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Modification of electrode surface with covalently functionalized graphene oxide by L-tyrosine for determination of dopamine

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ABSTRACT

An L-tyrosine (L-Tyr) covalently functionalized graphene oxide (GO) composite (Tyr–GO) has been prepared through amide bonds, which is further used to modify glassy carbon electrode (GCE) by simple dipping-drying method. The differential pulse voltammetry (DPV) peaks of dopamine (DA) and ascorbic acid (AA) can be completely separated with a peak potential difference of 414 mV by using the fabricated Tyr–GO/GCE, holding promise for simultaneous determination of DA and AA. The peak currents are linearly with the concentration of DA in the range from 1.0×10^{-6} to 5.0×10^{-4} mol/L with a detection limit of 2.8×10^{-7} mol/L. In addition, the modified electrode exhibits excellent reproducibility and stability.

1. Introduction

L-Tyrosine (L-Tyr), an essential amino acid, plays important roles in mammalian central nervous systems and photosynthesis by virtue of its asymmetric structure and phenol functionality [1]. For example, the absence of L-Tyr could cause albinism and alkaptonuria, while a high L-Tyr concentration in culture medium can result in increased sister chromatid exchange [2]. The structure of L-Tyr is shown in Fig. 1. So far, great efforts have been made to apply Tyr in chemical modification of electrodes and chromatographic separation due to their advantages of excellent biocompatibility, rich material resource and easy operation [3,4]. For example, Weng et al. prepared a copper-Tyr chiral complex by inserting pyridine segmental ligand [5]. Long et al. fabricated a hydrogen peroxide biosensor by electropolymerization of the L-Tyr derivatives and phenolic film onto the electrode surface [6]. The tyrosine and its decyl ester derivatives can be easily electropolymerized to create stable thin films on a Pt electrode surface. All of the thin film-modified electrodes have sensitive and stable responses to H_2O_2. They also have illustrated the capability of the films derived from tyrosine and its derivatives to form a biosensor incorporating the Horse radish peroxidase (HRP) . Yang et al. developed a DNA sensor based on polyaniline-(mesoporous nanozirconia)/poly-Tyr film, which was used for highly sensitive detection of phosphinothricin acetyltransferase gene sequence [7]. The dynamic detection range was from 1.0×10^{-13} mol/L to 1.0×10^{-6} mol/L, and the detection limit was 2.68×10^{-14} mol/L. Compared with other electrochemical DNA biosensors based on zirconia-based materials, the proposed biosensor showed its own performance of simplicity, good stability, fine selectivity and high sensitivity. Recently, Wang et al. developed a novel poly(Tyr)/functionalized multi-walled carbon nanotubes composite film modified electrode for simultaneous determination of ascorbic acid (AA), dopamine (DA) and uric acid (UA) [8]. Based on the poly (Tyr) film is a stable multilayer conductive polymer film, which possessed the larger real surface area, π–π conjugated bond, a great deal of active sites and better conductivity. The prepared electrode not only separated the cyclic voltammetric signals of AA, DA and UA, respectively, but also showed higher oxidation current for these molecules. The detection limits for AA, DA and UA were 2.0 μmol/L, 0.02 μmol/L and 0.30 μmol/L, respectively. The method has good selectivity and sensitivity.

Graphene has become the focus of scientific research due to its outstanding chemical, mechanical and electrical properties. It has been found that graphene has the ability to promote electron-transfer reactions, which has been used as an excellent electrode

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material. In addition, the polymer film modified electrodes prepared by electropolymerization method has shown excellent properties in the fabrication of electrochemical sensor, such as high specific surface area, high thermal conductivity and electron transport capabilities [9–13]. Recently, electropolymer/graphene modified electrodes have been extensively studied because incorporation of graphene into conducting polymers can make the new composite materials possess excellent electrocatalytic properties for biomolecules with a synergistic effect, which would be useful in biochemical analysis [14].

However, graphene has poor dispersibility in solution due to the large conjugated effects between the sheet layers, which limits its application in bioanalysis [15]. The suitable functionalization of graphene can not only avoid the agglomeration and aggregation of graphene in a solvent, but also maintain the excellent inherent properties of graphene. Graphene oxide (GO) can be considered as a derivative of graphene; it can be synthesized by chemical or thermal reduction methods. The presence of various oxygen-containing functional groups on GO renders it strongly hydrophilicity, which enables GO to be easily modified on electrodes by simple methods, such as drop-casting, spraying, or spin-coating [9,16]. Moreover, the functional groups on GO can serve as the active sites for chemical modification and functionalization of GO, which in turn can be employed to immobilize various electroactive species through covalent or noncovalent bonds. Especially, covalently functionalization of GO with modifying molecules through π–π interaction and functional groups such as carboxyl and hydroxyl group can not only improve the dispersibility of GO but also enhance the interfacial interaction between GO and the matrix. In addition, the synergism between the adhesion stability of modifying molecule and the catalysis of GO results in excellent properties of the composite materials, this has become an outstanding material for electrode modification. Recently, the preparation of GO and polymer composite materials has attracted much attention [17–19].

Dopamine (DA) is an important neurotransmitter in the mammalian central nervous system. Ascorbic acid (AA) usually coexists with DA in real biological samples. Therefore, the development of a sensitive and selective biosensor for simultaneous determination of DA and AA is of great importance for bioanalytical applications and diagnostic research [20–25].

In this work, a novel electrochemical biosensor has been developed for highly sensitive determination of DA based on L-Tyr–GO composite modified GCE. From the results of FT-IR, Tyr was covalently bonded with GO through amide bonds. The fabricated Tyr–GO/GCE can completely separate the DPV peaks of DA and AA, holding promise for simultaneous determination of DA and AA. This work provided potential application of graphene-based materials in analysis, separation and recognition of biomolecules.

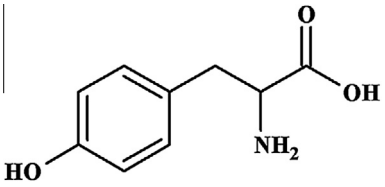

Fig. 1. Chemical structure of L-Tyr.

2. Materials and methods

2.1. Apparatus and materials

DA and AA were purchased from Sinopharm Chemical Reagent Co., Ltd (China). L-Tyrosine (L-Tyr), thionyl chloride ($SOCl_2$), dimethylformamide (DMF), triethylamine (TEA) and sodium hydroxide (NaOH) were obtained from Beijing chemical reagent company (China). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using a CHI-660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) coupled with a conventional three-electrode cell. Glassy carbon electrode (GCE) or the modified GCEs were used as the working electrodes. The auxiliary electrode was a platinum wire. All the potentials quoted in this work were referred to a saturated calomel electrode (SCE) as the reference. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet-5700 infrared spectrometer (Madison, USA). The transmission electron microscope (TEM) images were obtained with Hitachimodel H-800 TEM opened at an accelerating voltage of 100 kV.

The supporting electrolyte was a 0.2 mol/L phosphate buffer saline (PBS, pH 6.5), which was prepared by using $Na_2HPO_4{\cdot}12H_2O$ and NaH_2PO_4. The working solutions of DA and AA were prepared by PBS. All reagents were of analytical-reagent grade. All solutions were prepared with doubly distilled water.

2.2. Synthesis of Tyr–GO

Graphene oxide (GO) was prepared by a modified Hummers method [26]. The scheme for preparation of Tyr–GO is shown in Fig. 2. Firstly, 50 mg GO, 25 mL of $SOCl_2$, and 0.15 mL DMF were mixed and heated to 70 °C under reflux for 24 h. The unreacted $SOCl_2$ was distillated at atmospheric pressure, and then under reduced pressure for 10 min to make sure the unreacted $SOCl_2$ was distillated completely. Subsequently, 0.2 g Tyr and 2 mL of TEA were added at 80 °C and reacted for another 24 h with the 40 mL of DMF as the solvent. After cooling the solution to room temperature, 0.45 μm microporous filtration membrane was used to remove DMF and TEA. The filter cake was ultrasonically washed for 5 min using 50 mL of 0.1 mol/L NaOH. The suction and washing repeated five times to completely remove the DMF and TEA. The resulting filter cake was washed with water, ultrasonicated with 50 mL of 0.1 mol/L HCl for 5 min, then washed with distilled water to pH = 7, followed by vacuum drying at 90 °C for 24 h.

2.3. Preparation of modified electrodes

Prior to surface modification, the GCE was polished successively using chamois leather containing Al_2O_3 slurry (0.05 μm after 0.3 μm) and then rinsed ultrasonically with doubly-distilled water

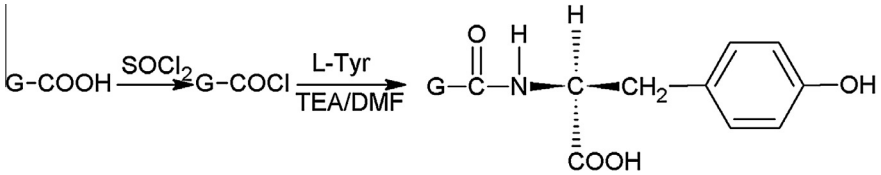

Fig. 2. Scheme of the preparation of Tyr–GO.