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Sensitive electrochemiluminescence sensor based on ordered mesoporous carbon composite film for dopamine

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ABSTRACT

This work reports a sensitive electrochemiluminescence (ECL) detection strategy based on $Ru(bpy)_3^{2+}$/ordered mesoporous carbon/Nafion composite films modified glassy carbon electrode (GCE). Electrochemical and ECL behaviors of the prepared ECL sensors were studied with tri-n-propylamine (TPA) as coreactant. The proposed ECL sensor showed good reproducibility and high sensitivity to TPA with a wide linear range (4.75×10^{-9} to 6.25×10^{-4} M) and low detection limit (1.58×10^{-9} M). Under the optimized conditions, the ECL sensor with TPA as coreactant was employed to detect a neurotransmitter dopamine (DA), for estimating its practical application in the medicine analysis. The present sensor displayed a good response to the concentration of DA from 5.0×10^{-9} M to 5.0×10^{-4} M. Moreover, the ECL sensor could be successfully applied to detect DA in real samples. The proposed signal amplification strategy for the preparation of ECL sensor could be easily attained and hold great promise for ultrasensitive medicine analysis.

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1. Introduction

Electrochemiluminescence (ECL), the production of light emission from electrochemically generated luminophore [1], is a noteworthy versatile and sensitive analytical method [2]. Due to the inherent advantages of electrochemistry and chemiluminescence, ECL has emerged in various research fields such as chemical sensing [3,4], imaging [5] and optical studies [6]. It also has a widespread application in environmental, clinical and medicine analysis [7]. Among various ECL compounds, $Ru(bpy)_3^{2+}$ with the superior properties including good electrochemical stability, high sensitivity and efficiency [8] has received great attention. So far, extensive efforts have been made to create a solid-state ECL sensor [9] due to its low consumption, simple operation, reproducibility and stability [10,11]. And the approaches for immobilization of $Ru(bpy)_3^{2+}$ onto electrode surfaces include Langmuir–Blodgett film (LB) [12], self-assembly monolayer (SAM) [13] and sol–gel technology [14]. Although a great progress of the ECL sensor has been made, those methods still cannot be applied widely as they suffer from instability at positively biased potentials and possible desorption in organic solvent [15]. To circumvent these disadvantages, ECL sensors based on various nano-materials which act as favorable electric conductors and excellent matrixes for immobilizing $Ru(bpy)_3^{2+}$ are being developed [16,17].

As one of novel carbon materials, ordered mesoporous carbons (OMC) have attracted increasing attention in many fields including adsorption, catalysis, capacitor, sensors, energy storage and etc [18,19], which greatly attribute to their excellent conductibility, high specific surface areas, large pore volume and remarkable π-conjunction [20–22]. Furthermore, when used as a platform for immobilizing organic and inorganic molecules onto electrode surfaces, OMC can effectively promote electron-transfer reactions of important molecules. This outstanding property promotes the increasing application of OMC-based sensors in the electrochemistry analysis [23–25]. Therefore, OMC will be a promising alternative candidate for ECL sensor material.

In this work, the OMC@Nafion-based composite film was used to immobilize $Ru(bpy)_3^{2+}$ onto a glass carbon electrode (GCE) surface. Due to the excellent ion-exchange ability of Nafion [26] and strong adsorption of OMC [27], $Ru(bpy)_3^{2+}$ would be easily immobilized into the composite film. Moreover, this strategy can effectively prevent the immobilized ECL reagents from leaking into the solution, since the ion-exchange selectivity coefficient of Nafion for $Ru(bpy)_3^{2+}$ is as high as 5.7×10^6 [28]. The presented $Ru(bpy)_3^{2+}$/OMC@Nafion composite film-modified GCE displayed good sensitivity for the ECL determination of coreactant tripropylamine (TPA). Under the optimal condition, the $Ru(bpy)_3^{2+}$–TPA system could be applied in the determination of dopamine (DA), which is an important neurotransmitter in the mammalian central nervous system and plays a significant role in the function of the renal, hormonal, and cardiovascular systems [29]. Some brain functions such as learning and memory formation are sensitive

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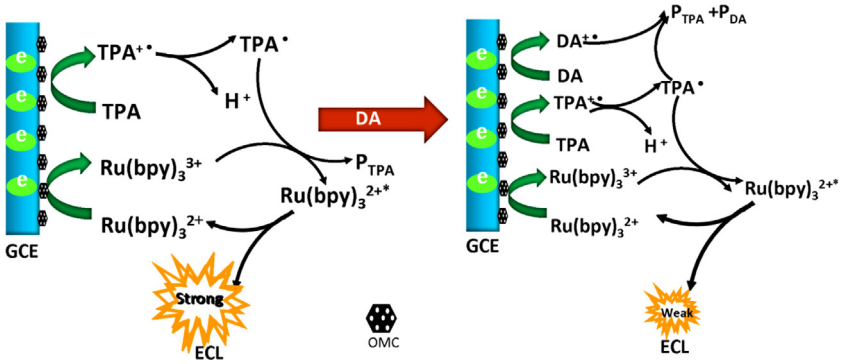

Scheme 1. Schematic illustration of the mechanism for ECL reaction of $Ru(bpy)_3^{2+}$ with TPA and DA. P_{TPA} is the oxidation product of TPA$^{\cdot}$; P_{DA} is the reduced product of $DA^{+\cdot}$.

to the change in the level of DA [30]. Additionally, it may lead to physiological and pathological process of Pakinson when DA concentration levels are extreme abnormalities [31]. Generally, a wide variety of conventional methods, including the capillary electrophoresis [32], high-performance liquid chromatography [33], liquid chromatography–electrospray tandem mass spectrometry [34] and radioimmunossay [35] have been carried out for quantitative analysis of DA. In spite of their high reliability, these assays still have some limitations such as complicated extraction or derivatization procedure, intensive labor and long analysis time. Therefore, it is necessary to develop a simple, rapid, and inexpensive method for quantitative detection of DA. As shown in Scheme 1, ECL response of the proposed $Ru(bpy)_3^{2+}$–TPA reaction system is decreased with the adding of DA. Therefore, the ECL sensor could be employed in quantitative determination of DA.

2. Experimental

2.1. Reagents and materials

Tris (2,2-bipyridyl) dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2{\cdot}6H_2O$) and TPA were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Dopamine hydrochloride ($C_8H_{11}NO_2{\cdot}HCl$) and potassium chloride (KCl) were purchased from Aladdin Chemistry Co. Ltd. Ordered mesoporous carbon (OMC) was obtained from XF Nano company (Nanjing, China). Nafion (5 wt%) was purchased from Fluka. Other reagents were of analytical grade and used as received. Freshly prepared solutions of DA and the ultrapure water were used throughout the work.

2.2. Apparatus

The electrochemical measurements were carried out on a CHI 660B electrochemical workstation (Shanghai CH Apparatus Inc., China). All electrochemical experiments were carried out with a conventional three-electrode system. The three-compartment electrochemical cell contains a platinum wire as auxiliary electrode, an Ag/AgCl (3 M KCl) as reference electrode and $Ru(bpy)_3^{2+}$/OMC@Nafion modified GCE (3 mm in diameter) as working electrode, respectively. The ECL emission was monitored with a model MPI-E electrochemiluminescence analyzer (Xi'An Remax Electronic Science & Technology Co. Ltd., Xi'An, China) at room temperature.

The small-angle and wide-angle X-ray diffraction (XRD) measurements were performed on a Rigaku D/max B diffractometer using Cu Kα radiation (40 kV, 30 and 40 mA). Transmission electron microscopy (TEM) images of the samples were taken with a JEOL 2011 instrument (Hitachi) operating at 200 kV.

2.3. Preparation of $Ru(bpy)_3^{2+}$/OMC@Nafion modified electrodes

Before modified, GCE was polished to a mirror-like with 1.0, 0.3, and 0.05 μm alumina slurry. The electrodes were successively sonicated in 1:1 anhydrous ethanol and doubly distilled water, then allowed to dry under N_2 stream. The OMC@Nafion solution was firstly prepared by dispersing 2.0 mg of the OMC into 1 mL (0.5 wt%) Nafion mixture with ultrasonic oscillation to give a 2 mg mL^{-1} black suspension. Subsequently, eight microliter of as-prepared OMC@Nafion solution was cast on the surface of pretreated GCE and dried in a pressure desiccator to obtain the OMC@Nafion modified electrode. Finally, the modified electrode was immersed into 1.0 mM $Ru(bpy)_3^{2+}$ solution for 2 h and then carefully washed to remove the loose $Ru(bpy)_3^{2+}$ with distilled water. The mechanism of TPA and DA detection based on the prepared ECL sensor is shown in Scheme 1.

2.4. Determination of DA in real samples

Since DA is stable in acidic media, the dopamine hydrochloride injection (Shanghai Harvest Pharmaceutical Co. Ltd) samples were freshly prepared by appropriately diluting with PBS (0.01 mol L^{-1}, pH 5.0) and subjected directly to the ECL detection. Noted that the prepared solutions should avoid exposure to light and air, which ensures their acidity and stability will not affect by external environment.

3. Results and discussion

3.1. Characterization of ordered mesoporous carbon and its composite film

TEM was first used to investigate the morphologies and structures of OMC materials. Fig. 1A displays TEM images of the carbon materials viewed perpendicular to the channel direction. It can be seen that the OMC consist of the ordered hexagonal array of carbon nanorods with an average size of about 5 nm in diameter. The hexagonally ordered arrangement leaded to the well-resolved XRD peaks, as evident from Fig. 1B, which can be indexed to (1 0 0), (1 1 0) and (2 0 0) in the range of 2θ below 3.0° reflections of the 2D hexagonal symmetry with the space group p6 mm. In addition, the nitrogen adsorption/desorption isotherm curves of the OMC revealed a high specific surface area of 852 $m^2\ g^{-1}$ with the average pore diameter of about 4.5 nm and the specific pore volume of 0.97 $cm^3\ g^{-1}$ (curve a, Fig. 1C). After the formation of OMC@Nafion composite film, the relatively high BET surface area (380 $m^2\ g^{-1}$) and the total pore volume (0.56 $cm^3\ g^{-1}$) were retained (curve b, Fig. 1C), which may vastly amplify the active surface area for immobilization of ECL reagent.

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