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Simultaneous electrochemical determination of ascorbic acid, dopamine and uric acid using poly (tyrosine)/functionalized multi-walled carbon nanotubes composite film modified electrode

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ABSTRACT

A novel poly (tyrosine)/carboxyl functionalized multi-walled carbon nanotubes composite film modified electrode has been fabricated and used as electrochemical sensor for simultaneous determination of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The prepared electrode not only separated the cyclic voltammetric signals of AA, DA and UA with oxidation potential difference of 160 and 150 mV between AA–DA and DA–UA, respectively but also showed higher oxidation current for these molecules in pH 7.4 phosphate buffer solution. Because it exhibited excellent selectivity towards the oxidation of AA, DA and UA, the modified electrode was used for simultaneous voltammetric measurement of the three analytes by differential pulse voltammetry. Under the optimum conditions, the detection limits for AA, DA and UA were 2.0 μ mol L^{-1}, 0.02 μmol L^{-1} and 0.30 μ mol L^{-1}, respectively (S/N of 3). The method has good selectivity and sensitivity and was successfully applied to the simultaneous determination of AA, DA and UA in spiked human serum.

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1. Introduction

Dopamine (DA) is one of the most important neurotransmitters which play vital role in the function of the central nervous, renal, hormonal and cardiovascular systems. Abnormal DA transmission is associated with neurological disorders such as schizophrenia, Parkinson's disease, and Huntington's disease [1,2]. Uric acid (UA) is the terminative oxidation product of purine degradation metabolism in human beings. Its concentration level in body fluids such as human serum and urine is marker of many clinical conditions, including hyperuricemia, gout, and the Lesch–Nyan disease [3,4]. Ascorbic acid (AA) is an antioxidant and free radical scavenger which is used for the prevention of scurvy and treatment of common cold, mental illness and cancer [5]. Since AA, DA and UA usually coexist in real biological samples, the development of a selective and sensitive method for their simultaneous determination is highly desirable for analytical and diagnostic applications.

The fact that AA, DA and UA are easily oxidized makes their detection feasible by electrochemical methods. However, these biomolecules oxidized at a potential rather close at bare electrode and always interference to each other for the determination of any one of the analytes [6,7]. Therefore, improvement of selectivity and sensitivity of the working electrode towards the three compounds has been a long-standing issue in electroanalysis. In recent years, chemically modified electrodes (CMEs) have become important electrochemical detection methods for the determination of biologically important compounds because of its good sensitivity, selectivity and stability [8–10]. There have been some reports on the application of CMEs for the simultaneous determination of AA, DA and UA [11–20], such as poly (oracet blue) modified glassy carbon electrode (GCE) [11], GCE modified with poly (evans blue) film [12], GCE modified with poly(eriochrome black T) [13], Pt–Au hybrid film modified electrode [14], palladium nanoparticle-loaded carbon nanofibers modified electrode [15], pyrolitic graphite modified electrode [16], zinc oxide composite film modified electrode [17], functionalized-graphene modified graphite electrode [18], $LaFeO_3$ nanoparticles modified electrode [19], poly(L-arginine) modified carbon paste electrode [20], etc. However, the reported modified electrodes need expensive material and prolonged fabrication time, lack stability and sensitivity. So development of new materials to accomplish rapid speed, good sensitivity and low cost of analysis has still been one of the attractive subjects. In this paper, we prepared a new poly (tyrsine)/functionalized multi-walled carbon nanotubes composite film modified electrode to catalyze the oxidation of AA, DA and UA, which provided a simple and sensitive voltammetric method for determining the concentrations of the three compounds simultaneously.

Since carbon nanotubes (CNTs) were discovered in 1991, they have become the focus of scientific research due to their outstanding chemical, mechanical and electrical properties [21]. Chemically modified electrodes utilizing CNTs have been the subjects of many recent research

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reports because CNTs have the ability to promote electron-transfer reactions when used as an electrode material in electrochemical reactions [22–25]. Recently, the polymer film modified electrodes prepared by electropolymerization method have showed very much excellent characteristics in acting as electrochemical sensor, such as good stability, reproducibility, more active sites, and homogeneity. Moreover, electropolymer/CNTs modified electrodes have been extensively studied because incorporation of CNTs into conducting polymers can lead to new composite materials possessing the properties of each component composites with a synergistic effect, which have demonstrated excellent electrocatalytic ability for some biological molecules and would be useful in biochemical analysis [26]. However, few reports about poly (amino acid)/CNTs modified electrode have been reported [27].

Tyrosine (Tyr) is one of the 20 standard amino acids that are used by cells to synthesize proteins. It also plays an important role in photosynthesis by virtue of its phenol functionality. Multi-walled carbon nanotubes functionalized with carboxylic acid group (MWCNTs-COOH) have high dispersion quality, binding activity for molecular recognition and redox activity of carboxylic acid groups on the surface of MWCNTs. In this work, we reported for the first time on a poly (Tyr)/carboxylated multi-walled carbon nanotubes composite film to modify glassy carbon electrode (GCE). The prepared new composite film possessed the advantages of both MWCNTs-COOH and poly (Tyr) with a synergistic effect, which indicated excellent electrocatalytic activity for oxidation reactions of AA, DA and UA at the surface of the modified electrode. Moreover, the modified electrode showed good sensitivity, selectivity and reproducibility for the simultaneous determination of AA, DA and UA. Based on its excellent characteristics compared to other electrochemical sensors reported in terms of high sensitivity, wide linearity and good stability, the poly (Tyr)/carboxylated multi-walled carbon nanotubes composite film modified glassy carbon electrode (poly (Tyr)/MWCNTs-COOH/GCE) was satisfactorily used for the simultaneous determination of AA, DA and UA in human serum by differential pulse voltammetry (DPV).

2. Experimental

2.1. Reagents

DA and UA were purchased from Sigma (USA). DL-Tyr and AA were obtained from Shanghai Chemical Factory (Shanghai, China). Multi-walled carbon nanotubes with carboxylic acid groups (MWCNTs-COOH, 20–30 nm outer diameter, 0.5–2 μm length and >95% purity) were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. All chemicals were of analytical grade and were used without further purification. The 0.067 mol L^{-1} phosphate buffer solutions (PBS) with various pH values were prepared by mixing the stock solutions of 0.067 mol L^{-1} KH_2PO_4 and Na_2HPO_4. The working solutions of AA, DA and UA were prepared just prior to use. All solutions were prepared with Millipore ultrapurewater (Millipore, Bedford, MA, USA).

2.2. Apparatus

Electrochemical measurements were performed with a LK2005 Microcomputer-based electrochemical system (LANLIKE, Tianjin, China). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a platinum sheet electrode as the counter electrode and a bare or modified glassy carbon disk electrode (GCE) with a diameter of 3 mm used as working electrode. All pH measurements were made with a pHS-3C digital pH meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass electrode. A KQ-250B ultrasonic washer (Kunshan Ultrasonic Instrument Works, Kunshan, China) was used to wash the electrode.

2.3. Preparation of the poly (Tyr)/MWCNTs-COOH/GCE

Prior to its modification, the bare GCE was polished with 0.05 μm α-alumina powder and rinsed with 1:1 HNO_3 solution, ethanol, and doubly distilled water for 10 min successively. The MWCNTs' suspension was prepared by dispersing 1.0 mg MWCNTs-COOH in 10 ml dimethyl formamide (DMF) under sonication for 30 min. A 10 μL aliquot of black suspension was dropped directly onto the surface of clean GCE and it was dried at room temperature. The obtained electrode was taken as MWCNTs-COOH/GCE. The poly (Tyr)/MWCNTs-COOH/GCE was prepared by electropolymerization. The polymeric film was deposited on MWCNTs-COOH/GCE by cyclic sweeping from −0.8 to 1.8 V at 100 mV s^{-1} for sixteen cycles in pH 6.0 phosphate buffer solution containing 1.0×10^{-3} mol L^{-1} Tyr. After polymerization, the modified electrode was washed with doubly distilled water, and then air-dried.

2.4. Experimental methods

Cyclic voltammetric and differential pulse voltammetric measurements were carried out with three electrodes in phosphate buffer solution. The cyclic voltammograms were recorded by cycling the potential between −0.2 and +0.6 V at a scan rate of 100 m Vs^{-1}. The differential pulse voltammetric measurements were performed by applying a sweep potential from −0.6 to +0.6 V at pulse amplitude of 50 mV and pulse width of 0.1 s. All experiments were carried out at room temperature. The modified electrode could be used repeatedly after rinsed with doubly distilled water and blotted with filter paper.

2.5. Sample preparation

Blood samples were collected from healthy volunteers at the Hospital of Shandong Normal University. A 1.0 mL of fresh blood sample was obtained and centrifuged at 3000 rpm for 20 min to remove all precipitating materials. The spiked serum samples were prepared as follows: 0.5 mL of the separated serum was transferred to a color comparison tube. After spiked with different quantities of DA and AA, the mixture solution obtained was diluted to 10 mL with pH 7.4 phosphate buffer. Then the synthesized serum samples were placed in the electrochemical cell to detect AA, DA and UA simultaneously by the proposed DPV method.

3. Results and discussion

3.1. Preparation and characterization of poly (Tyr)/MWCNTs-COOH composite film at the GCE surface

Fig. 1b showed the cyclic voltammogram of the MWNTs-COOH/GCE in phosphate buffer solution (pH 6.0). In the potential range from 0.4 to −0.4 V, a pair of stable redox waves appeared with the cathodic peak potential of 0.002 V and the anodic peak potential of 0.055 V, which was related to the redox of the carboxylic acid group [25]. Compared with the bare GCE (Fig. 1a), the background current of the MWNTs-COOH/GCE was apparently large. This could be attributed to the increased surface area.

Cyclic voltammetry was used to form the electropolymerization film of Tyr on MWNTs-COOH/GCE. Compared with other supporting electrolyte used in electrodeposition process of polymeric film, the obtained polymeric film was observed to be more complete, uniform and compact, which showed better electrocatalytic activity to the oxidation of DA when pH 6.0 phosphate buffer solution was used as supporting electrolyte during polymer formation. Thus it was chosen as supporting electrolyte for electropolymerization in this work. The potential scan range was the most important factor in preparing poly (Tyr) film. If the positive potential value was below 1.5 V or if the negative one was above −0.6 V, no polymer

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