6 h. By changing the TIP/MWCNT mass ratios, different samples were obtained.

2.4. 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, and ethanol, respectively. To obtain the best conditions in the preparation of the DDF-CNT-TiO_2/IL/GC, we optimized the ratio of DDF, CNT-TiO_2 and IL. The results of our study showed that the maximum peak current intensity of IP could be obtained at the surface of DDF-CNT-TiO_2/IL/GC with optimum ratio of DDF, CNT-TiO_2 and IL.

The DDF-CNT-TiO_2 composites were prepared by mixing 10 mg of DDF and 10 mg of CNT-TiO_2 in 15 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 DDF or unadsorption DDF from CNT-TiO_2 surface and then dried at 40 °C under vacuum overnight to obtain the DDF-CNT-TiO_2 composites.

The DDF-CNT-TiO_2 modified electrode was prepared by dropping 8 μL of 3 mg/mL DDF-CNT-TiO_2 (dispersed in ethanol) on the surface of GC electrode. A beaker was covered over the electrodes so that ethanol can evaporate slowly in air and a uniform film electrode can be formed. For the preparation of DDF-CNT-TiO_2/IL/GC, 15 mg DDF-CNT-TiO_2 was uniformly dispersed in 5 mL double distilled water with the aid of ultrasonic agitation. Then, 250 μL of IL was added to the obtained DDF-CNT-TiO_2 solution and with the aid of ultrasonic agitation, a uniform solution was prepared. The DDF-CNT-TiO_2/IL/GC electrode was prepared by dropping 8 μL prepared DDF-CNT-TiO_2/IL composite was dropped onto the GC electrode surface and the solvent was evaporated in air.

3. Results and discussion

3.1. Characterization of the CNT-TiO_2

The response of a modified electrode is related to its physical morphology. Scanning electron microscopy (SEM) was performed to the CNT-TiO_2 particles and it was indicated that CNT-based composites were obtained under our experimental conditions. Fig. 1A shows a representative SEM image of the sample prepared with the TIP/CNT, which clearly illustrates that the CNTs were homogeneously decorated with well-dispersed nanoparticles. The SEM image of the primary CNTs is displayed as an inset of Fig. 1A.

The XRD pattern of the sample prepared with the TIP/CNT Fig. 1B, which demonstrates the highly crystalline nature of the composites. The diffraction peak at $2\theta = 26.5^\circ$ can be well indexed as the 002 reflection of graphite, while the other diffraction peaks in the range of $15^\circ < 2\theta < 80^\circ$ correspond to the 101, 004, 100, 200, 105, 211, 204, 116, 220 and 215 reflections of anatase [26], respectively, which suggests that the nanoparticles decorated on the MWCNTs were anatase. This indicates that the precursor, titanium (IV) isopropoxide, was converted to anatase, which deposited on the CNTs under the experimental conditions.