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ORIGINAL ARTICLE

Simultaneous detection of ascorbic acid, dopamine, uric acid and tryptophan with Azure A-interlinked multi-walled carbon nanotube/gold nanoparticles composite modified electrode

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Abstract In this paper, multi-walled carbon nanotube/Azure A/gold nanoparticle composites (Nafion/AuNPs/AzA/MWCNTs) were prepared by binding gold nanoparticles to the surfaces of Azure A-coated carbon nanotubes. Nafion/AuNPs/AzA/MWCNTs based electrochemical sensor was fabricated for the simultaneous determination of ascorbic acid, dopamine, uric acid, and tryptophan. Cyclic voltammetry and electrochemical impedance spectroscopy were used to characterize the electrochemical properties of the modified electrodes. The modified electrode showed excellent electrocatalytic activity toward ascorbic acid, dopamine, uric acid, and tryptophan (pH 7.0). The experiment results showed that the linear response range for simultaneous detection of AA, DA, UA and Trp were 300–10,000 μM, 0.5–50 μM, 0.5–50 μM and 1.0–100 μM, respectively, and the detection limits were 16 μM, 0.014 μM, 0.028 μM and 0.56 μM (S/N = 3). The proposed method offers promise for simple, rapid, selective and cost-effective analysis of small biomolecules. The procedure was also applied to the determination of tryptophan in spiked milk samples.

1. Introduction

Ascorbic acid (AA), dopamine (DA), uric acid (UA) and tryptophan (Trp) are seen as crucial small biomolecules for physiological processes in human metabolism. It is well known that AA, DA, UA and Trp usually coexist in biological matrixes. Unnatural levels of these species will contribute to various diseases and disorders (Cooper et al., 1982; Damier et al., 1999; Mazloum-Ardakani et al., 2009; Liu et al., 2007). Tryptophan is an important amino acid owing to its essential functions in biological systems. It is a vital constituent of proteins and

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indispensable in human nutrition for establishing and maintaining a positive nitrogen balance (Fiorucci and Cavalheiro, 2002). Thus, the purpose of their concentration is significant not only for biomedical chemistry and neurochemistry but also for diagnostic and pathological research.

It is well known that AA, DA, UA and Trp usually coexist in biological matrixes. As the oxidation potentials of these species are very close, thus, the interference from each other should be expected. Thus, the subject area of the ability to selectively determine these species in a mixed solution is required. Latterly, for this design, various chemically modified electrodes have been constructed and applied for the simultaneous determination of AA, DA, UA and Trp in their mixture (Ghoreishi et al., 2014; Wang et al., 2012, 2013; Yang et al., 2011; Zhang et al., 2012; Noroozifar et al., 2011; Li et al., 2014; Kaur et al., 2013). A variety of materials have been used for the modification of electrode, such as gold nanoparticles/over oxidized-polyimidazole composite (Wang et al., 2012), graphene hybrid tube-like structure and 3,4,9,10-perylenetetracarboxylic acid (GS–PTCA) (Zhang et al., 2012), iron ion-doped natrolite zeolite–Multiwall carbon nanotube (Noroozifar et al., 2011), a hybrid of graphene sheets (GS) MWNTs bridged mesocellular graphene foam (MWNTs/MGF) (Li et al., 2014) and silver nanoparticle-decorated reduced graphene oxide composite (AgNPs/rGO) (Kaur et al., 2013). Carbon nanotubes (CNTs) have drawn special research attention because of their unique properties and possible applications. To improve upon the attributes of the CNTs, low-cost and industrially feasible approaches to their modifications are always being sought by chemists and materials scientists. The recently developed chemical and electrochemical functionalization schemes that have significantly broadened the application spectrum of CNTs. Functionalization of carbon nanotubes (CNTs) has attracted considerable interest in the fields of physics, chemistry, material science and biology. Combining hybrid nanostructures of metal nanoparticles (NPs) and carbon nanotubes could afford a novel scheme to prepare promising nanomaterials for the highly sensitive sensors and imaging science applications. Surface-linked Au–CNT nanocomposites may further be classified as covalently linked and non-covalently linked (Zhang and Olin, 2011). For non-covalent bonding, there are several ways to attach linking molecules to carbon nanotubes, including π stacking (Chen et al., 2008; Liu et al., 2003; Wang et al., 2002, 2012, Wang and Bi, 2013; Ou and Huang, 2006; Wang et al., 2007), hydrophobic forces (Richard et al., 2003; Cao et al., 2008; Xiao et al., 2008; Alexeyeva et al., 2006), and electrostatic interactions (Zhang and Olin, 2011; Jiang et al., 2003; Yao and Shiu, 2008). CNT/nanoparticle hybrid materials, in which nanoparticles are attached to CNT surfaces, have been reported to exhibit catalytic activity, enhanced electrical conductivity, and hydrogen-sensing capability, suggesting broad potential application in optoelectronics, molecular sensors and heterogeneous catalysis. Certain attributes of gold nanoparticles suggest that gold-nanoparticle-functionalized CNTs may prove applicable in future fabrication of nanodevices, enabling further miniaturization of integrated circuits (Wang et al., 2006). Thionine (Zhuo et al., 2005, 2006) and N,N-bi(2-mercaptoethyl)-perylene-3,4,9,10-tetracarboxylic diimide (MEPTCDI) are also used to link carbon nanotubes and gold nanoparticles through π stacking (Wang et al., 2007; Zhou et al., 2007).

In this study, we have prepared Nafion/AuNPs/AzA/MWCNT composites using N′,N′-dimethylphenothiazin-5-ium-3,7-diamine (AzA) molecules as interlinkers for depositing metal nanoparticles on CNTs. AuNPs were non-covalently attached to MWCNTs in the presence of Azure A. Azure A/Azure I molecules (Dezhampanah and Aghajani, 2013; Li et al., 2007) can easily interact with the MWCNTs to form a young kind of stable AzA–MWCNTs nanostructure. Chemically oxidized carbon nanotubes have many carboxyl groups, which lead to negatively charged surfaces of carbon nanotubes. Electrostatic interactions will result between these carboxyl groups and positively charged molecules (AzA^+) (Li et al., 2007). Upon subsequent addition of negatively charged gold nanoparticles, electrostatic interaction with AzA serves to "glue" the AuNPs onto the MWCNTs (Zhou et al., 2007). The resulting Nafion/AuNPs/AzA/MWCNTs hybrid films were used for electrochemical sensing of AA, DA, UA and Trp in their quaternary mixture. Satisfactory results were also obtained from analyzing real samples using this Nafion/AuNPs/AzA/MWCNTs nanocomposite modified electrode. The attractive response performances of the proposed method for simultaneous detection of the four biomolecules were presented in detail.

2. Experimental

2.1. Apparatus

The voltammetric experiments were performed in an electrochemical assembly with a platinum wire as the counter electrode, a glassy carbon electrode (Φ = 3 mm) as working electrode and a Ag/AgCl reference electrode. Cyclic voltammetry (CV) experiments were taken out with a Gamry Reference 600 potentiostat (Gamry, USA). All experiments were done at room temperature (25 °C). Before each experiment, the working electrode was polished with a slurry containing 0.3 μm and then with 0.05 μm sized aluminum oxide particles for 5 min. After each treatment, the electrode was washed and ultrasonicated in distilled water for 5 min to remove retained aluminum oxide particles on the electrode surface. Multiwalled carbon nanotubes (MWCNTs, φ = 6–9 nm) were purchased from Sigma Aldrich Co. The pH values of the solutions were assessed by a Hanna HI 221 pH-meter using the full range of 0–14.

2.2. Reagents and materials

All chemicals used were of analytical-reagent grade, and distilled water was used throughout. Ascorbic acid, dopamine and uric acid were obtained from Sigma (St. Louis, MO, USA), and they were all used as received. The stock solutions of dopamine (1.0×10^{-2} mol L^{-1}) and ascorbic acid (1.0×10^{-2} mol L^{-1}) were made daily by dissolving dopamine hydrochloride and ascorbic acid (Merck) in ethanol and distilled water, respectively. Uric acid solution (1.0×10^{-2} mol L^{-1}) was prepared by dissolving the solid in a small volume of 1.0×10^{-2} mol L^{-1} NaOH solution and diluted to the desired concentration. The solutions were protected from light and stored at 4 °C. Before usage, all sample solutions were prepared by appropriate dilutions to the desired concentration with distilled water. Trisodium citrate (99.5%) and