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Structural and characteristic analysis of carbon nanotubes-ionic liquid gel biosensor

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Abstract

The structure and characteristic of carbon nanotubes-ionic liquid gel biosensor were studied by voltammetry, microscopy and spectroscopy. Various biomolecules were electrochemically detected with this gel biosensor such as glucose oxidase and NADH. The excellent electrochemical behavior of this gel biosensor might be due to the following three main factors: (1) the inherently perfect electrochemical characteristic of multi-wall carbon nanotubes (MWNTs); (2) the better solvent effect and conductivity of ionic liquid as well as the proper interactions between MWNTs and ionic liquid; (3) the proper mixing ratio of MWNTs to ionic liquid. Meanwhile, the interactions between MWNTs and ionic liquid were carefully studied as well. It can be concluded that the non-covalent (π–π) interaction between the imidazole loop of ionic liquid and MWNTs side wall should play an important role. This work gives a further understanding of what results in the high sensitivity and selectivity of such a biosensor to some biomolecules, and provides a simple and easy approach to design new biosensors with various nano-particles and versatile ionic liquid.

Keywords: Carbon nanotubes; Ionic liquid; Voltammetry; Spectroscopy; Biosensor

1. Introduction

Since Fukushima found that carbon nanotubes (CNTs) could form gels when mixing them with imidazolium ion-based room-temperature ionic liquid (RTILs) by simply grinding in 2003 [1], several scientists have developed the excellent electrocatalytic properties of such a gel in the redox behavior of different biomolecules [2–5]. Our group has been involving in the development of chemically modified electrode based on CNTs and RTILs. For example, the MWNTs gel of 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) was coated on a glassy carbon electrode, where the direct electrochemistry of proteins could be studied. The preliminary investigation has demonstrated that such a gel electrode is thermally stable with high conductivity, and that the proteins adsorbed on the electrode can still retain their activities [6]. We have also reported the selective detection of dopamine in the presence of ascorbic acid and uric acid at another MWNTs gel modified electrode of 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) [7]. The oxidation peaks of dopamine, ascorbic acid and uric acid in their mixture can be well separated since the peak potential of ascorbic acid is shifted to more negative value, while that of uric acid is shifted to more positive value due to the modified electrode. As a result, dopamine can be determined in the presence of uric acid and more than 100 times excess of ascorbic acid. The modified electrode has been successfully applied for the assay of dopamine in human blood serum as well. Furthermore, we reported the detection of uric acid and adenine on this gel biosensor [8]. There was a significant two-way electrocatalytic activity upon both oxidation and reduction of uric acid. A diimine, the oxidation product of uric acid, was found to be an unstable intermediate, which was converted by a follow-up hydration reaction to an imine alcohol, with the reaction rate constant of

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$8.5 \pm 0.3\ M^{-1}\ s^{-1}$. Based on the signal-to-noise ratio of 3, the detection limit of the current technique was found to be as low as 9.0×10^{-8} M (uric acid) and 2.0×10^{-6} M (adenine), respectively. This kind of modified electrode provides a platform for fabrication of biosensors, which shows promising application to detect various biomolecules.

Recently, scientists have been investigating the internal physicochemical characteristics of the carbon nanotubes-ionic liquid gel, such as the structure and viscosity [9], solubility [10–12], dispersibility [13,14] and photovoltaic property [15]. For example, it is found that the characteristic rheological behaviors, such as high shear thinning, dynamic yield stress, and frequency independent dynamic behavior, not only support the gel formation due to the uniform dispersion of single-wall carbon nanotube (SWNT) in the ionic liquid medium, but also explain the formation of network structure induced by a strong interaction between ionic liquid and SWNT [9]. Ionic liquid-modified carbon nanotubes with reversibly switchable solubility between aqueous and organic solvents can be induced by anion exchange coupled with cationic imidazole rings, which represents a simple and convenient way to alter the solubility of CNTs by simply switching salt solutions under neutral conditions [10–12]. Usui et al. found that there were notable effects in photocurrent density and voltage measurements when the dye-sensitized solar cells (DSCs) were assembled with CNT ionic nano-composite gel electrolyte [15]. Their energy conversion efficiency is significantly improved and increased compared with a DSC using a bare ionic liquid electrolyte.

However, to our knowledge, there are no integrated reports regarding the gel of carbon nanotubes-ionic liquid to explain the internal relationship between those characteristics and chemical behaviors. The purpose of this work is to study the voltammetric behavior of the carbon nanotubes-ionic liquid gel biosensor as well as its structural and physicochemical characteristics. The interactions between MWNTs and ionic liquid were investigated by various spectrometric methods. And new approaches to design biosensors are prospected.

2. Experimental

MWNTs were obtained from the Department of Chemical Engineering of Tsinghua University of China as gifts. They were produced by catalytic chemical vapor deposition (CCVD) method, and the details of synthesis were reported elsewhere [16,17]. The purity of the MWNTs is about 99%. The ionic liquids of 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) were synthesized according to the procedures described in Refs. [18,19]. They were characterized by ^1H NMR and IR, and their purities were proven to be very high. Glucose was purchased from Beijing Chemical Reagent Company or Tianjin Chemical Reagent Company. Nicotinamide adenine dinucleotide hydrogen (NADH) was purchased from Sigma. Triply distilled water was used. All other reagents were of analytical grade.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a CHI 660 electrochemical workstation (Shanghai, China). The working electrode was a glassy carbon electrode or a modified glassy carbon 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). The atomic force microscope (AFM) image was obtained using a NANOSCOPE IIIa (Digital instruments, USA). The Raman spectra were obtained with a SYSTEM 1000 (Renishaw, UK). The FT-IR was performed with a FTS-65A (Nicolet, USA). A CARY 1E UV–Vis spectrometer (Varian, Australia) was used to obtain UV–Vis spectra. An F-4500 spectrometer (Hitachi, Japan) was used to acquire the fluorescence spectra.

The gel was produced by grinding 12 mg MWNTs and 0.2 mL ionic liquid ($OMIMPF_6$ or $BMIMPF_6$) in an agate mortar for about 20 min, and it would be available for at least three months. The multi-walled carbon nanotubes-ionic liquid gel modified glassy carbon electrode (denominated as MWNTs-IL-Gel/GCE in this paper) was fabricated as described before [7]. As the thickness of the modified layer has great effect on the electrochemical properties of MWNTs-IL-Gel/GCE, it was carefully controlled to be consistent during each exploration. All voltammograms of MWNTs-IL-Gel/GCE were recorded after reaching equilibrium within the tested aqueous solution.

3. Results and discussion

As shown in Fig. 1a, in the 0.1 M phosphate buffer containing 20 mM glucose (pH 7.00), no other obvious redox peak appears at the MWNTs/GCE except the oxidation peak at about 0 V due to the MWNTs' partly structural deficiency. It can be demonstrated that this oxidation peak is getting clearer after treating MWNTs with mixed nitric acid and sulfuric acid (1:3). However, a small but clear reduction peak (about −0.10 V) was observed at a MWNTs-$BMIMPF_6$-Gel/GCE (Fig. 1b). Meanwhile, similar results were obtained when $BMIMPF_6$ was replaced by $OMIMPF_6$ in the gel. The only difference was that the current response was higher when using $BMIMPF_6$ rather than $OMIMPF_6$, which might be owing to both the higher viscosity of $OMIMPF_6$ and stronger interaction between $OMIMPF_6$ and MWNTs, thus hindered the unwrapping of electrochemically active sites of MWNTs in a way.

The electrochemical determination of glucose concentration without using enzyme is one of the dreams that many researchers have been trying to make come true. In recent years, the non-enzymatic glucose sensor keeps coming closer to practical applications with new electrode materials being reported. But almost all of them are related to direct electrochemical oxidation of glucose. There is no report