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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.

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].

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

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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 derivates 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 callled 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, antitumor, 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 ~4 °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 ($150 \times 4.6\ mm^2$ i.d., 5 μm, 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 × 75 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 CH_2Cl_2/CH_3OH (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).

2.4. Preparation of the polymerized ionic liquid film modified electrode

Prior to modification, glassy carbon electrode was polished with emery paper and alumina slurries followed by rinsing thoroughly with ultrapure water. The electrodes were successively ultrasonicated in nitric acid, ethanol and water, and then allowed to dry at room temperature. 1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate ionic liquid was homogeneously dispersed into 0.1 mol L^{-1} sodium tetrafluoroborate solution with ultrasonication to give a 1.0 mmol L^{-1} solution. Electrochemical polymerization of 1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate was performed with potential step technique with the potential being varied from 0 V to 1.2 V. Step time for 0 V and 1.2 V was set as 2 s and 5 s, respectively. After 15 cycles, the polymeric film modified electrode was washed with ultrapure water to remove all chemicals which were physically absorbed. Subsequently, the film modified electrode was incubated into a saturated solution of sodium dodecyl sulfate for 2 min under stirring to exchange tetrafluoroborate anion with dodecyl sulfate, and washed thoroughly with ultrapure water to remove all chemicals which physically adsorbed on the electrode surface, thus to obtain a poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium dodecyl sulfate} film modified glassy carbon electrode.

2.5. Samples preparation

M. officinalis were bought from local hospital, and were ground into powder, then dried at 60 °C for 4 h. Subsequently, magnolol was extracted according to the reported procedure [42]. Two grams of *M. officinalis* powder were weighted, and dispersed into 100.0 mL methanol. The mixture was stirred for 3 h at 60 °C. After being cooled to room temperature, it was then treated with ultrasonic stirring for 30 min. After that, the mixture was filtered with 0.45 μm filter membrane, and the filtrate was used as sample for magnolol analysis.

2.6. Electrochemical measurements

Cyclic voltammograms of magnolol at the ionic liquid polymeric film electrode were recorded in the potential range from 0 V to 0.8 V. After accumulating for 150 s with stirring under 0 V, differential pulse voltammograms of magnolol at the ionic liquid polymer film electrode were recorded. The oxidation peak current was used for quantitative analysis of magnolol. The pulse amplitude, pulse period, and pulse width of differential pulse voltammetry were 50 mV, 0.2 s, and 50 ms, respectively.

3. Results and discussion

3.1. Scanning electron microscopy characterization

Morphology of the unmodified glassy carbon electrode and the poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium dodecyl sulfate} film modified electrode surface were characterized with scanning electron microscopy. As shown in Fig. 1(a), before being modified, a smooth and homogeneous surface was observed. Fig. 1(b) corresponds to the image of the polymeric film modified electrode surface and exhibits a homogeneous and compact layer with nanopores and full coverage. This micrograph is different from the image of the unmodified electrode surface demonstrating that the electropolymerization of ionic liquid during the potential-step process. Moreover, pores in the diameter varied from 50 nm to 100 nm can be seen obviously. These nanopores not only supply some channels for the mass transfer of target molecules, but also enhance the electroactive electrode surface, thus to improve the accumulation efficiency and the response sensitivity.

3.2. X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy is one of the most widely used surface techniques in materials science and chemistry. It allows the determination of atomic composition of the sample in a non-destructive manner. Thus, X-ray photoelectron spectroscopy was used to analysis ionic liquid polymeric film modified electrode before and after being treated with sodium dodecyl sulfate solution. From Fig. 2(a), we can know that C_{1s} levels at 284.0 eV, O_{1s} level at 532.0 eV, B_{1s} level at 193.5 eV, N_{1s} level at 400.0 eV and F_{1s} level at 685.2 eV existed in poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate} film modified electrode.

In the case of poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium dodecyl sulfate} film modified electrode (Fig. 2(b)), B_{1s} and F_{1s} energy level disappeared, reversely S_{1s} energy level at 168.5 eV appeared obviously, which means that tetrafluoroborate anions have been substituted by dodecyl sulfate anions completely. These results also indicated the successful fabrication of poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium dodecyl sulfate} film modified electrode.

3.3. Cyclic voltammetric behavior of magnolol

Cyclic voltammetry was used to investigate the electrochemical behavior of magnolol at the polymerized ionic liquid film electrode which was fabricated with 15 cycles of potential step from 0 V to 1.2 V. Fig. 3 shows the cyclic voltammograms of 5.0×10^{-4} mol L^{-1} magnolol at the polymerized ionic liquid film electrode (a) and the unmodified glassy carbon electrode (b). An oxidation

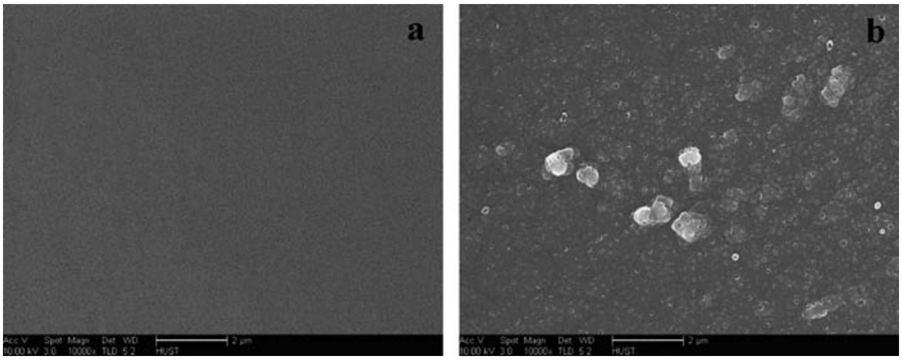

Fig. 1. Scanning electron microscopic images of an unmodified glassy carbon electrode (a) and a poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium dodecyl sulfate} nanoporous film modified electrode (b).

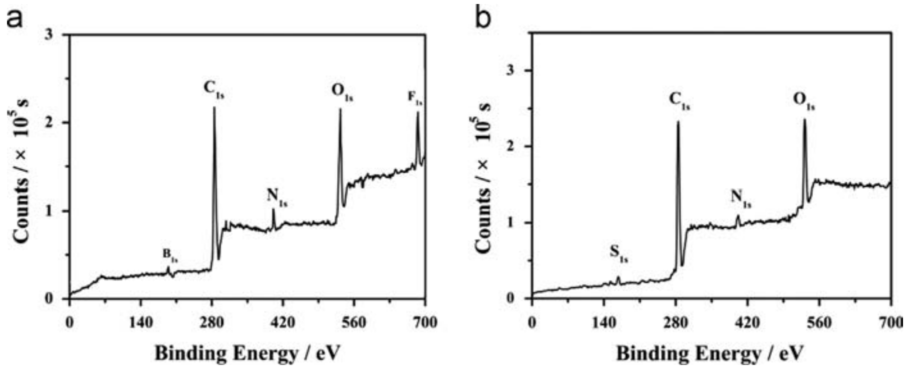

Fig. 2. X-ray photoelectron spectroscopy characterization of poly{1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate} (a) and poly{1-butyl-3-[3-(N-pyrrolyl) propyl]imidazolium dodecyl sulfate} (b) nanoporous film modified glassy carbon electrode surface.

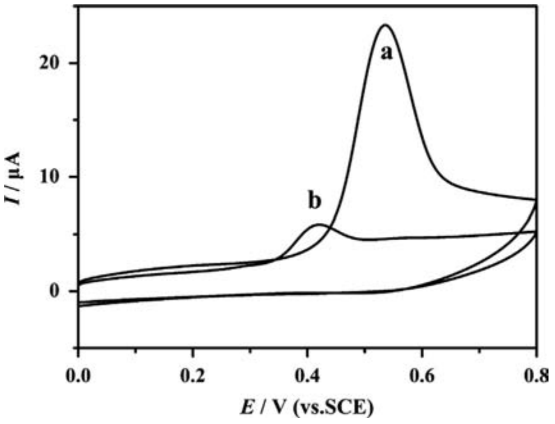

Fig. 3. Cyclic voltammograms of 5.0×10^{-4} mol L^{-1} magnolol on the polymerized ionic liquid film electrode (a) and the unmodified glassy carbon electrode (b) at the scan rate of 0.1 V s^{-1}. Supporting electrolyte solution: 1/15 mol L^{-1} phosphate buffer solution at pH 7.0.

peak located at 0.42 V was observed at the unmodified glassy carbon electrode. Nevertheless, in the case of ionic liquid polymeric film electrode, the oxidation peak shifts positively to 0.54 V, indicating a retarded effect on the electron transfer of magnolol. Meanwhile, the oxidation peak current increased significantly, meaning the effective accumulation of amagnolol onto the ionic liquid polymeric film electrode surface, and thus enhance the sensitivity for magnolol determination. This may be attributed to the nanoporous structure of the polymeric film which increases the specific surface of the electrode, and can also be interacted with magnolol through hydrophobic and π–π interaction.

In order to verify the facts that the ionic liquid film has been polymerized onto the glassy carbon electrode surface and magnolol has been accumulated to the electrode surface through adsorption. The polymerized ionic liquid film electrode was incubated into a magnolol solution for a controlled time interval, and then washed with water thoroughly. After that, the electrode was transferred into a phosphate buffer solution without magnolol to test its electrochemical behavior using cyclic voltammetry. As shown in Fig. S1, an oxidation peak corresponding to the electrochemical oxidation of magnolol was observed obviously. In addition, an unmodified glassy carbon electrode was also used to carry out this experiment. It was found that electrochemical response of magnolol on the unmodified electrode is much lower than that on the film electrode.

Cyclic voltammograms of 1.0×10^{-5} mol L^{-1} magnolol on the polymerized ionic liquid film electrode at different scan rates were shown in Fig. S2(A). When scan rate varied from 0.05 V s^{-1} to 0.9 V s^{-1}, the oxidation peak current increased gradually, and the oxidation peak potential shifted slightly towards positive potential. It was seen from Fig. S2(B) that the oxidation peak currents (Ip) were linearly related to scan rates (ν). The regression equation can be expressed as Ip (μA)=39.45ν (V s^{-1})+0.921 (R=0.996). A linear dependence of the peak current on scan rate is characteristic of an electrode process involving immobilized species, i.e, with absence of mass transport. The result also indicates that the oxidation of magnolol at the polymerized ionic liquid film electrode surface was controlled by an electronic transference process.

As shown in Fig. S2(C), a linear relationship was found between the oxidation peak potential (E_{pa}) and the natural logarithm of scan rate (ln ν), the regression equation can be expressed as E_{pa} (V)=0.02939 ln ν (V s^{-1})+0.5969 (R=0.9988). For a totally irreversible electrode process, the relationship between E_{pa} and ln ν can be expressed by Laviron equation [43]

$$E_{pa}=E^{o}+(RT/\alpha nF)\ln(RTk_s/\alpha nF)+(RT/\alpha nF)\ln\nu$$

where α is the transfer coefficient, which is assumed to be 0.5 in totally irreversible electrode process [44]; k_s is the standard rate constant of the reaction; n is the electron transfer number; ν is the scanning rate; E° is the formal redox potential; R is the gas constant; T is the absolute temperature, and F is the Faraday constant (T=298 K, R=8.314 J K^{-1} mol^{-1}, and F=96485 C mol^{-1}).

According to the linear correlation of E_{pa} vs ln ν as mentioned above, the slope of the line is equal to $RT/\alpha nF$, and the electron transfer number (n) is therefore calculated to be 1.8. Thus, the electrochemical oxidation of magnolol at the ionic liquid polymeric film electrode should be a two-electron transfer process.

3.4. Optimization of experimental conditions

3.4.1. Influence of the number of potential step cycles

The film thickness is an important factor that will influence the current response of magnolol at the polymerized ionic liquid film electrode, and further affects electrochemical sensitivity towards its determination. It will be the fact that the thickness of the polymerized ionic liquid film will be influenced by the cyclic numbers of potential step. Therefore, dependence of the oxidation peak current of 1.0×10^{-6} mol L^{-1} magnolol on the cyclic numbers of potential step was investigated by differential pulse voltammetry in a phosphate buffer solution at pH 7.0. The voltammograms were presented in Fig. 4. It was obvious to see that the oxidation peak current increased remarkably with the cyclic numbers of potential step increasing from 5 cycles to 15 cycles. Nevertheless, the oxidation peak current decreased reversely when the cyclic number of potential step further increasing from 15 cycles to 50 cycles. The reason for the current decrease should be ascribed to the formation of a thick film which will retard the mass- and

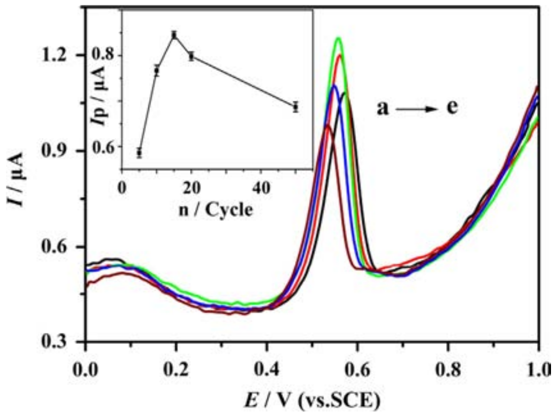

Fig. 4. Typical differential pulse voltammograms of 1.0×10^{-6} mol L^{-1}magnolol at the polymerized ionic liquid film electrodes which were fabricated with 5 (a), 10 (b), 15(c), 20 (d) and 50 (e) cycles of potential step. The insert is the plot between the oxidation peak current and the cyclic number of potential step.

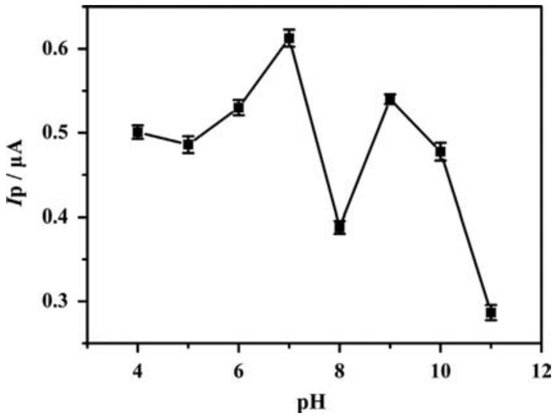

Fig. 5. Influence of pH values on the oxidation peak current of 1.0×10^{-6} mol L^{-1} magnolol at the ionic liquid polymeric film electrode.

electron-transfer process. Accordingly, 15 cycles were selected as the optimal cyclic number of potential step for the fabrication of the polymerized ionic liquid film electrode in following experiments.

3.4.2. *Influence of pH value*

When pH values being regulated from 4.0 to 11.0, the influence of pH values on the voltammetric response of magnolol at the ionic liquid polymeric film electrode was investigated and presented in Fig. 5. It was obvious to see that the current response of magnolol gradually increased with pH values increasing from 4.0 to 7.0, and a maximum value was obtained at pH 7.0. A dramatic decreasing was observed at pH 8.0. While at pH 9.0, the current response recovered in some degree. Whereas, with the pH values further increasing, the oxidation peak current of magnolol also has a tendency to decrease. Therefore, a phosphate buffer solution at pH 7.0 was selected for the determination of magnolol at the ionic liquid polymeric film electrode.

The relationship between the oxidation peak potential and the solution pH values was also studied. It was found that the oxidation peak potential was linearly related to the pH values in the range from 4.0 to 8.0. Whereas, the oxidation peak potential deviated from the linearity as pH values increasing from 8.0 to 11.0. The regression equation can be described as following: E_{pa} (V)=−0.0524 pH+0.8608 ($R=-0.9974$). A slope of 52.4 mV/pH suggests that the overall process was proton dependent, and the electron transfer was accompanied by the transfer of an equal number of protons, i.e., two electrons and two protons were involved. Although the electrochemical oxidation of phenolic compounds has proven to generate phenoxy radical, or phenoxonium ion and quinone via one-electron or two-electron transfer process, the complete mechanism is also undiscovered. According to previous reports about the electrochemical oxidation of phenolic compounds [45,46], the anodic oxidation of magnolol could be attributed to the aromatic-ring in the magnolol and the formation of phenoxonium ion via a two-electron and two-proton process. The radicals could either be further oxidized to be quinones or couple with another radical to form dimeric products irreversibly, and/or, the generated quinones and phenoxy radicals undergo chemical reactions or a free radical multistep growth polymerization to form various products through C–O, C–C and/or O–O coupling. The mechanism of the overall reaction can be described as oxidation, followed by deprotonation, another oxidation and deprotonation process, and the final coupling. The resulting magnolol dimer is non-conducting film, which could insulate the electrode. Therefore, no further oxidation peak was observed at the electrode surface.

3.4.3. *Influence of accumulation potential and time*

Accumulation time and accumulation potential were important parameters for improving the sensitivity for magnolol analysis. Thus, their influences on the current response of 1.0×10^{-6} mol L^{-1} magnolol at the ionic liquid polymeric film electrode were investigated and presented in Fig. 6. As shown in Fig. 6(a), in the accumulation potential range from −0.1 V to 0 V, no obvious change was observed for the oxidation peak current. While, a significant decrease appeared in the accumulation potential range from 0 V to 0.4 V. Consequently, the accumulation of magnolol was carried out at 0 V. Effects of accumulation time on the oxidation peak current of magnolol were shown in Fig. 6(b). It was found that the peak current increases rapidly with increasing accumulation time from 0 to 150 s and levels off at 180 s. Taken efficiency and sensitivity into accounts, accumulation time of 150 s was selected for magnolol analysis.

3.5. *Reproducibility and selectivity*

The reproducibility for the fabrication of ionic liquid polymeric film electrode was demonstrated by determining 1.0×10^{-6} mol L^{-1} magnolol with seven electrodes which were prepared independently. Relative standard deviation for the peak current response of magnolol was calculated to be 1.97%, suggesting an acceptable reproducibility for the ionic liquid polymeric film electrode fabrication. When an identical ionic liquid polymeric film electrode was reused to determine magnolol, the current response decreased significantly. It was found that the reuse of the modified is limited by the nature of the oxidation products of phenolic compounds. A non-conducting film will be formed on the modified electrode surface due to the polymerization of phenolic compounds, thus leading to the inefficient accumulation of magnolol and the significant decrease in the current response. As a result, the modified electrode should be freshly prepared after each voltammetric determination.

The selectivity of the ionic liquid polymer film electrode for the determination of 1.0×10^{-6} mol L^{-1} magnolol was investigated using some substances as potential interferents. It could be obviously seen, from Fig. S3, that dopamine, L-cysteine, m-dihydroxybenzene, ascorbic acid and L-lysine have no interference on the determination of magnolol at the concentration of 1.0×10^{-5} mol L^{-1} (SD < 5%). he interference of hanokiol on the magnolol determination was also investigated. From the cyclic voltammogram, which is shown in Fig. S4, it is obvious to see that peak-to-peak potential difference

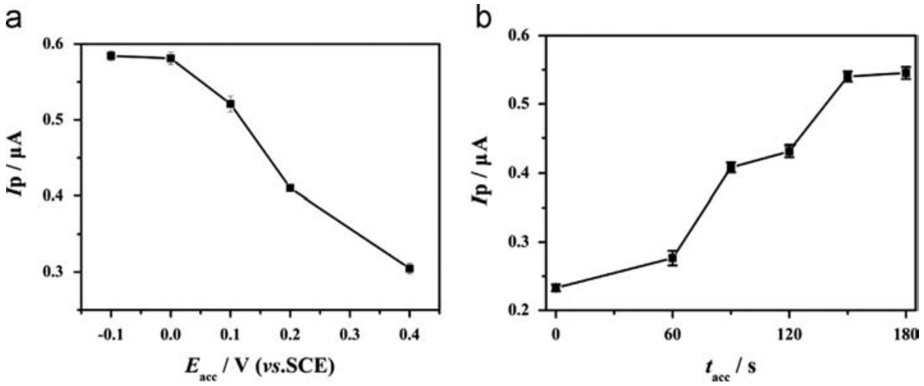

Fig. 6. Influence of accumulation potential (a) and time (b) on the oxidation peak current of 1.0×10^{-6} mol L^{-1} magnolol at the ionic liquid polymeric film electrode.

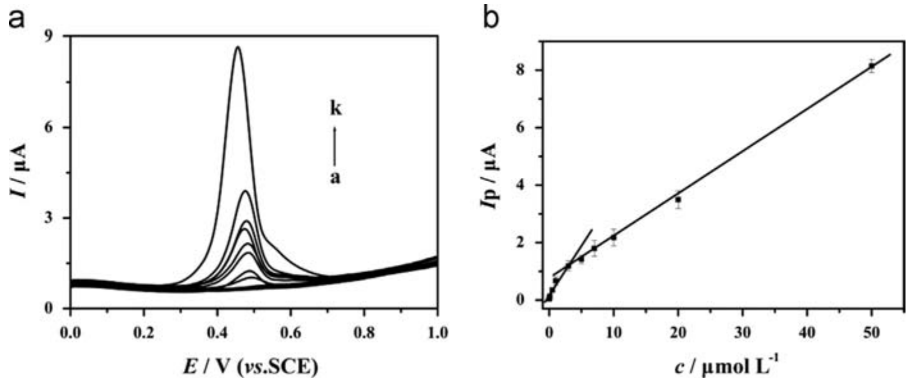

Fig. 7. (a) Typical differential pulse voltammograms of 0.01 (a), 0.05 (b), 0.1 (c), 0.5 (d), 1.0 (e), 3.0 (f), 5.0 (g), 7.0 (h), 10.0 (i), 20.0 (j) and 50.0 (k) μmol L^{-1} magnolol at the polymerized ionic liquid film electrode which was fabricated with 15 cycles of potential step and (b) calibration curve for the magnolol determination. Supporting electrolyte solution: 1/15 mol L^{-1} phosphate buffer solution at pH 7.0. Accumulation was performed under 0 V for 150 s.

Table 1
Results for the determination of magnolol in *M. officinalis* samples ($n=3$).

This method			HPLC method			Recovery method			
Measured (μmol L^{-1})	Average (μmol L^{-1})	RSD (%)	Measured (μmol L^{-1})	Average (μmol L^{-1})	RSD (%)	Added (μmol L^{-1})	Found (μmol L^{-1})	Recovery (%)	RSD (%)
3.715 3.737 3.721	3.724	0.31	3.708 3.686 3.676	3.690	0.44	1.0 1.0 1.0	4.768 4.781 4.761	104.4 105.7 103.8	0.93

between the oxidation peak of magnolo and hanokiol is 130 mV, meaning the possibility for the respective determination of them. All results indicate that the polymerized ionic liquid film electrode possesses superior selectivity towards magnolol determination.

3.6. Analytical characteristics

Fig. 7(a) exhibits differential pulse voltammograms of magnolol at the ionic liquid polymeric film electrode with different concentrations. As it can be seen, the oxidation peak current increased with magnolol concentration increasing, being accompanied by the slightly negative shift of the oxidation peak potential. The voltammograms of magnolol at low concentration were enlarged and shown in Fig. S5. From Fig. 7(b), it was obviously observed that the oxidation peak current is linearly related to the magnolol concentration in the range of 1.0×10^{-8}–1.0×10^{-6} mol L^{-1} and 1.0×10^{-6}–5.0×10^{-5} mol L^{-1}. The detection limit was estimated to be 4.55×10^{-9} mol L^{-1} (S/N=3). It was noted that two linear regions were presented for magnolol determination. In lower concentration, the adsorption of magnolol to the polymerized ionic liquid film modified electrode surface seems to be a single monomolecular layer. Thus, high sensitivity should be obtained for magnolol sensing. Nevertheless, with the magnolol concentration increasing, the active sites for adsorption would be occupied. Therefore, the accumulation will be more ineffective, leading to a low sensitivity towards magnolol. The analytical performance of the polymerized ionic liquid film modified glassy carbon electrode was compared with those methods that have been developed previously (Table S1). It can be found that the polymerized ionic liquid film electrode exhibited a wider linear range in the detection of magnolol. In addition, a lower detection limit was also obtained for magnolol determination. The results suggested that the polymerized film electrode possesses superior electrochemical sensing property towards magnolol.

High sensitivity of the ionic liquid polymeric film electrode encouraged us to determine magnolol in real samples with the recommended method. Magnolol concentration in the *M. officinalis* samples was determined using the standard addition method. The results were summarized in Table 1. The accuracy of the developed method was evaluated with high performance liquid chromatography [47] and recovery method. T-test method was also used to compare the average values obtained by the polymerized ionic liquid film electrode and HPLC method. The calculated *t* value was 2.95 (confidence coefficient 95%), which was less than the standard value (3.18). These data indicated that there is no systematic error. All results indicated that the polymerized ionic liquid film electrode was accurate and promising in the analysis of magnolol without interferences from the real samples.

4. Conclusions

1-Butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate ionic liquid was synthesized, and was used to fabricate a polymeric film modified electrode using potential-step technique. After being treated with sodium dodecyl sulfate solution, a poly{1-butyl-3-[3-(N-pyrrole) propyl]imidazole dodecyl sulfate} film modified glassy carbon electrode with a hydrophobic interface was obtained. Electrochemical behaviors of magnolol at the obtained film modified electrode were investigated. Subsequently, the voltammetric method for magnolol determination was developed, and proved to be high sensitivity, good reproducibility and acceptable stability. The successful determination of magnolol in *M. officinalis* using the ionic liquid polymeric film electrode was achieved, suggesting its potential application in real sample analysis.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.11.055.

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