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A novel nanoporous film electrode based on electrochemical polymerization of ionic liquid and its application in sensitive determination of magnolol

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ABSTRACT

A polymeric film modified glassy carbon electrode was electrochemically fabricated with potential step technique using 1-butyl-3-[3-(N-pyrrole)propyl] imidazolium tetrafluoroborate ionic liquid as a monomer. Followed by being treated with sodium dodecyl sulfonate solution, a hydrophobic film bearing poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium dodecyl sulfonate} moiety was modified onto electrode surface. The substitution was confirmed by X-ray photoelectron spectroscopy. The morphology of the polymeric film electrode surface was characterized with scanning electron microscopy. Electrochemical behaviors of magnolol at the hydrophobic polymeric film electrode were systematically investigated with voltammetry. Compared with the unmodified glassy carbon electrode, the oxidation peak shift slightly towards positive potential and the oxidation peak current significantly increased. Under optimal conditions, the oxidation peak current was linearly related to the magnolol concentration in the range of 1.0×10^{-8} to 1.0×10^{-6} mol L⁻¹ and 1.0×10^{-6} to 5.0×10^{-5} mol L⁻¹. The detection limit was estimated to be 4.55×10^{-9} mol L⁻¹ ($S/N=3$). The polymerized ionic liquid film electrode was successfully used to analysis magnolol in *M. officinalis*. The result was consistent with that obtained by high performance liquid chromatography.

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1. Introduction

Ionic liquids are specific organic salts composed of big organic cations and small inorganic anions. Ionic liquids often exist in liquid state at around room temperature, and are considered as green solvents due to their superior properties. They exhibit a series of attractive characteristics such as high chemical and thermal stability, lower flammability, negligible vapor pressure, high ionic conductivity, and wide electrochemical window [1–3]. Furthermore, the most important feature of ionic liquid is that their amphiphilicity can be easily tuned by proper selection of cation, anion and substituent [4]. Therefore, ionic liquids are encouraged to be extensively used in many research fields including organic synthesis, material science, biochemistry, electrochemistry and analytical chemistry [5–10].

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Unfortunately, when ionic liquids are used as electrolyte materials or functional materials for modified electrodes, they have a fatal drawback that the component ions of ionic liquids will migrate along with the potential gradient [11]. Even using a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, to develop a thin film modified electrode, it is difficult to retain the long-term stability of the ionic liquid film [12]. In addition, there is also a fear of leakage of ionic liquids in battery technology as well as other organic electrolyte solutions. Some kinds of polymer gel electrolytes containing ionic liquids have been investigated to realize both high ionic conductivity and good mechanical property. For example, polymerization of vinyl monomers in ionic liquids [13,14] or ionic liquids containing vinyl group [15,16] were both conducted to fabricate conductive polymer electrolytes. Ionic liquid-based polymer electrolytes are commonly prepared by two methods [17]. The first is to dissolve a polymer and an ionic liquid into a volatile solvent followed by removing of the solvent [18,19]. The second is to polymerize a monomer-ionic liquid mixture (alternatively ionic liquids with vinyl groups) through thermal or UV (or visible) light initiation in the presence of suitable initiators [20,21]. High temperature and long reaction time limit the polymerization process induced by thermal

initiators. The light-induced polymerization seems to be especially useful due to the short polymerization time and low reaction temperature. However, only in several works photochemical reactions were used for preparation of polymer electrolytes based on ionic liquid [22–24]. Electrochemical techniques were also employed to prepare polymer film [25,26]. The electrochemical polymerization process is more accurate and gives the chance to have a better control of synthesis parameters and reactions than the chemical route [27]. The electrochemical oxidation of monomers, pyrrole for example, initiates a polymerization process at the electrode/electrolyte interface that promotes the formation of a polymeric film that adheres to the electrode [28]. Electrochemically initiated polymerization of conducting polymers comprises fast and complex reactions giving a mix of polymer chains with different properties [29].

In this paper, an ionic liquid bearing pyrrole moiety, 1-butyl-3-[3-(N-pyrrole)propyl]imidazolium tetrafluoroborate, was synthesized and employed as a monomer for fabrication of a polymeric film onto a glassy carbon electrode surface using potential step technique. The mechanism for the polymerization of the as-prepared ionic liquid is based on the electrochemical oxidation of pyrrole moiety. The electrochemical polymerization of pyrrole and its derivatives on the electrode surface has been well studied [30–32]. Although a chromatic film can be obviously observed after electrochemical polymerization, the stability of the as-prepared polymerized ionic liquid film is dissatisfied. It was found that the film will totally disappear when was incubated into an electrochemical cell with phosphate buffer solution for cyclic voltammetric scanning. In order to improve stability of the polymerized ionic liquid film in aqueous solution, tetrafluoroborate anions were substituted by dodecyl sulfate anions to obtain a hydrophobic interface. To evaluate the characteristics of the poly(1-butyl-3-[3-(N-pyrrole)propyl]imidazolium dodecyl sulfate) film electrode, electrochemical behaviors of magnolol were investigated systematically. A sensitive method for magnolol determination was also proposed.

Magnolol is the active ingredient of *M. officinalis* (also called houpo in Chinese) that is extensively used in herbal prescriptions of traditional Chinese medicine for the treatment of thrombotic stroke, typhoid fever and headache. The practical applications in medical treatment demonstrated that magnolol possesses antioxidant, anti-tumor, anti-platelet aggregation and antimicrobial activities. Therefore, it is of great importance to develop a convenient and sensitive method for the magnolol assay because that the quantification of this active compound is also very vital for the production of pharmaceutical preparations. Till now, a wide range of analytical techniques include liquid chromatography [33], liquid chromatography with mass spectrometry [34], capillary electrophoresis [35] and fluorescence spectroscopy [36] have been applied to determine magnolol. Furthermore, electrochemical techniques were also reported for magnolol analysis due to its electrochemical activity [37–40]. However, to the best of our knowledge, electrochemical fabrication of a poly(1-[3-(N-pyrrole)propyl]-3-butylimidazolium dodecyl sulfate ionic liquid) film electrode and its application in magnolol determination were firstly reported in this work. The polymerized ionic liquid film electrode exhibited an attractive ability such as excellent sensitivity, selectivity and stability for the sensitive determination of magnolol. The practical application of the ionic liquid polymeric film modified electrode for the determination of magnolol in *M. officinalis* samples was also performed successfully.

2. Experimental

2.1. Reagent and materials

1,3-Dibromopropane, sodium tetrafluoroborate and sodium dodecyl sulfonate were purchased from Sinopharm Chemical Reagent

Co., Ltd. (Shanghai, China). 1-Butylimidazolium was bought from Wuhan Talerace Chemistry & Technology Co., LTD. (Wuhan, China). Magnolol were purchased from Aladdin (Shanghai, China). Magnolol stock solution was prepared with ethanol and kept in a refrigerator at $\sim 4^\circ\text{C}$. Phosphate buffer solution was prepared by mixing of K_2HPO_4 and NaH_2PO_4 solution. Other chemicals were of analytical grade and were used as received. All of the solutions were prepared with ultrapure water obtained from a Molecular water purification system (Shanghai, China).

2.2. Apparatus

Electrochemical measurements were carried out on a CHI660C electrochemical workstation (Chenhua Corp., Shanghai, China) with a conventional three-electrode system. An ionic liquid polymeric film modified glassy carbon electrode (3 mm in diameter) was employed as working electrode. A Pt wire electrode and a saturated calomel electrode (SCE) were used as auxiliary electrode and reference electrode, respectively. NMR was measured using an Avance 400 MHz NMR Spectrometer (Bruker, Switzerland). Scanning electron microscopy (SEM) images were obtained on JSM-6700F field emission scanning electron microscopy (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (Thermo Electron Corp., USA) was used for analysis of the composition of the ionic liquid polymeric film. High performance liquid chromatography analysis was performed on a Hitachi L-7000 equipped with a L-4000 UV detector (Hitachi, Japan) and an Alltima C18 column ($150 \times 4.6 \text{ mm}^2$ i.d., $5 \mu\text{m}$, Alltech, Deerfield, IL, USA). A mixing solution of methanol and water (70:30, v/v) was used as mobile phase. Two hundred ninety nanometers were selected as the detection wavelength for magnolol analysis. All electrochemical measurements were performed at 298 K unless otherwise stated.

2.3. Synthesis of 1-butyl-3-[3-(N-pyrrole)propyl]imidazolium tetrafluoroborate

N-(3-bromopropyl)pyrrole was synthesized according to the reported procedure [41]. Pyrrole (15 mmol) was added drop-wise at 0°C to a dry DMF solution (150 mL) containing 1,3-dibromopropane (43 mmol) and NaH (43 mmol), and the resulting solution was stirred overnight. Ultrapure water (150 mL) was added and the resulting mixture was extracted with anhydrous diethyl ether ($4.0 \times 75 \text{ mL}$). The ether was dried over MgSO_4 and evaporated to afford a clear, brownish liquid. The crude product was purified by chromatography on silica gel with petroleum ether as an eluent. This afforded the desired substance as brownish oil (yield: 65%).

N-(3-bromopropyl)pyrrole (12 mmol) was dissolved into 100 mL toluene, and was added drop-wise to a toluene solution containing 1-butylimidazolium (12 mmol), then the resulting solution was stirred at 80°C for 12 h under the protection of nitrogen. The melt was decanted from the hot solution and the toluene phase was evaporated. The crude product was purified by chromatography on silica gel with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (1:1) as an eluent, affording 1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium bromide as brownish oil (yield: 78%).

Under vigorous stirring, 1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium bromide (5 mmol) was added dropwise to a solution of sodium tetrafluoroborate (10 mmol) in 100 mL of acetone. The mixture was stirred at room temperature for 48 h. The solid was filtered off, and the filtrate was evaporated to remove the solvent. The residue was purified by silica column chromatography to give 1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate ionic liquid (yield: 75%).

^1H NMR (D_2O): 8.49 (s, 1H); 7.28 (d, 2H); 6.63 (d, 2H); 6.03 (dd, 2H); 4.04 (t, 2H); 3.99 (t, 2H); 3.91 (t, 2H); 2.26 (tt, 2H); 1.68 (tt, 2H); 1.18 (tq, 2H); and 0.78 (t, 3H).

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