



Electropolymerized toluidine blue O functionalized ordered mesoporous carbon-ionic liquid gel-modified electrode and its low-potential detection of NADH

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ABSTRACT

A novel gel was developed based on the polymerization of a composite containing toluidine blue O (TBO) functionalized ordered mesoporous carbon (OMC) by a π - π stacking interaction and ionic liquid (IL). The poly (toluidine blue O) (PTBO)-OMC-IL composite film distributes almost homogeneously with unique structure on the surface of substrate. The PTBO-OMC-IL gel modified glass carbon (GC) electrode displays high conductivity investigated by electrochemical method. Electrochemical studies suggest that the PTBO-OMC-IL gel/GC electrode provide a positively synergistic effect among PTBO, OMC and IL on the electrochemical oxidation of NADH. Under a low applied potential of -0.034 V, NADH could be linearly detected from $1.0 \mu\text{mol L}^{-1}$ up to 6.0mmol L^{-1} with a low detection limit of $0.4 \mu\text{mol L}^{-1}$ ($S/N=3$) and fast response time of 2 s. So the PTBO-OMC-IL gel modified electrode may be used as electrochemical transducers and has potential application for designing a variety of NAD^+ -dependent electrochemical biosensors.

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1. Introduction

Ordered mesoporous carbon (OMC) has become a hot subject since it was synthesized in 1999 [1]. Compared with the different forms of carbon materials, OMC possesses special properties (well-ordered pore structure, high specific pore volume and high specific surface area) which make it attractive in the field of electroanalytical applications for the low potential determination of different bioanalytes [2,3]. The oxidation of ascorbic acid and uric acid was investigated by Ndamanisha et al. at the OMC functionalized with ferrocenecarboxylic acid modified electrode [4,5]. Recently, studies have been developed by preparing composite films composed of both OMC and conjugated polymers [6,7]. These new composite materials possess the properties of each component with a synergistic effect that would be useful for the detection of electroactive species, including β -nicotinamide adenine dinucleotide (NADH) [8], hydrogen peroxide [9] and etc.

On the other hand, ionic liquids (IL) have been the targets of numerous investigations because of their characteristics such as good chemical and thermal stability, almost negligible volatility, good ionic conductivity and wide electrochemical window. Hence

they have been extensively used to prepare modified electrode and biosensors in electrochemistry and biocatalysis. For example, several groups have reported that IL can form gels with carbon nanotubes or OMC by grinding to fabricate several modified electrodes in order to selective detection of dopamine in the presence of ascorbic acid and uric acid [10,11].

NADH and its oxidized form (NAD^+) are cofactors of more than 500 kinds of dehydrogenase enzymes widely used for the construction of electrochemical biosensors. However, the direct oxidation of NADH at conventional bare electrodes, such as carbon, gold and platinum, is highly irreversible and needs a considerable overpotential [12,13]. Consequently, considerable efforts have been devoted toward the goal of identifying new electrode materials and new methods that will reduce the overpotential for oxidation of NADH and minimize surface passivation effects. Some nanomaterials such as carbon nanotubes (CNT) [14] and OMC [15], water soluble dye compounds [16], phenothiazine derivatives [17] and various redox polymers [18] as electron transfer mediators have been used successfully to decrease the high overpotential for electrocatalytic oxidation of NADH and minimizing surface fouling. Zeng et al. [14] electrodeposited toluidine blue O (TBO) functionalized CNT for a stable low-potential amperometric detection of NADH. Lu et al. [15] fabricated composite film which contains OMC along with the incorporation of poly (neutral red) for determination of NADH.

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In this article, a new gel was developed based on the polymerization of a composite containing TBO functionalized OMC by a π - π stacking interaction and IL and was used to modify glassy carbon (GC) electrode. The PTBO-OMC-IL gel/GC electrode exhibited high conductivity and good electrocatalytic activity toward NADH due to a positively synergistic effect among PTBO, OMC and IL.

2. Experimental

2.1. Apparatus and reagents

All electrochemical experiments were performed with a CHI 660C electrochemical workstation. A conventional three-electrode system was used with a modified grass carbon (GC, 3 mm in diameter) electrode as working electrode, a Ag/AgCl/3 mol L⁻¹ KCl electrode as reference electrode, and a platinum foil electrode as counter electrode. Amperometric measurements were carried out under stirred conditions, and the response current was marked with the change value between the steady state current and the background current. The scanning electron microscopy (SEM) images were performed on a JSM-6360LV SEM (JEOL, Japan). All experiments were performed at room temperature.

OMC was synthesized following a published procedure [19]. N,N'-dimethylformamide (DMF) (HPLC grade) was purchased from Sangon Biotech Co., Ltd. (China). IL of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) was purchased from Lan zhou Institute of Chemical Physics (China). NADH (reduced form, in the form of sodium salt, >92% purity) was purchased from J&K Scientific Ltd. (China). TBO was purchased from Sigma-Aldrich (USA). McIlvaine buffer solution (pH 4.0, consisted of 0.1 mol L⁻¹ citric acid and 0.2 mol L⁻¹ solution of Na₂HPO₄ containing 0.1 mol L⁻¹ KCl) was used for electropolymerization and phosphate buffer solution (PBS, 0.067 mol L⁻¹, pH 7.0) was used as buffer solution for other electrochemical experiments. All other chemicals reagents were of analytical reagent grade and used as received. Double-distilled water was used throughout.

2.2. Preparation of the OMC functionalized with TBO composite

The OMC functionalized with TBO (TBO-OMC) composite was firstly prepared by sonicating a mixture of 25 mg OMC and 40 mg TBO in 100 mL DMF for 6 h at room temperature. The resulting suspension was centrifuged with high speed, and then evaporated on a rotary evaporator. Finally, the obtained sample was dried at 75 °C for 5 h to obtain TBO-OMC composite.

2.3. Preparation of the modified electrode

Firstly, 12 mg TBO-OMC composite was mixed with 0.16 mL IL by grinding in an agate mortar for about 20 min to form a black TBO-OMC-IL gel [20]. Meanwhile, the GC electrode was polished with 0.3 and 0.05 μ m alumina powder, respectively, followed with being ultrasonically cleaned with ethanol and double-distilled water and dried in nitrogen. Then, the GC electrode was rubbed over the TBO-OMC-IL gel for about 15 min placed on a smooth glass slide, and the gel was mechanically attached to the electrode surface. After the gel on the electrode surface was smoothed with a spatula, a thin gel film was left on the GC electrode surface. Finally, the TBO-OMC-IL gel modified GC electrode was transferred to a McIlvaine buffer solution (pH 4.0) and electropolymerized by cyclic voltammetry between -0.6 and +1.0 V at 50 mV/s for 30 cycles. The begin potential was -0.6 V and the forward scan direction is positive. The electrodeposited gel modified GC electrode (denominated as PTBO-OMC-IL gel/GC electrode in this paper) was fabricated. Similarly, the OMC-IL gel could also be formed by grinding 12 mg OMC and

0.16 mL IL in an agate mortar together. Then the OMC-IL gel modified GC electrode was fabricated by the rubbing method, and was denoted as OMC-IL gel/GC electrode hereafter.

3. Results and discussion

3.1. The micrograph of the composite film

Fig. 1 displays the morphologies of the OMC, TBO-OMC and PTBO-OMC-IL composite films characterized with SEM. It is clear that OMC dispersed in DMF by sonication is highly entangled. The TBO-OMC composite was also dispersed in DMF by sonication and its image of SEM indicates that the OMC is untangled after functionalized with the TBO as comparison with Fig. 1(A), because TBO is hydrophilic and hydrophobic OMC could interact strongly with TBO by a π - π stacking interaction. From Fig. 1(C), it can be observed that the PTBO-OMC-IL composite film distributes almost homogeneously with unique structure on the surface of substrate.

3.2. Electropolymerization of TBO and electrochemical characterization of the PTBO-OMC-IL gel/GC electrode

According to the reports, the initial step for the TBO polymerization is one-electron oxidation of NH₂ group and forms a cation radical [14,21]. The unpaired electron can be delocalization through the TBO molecule, but the unpaired electron may be sited with high probability on either amine group and at position ortho to them. Radical dimerization can occur via carbon-nitrogen coupling routes as shown in Scheme 1. The oxidation of the NH₂ group in the dimer can occur again, the polymerization can take place readily to form the PTBO. The consecutive cyclic voltammograms indicate the formation process of the PTBO film on the modified electrode [14]. Fig. 2 shows cyclic voltammograms of the PTBO-OMC-IL gel/GC electrode obtained from the electropolymerization process of TBO with consecutive potential scan. As we can see, the first cyclic voltammogram (initial potential is -0.6 V) exhibits a pair of sharp reversible peaks at the region of the monomer redox peak. The current of the monomer of TBO at about -0.14 V decreased while the current of PTBO at about +0.04 V increased step by step, which means that TBO could be electropolymerized and formed conducting polymer successfully. With increasing scan cycles, a pair of new reversible peaks with a cathodic peak potential of -0.02 V and an anodic peak potential of +0.04 V appear and increase gradually. The above result indicates that the polymer film grows with elapse of time.

The cyclic voltammograms responses of the bare GC (curve 1), OMC-IL gel/GC (curve 2) and PTBO-OMC-IL gel/GC (curve 3) electrodes in PBS (0.067 mol L⁻¹, pH 7.0) are shown in Fig. 3. At the bare GC (curve 1) electrode, no redox peaks could be observed. At the OMC-IL gel/GC electrode (curves 2), a small pair of perks appears which could be ascribed to the redox process of the acidic groups at the surface of OMC [22]. However, the PTBO-OMC-IL gel/GC (curve 3) electrode shows evidently reversible redox responses of the PTBO and the formal potential $E_{1/2}$ is calculated around at -89.9 mV which is taken as the mid-point of the anodic and cathodic peak potentials. Compared with the other two, the PTBO-OMC-IL gel/GC electrode displays the highest background current. To explain the above results, the following three reasons are formulated. Firstly, OMC has larger hydrophobic surface area and could interact strongly with TBO, which is contributed to larger adsorption amount of TBO. Secondly, the OMC-induced enhancement in the behavior of PTBO could be ascribed to improved electronic and ionic transport capacity of the PTBO-OMC-IL gel. Thirdly, PTBO, OMC and IL exhibit some unique characteristics such as high conductivity and good electronic structure, respectively. So, there is a positive synergistic conductivity among PTBO, OMC and IL.

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