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Simultaneous detection of dopamine and ascorbic acid using silver/silver sulfide modified carbon nanotube electrodes

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ABSTRACT

In this study, silver/silver sulfide (Ag/Ag_2S) was applied on an electrochemical system for the simultaneous determination of dopamine (DA) and ascorbic acid (AA) in phosphate buffer solution (pH 7.0). The Ag/Ag_2S nanoparticles were dispersed with carbon nanotube (CNT) in Nafion to be an Ag/Ag_2S-immobilized CNT electrode. The electrochemical behaviors of DA and AA were examined using the differential pulse voltammetry (DPV) technique. The characteristic peaks of DA and AA in the differential pulse votammogram were well separated. Without Ag/Ag_2S, CNT electrode cannot detect AA. When Ag/Ag_2S nanoparticles were immobilized on the CNT electrode, the sensitivity to DA increased from 0.637 to 1.000 $\mu A\ \mu M^{-1}\ cm^{-2}$, and the sensitivity to AA became 0.020 $\mu A\ \mu M^{-1}\ cm^{-2}$ in the linear concentration range of 250–2000 μM.

1. Introduction

Dopamine (DA) is a crucial neurotransmitter that contains a catecholamine group and plays a very important role in the central nervous, renal, hormonal and cardiovascular systems. The abnormal secretion of DA in the human body can lead to diseases, such as schizophrenia and Parkinson's disease [1–3]. Monitoring the DA concentration in blood or urine is important because these concentrations can be used as an effective early warning sign for central nervous system diseases.

The DA concentration is very low in human blood, whereas the concentration of ascorbic acid (AA) which largely coexists with DA is generally 100–1000 times higher than that of DA [4]. The oxidation product of DA can be homogeneously reduced by AA [5], which is an abundant antioxidant in the human body. The oxidation potentials of DA and AA are very close, so their characteristic peaks in a voltammogram usually overlap [6]. Therefore, selectivity is as important as sensitivity when electrochemically determining DA and AA.

Glassy carbon electrodes (GCE) modified by polymeric film, such as cation-exchange membrane [7–9], prussian blue [10], ruthenium (III) diphenyldithio-carbamate [11] and polypyrrole(-dodecyl sulphate) [12], could expel one of the two species to detect the other [13]. Previous researchers have developed various modifying polymer films for simultaneously detecting DA and AA, including poly (N,N-dimethyl aniline) [14] and poly(acid chrome blue K) [15]. The modification of self-assembled monolayers (SAMs), such as thiol monolayers on a gold electrode, is feasible [16,17] for simultaneously detecting DA and AA. 2,2′-Dithiobisethaneamine and 6,6′-Dithiobishexaneamine were two examples. However, low conductivities and diffusion coefficients of these modified films would give long response times. Therefore, conducting polymer-coated carbon fiber/tube electrodes were applied [18–20].

Carbon nanotubes (CNT) [21] are generally classified into two categories: single-wall and multi-wall. CNT are attractive nanomaterials with specific electronic, mechanical and chemical properties that can facilitate the electron transfer between an electro-active species and an electrode [22,23]. CNT also provides a large surface area due to nanostructure. The potential applications of CNT in fabricating electrochemical sensors have been previously reported [24,25]. CNT also has been applied for the selective detection of DA and UA [26–29]. In several studies, biomolecules, polymers or catalysts were immobilized by CNT on electrodes to improve sensing performance [30–35].

Silver (Ag) is a material with high electron conductivity and good stability in solution. An Ag-dispersed ceramic-graphite composite was developed to detect DA using the sol-gel technique [36]. Ag was deposited on indium-tin-oxide glass (ITO) in a vacuum and then electrochemically oxidized to silver sulfide (Ag_2S) to

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detect DA and AA [37]. A silver hexacyano-ferrate nanoparticles/carbon nanotubes modified glassy carbon electrode was applied for the simultaneous detection of DA, AA and UA by cyclic voltammetry [38].

In this work, a simple and fast procedure (silver mirror reaction) was used to prepare the silver/silver sulfide (Ag/Ag_2S) particles. A layer of Nafion containing Ag/Ag_2S and CNT was spread on an ITO electrode. The simultaneous determination of DA and AA with this Ag/Ag_2S-immobilized CNT electrode by differential pulse voltammetry in phosphate buffer solution is described. It is shown that the oxidation peaks for DA and AA can be well separated. A sensitive and selective electrochemical sensor for simultaneous determination of DA and AA has been established. The performance of this sensor in real samples is under investigation.

2. Research methodology

2.1. Materials and reagents

Multi-walled carbon nanotubes (length, 0.5–2 μm; outer diameter, 20–50 nm; wall thickness, 1–2 nm) and Ag_2S particles were purchased from Aldrich Company. Sodium sulfide, silver nitrate and DA were obtained from Sigma. Trisodium citrate dihydrate and formaldehyde were obtained from SHOWA Chemical, and Tedia Company, respectively. AA was provided by Riedel-deHaen. Nafion and ITO glass (surface resistance <10 ohm/□) were obtained from DuPont, and Shinan SNP Co Ltd, respectively. The solutions were prepared in double distilled water.

2.2. Instrumentation

Electrochemical experiments were performed in a 100-mL cell at room temperature (approximately 25 °C). The electrolyte used for these experiments was a phosphate buffer solution (PBS) containing the detected species at pH 7.0. A transmission electron microscopy (TEM, Hitachi, H-7500) and X-ray diffraction (XRD, RIGAKU, D/MAX) were used to observe the structure of Ag/Ag_2S, Ag and Ag_2S particles. Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) were performed with an electrochemical system Autolab (ECO CHEMIE BV, PGSTAT-302N).

2.3. Synthesis of Ag/Ag_2S nanoparticles

A chemical reduction (silver mirror reaction) was employed to synthesize Ag/Ag_2S particles. Two aqueous solutions were prepared: a silver solution containing 0.1 M $Ag(NH_3)_2^+$ and 0.1 M trisodium citrate as well as a reduction solution containing 12.3 M formaldehyde and 0.5 M trisodium citrate. Fifty milliliters silver solution was added dropwise to 500 mL reduction solution under magnetic stirring at room temperature (approximately 25 °C) for 1 hr to prepare Ag particle suspension. Ten milliliters of 0.5 M sodium sulfide solution was then added into the mixed solution. Finally, the produced particles were filtrated, rinsed with deionized water, and desiccated in a vacuum oven at 60 °C. For pure Ag particles, the Ag suspension was not mixed with sodium sulfide solution.

2.4. Fabrication of Ag/Ag_2S-immobilized CNT and Ag/Ag_2S electrodes

A three-electrode system was used with an Ag/AgCl (saturated KCl) reference electrode and a Pt counter electrode. The working electrode, denoted as the Ag/Ag_2S-immobilized CNT electrode, was an ITO glass electrode coated with a layer containing CNT, Nafion, and Ag/Ag_2S. Prior to each electrode coating, a bare ITO glass electrode (3 mm in diameter) was first sonicated in acetone for 20 min, followed by rinsing with water, ultrasonic cleaning in water:ethanol (1:1) mixed solvent, and rinsing with water again.

The ITO glass electrode was coated with an Ag/Ag_2S-immobilized CNT solution: 6 mg of CNT dispersed in 1 mL of 0.5% Nafion solution containing 15 mg Ag/Ag_2S. This suspension solution was mixed in an ultrasonic bath for 2 h. Five microliters of the mixture were transferred onto the ITO glass electrode with a micro-pipette and then dried in an oven at 60 °C. Nafion was used as a binder. As a control, some of the suspension solutions did not contain Ag/Ag_2S. The electrode without Ag/Ag_2S immobilization was denoted as the CNT electrode.

An Ag/Ag_2S electrode was prepared by electrochemical deposition method. Firstly, an Ag electrode was electrodeposited on a bare ITO glass electrode surface from 0.05 M $AgNO_3$ solution by scanning the potential between 0 and −1.0 V (vs. Ag/AgCl) at a rate of 50 mV/s for 10 cycles. Then, the Ag electrode was soaked in 0.5 M sodium sulfide solution to form the Ag/Ag_2S electrode for 10 min.

2.5. Electrochemical analysis

Before measurement, the electrodes were cleaned in PBS (pH 7.0) with the CV method. The potential was swept over a range of 0–0.6 V (vs. Ag/AgCl) at a rate of 50 mV/s for 10 cycles. Electrochemical impedance spectroscopy was performed with an amplitude of 15 mV at a bias of −0.02 V (vs. Ag/AgCl). The frequency ranged from 5 kHz to 0.01 Hz. For DPV, the scan rate, pulse amplitude, step potential, and pulse width were 10 mV/s, 25 mV, 5 mV, and 50 ms, respectively.

The concentrations of DA and AA ranged from 0 to 40 μM and 0 to 2 mM, respectively, in PBS (pH 7.0).

3. Results and discussion

3.1. Characterization of Ag/Ag_2S particles

The synthesis of Ag/Ag_2S nanoparticles by chemistry methods allows good control of particle size distribution, particle size and particle shape. The characteristic such as the nanoparticles can be maintained in suspension and present differentiated active surface area. Fig. 1 shows the typical TEM image of the Ag/Ag_2S nanoparticles with a size distribution that indicates those spherical Ag/Ag_2S nanoparticles were well synthesized and had a mean diameter of approximately 48 nm.

Fig. 2 shows the XRD patterns of pure Ag, Ag_2S and Ag/Ag_2S. Pure Ag is a crystal with four sharp peaks at $2\theta = 38^\circ, 44^\circ, 64^\circ$, and 77° corresponding to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) silver planes, respectively, which coincide well with those observed in the literature (JCPDS No. 04-0783). Pure Ag_2S is a crystal and has many characteristic peaks. The XRD pattern of the synthesized particles in this study revealed the presence of Ag and Ag_2S, indicating that the particles were a mixture of Ag and Ag_2S.

3.2. The electrochemical behavior of DA and AA

The sensing behaviors of DA and AA were studied on CNT (dashed line) and Ag/Ag_2S-immobilized CNT (solid line) electrodes using DPV, as shown in Fig. 3A. No peak appeared in the blank electrolyte with either the CNT electrode (curve a) or the Ag/Ag_2S-immobilized CNT (curve b). A similar peak appeared at 0.15 (±0.01) V (vs. Ag/AgCl) for DA oxidation on both the CNT electrode (curve c) and the Ag/Ag_2S-immobilized CNT electrode (curve d) in the solution containing DA. An oxidation peak appeared at −0.02 V (vs. Ag/AgCl) for AA on the Ag/Ag_2S-immobilized CNT electrode (curve e) but not on the CNT electrode (curve f) in the solution containing AA. Apparently, Ag/Ag_2S worked as an electrocatalyst for AA, and the immobilization