



Electrochemical preparation of two nanostructured poly(sulfosalicylic acid) films with different morphologies and properties for selective sensing of dopamine: Comparative study



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ABSTRACT

Two nanostructured poly(sulfosalicylic acid) (PSA) films were synthesized from room temperature ionic liquid (RTIL) or aqueous solution on a glassy carbon electrode (GCE) via potentiodynamic electropolymerization. The morphology and properties of the PSA films were characterized with scanning electron microscopy (SEM), scanning probe microscopy (SPM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). It was found that solvent had a major influence on the morphology and electrochemical properties of the resultant PSA films. The PSA(I) film, which was prepared from RTIL, consists of granular particles with cracks, whereas the PSA(II) film prepared from aqueous solution consists of nano-triangles with a more compact surface. The blocking effect of the PSA(I) film for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ electrochemical probe is much stronger, and a remarkably enhanced voltammetric response of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ electrochemical probe can be observed for the PSA(II) film. When it is used to detect dopamine in the presence of a high concentration of ascorbic acid, PSA(II)/GCE has three linear parts with better discrimination and a detection limit of 0.03 μM . For PSA(I)/GCE, there are two linear parts with a detection limit of 0.05 μM . However, the reproducibility and storage stability of PSA(I)/GCE are better than those of PSA(II)/GCE.

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1. Introduction

Owing to the high permselectivity for cationic analytes, poly (sulfosalicylic acid) (PSA) has attracted the interest of many researchers for electrochemical sensing as an electrode modification material. In 2001, Zhao et al. first reported the application of 5-sulfosalicylic acid (SA) as a monomer to prepare PSA-modified glassy carbon electrodes (PSA/GCE) at pH 5.5 in phosphate buffer solution (PBS) via electropolymerization. The high surface concentrations of negatively charged functional groups, such as $-\text{SO}_3^-$ and $-\text{COO}^-$, made PSA/GCE highly active towards oxidation of dopamine (DA) cation, and they could efficiently eliminate the interference of ascorbic acid (AA) anions that usually co-exist with DA in biological environments [1]. Since then, the PSA-modified electrode has been used to detect many other analytes, such as xanthine [2], glucose [3], l-tryptophan [4] and roxithromycin [5]. To improve the performance of the PSA-modified electrode, composite films, such as PSA/nano-gold composite [6] and PSA/functionalized graphene composite [7–9], were also prepared. PSA with a well-defined nanostructure, as for PSA nanorods, was also

prepared, with an anodic aluminum oxide membrane serving as the template [2]. Feng et al. used the electrostatic interaction between DNA and SA to make PSA grow along the DNA strands and prepared a PSA–DNA composite electrode that could be used for the simultaneous determination of adenine, guanine, and thymine [10]. In these studies, all PSA films were electrochemically synthesized in aqueous solution. Because the focus of such studies was on applying PSA in electroanalysis, the mechanism of electropolymerization and the influential factors on the morphology and properties of the PSA film have rarely been studied.

The electropolymerization can be performed in different systems, such as aqueous solutions or organic solutions containing supporting electrolytes. Some novel electrolytic media, such as ionic liquid, microemulsion, and eutectic mixture, were also used [11,12]. The physical properties of the solvents, such as the polarity, permittivity, nucleophilicity, basicity and potential window, usually affect the polymerization by changing the morphology and properties of the resultant polymer films [13–15]. The polymer films with different morphologies and electrochemical properties can be applied for different purposes [16]. Because water is an ideal solvent for pollution-free large-scale use and much electropolymerization can be achieved in water, electropolymerization in aqueous solution is an enduring approach in

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this field. Many organic solvents with high polarity and low nucleophilic activity, such as acetonitrile, benzonitrile, and dichloromethane, have also been used. However, the high volatility, flammability and toxicity of these organic solvents limit their further application [12]. By contrast, room temperature ionic liquids (RTIL) with extremely low nucleophilicity, volatility and a wide potential window (4–6 V) may be more promising electrolytes and solvents for electropolymerization [17]. To the best of our knowledge, no research on the electropolymerization of a PSA film from RTIL has been reported yet.

Nanomaterial-modified (bio)sensor systems are becoming increasingly important due to their function tunability, versatility, and novel properties [18–19]. Dopamine (DA) is among the model neurotransmitter analytes that has been studied most widely by electrochemical means. Nanomaterial-based modifiers that are used for DA detection are mainly prepared from carbon nanotubes [20], reduced graphene oxide [21], metal or metal oxide nanoparticles [22], polymers [23] and their composites [24]. In this study, two nanostructured PSA films were electrochemically synthesized on the surface of glassy carbon electrodes (GCE) from RTIL (PSA (I)) and aqueous solution (PSA (II)). A comparative study between these PSA films was performed to evaluate the effect of different solvents on the morphology and properties of the PSA films. The sensing characteristics of these two PSA-modified GCEs (PSA/GCE) were also studied by using DA as a model analyte.

2. Experimental procedures

2.1. Chemicals and materials

5-Sulfosalicylic acid, dopamine hydrochloride, ascorbic acid and other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄, RTIL) (>99%) was purchased from the Center for Green Chemistry and Catalysis (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). Phosphate buffer solution (PBS) at pH 7.4 was prepared by dissolving 0.019 M NaH₂PO₄, 0.081 M Na₂HPO₄ and 0.1 M NaCl in deionized water. PBS at pH 5.7 was prepared by dissolving 0.094 M NaH₂PO₄, 0.006 M Na₂HPO₄ and 0.1 M NaCl in deionized water. All reagents were of analytical grade and were used without further purification. Ultrapure water (Millipore, 18.25 MΩ cm, Ulupure Science and Technology Co., Ltd., Chengdu, China) was used for solution preparation.

2.2. Apparatus

The electrochemical measurements were performed using a CHI660E Electrochemistry Workstation (CH Instrument Inc., Shanghai, China). A conventional three-electrode system was used with the GCE (0.07 cm² geometric areas, Gaossunion Technology Ltd., China) or PSA/GCE serving as the working electrode and a platinum foil (2 cm² geometric areas, self-made) as the counter electrode. Because the silver chloride of the Ag/AgCl reference electrode dissolves in RTIL and Ag wire can only constitute a pseudo reference electrode, the Ag/AgCl electrode and Ag wire are not suitable reference electrodes in RTIL. Hence, a calomel electrode with an internal solution of 0.3 M tetraethyl ammonium chloride (TEAC)/RTIL was used as the reference electrode for the electropolymerization of SA in RTIL. A commercial saturated calomel electrode (SCE) was used as the reference electrode for electrochemical measurements in aqueous solution. The reference electrode was placed with the Luggin capillary 2 mm away from the working electrode surface.

The surface morphology of the PSA films was characterized using a JSM-6700F field emission scanning electron microscope (JEOL, Japan) at an acceleration voltage of 3 kV. The atomic force microscopic images were obtained using a dimension icon scanning probe microscope (Veeco, USA) in the ScanAsyst mode operating in air. The Nanoscope Analysis 1.5 software was employed for image analysis.

2.3. Preparation of PSA-modified glassy carbon electrodes

Prior to electropolymerization, a glassy carbon electrode was polished with 0.3 μm α-Al₂O₃, rinsed with deionized water, and then sonicated in 1:1 HNO₃, acetone and deionized water for 1 min. The electrode was then immersed in RTIL or aqueous solution containing 10 mM 5-sulfosalicylic acid, and cyclic voltammetry was conducted for different cycles to obtain PSA films with different thicknesses. After electropolymerization, the PSA-modified glassy carbon electrodes (PSA/GCE) were rinsed with deionized water to remove the residual RTIL and 5-sulfosalicylic acid, and they were then dried with nitrogen flux for 3 min. To evaluate the storage stability, the PSA/GCE electrodes were sealed in a plastic package and stored in a refrigerator at 2 °C for two weeks.

2.4. Electrochemical impedance spectroscopy (EIS)

For the EIS characterization of the PSA films, 0.1 M NaCl aqueous solutions with 5.0 mM [Fe(CN)₆]^{3-/4-}, serving as anionic electrochemical probe, were used. The EIS measurements were performed at open circuit potential with the signal amplitude of 5 mV in the frequency range of 10⁵ Hz–10⁻² Hz. EIS spectra were fitted using the ZSimpWin 3.10 software.

2.5. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV)

CV and DPV measurements were performed within a potential range of -0.2 V to 0.6 V vs. SCE with a scan rate of 100 mV·s⁻¹ for CV. DPV parameters were set as follows: increment potential 4 mV; amplitude 50 mV; pulse width 0.05 s; sampling width 0.0167 s; pulse period 0.5 s; and quiet time 2 s. During electrochemical measurements, solutions were purged with high purity nitrogen prior to and throughout the experiments to remove oxygen from the solutions.

All experiments were performed at room temperature (20 ± 1 °C) and atmospheric pressure.

3. Results and discussion

3.1. Electropolymerization of 5-sulfosalicylic acid

For the electrochemical synthesis of PSA films on GCE from RTIL or aqueous solution using potentiodynamic polymerization, the corresponding voltammograms are shown in Fig. 1. For easy comparison, the potentials indicated in Fig. 1(a) have been converted to the values with respect to SCE. During electropolymerization, the phenolic hydroxyl group of 5-sulfosalicylic acid is the reactive site, and polymerization reaction occurs in the ortho position of phenol hydroxyl according to Schematics 1 [25,26].

In Fig. 1, the CV curves recorded in RTIL and aqueous solution are different, which suggests substantial differences in the polymerization processes for these two solvents. The first cycles that correspond to the electropolymerization of SA on a bare GCE electrode are different from the subsequent cycles. This different CV behavior can be attributed to the differences in the nucleation and subsequent growth of nuclei, which has been noted in the literature [27]. For CV curves that are recorded in aqueous solution (Fig. 1b), there are five anodic peaks; in contrast, for CV curves that are recorded in RTIL (Fig. 1a), only three anodic peaks can be observed. In Fig. 1(b), the anodic peaks a₄ and a₅ correspond to the oxidation of adsorbed monomer on the modified electrode surface, whereas the anodic peaks a₁, a₂, and a₃ correspond to the oxidation of monomer radicals and dimers or oligomers formed during polymerization [28–29]. The high potentials of anode peaks, especially for a₃ in Fig. 1(a) and a₄ and a₅ in Fig. 1(b), are due to the electron-withdrawing effect of the sulfo group [12]. The peak currents of a₄ at 1.2 V and a₅ at 1.4 V in aqueous solution are exceptionally large, which can be ascribed to the decomposition of water when the potential

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