



Electrochemical serotonin sensing interface based on double-layered membrane of reduced graphene oxide/polyaniline nanocomposites and molecularly imprinted polymers embedded with gold nanoparticles



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ABSTRACT

A double-layered membrane sensing interface was fabricated for sensitive and selective detection of serotonin (5-hydroxytryptamine, 5-HT) based on reduced graphene oxide (rGO)/polyaniline (PANI) nanocomposites and molecularly imprinted polymers (MIPs) embedded with gold nanoparticles (AuNPs). rGO/PANI nanocomposites were synthesized via electro-deposition process, in which protonated anilines were first anchored on the rGO sheets through electrostatic adsorption, and then the rGO/PANI membrane was formed on the bare electrode via cyclic voltammetry method. Functionalized AuNPs (F-AuNPs) were prepared to fabricate the MIPs embedded with AuNPs (AuNPs@MIPs) membrane on the modified electrode by constant potential method in the presence of 5-HT and p-aminothiophenol. The materials prepared in this work were examined by ultraviolet-visible (UV-Vis) and Raman spectroscopy, and the as-prepared membranes were characterized by scanning electron microscope, energy dispersive spectroscopy, and electrochemical methods. In addition, the obtained sensor allowed remarkable selectivity to 5-HT against the interferences caused by ascorbic acid and other interferents. A linear dependence of peak current in differential pulse voltammograms was obtained over 0.2–10.0 $\mu\text{mol L}^{-1}$ 5-HT with the limit of detection of 11.7 nmol L^{-1} ($S/N=3$). Furthermore, the obtained biomimetic sensor was employed to detect 5-HT in human serum samples.

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1. Introduction

Serotonin (5-hydroxytryptamine, 5-HT), an important monoamine neurotransmitter widely dispersed throughout the central nervous system, plays crucial roles in the regulation of mood, sleep, and appetite [1,2]. Therefore, the detection of 5-HT is of great value in diagnosing some diseases and can aid in understanding the role of 5-HT in some neurological disorders [3,4]. A variety of analytical methods including fluorimetry [5], enzyme immunoassay [6], chemiluminescence [7], and mass spectrometry [8] have been used for its analysis. These techniques are time-consuming and often require sample pretreatment.

Some novel researches for electrochemical determination of neurotransmitters have been reported based on polymeric film in recent years. Hrbac et al. have focused on the preparation of novel phenolic cyclopentenedione-based permselective layer for

dopamine (DA) amperometric sensing [9]. Zou et al. have reported a new voltammetric epinephrine (EP) sensor based on gold nanoparticles (AuNPs)/polyaniline (PANI) nanocomposite thin film [10]. Liu et al. have presented a sensing strategy for DA analysis based on polystyrene-grafted graphene hybrid [11].

Meanwhile, 5-HT is an electroactive compound and thus can be determined by electrochemical methods [12–15]. However, some factors limit the electrochemical detection of 5-HT under physiological conditions. One is that the concentration of 5-HT is too low to detect in human tissue [16]. Another is the presence of ascorbic acid (AA), uric acid (UA), and DA, and their oxidation potential overlaps with that of 5-HT at common electrodes [17,18]. To resolve these problems, the most effective approach is to choose conductive and selective materials to modify the electrode to improve the measuring sensitivity and selectivity to 5-HT.

Polyaniline has been considered as one of the most promising electrode materials to enhance the sensing sensitivity because of its low cost, easy synthesis, and relatively high conductivity [19–21]. To further exploit the electrochemical performance of PANI, nanometer-sized PANI composites should be considered

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[22,23]. Compared with other carbon-based materials, graphene, a two-dimensional structure consists of carbon atoms by sp^2 -hybridized bond, is predicted as an remarkable supporting material due to their high surface area, excellent mechanical strength, and outstanding conductivity [24–26]. However, there are few reports related to the graphene/PANI nanocomposites for electrochemical sensor.

Molecularly imprinted technique (MIT) has been so far demonstrated as a desirable technique in the sensor field for analytical purposes [23,27–29]. Molecularly imprinted polymers (MIPs), which were generated via MIT and possessed some advantages, such as high selectivity, low cost, chemical stability, and easy preparation, can act as artificial antibodies toward the target molecules for analytical purposes due to the complementarity in functional group orientation and spatial structure [30–33]. Literature reports on the preparation of MIPs for 5-HT recognition are limited and very recent in the field of electrochemical sensor. However, the molecularly imprinted electrochemical sensor (MIES) typically suffers from low sensitivity, since MIPs are lack of conductivity and electrocatalytic activity [34]. Therefore, molecularly imprinted conducting polymers have attracted tremendous attention due to their excellent electrochemical properties [35]. AuNPs have caused considerable interest and been extensively applied in fabrication of various sensors because of their excellent conductivity, good catalytic activity, further functionalization performance, and other related properties [36–38]. Thus, the integration of AuNPs into MIPs could overcome the electrochemical defects of MIPs by enhancing the conductivity and catalytic activity of MIPs, which in turn could significantly improve the sensitivity of imprinted sensor [39,40]. In addition, the functionalized monolayer-modified AuNPs can give access to producing MIPs embedded with AuNPs (AuNPs@MIPs) [41,42].

Herein, nanocomposites of PANI-coated reduced graphene oxide (rGO) (rGO/PANI) were synthesized through one-step electro-deposition on the surface of glassy carbon electrode (GCE). Then, the conducting membrane of AuNPs@MIPs was constructed on the rGO/PANI nanocomposites modified GCE by the electro-polymerization at a constant potential using 5-HT as template molecules, functionalized AuNPs (F-AuNPs) as functional monomers and p-aminothiophenol (p-ATP) as cross-linkers. The double-layered membrane sensing interface was evaluated to confirm its electrochemical properties, such as selectivity, conductivity, electrocatalytic activity, and stability. Furthermore, the sensing performance of obtained sensor used for the detection of the 5-HT in human serum samples was introduced in detail.

2. Experimental

2.1. Reagents and materials

Graphite powder (99.9995%, 325 mesh) was purchased from Alfa Aesar. Hydrazine hydrate, chloroauric acid, and sodium borohydride (NaBH_4) were purchased from Sinopharm Chemical Reagent Co. Ltd. 5-HT, DA, AA, UA, and EP were obtained from Sigma-Aldrich. Aniline monomer was obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd. and distilled prior to the electro-deposition. p-Aminothiophenol was purchased from Aladdin Reagent Co. Ltd. Other chemicals were of analytical grade, without further purification. All aqueous solutions were prepared in ultrapure water.

2.2. Apparatus

The electrochemical measurements were performed in a conventional three-electrode cell, using a CHI 660D workstation

(Shanghai Chenhua Co., China) with a platinum electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The modified GCE ($\Phi=3$ mm, polished before using) was used in this study. High-purity nitrogen was used for the deaeration of the solutions.

UV-Vis spectra were obtained on a Shimadzu UV-2450 spectrophotometer. Scanning electron microscope (SEM) images and energy dispersive spectroscopy (EDS) were recorded with S-4800 and S-3400N (Hitachi, Japan). Raman spectra were performed by using DXR Smart Raman Spectrometer excited with 633 nm laser radiation (Thermo Scientific, USA).

2.3. Synthesis of reduced graphene oxide

The exfoliated GO was synthesized from graphite powder by a modified Hummers method as described in the previous works [43]. The obtained GO (50 mg) was loaded in a 250-mL round-bottom flask and water (100 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated until it became clear with no visible particulate matter. Hydrazine hydrate (0.5 mL, 16 mmol) was then added and the solution heated in an oil bath at 85°C under a water-cooled condenser for 10 h over which the rGO gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed copiously with water to obtain rGO [45].

2.4. Preparation of rGO/PANI membrane

Hundred microliters of rGO (1 mg mL^{-1}) was added into 10 mL H_2SO_4 (0.2 mol L^{-1}) solution and ultrasonicated for 2 h to form a uniform suspension. And then, $73\ \mu\text{L}$ aniline was added into the above solution, and ultrasonicated for another 1 h under nitrogen. The electro-deposition process was carried out with a three-electrode system using cyclic voltammetry (CV) method in a sweeping potential range between -0.2 and 0.8 V at a scan rate of 50 mV s^{-1} for 20 cycles. The resultant electrode was rinsed by 0.2 mol L^{-1} H_2SO_4 solution and water in sequence and then dried at 45°C for 12 h.

2.5. Synthesis of functionalized AuNPs

According to a modified method [41], the F-AuNPs were synthesized by mixing a 10 mL solution containing 32 mg of HAuCl_4 in ethanol and a 5 mL solution containing 6 mg p-ATP in methanol. The mixed solution was stirred in the presence of 0.3 mL of glacial acetic acid in an ice bath for 1 h. Subsequently, 2.5 mL of aqueous solution of 0.5 mol L^{-1} NaBH_4 was added dropwise, resulting in a brown solution. The solution was stirred for an additional hour in an ice bath and then for 10 h at room temperature. The product was successively washed and centrifuged with methanol and ethanol, respectively.

2.6. Preparation of AuNPs@MIES

An electrolyte solution containing 1 mmol L^{-1} 5-HT, $24\ \mu\text{g mL}^{-1}$ F-AuNPs, 8 mmol L^{-1} p-ATP, and 0.1 mol L^{-1} PBS (pH 7.5), was kept in dark under a nitrogen atmosphere at room temperature for 4 h to complete the preassembly between 5-HT and F-AuNPs through the hydrogen-bond interaction. The rGO/PANI modified electrode was immersed into the electrolyte solution and the AuNPs@MIES was obtained by the electro-polymerization at a constant potential of 0.9 V for 400 s. After that, the electrode was immersed in 0.5 mol L^{-1} H_2SO_4 and treated with a constant potential of -0.4 V for 400 s to remove the templates and dried under nitrogen flow. The fabrication process of AuNPs@MIES was indicated in Scheme 1.

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