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Selective detection of dopamine in the presence of ascorbic acid and uric acid by a carbon nanotubes-ionic liquid gel modified electrode

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Abstract

The electrochemistry of dopamine (DA) was studied by cyclic voltammetry at a glassy carbon electrode modified by a gel containing multi-walled carbon nanotubes (MWNTs) and room-temperature ionic liquid of 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$). The thickness of gel on the surface of the electrode has to be controlled carefully because the charging currents increase with the modified layer being thicker. The anodic peaks of DA, ascorbic acid (AA) and uric acid (UA) in their mixture can be well separated since the peak potential of AA is shifted to more negative values, while that of UA is shifted to more positive values due to the modified electrode. At pH 7.08 the three peaks are separated ca. 0.20 and 0.15 V, respectively; hence DA can be determined in the presence of UA and more than 100 times excess of AA. Under optimum conditions linear calibration graphs were obtained over the DA concentration range 1.0×10^{-6} to 1.0×10^{-4} M. The detection limit of the current technique was found to be 1.0×10^{-7} M based on the signal-to-noise ratio of 3. The modified electrode has been successfully applied for the assay of DA in human blood serum. This work provides a simple and easy approach to selectively detect dopamine in the presence of ascorbic acid and uric acid.

Keywords: Carbon nanotubes; Ionic liquid; Dopamine; Ascorbic acid; Modified electrode

1. Introduction

Since the discovery of carbon nanotubes (CNs) in 1991, they have been the targets of numerous investigations due to their unique properties [1,2]. Several authors have reported the excellent electrocatalytic properties of nanotubes for the redox reaction of different biomolecules [3–5]. Room-temperature ionic liquids (RTILs), which are compounds that consist only of ions, are liquids at around room temperature. They have great potential as the green reaction media due to the advantages such as no measurable vapor pressure, good thermal and chemical stability, high conductivity, and low toxicity [6–8]. Fukushima et al. have recently demonstrated that pristine single-walled carbon nanotubes can form gels when mixing them with imidazolium ion-based RTILs by grinding [9]. Our group has been involving in the development of chemically modified electrode based on CNs and RTILs to multi-walled carbon nanotubes gel of 1-butyl-3-ethylimidazolium hexafluorophosphate on a glassy carbon electrode and studying the direct electrochemistry of proteins. The preliminary investigation has demonstrated that such gel electrode is thermal stable with high conductivity, and that the proteins adsorbed on the electrode can still retain their activities [10]. This kind of modified electrode provides a platform for fabrication of biosensors, which shows promising application to detect various biomacromolecules.

DA is an important neurotransmitter in mammalian central nervous system [11]. In the extra-cellular fluid of the central nervous system the basal DA concentration is very low (0.01–1 μM) [12]. A major problem in its determination

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is the lack of resolution between DA and coexisting AA, and its concentration is generally much higher than DA. At traditional solid electrodes, AA is oxidized at potentials close to that of DA, resulting in an overlapping voltammetric response. Various approaches have been made to overcome these difficulties [13–23]. For example, the voltammetric behavior of DA was studied at an unmodified, exfoliated graphite electrode [20] and surface modified electrodes with organic polymers [19,21,22] and metal complexes [15,16] and so on. Recently, carbon nanotubes as modified material on the electrodes have been developed to detect DA with satisfactory results [30–34]. Measurement at higher than ambient solution temperatures has also been made as an alternative approach to tackle such problem [35].

Here, we describe a cyclic voltammetric and differential pulse voltammetric studies of DA both in the absence and presence of AA at a MWNTs-ionic liquid gel modified electrode. Since the anodic peak potential of AA is shifted to more negative values than that of DA, their overlapped anodic peaks can be separated, which results in both compounds to be quantitatively determined. Moreover, the presence of UA has no effect on the detection of DA.

2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a BAS 100B electrochemical workstation (Bioanalytical System, USA). The working electrode was a glassy carbon (GC) electrode or a modified GC electrode, the auxiliary and reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. The transmission electron microscope (TEM) image was obtained using a JEOL 200CX TEM (JEOL, Japan).

2.2. Reagents and solutions

MWNTs were produced by catalytic chemical vapor deposition (CCVD) method, and provided by the Department of Chemical Engineering of Tsinghua University of China as gifts. The details of synthesis were reported elsewhere [24,25]. The purity of the MWNTs is about 99%.

The ionic liquid of 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) was synthesized according to the procedures described in the references [26,27]. The $OMIMPF_6$ has been characterized by ^1H NMR and IR, and its purity was proven to be very high.

Dopamine (3-hydroxytyramine hydrochloride) was purchased from Fluka. L(+)-Ascorbic acid was purchased from Northeast Pharmacy Institute of China. Uric acid was purchased from Merck. Water was triply distilled with a quartz apparatus. Highly purity nitrogen was used for deaeration. All other reagents were of analytical grade.

The human blood serum was obtained from Campus Hospital of Peking University and was diluted 10 times with 0.1 M phosphate buffer (pH 7.08) before using.

The buffer and sample solutions were purged with highly purified nitrogen for at least 5 min prior to the experiments. Nitrogen atmosphere was maintained over the solutions during the experiments. All experiments were carried out at room temperature ($18 \pm 2\,^{\circ}C$).

2.3. Fabrication of the modified electrode

First, 12 mg MWNTs mixed with 0.2 mL $OMIMPF_6$ were ground with an agate mortar for about 20 min, and a black gel was formed [9]. Meanwhile, a glassy carbon disk electrode with the diameter of 4 mm was polished with alumina, followed with being washed in triply distilled water and ethanol, respectively. Then, the GC electrode was rubbed over the carbon nanotubes gel placed on a smooth glass slide, and the gel was mechanically attached to the electrode surface. Finally, after the gel on the electrode surface was smoothed with a spatula to leave a thin gel film on the GC electrode surface, the gel modified glassy carbon electrode (denominated as MWNTs-IL-Gel/GC electrode in this paper) was fabricated. All voltammograms of the MWNTs-IL-Gel/GC electrode were recorded after reaching equilibrium within the tested aqueous solution.

3. Results and discussion

3.1. Characterization of the MWNTs-IL-Gel/GC modified electrode

The MWNTs-IL-Gel/GC modified electrode is first characterized by the TEM. Fig. 1 shows the typical TEM image of the MWNTs, which were dispersed in ethanol by sonication. It is clear that MWNTs are highly entangled with the diameter of several tens of nanometers. As comparison, the MWNTs gel of the $OMIMPF_6$ was dispersed in triply distilled water by sonication, and its image of TEM (Fig. 2) indicates the MWNTs are untangled after being treated with

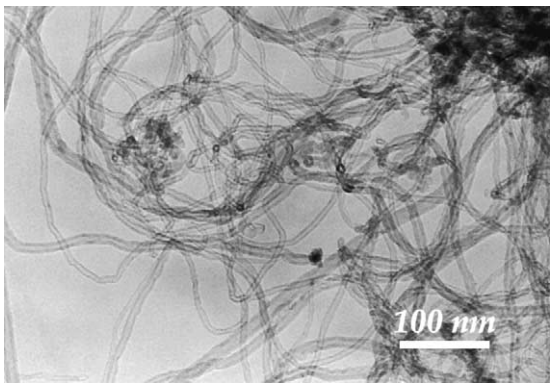

Fig. 1. TEM image of MWNTs dispersed in ethanol by sonication.