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Electrochemical oxidation of guanosine-5′-triphosphate on a graphene and ionic liquid composite modified carbon molecular wire electrode

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ABSTRACT

A graphene, chitosan and 1-ethyl-3-methylimidazolium tetrafluoroborate composite was prepared and modified on the surface of a carbon molecular wire electrode. The fabricated electrode was characterized by different methods such as scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. Electrochemical behaviors of guanosine-5′-triphosphate (GTP) were carefully studied on the modified electrode. The electrochemical parameters such as the charge transfer coefficient (α) and the electrode reaction standard rate constant (k_s) were calculated with the results as 0.57 and $1.56 \times 10^{-4}\ s^{-1}$. Under the optimized conditions, the oxidation peak current was proportion to the GTP concentration in the range from 0.007 to 70.0 μmol/L with the detection limit of 0.232 nmol/L (S/N = 3). Moreover, the proposed method showed good selectivity to the GTP detection without the interference of coexisting substances, and was further applied to the artificial samples determination with satisfactory results.

1. Introduction

Guanine nucleotides are served as energy sources and play important roles in regulatory systems in a wide variety of tissues and organisms, which can facilitate the maintenance of the internal milieu [1,2]. Guanosine-5′-triphosphate (GTP) is one of guanine nucleotides in which triphosphate is attached at the 5′ position of guanosine. GTP is also present along with ATP in the extracts of starfish and sea urchin [3] and in enzyme nucleoside diphosphate kinase [4]. The detection of GTP by electrochemical method has attracted intensive interests. Goyal et al. investigated the electrochemical oxidation mechanism of GTP at a pyrolytic graphite electrode [5]. They also used a nanogold modified ITO electrode for the simultaneous determination of guanosine and GTP in the human blood plasma samples [6]. Our group also used an ionic liquid (IL) modified carbon paste electrode (CPE) for the detection of GTP [7]. Ionic liquids (ILs) are compounds composed entirely of ions and exist in the liquid state around room temperature [8,9], which are generally consisted of an organic bulky cation weakly coordinated to an inorganic anion. ILs have attracted much attentions in recent years due to their unique chemical and physical properties, such as high chemical and thermal stability, almost negligible vapor pressure, high conductivity and wide electrochemical potential windows [10–12]. The applications of ILs in electrochemistry and electrochemical sensor such as the electrolyte and the modifier or the binder in chemically modified electrode have been widely investigated. Our group had applied different kinds of IL-CPEs for the investigation on protein electrochemistry and the detection of electroactive molecules [13–15].

Graphene (GR) is a flat monolayer of carbon atoms that tightly packed into a two-dimensional honeycomb lattice. Recently it has attracted extensive attentions in various research fields due to good electrical conductivity, high surface-to-volume ratio, fast electron transfer rate and exceptional thermal stability [16–18]. Many researchers have investigated the feasibility of GR in electroanalytical chemistry as a novel electrode modified material. For example, Kim et al. applied a GR modified electrode for electrochemical detection of dopamine in the presence of ascorbic acid [19]. Li et al. used GR-modified electrode for the selective detection of dopamine [20]. Ai et al. fabricated a GR–chitosan composite film modified glassy carbon electrode (GCE) to determine 4-aminophenol [21].

Molecular wires (MW) have received great attentions due to their specific characteristics such as good chemical and thermal stability, high conductivity and wide electrochemical windows [22,23]. Diphenylacetylene (DPA) is one of the smallest conjugated oligomers, which can be viewed as the structural unit of the conjugated molecules. DPA can provide a good theoretical model for exploring the structural and electronic properties that control the electron transport in phenylene–acetylene oligomers. Recently a MW modified carbon paste electrode (which was named as carbon

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molecular wire electrode, CMWE) was reported, which exhibited better performances than the traditional GCE [24].

In this paper a GR, chitosan (CTS) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) composite modified CMWE was fabricated firstly. Then different methods such as scanning electron microscopy (SEM), cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to characterize the modified electrode. Then electrochemical behaviors of GTP on the modified electrode were carefully investigated with the electrochemical parameters calculated. The prepared electrode showed high sensitivity and stability to the GTP detection over the concentration range from 0.007 to 70.0 μmol/L.

2. Experimental

2.1. Reagents

Guanosine-5′-triphosphate (GTP, ≥98.0%, Shanghai Kayon Biological Technology Co. Ltd., China), adenosine-5′-triphosphate (ATP, ≥98.0%, Shanghai Kayon Biological Technology Co. Ltd., China), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4, Lanzhou Greenchem ILS. LICP. CAS., China), diphenylacetylene (DPA, 99%, Aladdin Chemistry Co. Ltd., China), chitosan (CTS, minimum 95% deacetylated, Dalian Xindie Chemical Reagents Co. Ltd., China), graphene (GR, ≥98.3%, Sinocarbon Technology Co. Ltd., China) and graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Plant, China) were used as received without further purification. The stock solution (10.0 mmol/L) of GTP was prepared just before use and stored in 4 °C refrigerator. 0.2 mol/L 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

All the voltammetric measurements such as cyclic voltammetry and differential pulse voltammetry were performed on a CHI 1210A electrochemical workstation (Shanghai CH Instruments, China), and electrochemical impedance spectroscopy (EIS) was performed on a CHI 750B electrochemical workstation (Shanghai CH Instruments, China). A conventional three-electrode system was used with a CTS–GR–IL/CMWE as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. Scanning electron microscopy (SEM) was conducted with a JSM-6700F scanning electron microscope (Japan Electron Company, Japan).

2.3. Preparation of CTS–GR–IL/CMWE

According to Ref. [24] CMWE was prepared by hand-mixing of graphite powder with DPA at a ratio of 70/30 (w/w) in a porcelain mortar for 20 min. Then a portion of the composite was filled firmly into one end of a glassy tube ($\Phi = 4$ mm) and the electrical contact was provided by inserting a copper wire to the paste in the inner hole of the tube. Then CMWE was heated at 65 °C for 60 s, which was higher than the melting point of DPA (m.p. = 62.5 °C) for the completely mixture. A new surface was obtained by smoothing the electrode onto a weighing paper just before use. The modified electrode was prepared with the following procedure. 1.0 mg GR was added into 1.0 mL 0.1% chitosan (1.0% HAC) solution and followed by ultrasonication for 2 h to form a homogenous mixture of CTS–GR solution. Then ionic liquid [EMIM]BF_4 was dispersed into the above CTS–GR solution (v/v, 1.8%) to give a homogeneous CTS–GR–IL suspension. 10.0 μL of the CTS–GR–IL suspension solution was spread gently over the entire surface of CMWE and dried at room temperature to prepare the modified electrode. The obtained electrode was noted as CTS–GR–IL/CMWE and other electrodes such as CTS–GR/CMWE and CTS–IL/CMWE were also fabricated with the similar procedures for comparison.

3. Result and discussion

3.1. Characteristics of the modified electrodes

The typical scanning electron microscopic (SEM) images of different electrodes were shown in Fig. 1. It can be seen that on the CMWE (Fig. 1A) a very smooth and flat interface appeared, which indicated that MW was an efficient binder to connect the carbon powder together. On the CTS–IL/CMWE (Fig. 1B) a regular layer structure could be found. CTS is a good film forming biomaterial and the addition of IL with high viscosity can result in the film formed on the electrode surface. The image of the CTS–GR/CMWE (Fig. 1C) showed clearly large sheet-like shape materials on the electrode surface, indicated that GR had been successfully immobilized on the CMWE surface. On the CTS–GR–IL/CMWE (Fig. 1D) the increase of the size of the nanosheets appeared, indicating the interaction between the materials and the apparent surface area of the modified electrode was greatly increased.

Electrochemical impedance spectroscopy (EIS) is commonly used to characterize the interface properties of electrodes after different surface modification process. Fig. 1E showed the typical EIS results of the modified electrodes in 10.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ solution. Here Z′ and Z″ are the real and imaginary parts of experimental data, and then the Randles circuit is used to fit the impedance spectra (inset of Fig. 1E). In the Randles circuit it is assumed that the electron transfer resistance (Ret) and the diffusion impedance (W) are both in parallel to the interfacial double layer capacity (C). This parallel combination of Ret and C give rise to a semicircle in the Randles circuit. For the CTS–GR/CMWE (curve b) and CTS–IL/CMWE (curve c), the values of Ret were got as 8.16 Ω and 1.52 Ω, respectively, which was much lower than that of the bare CMWE (518.98 Ω, curve a). The results indicated that the presence of GR and IL could greatly facilitate the electron transfer rate between $[Fe(CN)_6]^{3-/4-}$ and electrode, which could be attributed to the higher conductivity of GR and IL on the electrode surface. While the Ret value of CTS–GR–IL/CMWE was further decreased with a nearly straight line appeared and the value was close to zero (curve d). The result indicated that CTS–GR–IL had been successfully immobilized on the CMWE surface, which could further accelerate the electron transfer rate of probe. GR can interact with the imidazolium group of [EMIM]BF_4 with the π–π or/and π–cationic, hydrophobic and electrostatic attraction, which resulted in a stable GR–IL composite material with higher conductivity.

Electrochemical characteristics of different modified electrodes were further proved by the cyclic voltammetric method. Fig. 1F showed the cyclic voltammograms of CMWE (a), CTS–GR/CMWE (b), CTS–IL/CMWE (c) and CTS–GR–IL/CMWE (d) in 1.0 mmol/L $K_3[Fe(CN)_6]$ solution containing 0.5 mol/L KCl. On the CMWE a couple of well-defined quasi-reversible redox peaks appeared with the peak-to-peak separation (ΔE_p) of 172 mV (curve a). After the CMWE was modified with CTS–GR (CTS–GR/CMWE) and CTS–IL (CTS–IL/CMWE), the values of ΔE_p were decreased to 144 mV (curve b) and 99 mV (curve c) with the increase of redox peak currents gradually. The results indicated that the presence of good conductivity of GR and IL on the CMWE surface could accelerate the electron transfer rate between $[Fe(CN)_6]^{3-/4-}$ and electrode. On the CTS–GR–IL/CMWE (curve d) the redox peak currents were further increased. This informed that the CTS–GR–IL/CMWE could provide an increased electrochemical response and better reversibility