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Application of graphene-ionic liquid-chitosan composite-modified carbon molecular wire electrode for the sensitive determination of adenosine-5′-monophosphate

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ABSTRACT

In this paper, a graphene (GR) ionic liquid (IL) 1-octyl-3-methylimidazolium hexafluorophosphate and chitosan composite-modified carbon molecular wire electrode (CMWE) was fabricated by a drop-casting method and further applied to the sensitive electrochemical detection of adenosine-5′-monophosphate (AMP). CMWE was prepared with diphenylacetylene (DPA) as the modifier and the binder. The properties of modified electrode were examined by scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. Electrochemical behaviors of AMP was carefully investigated with enhanced responses appeared, which was due to the presence of GR-IL composite on the electrode surface with excellent electrocatalytic ability. A well-defined oxidation peak of AMP appeared at 1.314 V and the electrochemical parameters were calculated by electrochemical methods. Under the selected conditions, the oxidation peak current of AMP was proportional to its concentration in the range from 0.01 μM to 80.0 μM with the detection limit as 3.42 nM (3σ) by differential pulse voltammetry. The proposed method exhibited good selectivity and was applied to the detection of vidarabine monophosphate injection samples with satisfactory results.

1. Introduction

Purine nucleoside is a fundamental and important compound in biological system, which can be involved in a lot of biochemical process. The variation of nucleoside concentration in body fluid can cause some diseases such as carcinoma and liver disease [1]. Hence, the sensitive detection of purine nucleosides is very important in bioanalytical chemistry. Because nucleosides have electroactive groups in its molecular structure, electrochemical methods can be used for the direct detection, which exhibit many advantages such as rapidity, low cost and high sensitivity and selectivity with cheaper instrumentation [2,3]. For example, Lin et al. [4] combined capillary electrophoresis with electrochemical detection for the detection of purine bases on a copper electrode. Radecka et al. [5] fabricated a macrocyclic polyamine-modified gold electrode for the voltammetric detection of adenine nucleotides. Zhu et al. [6] applied an ordered mesoporous carbon-modified electrode for the electrochemical detection of dsDNA. Gao et al. [7] used a 1-ethyl-3-methylimidazolium ethylsulfate modified carbon paste electrode for the simultaneously detection of guanosine and adenosine. Adenosine-5′-monophosphate (AMP) is one kind of nucleosides with many specific functions in biological process [8]. The effect of AMP on the kinetics of glutamate dehydrogenase was studied by chronoamperometry and cyclic voltammetry [9]. Gao et al. [10] applied a hydroxyl functionalized ionic liquid (IL)-modified electrode for the sensitive detection of AMP.

As a two-dimensional nanosheet graphene (GR) has exhibited many specific properties such as big surface-to-volume ratio, good conductivity and high-electrocatalytic activity [11,12]. Due to its specific electrochemical behaviors, GR has been widely used in the field of electrochemistry and electrochemical biosensors [13,14]. With the usage of GR as the modifier on the electrode surface, electrochemical performance of the GR-modified electrode can be greatly enhanced [15]. In recent years, GR-based composites have been synthesized and used, which greatly extend the application of GR [16]. Among them, GR and IL composite had been explored. Due to the specific properties of IL such as negligible vapor pressure, high conductivity and good stability, IL has attracted great attentions in the field of electrochemistry [17,18]. The combination of GR with IL can result in a specific hybrid material due to their interactions. Shan et al. used an IL functionalized GR-modified glassy carbon electrode (GCE) for the sensitive detection of NADH and ethanol [19]. Guo et al. [20] applied a GR-IL composite as the advanced electrode material for the detection of trinitrotoluene. Peng et al. [21] investigated the electrochemical behaviors of azithromycin at a GR-IL composite-modified GCE. Sun et al. [22] also applied a GR-IL composite-modified electrode for the electrochemical oxidation of guanosine-5′- triphosphate.

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In this paper, a GR, a hydrophobic IL 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) and chitosan (CTS) composite, was prepared and used as the modifier for the electrode modification. As a new kind of chemically modified carbon paste electrode with better performance, carbon molecular wire electrode (CMWE) was used as the substrate electrode, which was fabricated with molecular wire (MW) as the binder and/or the modifier. MW exhibits some specific characteristics such as good chemical and thermal stability, high conductivity and wide electrochemical windows, so it can be used in the chemically modified electrode. Safavi et al. [23] reported the preparation of CMWE with DPA as the binder. Our group also applied CMWE [24] or GR-modified CMWE [25] for the sensitive detection of adenosine-5′-triphosphate. To further enhance the electrochemical performance, a GR-IL composite was prepared and used for the modification of CMWE. By combining the advantages of GR, IL and CMWE, a new modified electrode was devised and further used for AMP detection. Electrochemical behaviors of AMP on the modified electrode were carefully investigated with the electrochemical parameters calculated. The results indicated that CTS-GR-IL/CMWE exhibited excellent performances for the sensitive detection of AMP, which was further applied to the drug samples detection with satisfactory results.

2. Experimental

2.1. Reagents

Adenosine-5′-monophosphate (AMP, ≥98.0%) and guanosine-5′-monophosphate (GMP, ≥98.0%) were purchased from Shanghai Kayon Biological Tech. Ltd. Co. (China). The AMP stock solution (10.0 mM) was prepared and stored in 4 °C refrigerator. 1-Octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$, Hangzhou Kemer Chemical Ltd. Co., China), diphenylacetylene (DPA, 99%, Aladdin Chemistry Ltd. Co., China), chitosan (CTS, minimum 95% deacetylated, Dalian Xindie Chemical Reagents Ltd. Co., China), graphene (GR, ≥98.3%, Sinocarbon Technology Ltd. Co., China) and graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Plant, China) were used as received. 0.2 M Britton–Robinson (B-R) buffer solutions with various pH values were used as the supporting electrolyte. All the reagents were of analytical reagent grade and the redistilled water was used throughout the experiments.

2.2. Apparatus

A CHI 1210A electrochemical workstation (Shanghai CH Instruments, China) was used for voltammetric measurements and CHI 750B electrochemical workstation (Shanghai CH Instruments, China) was used for electrochemical impedance spectroscopic (EIS) experiment. A conventional three-electrode system was used throughout with a CTS-GR-IL modified CMWE as working electrode ($\varphi = 4.2$ mm), a platinum wire electrode as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. Scanning electron microscopy (SEM) was conducted with a JSM-6700 F scanning electron microscope (Japan Electron Company, Japan). Transmission electron microscopy (TEM) was performed on an FEI Tecnai G20 transmission electron microscope (FEI Company, USA).

2.3. Preparation of CTS-GR-IL/CMWE

Based on the reported procedure [24], CMWE was prepared by mixing graphite powder with DPA and the surface of CMWE was polished to a mirror-like interface just before use. The modifier was prepared with the following procedure. GR (5.0 mg) was added into a 5.0-mL 0.1% CTS solution with ultrasonication for 2 h to get a homogenous CTS-GR mixture. Then $OMIMPF_6$ was added in the CTS-GR mixture at the ratio of 3% (v/v) and sonicated to get a homogeneous CTS-GR-IL solution. CTS-GR-IL suspension solution (6.0 μL) was casted on CMWE surface to get the modified electrode, which was denoted as CTS-GR-IL/CMWE and dried at room temperature. Other modified electrodes such as CTS-GR/CMWE and CTS-IL/CMWE were also fabricated with the similar procedures and used for comparison.

3. Result and discussion

3.1. Characteristics of the modified electrodes

The morphologies of GR and GR-IL hybrid were recorded with the TEM results shown in Fig. 1 A and B, which gave the typical flake-like shapes on both images. It can be seen that GR appeared as few-layer sheets (Fig. 1A), which was attributed to the partly aggregation of GR nanosheets due to its poor solubility, while the TEM image of GR-IL exhibited as transparent with some wrinkled topology (Fig. 1B), which was often observed for single-layer GR. GR and $OMIMPF_6$ can interact with each other via cation-π and/or π-π interactions, which result in a stable composite with good dispersion. The SEM images of composite on the surface of the modified electrodes were further recorded. On CTS-GR/CMWE (Fig. 1C), a clearly flake-like shape appeared with layer-by-layer structure, which was the typical characteristic of GR nanosheets. On CTS-GR-IL/CMWE (Fig. 1D), the size of the nanosheets was increased with the layered structure connected to form a continuous and smooth interface. The results could be attributed to the binding and blanketing effect of IL that had high viscosity. The interaction of IL with GR has been proven to form a

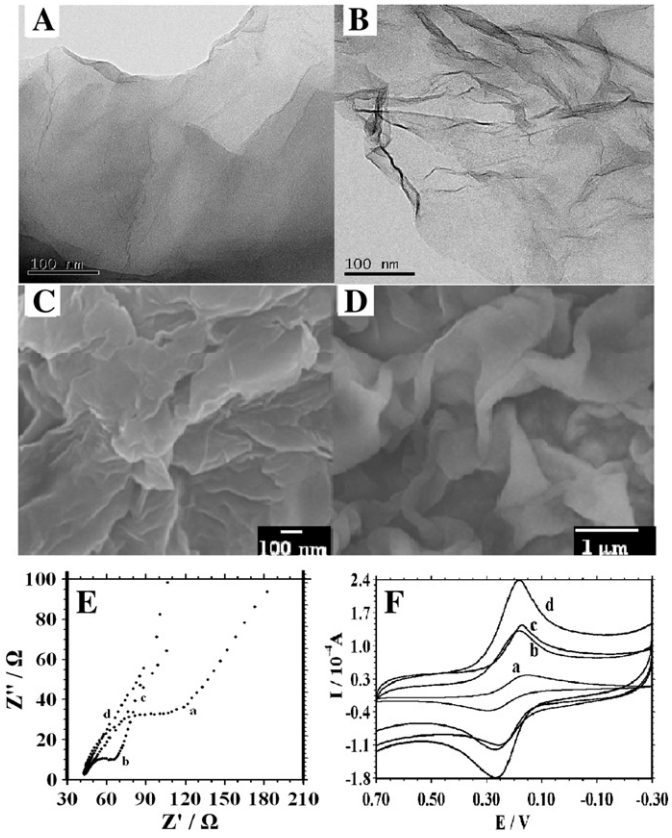

Fig. 1. TEM images of GR (A) and GR-IL (B). SEM images of CTS-GR/CMWE (C) and CTS-GR-IL/CMWE (D). (E) Electrochemical impedance spectra for CMWE (a), CTS-GR/CMWE (b), CTS-IL/CMWE (c) and CTS-GR-IL/CMWE (d) in a solution of 10.0 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl with the frequencies swept from 10^4 to 0.1 Hz. (F) Cyclic voltammograms of CMWE (a), CTS-GR/CMWE (b), CTS-IL/CMWE (c) and CTS-GR-IL/CMWE (d) in a solution of 1.0 mM $K_3[Fe(CN)_6]$ and 0.5 M KCl at a scan rate of 100 mV s^{-1}.