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Determination of L-tryptophan in the presence of ascorbic acid and dopamine using poly(sulfosalicylic acid) modified glassy carbon electrode

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ABSTRACT

In this work, a glassy carbon electrode modified with poly-sulfosalicylic acid (PSA/GCE) was prepared using electropolymerization method and applied for the determination of L-tryptophan (L-Trp) in the presence of ascorbic acid and dopamine. The morphologies and interface properties of PSA film were examined by scanning electron microscopy and electrochemical impedance spectroscopy. The electrocatalytic oxidation of L-Trp on the PSA/GCE from potentially interfering species, e.g. ascorbic acid (AA) and dopamine (DA) was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under optimum conditions, the proposed method exhibited wide linear dynamic range of 5×10^{-8} to 1×10^{-5} M with a detection limit (S/N = 3) of 6.8×10^{-9} M. Moreover, the modified electrode exhibited good reproducibility and high selectivity, demonstrating its feasibility for the analytical purpose.

1. Introduction

L-Tryptophan (L-Trp) is one of the essential amino acids for the human body and a vital constituent of protein biosynthesis of living organisms [1]. In many biochemical processes, it is an essential precursor of hormone for neurotransmitter serotonin and other relevant biomolecules [2,3]. Due to L-Trp cannot be synthesized directly in human body and the scarce presence in vegetables, it is commonly added to dietary, food products as a food fortifier and to pharmaceutical formulations. However, when improperly metabolized, a waste product will be created in the brain to cause hallucinations and delusions [4]. So, to establish a simple, accurate, rapid and inexpensive method for the determination of L-Trp in food, pharmaceutical products and biological fluids is very necessary.

Various methods have been developed for the determination of L-Trp, such as spectroscopy [5], high-performance liquid chromatography [6,7], fluorometric methods [8], capillary electrophoresis [9] and electroanalysis [10]. Among these methods, electrochemical techniques have gained much more attention for its high sensitivity, high accuracy, simple operation mode and low cost. However, the voltammertric response of L-Trp at bare electrode is not optimal because of sluggish electron transfer processes and high overpotential [11]. Hence, a lot of efforts have been devoted to promote the electron transfer and reduce the overpotential for the electrochemical oxidation of L-Trp [12].

Recently, various modified electrodes have been reported for the determination of Trp, such as poly-4-aminobenzoic acid [11], polyglutamic acid [12], 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone (4-FEPE) [13], Ni(II)/ACDA–AuNP–Au [14], gold nanoparticles [15] and nano-TiO_2/ferrocence carboxylic acid [16]. Among these electrodes, polymer film modified electrodes have been paid great attention due to their good stability, biocompatibility, homogeneity and strong adherence to electrode surface [17,18]. The thickness and permeation of the polymeric films can be controlled by the potential and current applied. Polymer films can significantly improve the electrocatalytic properties of substrates, decrease the overpotential, increase the reaction rate and improve reproducibility of the electrode response in the area of electroanalysis [19–21]. Studies [22–25] have indicated that polymer film modified electrodes show an enhanced response for the determination of various important biological and clinical species. Fabrication of conducting polymer film is flexible, hence, it provides an attractive mean of overcoming the problems caused by the solvent evaporation method [26,27].

In this work, we used sulfosalicylic acid as a modifier to obtain a polymer of poly(sulfosalicylic acid) film (PSA) at glassy carbon electrode (PSA/GCE) by electrochemical polymerization. Because of high electron density of carbonyl and sulfonic groups in sulfosalicylic acid molecule (COO^- and SO_3^-), the PSA film has high concentrations of negatively charged surface-functional groups. The modified electrode showed excellent electrocatalytic properties with obvious reduction of overpotential and

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enhancement of oxidation current, making it suitable for the analytical purpose.

2. Experimental

2.1. Apparatus

Electrochemical measurements were carried out on a CHI 660C electrochemical workstation (Shanghai Chenhua Co., Ltd., China) with a conventional three-electrode system. GCE (3 mm) was purchased from Shanghai Chenhua Co., Ltd., China. Poly(sulfosalicylic acid) modified GCE was used as the working electrode, while the platinum wire served as the auxiliary electrode and standard calomel electrode acted as the reference electrode. Scanning electron micrographs measurements and Fourier transform infrared (FTIR) spectra were carried out on a scanning electron microscope (JSM-6700F, 15.0 kV, Japan) and Fourier transform infrared spectrometer (AVATAR 370, America), respectively.

2.2. Chemicals

L-Trp, AA, DA, cysteine, alanine, phenylalanine and leucine were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Sulfosalicylic acid, citric acid were supplied from Shanghai No.1 Chemical Reagent Factory. Glutamic acid and other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals commercially available were of analytical grade and used without further purification.

2.3. Preparation of modified glassy carbon electrode

GCE was polished successively on chamois leather with 0.3 and 0.05 μm Al_2O_3 slurry, followed by washing with HNO_3 (1:1, v/v), ethanol and doubly distilled water in an ultrasonic bath. Then, the electrode was immersed in 10 mM sulfosalicylic acid using PBS of pH 5.5 and a potential step from −1.0 to 2.0 V at 100 mV s^{-1} was applied for 30 cycles until a reproducible CV characteristic was obtained (Fig. 1). Finally, the PSA/GCE was carefully washed with double distilled water for use.

2.4. Preparation of FTIR spectroscopy analysis

The poly(sulfosalicylic acid) was electropolymerized on the aluminum sheet working electrode. The working electrode was washed with ethanol and double distilled water, and was dried at room temperature. Then, it was immersed in 0.1 M PBS (pH 3.5) containing 0.1 M sulfosalicylic acid with repeated potential scan from −1.0 to 2.0 V at 100 mV s^{-1} for 30 cycles. The reference electrode and counter electrode in the progress were the same as Section 2.1.

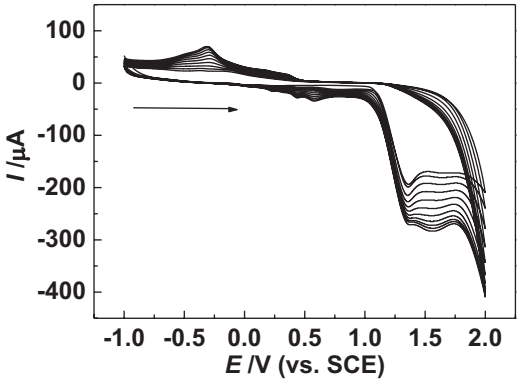

Fig. 1. The electro-polymerization of sulfosalicylic acid on GCE surface was carried out using cyclic voltammetry between −1.0 V and 2.0 V for 15 cycles in 0.1 M PBS (pH 5.5) containing 10 mM sulfosalicylic acid.

3. Results and discussion

3.1. Characterization

To investigate the morphology of the modified electrode, PSA film was prepared by electropolymerization of sulfosalicylic acid at GCE as described above. Fig. 2 shows the typical morphology of PSA film by scanning electron microscope (SEM), indicating that the film has a fine cluster-like structure. The surface of PSA film was smooth and homogeneous which verified that the PSA film was successfully polymerized on the electrode surface and may enhance the interaction between the modified electrode and the L-Trp [13].

Electrochemical impedance spectroscopy (EIS) was used as a powerful technique to study the interface properties of the electrode surfaces. Fig. 3(A) shows the typical Nyquist diagrams of the EIS in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ solution at the bare GCE (a), and PSA/GCE (b). Compared with the bare GCE (curve a), the electron-transfer resistance (R_{et}) for PSA/GCE was larger (curve b). This may be ascribed to the electrostatic repulsion force between the negatively charged $[Fe(CN)_6]^{3-/4-}$ and poly(sulfosalicylic acid) film [28]. Cyclic voltammetry (CV) experiments (Fig. 3B) were also studied in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ solution + 0.1 M KCl. It can be seen that the redox peaks at the bare GCE are well-shaped while the peak shape was deteriorated at PSA/GCE. The results of CV are according with EIS, indicating that the successful polymerization process of sulfosalicylic acid onto the surface of GCE.

The FTIR spectra (Fig. 4) illustrated the differences between the fine curves of sulfosalicylic (a) and disappears curve of PSA (b), which is attributed to the polyreaction of sulfosalicylic acid. In the FTIR absorption spectra of sulfosalicylic acid (a), the wide peaks between 3200 cm^{-1} and 3500 cm^{-1} is O—H stretching vibration and 3112 cm^{-1} is C—H stretching vibration peak. As shown in curve (b), the peaks at 3442 cm^{-1} and the peaks of S—O stretching vibration (1350 cm^{-1} and 1170 cm^{-1}) and —COO^- stretching vibration (1620 cm^{-1} and 1469 cm^{-1}) obviously broaden due to poly-reaction of sulfosalicylic acid, indicating that the monomer have been formed PSA polymer.

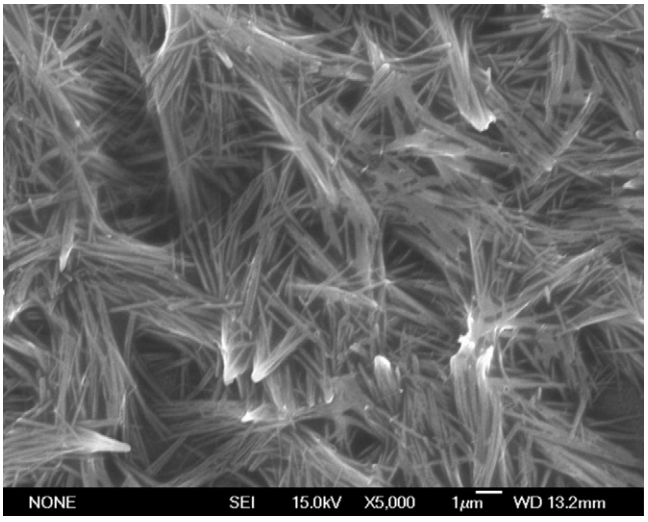

Fig. 2. Scanning electron micrographs of the PSA/GCE.

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