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A novel sensing platform based on ionic liquid integrated carboxylic-functionalized graphene oxide nanosheets for honokiol determination

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ABSTRACT

A novel ionic liquid, 4-hydroxy-1-methyl-[1-(3-pyrrolyl-propyl)]-piperidinium bromide, was synthesized and characterized. Carboxylic-functionalized graphene oxide nanosheets were modified with this ionic liquid to fabricate a nanocomposite which was denoted as GrO-COO-IL. Characterizations of FTIR, X-ray photoelectron spectroscopy, Raman spectroscopy and transmission electron microscopy confirmed the successful conjunction of these two components. GrO-COO-IL nanocomposites were homogeneously dispersed with utralpure water, and were then coated onto glassy carbon electrode surface. Followed by cyclic voltammetric scanning, a graphene oxide-polymerized ionic liquid film modified electrode (GrO-COO-Poly-IL/GCE) was prepared, and was studied with electrochemical impedance spectroscopy and scanning electron microscope. It was found that both honokiol and magnolol exhibit sensitive voltammetric response at the GrO-COO-Poly-IL/GCE. Simultaneous assay of honokiol and magnolol was realized with differential pulse voltametry. In the presence of magnolol, the oxidation peak current was linearly related to honokiol concentration in the range of $1.0 \times 10^{-8} \sim 1.0 \times 10^{-5}$ mol L^{-1} with a detection limit of 1.53×10^{-9} mol L^{-1} (S/N = 3). Meanwhile, in the presence of honokiol, a linear relationship between the oxidation peak current and magnolol concentration was found from 7.0×10^{-8} to 1.0×10^{-5} mol L^{-1}. The detection limit is calculated to be 8.27×10^{-9} mol L^{-1} (S/N = 3). In addition, GrO-COO-Poly-IL/GCE was successfully used for determination of honokiol in the traditional Chinese medicine, and was demonstrated to be an effective and sensitive method.

1. Introduction

Graphene comprises a 2D layer of sp^2-hybridized carbon atoms which are arranged in a hexagonal lattice. The lattice is composed of two equivalent sub-lattices of carbon atoms bonded together with σ bonds. Each carbon atom in the lattice has a π orbital that contributes to a delocalized network of electrons. Graphene possesses one-atom thickness and is considered as the thinnest material in our universe [1,2]. In recent years, graphene has received considerable attention due to its high surface area (~2600 m^2/g), high chemical stability, excellent conductivity and strong mechanical strength [3]. Graphene oxide is the derivative of grpahene, and is also a class of 2D carbon-based nanomaterial. Different from graphene, graphene oxide nanosheets are polar substrates which can be homogeneously dispersed into water or other common polar solvents, thus easy to be coated onto substrate to form a uniform film. Owing to its large specific surface area, good biocompatibility and ability to promote electron transfer [4], graphene oxide nanosheets have been extensively used to fabricate electrochemical sensing and biosensing devices to improve their sensing performance. For example, based on the enhanced effects of graphene oxide nanosheets, dopamine [5], caffeine [6], 2,4,6-trinitrotoluene [7] and glucose [8] were determined sensitively and selectively.

Ionic liquids, which melting points are often kept below ambient temperature, are a new type of compounds consisting entirely of ions. Recently, ionic liquids have been extensively used

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in organic synthesis, liquid-liquid extraction, electrochemistry, and electrochemical sensors. These applications are attributing to their unique properties such as extraordinarily high chemical and thermal stability, good conductivity, wide electrochemical windows, and good dissolving capability [9–13]. To combine the merits of ionic liquid and graphene, many nanocomposites have been synthesized, characterized and extensively used. For example, amine-terminated ionic liquids are grafted to the carboxylic acid groups of graphene oxide nanosheets [14,15] to produce a novel nanocomposite. The resultant nanocomposites can be dispersed in various organic solvents, and used to fabricate a non-volatile resistive crossbar memory. Using photoactive anionic porphyrin as counter anions towards the ionic liquid which was grafted onto graphene nanosheets through the noncovalent interactions of anion and/or cation, Karousis and coworkers [16] developed some optoelectronic devices. Recent studies [17,18] show that for a hydrophobic imidazolium based ionic liquid, the imidazolium ring slightly tilted to the surface plane, so that ionic liquid molecules can be orientated at the graphene surface. Applications of ionic liquid modified graphene are concentrated in the field of electrochemistry, particularly in the area of electrochemical sensing. As expected, modification with ionic liquids improves the stability and dispersion of graphene nanosheets as well as the electron transfer between the target species and graphene. Moreover, the combination of graphene and ionic liquid via physical or chemical interactions can provide a favorable microenvironment for the immobilization of enzymes/proteins, and enhance their catalytic activity. Till now, modified electrodes based on ionic liquid grafted graphene nanosheets have been successfully applied to analysis glucose [19–21], hydroquinone [22], catechol [22], guanine and adenine [23], ascorbic acid [23], dopamine [23] and DNA damage [24].

Honokiol and magnolol are the bioactive component isolated from the traditional Chinese medicine, Cortex Magnolia Officinalis, or other Magnoliaceae. They have been demonstrated possessing many physiological activities such as anti-inflammatory [25], antioxidant [26], anti-tumor [27], anti-bacteria [28], etc. The total content of honokiol and magnolol is an important parameter for evaluating the quality of Cortex Magnoliae Officinalis. The Pharmacopoeia of China requires that the total content of honokiol and magnolol in Cortex Magnoliae Officinalis is no less than 2.0% [29]. In addition, some concentrated composite herbal preparations containing Cortex Magnoliae Officinalis in their prescriptions are widely used in oriental countries for their convenient use [30].

Therefore, it is quite important and interesting to develop simple and sensitive method for the simultaneous determination of honokiol and magnolol. To date, liquid chromatography [31], liquid chromatography with mass spectrometry [32], capillary electrophoresis [33], fluorescence [34] and electrophoresis [30,35] have been extensively employed for honokiol and magnolol determination. Recently, direct determination of honokiol and magnolol using electrochemical methods have also attracted increasing attention with respect to high sensitivity, short analysis time, low cost and handling convenience.

Herein, 4-hydroxy-1-methyl-[1-(3-pyrrolyl-propyl)]-piperidinium bromide (HMPPPB) ionic liquid was successfully synthesized, and grafted onto graphene oxides surface to produce GrO-COO-IL nanosheets. Subsequently, GrO-COO-IL nanosheets were coated onto glassy carbon electrode surface to fabricate a film modified electrode, which was then treated with cyclic voltammetric scanning to obtain a polymerized ionic liquid-graphene oxides nanosheets film electrode (GrO-COO-Poly-IL/GCE). The GrO-COO-Poly-IL film possesses the advantages of ionic liquid and graphene oxide nanosheets, thus was employed to determine honokiol and magnolol sensitively and conveniently. The practical application of the GrO-COO-Poly-IL/GCE was also demonstrated by the determination of honokiol in Cortex Magnoliae Officinalis.

2. Experimental

2.1. Reagents

Honokiol and magnolol was obtained from National Institute for the Control of Pharmaceutical Biological Products (Beijing, China). Graphite powder was purchased from Qingdao Tianhe Graphite Co. Ltd. with an average particle diameter of 4 mm (99.95% purity). 1-(3-Bromopropyl) pyrrole was synthesized with the reported procedure [36]. 4-Hydroxy-1-methyl piperidine (98%) was obtained from Alfa Aesar. 0.1 mol L^{-1} phosphate buffer solution was prepared by mixing of K_2HPO_4 and NaH_2PO_4 solution. All the reagents were of analytical reagent grade, and used without any further purification. All aqueous solutions were prepared using ultrapure water (18.2 MΩ cm, Milli-Q, Millipore).

2.2. Instruments

All electrochemical experiments were performed on a CHI660C electrochemical workstation (CH Instrumental Co., China) with a conventional three-electrode system. A GrO-COO-Poly-IL/GCE modified glassy carbon electrode (3 mm in diameter) was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference electrode and auxiliary electrode, respectively. Voltammetric experiments were carried out in a 10 mL cell. The pH measurements were carried out on PHS-3C exact digital pH meter (Shanghai REX Instrument Factory, China). FTIR was recorded on a FTIR-8700 infrared sepectrophotometer (Shimadzu, Japan). Raman spectra were performed on a LabRAM HR800 confocal Raman microscopy system (Horiba JobinYvon, France) using 532 nm laser. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G^2 20S-TWIN instrument (FEI Company, Netherlands) operating at an acceleration voltage of 200 kV. Scanning electron microscope (SEM) images were performed on a Hitachi SU-8000 (Hitachi, Japan) to study the interfacial properties of the modified electrode. X-ray photoelectron spectroscopy (XPS, Thermo Electron Corp., USA) was used to analysis of the composition of GrO-COO-IL nanomaterials.

2.3. Synthesis of HMPPPB ionic liquid

4-Hydroxy-1-methyl piperidine and 1-(3-bromopropyl) pyrrole were added into 15 mL toluene, and stirred at 80 °C for 15 h under nitrogen atmosphere. After being cooled to room temperature, the mixture was extracted four times with acetic ether and ultrapure water. Subsequently, the aqueous layer was evaporated to obtain 4-hydroxy-1-methyl-[1-(3-pyrrolyl-propyl)]-piperidinium bromide (HMPPPB) ionic liquid. The synthetic route, NMR and mass spectroscopy of HMPPPB ionic liquid were shown in Fig. S1 – S3. Some data were shown as following:

^{1}H NMR(D_2O) δ: 6.76(d, 2H), 6.11(d, 2H), 3.98(t, 2H), 3.89(d, 1H), 3.38(t, 2H), 3.20(d, 2H), 3.12(d, 2H), 2.92(s, 3H), 2.16(t, 2H), 1.96(d, 2H), 1.74(d, 2H); m/z = 222.92.

2.4. Preparation of GrO-COO-IL nanocomposite

Graphene oxide (GrO) nanosheets were synthesized directly from graphite by a modified Hummers method [37]. In a typical process, 1.0 g graphite powder was ground with 50 g NaCl for 10 min. NaCl was then dissolved and removed by filtration with water. The remaining graphite was stirred in 23 mL of 98% H_2SO_4 for 8 h. $KMnO_4$ (3 g) was gradually added while keeping the