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Application of graphene to modified ionic liquid graphite composite and its enhanced electrochemical catalysis properties for levodopa oxidation

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ABSTRACT

A novel kind of structurally uniform and electrocatalytic activity material formed by combination of graphene (GR), 1-(6,7-dihydroxy-2,4-dimethylbenzofuran-3-yl) ethanone (DE) and ionic liquid (IL) and used to modify carbon paste electrode (GR–DE–IL/CPE). The electrochemical properties of DE (as a modifier) in graphene paste electrode-based ionic liquids were studied in the aqueous solution. The fabricated GR–DE–IL/CPE was further used for the successful determination of levodopa (LD), and it exhibited an excellent electrocatalytic activity toward LD with a lower overvoltage, good electrochemical performances with higher conductivity and lower electron transfer resistance. It has been found that under optimum condition in CV, the oxidation of LD occurs at a potential about 400 mV less positive than that of an unmodified carbon paste electrode. Based on differential pulse voltammetry, the oxidation of LD exhibited a dynamic range between 0.015 and 1000 μM and a detection limit (3σ) of 5.0 ± 1 nM. Finally, this method was used for the determination of LD in real samples, using standard addition method.

1. Introduction

Graphene (GR) has enjoyed significant recent attention [1–3]. Carbon-based nanostructures such as carbon nanofibers [4], carbon nanotubes (CNTs) [5], mesoporous carbons [6] and GR [7] have been extensively used in fabrication of modified electrodes for applications in both analytical and industrial electrochemistry, because in addition to their low price, they exhibit suitable electrocatalytic activity for a variety of redox reactions, a broad potential window, and relatively inert electrochemistry [8,9]. There is a significant challenge in the synthesis and application of graphene sheets. As a rising star of carbon nanomaterials, graphene sheets, two-dimensional sheets of sp^2 conjugated atomic carbon, have stimulated intense research interest because of they have a high specific surface area, unless well separated from each other, tend to form irreversible agglomerates or even restack to form graphite through strong π–π stacking and van der Waals interaction [10]. With unique structure and properties, GR naturally becomes a versatile nanoscale building block for self-assembly to achieve novel structures and functionalities.

Another important class of novel materials for various electrochemical applications is ionic liquids (IL), due to their unique chemical and physical properties. IL is a liquid electrolyte which consists of a small anion and a bulky organic cation such as imidazolium and pyridinium [11]. ILs can meet the challenge about graphene sheets well, due to their high surface area, excellent electrical conductivity, easy of synthesis, and good dispersibility and long-term stability in various solvents, GR/IL-based composite materials have been widely used in fabricating electrochemical sensors [12,13]. Different advantages could be achieved by using this composite electrode, such as (i) a remarkable increase in the rate of electron transfer of different organic and inorganic electroactive compounds, (ii) a marked decrease in the overvoltage for biomolecules, (iii) higher current density for a wide range of compounds tested were observed. All these properties allow a sensitive, low-potential, simple, low-cost, and stable composite electrode for the detection of biomolecules and other electroactive compounds [14,15].

There are four principle enhancement techniques for voltammetric and amperometric modified electrodes, namely selective preconcentration, permselectivity, selective recognition and electrocatalysis [16]. Electrocatalysis at chemically modified electrodes is widely utilized for the determination of many drugs and biosubstrates. Various inorganic and organic materials have been used to fabricate modified electrodes which can enhance the electron

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transfer rate and reduce the overpotential for the oxidation of substrates [17,18]. The chemical modification of electrodes using electron transfer mediators is an interesting field in analytical chemistry [19,20]. One of the most important effects of any mediator is a reduction of the overpotential required for electrochemical reaction, which enhances the sensitivity (current) and selectivity of the method [21].

To the best of our knowledge, there is no reported to application of graphene to modified carbon paste electrode with electron transfer mediators. Therefore, we used graphene for the construction of novel nanostructured benzofuran derivative (1-(6,7-dihydroxy-2,4-dimethylbenzofuran-3-yl) ethanone (DE)) modified ionic liquid-based carbon paste electrode (GR–DE–IL/CPE). The experimental results indicate that modified electrode offers several advantages such as high repeatability, good stability and high apparent charge transfer rate constant. Utilizing the developed method, determination of the levodopa has been carried out in urine and human blood serum samples.

2. Experimental

2.1. Instruments and reagents

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302N, EcoChemie, Netherlands). A conventional three-electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and modified carbon paste electrode (GR–DE–IL/CPE) were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 691 pH/ion meter was used for pH measurements. Ultraviolet–visible (UV–Vis) spectra were obtained by an Optizen 3220UV UV–Vis spectrophotometer.

All solutions were freshly prepared with double distilled water. LD and all other reagents were of analytical grade from Sigma–Aldrich. Graphite powder and paraffin oil (*DC* 350, density = 0.88 g cm^{-3}), NH_3, H_3PO_4, H_2O_2, ethanol, HCl, $KMnO_4$, hydrazine monohydrate (N_2H_4, 98%) and sulfuric acid were purchased from Merck. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0.

2.2. Synthesis of 1-(6,7-dihydroxy-2,4-dimethylbenzofuran-3-yl) ethanone (DE)

DE was synthesized by electrosynthesis method according to the procedures described in the literature [22]. Briefly, 60 mL of 0.15 M sodium acetate in water, containing 1.0 mmol of 4-methylbenzene-1,2-diol and 1.0 mmol of acetylacetone was electrolyzed at controlled-potential (0.32 V) in a divided cell. The electrolysis was terminated when the current decayed to 5% of its initial value. At the end of electrolysis, a few drops of acetic acid were added to the solution and the cell was placed in a refrigerator overnight. The precipitated solid was collected by filtration and washed several times with water.

2.3. Synthesis of graphene sheets

Graphene oxide (GO) was obtained by oxidizing graphite using an improved method [23]. Briefly, a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to a mixture of graphite/$KMnO_4$ (3:18 g) at 50 °C and stirred for 12 h. The reaction was cooled to room temperature and transferred onto flask ice with 30% H_2O_2 (3 mL). The obtained solution was centrifuged, and then filtered. The solid material was then washed with water, 30% HCl, and finally washed twice with 200 mL of ethanol.

We synthesized GR using hydrazine together with ammonia solution. A colloidal suspension of GO in purified water (150 mg/50 mL) was prepared by sonication for 3 h. The suspension of GO was subsequently added to 50 μL of hydrazine solution (98%) with 200 μL of ammonia solution (30% in water). Then were refluxed at 90 °C for 12 h in a heating mantle and cooled to room temperature. Subsequently solutions were centrifuged, and GR precipitates were washed with deionized water and then dried at 60 °C in vacuum for 24 h.

2.4. Preparation of the electrode

To obtain the best conditions in the preparation of the GR–DE–IL/CPEs, we optimized the ratio of DE, GR and IL. The GR–DE–IL/CPEs were prepared by dissolving 0.006 g of DE in CH_3Cl and hand mixing with 0.55 g of graphite powder, 0.05 g of GR and 42 μL of IL using a mortar and pestle. Then ~0.5 mL of paraffin was added to the above mixture and mixed for 20 min until a uniformly wetted paste was obtained. This paste was then packed into the end of a glass tube. A copper wire inserted into the carbon paste provided an electrical contact. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing with weighing paper. For comparison, DE modified CPE (DE/CPE) without GR and IL, DE and IL modified CPE (DE–IL/CPE) without GR, and unmodified carbon paste electrode in the absence of DE, GR and IL were also prepared in the same way.

3. Results and discussion

3.1. Characterization of graphene

The morphology of graphene was characterized by a scanning electron microscopy (SEM), infrared spectroscopy (IR) and ultraviolet–visible (UV–Vis). Typical SEM image of graphene was shown in Fig. 1A. In Fig. 1A, graphene exhibited a morphology consisting of a thin wrinkling paper-like structure. For comparison, SEM images of GO and graphite were shown in Fig. 1S, Supplementary material. Fig. 1B shows UV–Vis absorption spectra of GO before and after reduction using hydrazine. UV–Vis spectra of GO shows strong absorption band that could be attributed to $\pi \rightarrow \pi^*$ transitions of aromatic C=C bonds [24]. The UV–Vis spectra of this material suggest that the more ordered structure of GO is due to greater retention of carbon rings in the basal planes the two spectra were recorded for an equal concentration of each material (Fig. 1B). The degree of remaining conjugation can be determined by the λ max of each UV–Vis spectrum. The more $\pi \rightarrow \pi^*$ transitions (conjugation), the less energy needs to be used for the electronic transition, which results in a higher λ max [23]. The as-prepared GO displays two characteristics bands: a strong absorption band with a maximum at 228 nm and a shoulder at around 300 nm. Reduction of GO aqueous suspension resulted in a red shift of the main absorption band to 273 nm. In addition, the intensity of the absorption tail in the higher λ has significantly increased (Fig. 1B). The result suggests that the GO nanosheets have been reduced and the electronic conjugation within the GO nanosheet was restored upon hydrazine reduction [25].

Infrared spectroscopy (Fig. 1C) evidences for presence of —COOH, —OH and —C—O at GO sheet. The IR spectrum of GO shows a C—O stretch at 1222 cm^{-1} and O—H stretch at 3500–3300 cm^{-1} as well as a C=O stretch at 1720–1690 cm^{-1} [26]. After the final reduction with hydrazine, the absence of the peaks at 1720–1690 and 1222 cm^{-1} indicates the epoxide and hydroxyl groups attached to the basal graphene layer have been removed (Fig. 1C).

3.2. Characteristics of the modified electrodes

The surface topography for GR/CPE showed a granular surface with the granules isolated and clearly distinguished (Fig. 2A). While