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A new electrochemiluminescent sensing interface for clonazepam based on titanate nanotubes self-assembled film

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ABSTRACT

A nanometer-sized titanic substance, titanate nanotube, was synthesized and used for investigating the electrochemiluminescence (ECL) behaviors of lucigenin. A self-assembled film of titanate nanotube was formed on the chitosan modified glassy carbon electrode (GCE) through electrostatic attraction. Comparing with the bare GCE, a dramatically enhanced (more than 50-fold) and more stable ECL emission of lucigenin could be achieved on the proposed TNTs/chitosan composite film-modified GCE under the cathodic potential scanning mode. Clonazepam was firstly found and employed as the coreactant to enhance ECL of lucigenin. Herein, this coreactant ECL system was investigated on the proposed ECL platform in detail. Under the optimum conditions, the proposed ECL sensor exhibited a linear response range of 1.0×10^{-8}–1.0×10^{-4} M with detection limit of 8.4×10^{-9} M and long-term stability for clonazepam. The possible mechanism for this sensor was also discussed.

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1. Introduction

The analytical methods based on electrochemiluminescence (ECL) have the advantages of high sensitivity and selectivity, good reproducibility and easy control. Thereby, it is becoming a powerful detection method in recent years. Lucigenin (N,N′-dimethyl-9,9′-biacrid-inium dinitrate) is an important ECL reagent, and considerable studies with regard to its chemiluminescence (CL) mechanism have been published [1,2]. However, owing to its low sensitivity and easy electrode fouling, less attention has been paid to the ECL of lucigenin than to its chemiluminescent. Especially, the adsorption of insoluble product of lucigenin after electrochemical process is the notorious problem which baffles the application of lucigenin ECL system. Hence, many efforts have been devoted to improve the sensitivity and stability of lucigenin ECL and expand its analytical application [3–5]. Okajima and Ohsaka investigated the ECL behavior of lucigenin on several kinds of modified electrodes, and found the modified electrodes could significantly enhance the ECL of lucigenin [3]. The electrodes modified by single-wall carbon nanotube film [4], gold nanoparticle self-assembled film [5] and so on have been used to improve the sensitivity and the stability of lucigenin ECL.

Recently, metal-oxide nanotubes which own unique one-dimensional (1D) nanostructures may offer uniform nanometer-sized channel, possess well electronic conductivity, high specific surface area and exhibit stable mechanical and chemical properties. Consequently, increasing attention has been paid to such metal-oxide nanotubes, especially to its application. Titanate nanotubes (TNTs), which are multilayered structures with a nanometer-scale inner-core cavity exposed to the outer surface [6], have attracted more interest due to their excellent electronic and optical characteristics. The surface of TNTs could be easily negatively charged after treatment by weak bases. Thus TNTs may possess broad application foreground in electroanalysis. However, up to the present, the ECL researches involved TNTs were still limited.

Clonazepam, 5-(2-chlorphenyl)-1,3-dihydro-7-nitro-2H-1,4-benzodiazepin-2-one, as a benzodiazepine derivative, is an anticonvulsant agent primarily used in the treatment of epilepsy for both adults and children [7–9]. Its use is based on daily administration of an oral dose to prevent seizures or intravenous infusions in status epilepticus [10] and neonatal convulsions [11], so it is necessary to monitor the concentration of clonazepam in the plasma of epileptic patients for controlling the dosage. In general, the accepted therapeutic concentration is in the range of 15–80 ng/ml at predose sampling [11,12]. Moreover, there is a risk of increased seizure frequency when the concentration of clonazepam in plasma exceeds 120 ng/ml [13]. Hence, it is essential to develop a sensitive and rapid method for detecting clonazepam in biological fluids. Several methods based on liquid chromatography (LC) [14–16], spectrophotometry [17,18], polarography [19] and gas chromatography [20] have been developed for determining clonazepam. Most of the above methods suffer from either time-consuming for sample preparation [21–23] or expensive equipment [24–26]. However, to the best of our knowledge, ECL

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method has been never applied to determine clonazepam. Herein, we chose clonazepam as a coreactant model to further evaluate the ECL behavior of lucigenin on the titanate nanotubes self-assembled film.

The objective of this work was to demonstrate the potential use of TNTs in the ECL application. The ECL behavior of lucigenin at the proposed TNTs/chitosan composite film-modified GCE has been investigated at cathodic potential. The results showed that lucigenin exhibited an obviously improved ECL response, including stability and sensitivity on the proposed modified electrode. Especially, this proposed modified electrode not only could amplify the ECL emmisson of lucigenin (more than 500-fold), but also evidently improve the stability of the ECL response of lucigenin at cathodic potentials below −0.6 V (versus Ag/AgCl). Meanwhile, clonazepam was firstly found to be a kind of enhanced coreactant for lucigenin ECL system. The effect of self-assemble time, pH, scan rate and ECL reaction medium on this ECL system were investigated in detail. The possible mechanism for the enhancement of ECL of lucigenin by clonazepam was also proposed.

2. Experimental

2.1. Reagents

Lucigenin and chitosan with a degree of deacetylation of 85% were purchased from Sigma Chemical Co. (USA) and used without further purification. Clonazepam was purchased from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Stock solution of 1.0×10^{-3} mol/L for clonazepam was prepared and stored at 4 °C in a refrigerator. The clonazepam working solutions were made by appropriate dilution with water. All other chemicals used in this study were analytical reagent or better. Double-distilled water was used throughout.

2.2. Electrochemiluminescence measurement

The equipment used for ECL measurement was a BPCL ultra-weak chemiluminescence analyzer controlled by a personal computer with BPCL program (Institute of Biophysics, Academia Sinica, China) and a electrochemical analyzer (CHI620, Shanghai Chenghua instrument Co., China). A conventional three-electrode system was used as the electrolytic system, which was composed of a chitosan/TNTs film-modified GCE as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (saturated KCl) electrode as the reference electrode. A commercial 5 ml cylindroid's glass cell was used as ECL cell. Before each measurement, the working electrode was fixed in the same position and directly faced the window of the pohotomultiplier tube. Transmission electron microscope (TEM) and field emission scanning electron microscope (FESEM) (FEI Nova Nano SEM 230, USA) were utilized to characterize the morphological characterization of the prepared titanate nanotubes and modified electrode.

2.3. Synthesis of TNTs and preparation of TNT colloidal suspensions

TNTs were synthesized by a hydrothermal process based on a previously reported procedure [27]. A colloidal suspension of TNTs was prepared as follows: a suitable amount of TNTs powder was dispersed in a 0.1 M HNO_3 solution under stirring and centrifugation. 2.5 mg TNTs was dispersed in 1 ml tetraethylammonium hydroxide (TEAOH) and the solution was then for ultrasounding until it dispersed equably.

2.4. Preparation of chitosan/TNTs composite film-modified GCE

A 1.0 wt.% chitosan solution was prepared by dissolving 1.0 g of chitosan flakes into 100 ml of 1.0% acetic acid and stirred for 3 h at room temperature, and the pH of the solution was then adjusted to 5.0. The chitosan solution was stored in refrigerator before using. The chitosan working solutions were made by appropriate dilution with water. The GCE was pretreated before using by polishing its surface with aqueous slurries of alumina powders (average particle diameters: 1.0 and 0.05 μm α-Al_2O_3) on a polishing microcloth and then rinsed with water and sonicated in acetone. Then it was allowed to dry at room temperature. As showed in Fig. 1A, 7 μL of 0.2% (w/w) chitosan solution was dropped onto the surface of GCE and left the solvent evaporate under the ambient temperature. After being washed with water, the resulting modified electrode was immersed in 2.5 mg/ml TNTs solution for required time and then rinsed thoroughly with water to move TNTs adsorbed physically.

3. Results and discussion

3.1. Morphological characterization of the prepared titanate nanotubes

Fig. 1A shows the scheme for fabrication of ECL sensor based on the ECL of lucigenin. Chitosan solution was first dropped onto the surface of GCE and left the solvent evaporate under the ambient condition. After being washed with water, the modified electrode was immersed in TNTs solution for required time and then rinsed thoroughly with water to move the TNTs adsorbed physically. Transmission electron microscope (TEM) images (see the inset of Fig. 1B) convincingly revealed that one-dimensional (1D) nanostructure material TNTs were successfully synthesized. It was clearly observed in the inset of Fig. 1B that the hollow nature of tubes with two ends open and have inner diameters of 5–7 nm, outer diameters of 8–18 nm, wall thickness of 3–6 layers with an interlayer spacing of ~0.4 nm, and the length up to micron. The surface morphological characterization of modified electrode was characterized by field emission scanning electron microscope (FESEM) (see Fig. 1B), from which we can obviously see that TNTs were attached and dispersed equably on the surface of chitosan.

3.2. Characterization of various modified electrodes

Fig. 1C shows the cyclic voltammograms (CVs) of different modified electrodes in 5.0 mM ferri/ferrocyanide solution containing 0.5 M KCl (versus Ag/AgCl as the reference electrode). Well-defined CVs, characteristic of the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ redox couple were observed at the bare GCE (see Fig. 1C(c)). When the electrode was modified with chitosan, the peak current increased dramatically due to the electrostatic force between ferri/ferrocyanide anions and chitosan, although chitosan might act as a mass transfer blocking layer. While the value of peak-to-peak separation (ΔE_p) became large, which suggested the lower electron transfer kinetics at chitosan modified electrode than that at bare glassy carbon electrode. Additionally, the amount of chitosan modified on GCE would determinate the electrochemical behavior of chitosan modified electrode in ferri/ferrocyanide solution. The increased amount chitosan on the modified electrode, the electrostatic force between ferri/ferrocyanide anions and chitosan would play the main role. In the self-assembled process of TNTs at the chitosan modified electrode, the net electric charge could change from positive to negative. Compared with the chitosan modified electrode, a decrease in the redox peaks was observed, which

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