



Electrochemical fabrication of polymerized imidazole-based ionic liquid bearing pyrrole moiety for sensitive determination of hexestrol in chicken meat



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ABSTRACT

1-[3-(tert-Butoxycarbonylamino)propyl]-3-[3-(N-pyrrole)propyl]imidazolium tetrafluoroborate [(*t*-Boc-APPPI)BF₄], which is a novel pyrrolyl-functionalized ionic liquid, was synthesized and characterized. Subsequently, it was electrochemically deposited onto a glassy carbon electrode surface to fabricate a polymerized ionic liquid film electrode. X-ray photoelectron spectroscopy, scanning electron microscope and electrochemical impedance spectroscopy were used to confirm the successful polymerization of ionic liquid. Voltammetric behaviors of hexestrol at the film electrode were investigated. The oxidation peak slightly shifted towards positive potential, however, dramatically increased in peak current. Experimental conditions for hexestrol determination were optimized. The oxidation peak current is linear with hexestrol concentration in the range of 1.0×10^{-8} – 1.0×10^{-5} mol L⁻¹. The detection limit is estimated to be 2.1×10^{-9} mol L⁻¹ (S/N = 3). Hexestrol in chicken meat was determined using the film electrode with good accuracy.

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1. Introduction

Ionic liquids are a typical type of low-melting organic salts that are mostly liquid at room temperature (Feng, Sun, Li, Liu, & Jiang, 2012). Ionic liquids possess many specific properties including very low measurable vapor pressure, high thermal stability, and superior conductivity. These properties promote their applications in many research fields. Besides being used as green solvent for organic synthesis or chemical processes, they have also been developed as functional reagents and materials for electrochemistry, analytical chemistry, biochemistry, catalysis, and material sciences (Fujita, Murata, Masuda, Nakamura, & Ohno, 2012; Li et al., 2013; Ma, Yu, & Dai, 2010). Enhanced effects of ionic liquid, which used as functionalized reagent in electrode modification, have been successfully demonstrated (Chen et al., 2013; Sun, Wang et al., 2013). For an electrode fabrication, the immobilization of ionic liquid onto a transducer surface is a vital step, which directly related to its sensitivity and selectivity. Physical mixing of ionic liquids into a composite matrix and then simply coated to electrode surface is considered to be the most convenient and available way

(Elyasi, Khalilzadeh, & Karimi-Maleh, 2013; Najafi, Khalilzadeh, & Karimi-Maleh, 2014; Ping, Wang, Wu, Ying, & Ji, 2012; Sun, Guo et al., 2013; Sun, Cao et al., 2013; Sun et al., 2014; Wang et al., 2014). However, due to their great solubility, the immobilized ionic liquids may easily detach from the electrode surface, especially during electrochemical measurements (Chu, Wu, Xiao, Zhang, & Chen, 2010). Unfortunately, even using a hydrophobic ionic liquid, such as 1-butyl-3-methylimidazolium hexafluorophosphate, to fabricate a thin film modified electrode, it is difficult to retain the long-term stability of the ionic liquid film (Zhu, Niu, Zhao, & Lan, 2014). To overcome this limitation, polymerization of desired ionic liquids onto electrode surface should be a powerful strategy. Specific composition and structure can be easily realized in the polymerization process, and thus leading to form a stable film which exhibits many particular characteristics (Zhang et al., 2008).

Ohno and his co-workers are the first group to develop polymerized ionic liquids. They used vinyl group functionalized ionic liquid as monomer to prepare polymer film, and demonstrated their practical applications in polyelectrolyte (Hirao, Ito, & Ohno, 2000; Ohno & Ito, 1998). Since polymerized ionic liquids are commonly in solid state, thus, some characteristics only for liquid state compound have disappeared partially or completely. For example, the ionic liquid after being polymerized has a lower conductivity

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than that of low molecular weight ionic liquid due to a large increase in bulk viscosity (Ohno & Ito, 1998). Fortunately, polymerized ionic liquids still maintain many special properties such as the nonflammability, thermal stability, and mechanical properties. Notably, the conductivity of polymerized ionic liquid is higher than other traditional polymers like polystyrene (Nakamura, Saiwaki, & Fukao, 2010). Since polymers are easily downsized and molded to make products, polymerized ionic liquids have also received much research interests for their potential applications including electrolytes in electromechanical transducers, artificial muscle fabrication etc. (Nakashima & Kawai, 2005; Tang et al., 2005).

Up to date, new developments on the synthesis and the characterization of polymerized ionic liquids are seldom reported. With respect to literature, most of them are based on vinyl, acrylic, or styryl moiety to produce polymers by chemical polymerization (Zhang et al., 2008). With a free-radical polymerization process, Ohno and coworkers have prepared imidazolium-based ionic liquid polymers (Masahiro & Ohno, 2001; Ohno, 2001). However, the polymer structure, molecular weight and polydispersity are difficult to be finely controlled in the process. As a substitute, an atom transfer radical polymerization (ATRP), which can supply a versatile living/controlled radical polymerization process for the preparation of (co)polymers with predictable molecular weights, low polydispersities, and well-defined architectures, was employed for polymerization of 1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate and 1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate ionic liquids (Matyjaszewski & Xia, 2001; Tang, Tang, Ding, Radosz, & Shen, 2005). Investigation demonstrated that polymers, which were derivative from styrenic ionic liquids, possess better stability than that obtained from methacrylate-based monomers. At ambient temperature, poly(ethylene glycol) methyl ether methacrylate and poly(ethylene glycol) dimethacrylate were also successfully prepared, and were found to form a gel polymer electrolyte (Ding, Tang, Radosz, & Shen, 2004). Nevertheless, there are still many challenges in using this method for ionic liquids polymerization or in highly polar solvents. Catalyst disproportionation, low halogenophilicity, and halogen loss by hydrolysis are considered to be the frequent problems (Matyjaszewski, 2012; Tsarevsky, Pintauer, & Matyjaszewski, 2004). Electrochemical polymerization is a well-established technique to fabricate polymer film with high conductivity. Compared with other approaches for polymerization, it has been proved to exhibit predominant advantages, such as combination of polymer synthesis during thin film formation, elimination of exogenous oxidants to initiate polymerization, and direct formation of polymer film onto electrode surface (Deepa & Ahmad, 2008; Lagoutte et al., 2013). In our previous studies, using 1-butyl-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate as functional monomer, a polymerized ionic liquid film was directly deposited onto glassy carbon electrode surface with potential step technique. Chromatic film can be obviously observed at the electrode surface. Unfortunately, the film will completely disappear when was used for voltammetric scanning in aqueous solution, indicating the polymerized ionic liquid film is also not robust (Wang et al., 2014).

Herein, a novel ionic liquid, 1-[3-(tert-butoxycarbonylamino)propyl]-3-[3-(N-pyrrolyl)propyl]imidazolium tetrafluoroborate, was synthesized and used as monomer to fabricate polymerized ionic liquid film electrode. The result demonstrated that the as-prepared polymerized ionic liquid film is very stable in aqueous solutions. In addition, using hexestrol as a model, the sensing characteristics of the electrode modified with a polymerized ionic liquid film were investigated thoroughly.

Hexestrol, a nonsteroidal synthetic estrogen, was widely used to promote growth rate in livestock production, and is also taken as a treatment for estrogen-deficiency disorders in veterinary medicine. However, the residual of hexestrol may interfere with the

normal physiological processes and creates teratogenic effect, mutagenic effects and carcinogenic effects on human. Thus, hexestrol was banned in most countries. Although the use of hexestrol is illegal, people still use it as additives surreptitiously. Therefore, it is very important to establish a sensitive, selective and rapid method for hexestrol determination. The traditional method for analysis of hexestrol is gas chromatography and liquid chromatography with mass spectrometry (Bagnati et al., 1990; Xu, Peng, Wang, Hao, & Jin, 2006; Xu et al., 2006). Although hexestrol possesses electroactive group, phenolic hydroxyl, electrochemical technique is seldom reported to determine hexestrol due to the high oxidation potential and poor sensitivity. Based on the as-prepared polymerized ionic liquid film electrode, voltammetric behavior of hexestrol was thoroughly investigated, and a sensitive and accurate method for determination was developed. The potential application of this method was also demonstrated by the determination of hexestrol in chicken meats.

2. Experiments

2.1. Reagents and apparatus

N-(3-Bromopropyl)pyrrole was synthesized according to the reported procedure (Zhao et al., 2009). 1-(3-Aminopropyl)imidazole, di-*t*-butyl-dicarbonate (DIBOC), sodium tetrafluoroborate, 1,3-dibromopropane and hexestrol were bought from Aladdin (Shanghai, China). Stock solution of hexestrol was prepared with anhydrous 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).

Electrochemical data were collected with CHI660C electrochemical workstation (Chenhua Corp., Shanghai, China) using a conventional three-electrode system. A polymerized ionic liquid film electrode (3 mm in diameter) was employed as the working electrode. A Pt wire electrode and a saturated calomel electrode (SCE) were used as the auxiliary electrode and reference electrode, respectively. NMR analysis was conducted on Avance 400 MHz NMR Spectrometer (Bruker, Switzerland). Mass spectra were acquired using an Agilent 6520 ESI quadrupole time-of-flight mass spectrometer with a standard ESI source in the positive-ion mode (Agilent Technologies, Inc., USA). The samples were directly introduced into the ESI source by a syringe pump at a flow rate of 6 mL min^{-1} . The gas temperature was 300 °C, the flow of drying gas was 10 L min^{-1} , and the nebulizer was at 30 psi. The voltage of the capillary was 3500 V and the fragmentor was 125 V. X-ray photoelectron spectroscopy (Thermo Electron Corp., USA) was used to characterize the composition of polymerized ionic liquid film. All electrochemical measurements were performed at 298 K (25 °C).

2.2. Synthesis of (*t*-Boc-APPPI) BF_4 ionic liquid

1-(3-Aminopropyl)imidazole (1.25 g, 0.1 mol) and di-*t*-butyl-dicarbonate (2.18 g, 0.1 mol) were dissolved into 50 mL anhydrous methanol. Triethylamine (3.3 mL, 21 mmol) was added into the mixed solution. Then, the resulting solution was stirred for 24 h under refluxing condition. The solvent was evaporated, and the product was purified to give 1-[3-(tert-butoxycarbonylamino)propyl]imidazolium.

N-(3-bromopropyl)pyrrole (10 mmol) was dissolved into 80 mL toluene, and was added dropwise to a toluene solution containing 1-[3-(tert-butoxycarbonylamino)propyl]imidazolium (10 mmol),

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