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ORIGINAL PAPER

Simultaneous determination of dopamine and uric acid on nafion/sodium dodecylbenzenesulfonate composite film modified glassy carbon electrode

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Abstract A novel electrochemical sensor has been constructed by using a glassy carbon electrode (GCE) coated with nafion/sodium dodecylbenzenesulfonate (SDBS). Differential pulse voltammetry (DPV) was used to study the electrochemical behaviors of dopamine (DA) and uric acid (UA). An optimum of 5 mM SDBS together with 0.05 wt% of nafion was used to improve the resolution and the determination sensitivity successfully. In 0.1 M phosphate buffer solution (pH 6.5), the modified electrode exhibited high electrocatalytical activity toward the oxidation of DA and UA with obvious reduction of overpotential. Compared with bare GCE, the modified electrode resolved the voltammetric response of DA and UA into two well-defined voltammetric peaks by DPV, which can be used for simultaneous determination of these species in mixture. The peak currents obtained from DPV were linearly related to the concentrations of DA and UA in the ranges of 4.0×10^{-7}–8.0×10^{-5} M and 4.0×10^{-6}–8.0×10^{-4} M, respectively. The detection limit of DA and UA (signal-to-noise ration was 3) were 5.0×10^{-8} and 4.0×10^{-7} M, respectively.

Keywords Sodium dodecylbenzenesulfonate (SDBS) · Nafion · Determination · Dopamine · Uric acid

1 Introduction

Dopamine (DA) is one of the most significant catecholamine, belongs to the family of excitatory chemical neurotransmitter and plays a significant role in the functioning of central nervous, renal and hormonal systems [1]. Low levels of DA may cause neurological disorders such as schizophrenia and Parkinson's disease [2]. DA is an important neurotransmitter in mammalian central nervous system [3]. In the extra-cellular fluid of the central nervous system the basal DA concentration is very low (0.01–1 μM) [4]. Therefore, it is of great clinical importance to measure DA level in the extracelluar fluid in order to monitor neurotransmission process and diagnose Parkinson's disease. Thus, there is a continuing interest in the development of simple, sensitive and reliable method for the determination of DA. Uric acid (UA) is the primary end product of purine metabolism in the human body [5]. Abnormal levels of UA are associated with a number of clinical situations such as gout, hyperuricemia, Lesch–Nyan disease, cardiovascular and kidney diseases, etc. [6, 7]. Since DA and UA commonly exist in body fluids, it is important to develop a simple method to detect these molecules selectively in routine assays. Simultaneous detection of UA and neurotransmitters, especially DA is important not only for clinical diagnostics but also for pathological research. Thus, considerable effort has been devoted to determine them utilizing various electrode materials, including clay-modified electrode [8], tetraphenylborate-modified electrode [9], polymer-modified electrode [10–14], carbon nanotube-modified electrode [15, 16], choline and gold nanoparticles-modified electrode [17]. Among the several strategies reported to solve the DA detection problem, a convenient way is to coat the working electrode with an anionic film such as nafion to protect the surface from the interferences [18–20]. Nafion, a cation-exchange polymer, is often employed to act as a covering to immobilize the desired film on the working electrode as well as an interfering barrier. However, this kind of electrode usually suffers from

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slow response and loss of sensitivity due to slow mass transportation of analytes in the films [21].

Surfactants, a special class of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other side, have been widely applied in electrochemistry to improve the property of the electrode/solution interface [22, 23]. The surfactant-modified electrodes have been reported previously [24, 25]. Chen et al. have reported a glassy carbon electrode (GCE) modified with cationic surfactant didodecyldimethylammonium bromide for simultaneous voltammetric determination of DA and ascorbic acid (AA) [24]. Zheng et al. have carried out the selective determination of DA in the presence of AA at sodium dodecyl sulfate-modified carbon paste electrodes [25]. Han et al. have reported sodium dodecylbenzenesulfonate (SDBS) self-assembled monolayers carbon paste electrode for studying the electrochemical behaviour of DA [26]. Cao et al. presented a differential pulse voltammetric (DPV) determination of AA, DA and their mixture at cetylpyridine bromide/chitosan composite film-modified electrode [27]. These studies indicate that surfactants offer an effective way for the simultaneous determination of bio-substances.

In this paper, we reported on the use of the nafion/SDBS composite film modified electrode for effective separation of DA and UA in 0.1 M phosphate buffer solution (PBS) of pH 6.5. Taking into account easy shed by using surfactant-modified electrode, nafion was used as an immobilizing agent to immobilize the surfactant SDBS, thereby the stability of electrode was strengthened. The DPV technique was used to study the catalytic oxidation of DA and UA at the nafion/SDBS composite film modified electrode. The nafion/SDBS composite film modified electrode showed a faster transfer rate compared to nafion-modified electrode or bare GCE. The nafion/SDBS composite film modified electrode exhibited high electrocatalytic activities toward the oxidation of DA and UA, and displayed good voltammetric peak separation between DA and UA.

2 Experimental

2.1 Reagents and apparatus

All reagents such as DA (Sigma-Aldrich), UA (Sigma-Aldrich), SDBS (Sinopharm Chemical Reagent Co. Ltd., SCRC, China) and nafion (SCRC, China), were used as received without further purification. All chemicals were of analytical grade. 0.1 M PBS with various pH values were prepared by mixing stock standard solution of KH_2PO_4 and $K_2HPO_4 \cdot 3H_2O$. Freshly prepared solution of DA and UA were used in all experiments. All solutions were prepared with doubly distilled water. All experiments were carried out at room temperature.

Electrochemical experiments were carried out using a CHI-660B electrochemical workstation (CHI, China). A conventional three-electrode system, consisting of nafion/SDBS composite film modified working electrode (3.0 mm in diameter), a saturated calomel reference electrode (SCE) and a platinum wire counter electrode, was employed. All experimental solutions were deoxygenated by purging with nitrogen gas prior to each experiment.

2.2 Preparation of the nafion/SDBS composite film modified electrode

Prior to modification, bare GCE (3 mm in diameter) was polished with 0.05 μm alumina slurry on the polishing cloth and then rinsed thoroughly with doubly distilled water, nitric acid (1:1), anhydrous ethanol, and doubly distilled water, and then allowed to dry at room temperature. SDBS of various concentrations together with 0.05 wt% of nafion were mixed. Then, 5 μL of the mixed solution was dropped on the electrode surface and dried at room temperature.

3 Results and discussion

3.1 Optimization of SDBS concentrations for DPV response of DA and UA oxidation

The effect of SDBS concentrations on the DPV response of DA and UA oxidation was investigated in the experiments. Figure 1 shows the DPV of 5.0×10^{-5} M DA and 1.0×10^{-4} M UA in 0.1 M PBS (pH 6.5) at the nafion-modified electrode containing different concentrations of SDBS. As it can be seen, using the nafion modified electrode without SDBS, the oxidation peaks of DA and UA overlap in part, and consequently determination of each species in the presence of the other is difficult. However, by introducing SDBS in the matrix of modified electrode, the anodic peaks of UA and DA can be easily separated. It was found in the experiments that the electrode containing 1 mM SDBS was able to resolve the anodic peaks of DA and UA (Epa for DA and UA is 0.17 and 0.42 V, respectively). The oxidation peak currents increased with increasing the concentration of SDBS from 2 to 5 mM, but did not change much for SDBS concentration higher than 5 mM. Hence, 5 mM SDBS was chosen for further experiments.

3.2 Oxidation of DA and UA at the nafion/SDBS composite film modified electrode

Figure 2 shows the electrocatalytic behavior of UA at the nafion/SDBS composite film modified electrode (Fig. 2A–M)

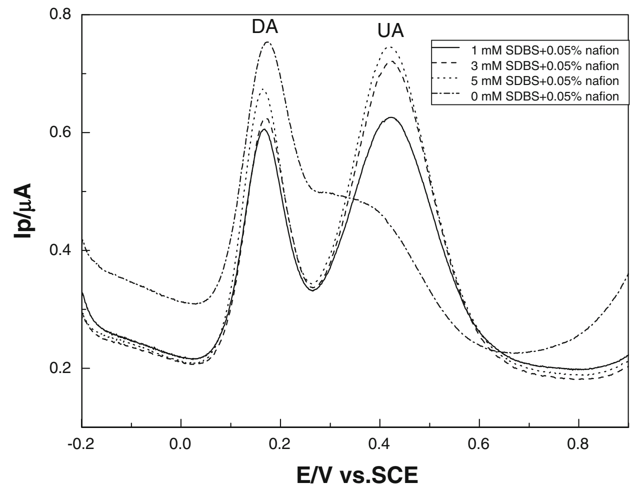

Fig. 1 DPV for a mixture of DA (5.0×10^{-5} M) and UA (1.0×10^{-4} M) in 0.1 M PBS (pH 6.5) at the nafion/SDBS composite film modified electrode containing various concentrations of SDBS

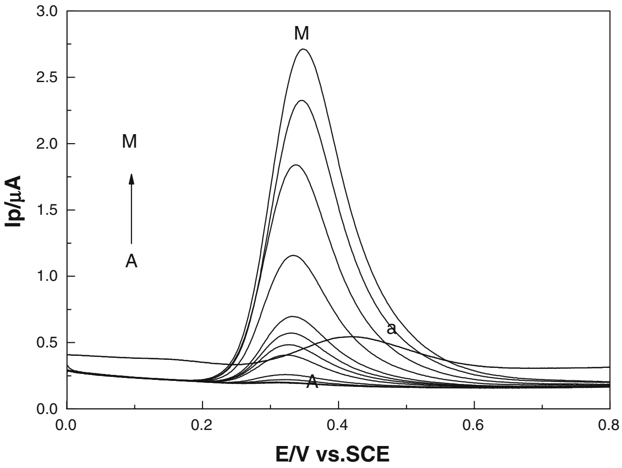

Fig. 2 DPV of the nafion/SDBS composite film modified electrode in 0.1 M PBS (pH 6.5) with different concentrations of UA: (A) 0.0; (B) 8.0×10^{-6}; (C) 2.0×10^{-5}; (D) 4.0×10^{-5}; (E) 6.0×10^{-5}; (F) 8.0×10^{-5}; (G) 1.0×10^{-4}; (H) 2.0×10^{-4}; (I) 3.0×10^{-4}; (J) 4.0×10^{-4} (K) 5.0×10^{-4}; (L) 6.0×10^{-4}; (M) 8.0×10^{-4}; (a) bare GCE, and the concentration of UA = 1.0×10^{-4} M

and bare GCE (Fig. 2a) in 0.1 M PBS (pH 6.5) that contained various concentrations of UA. It can be seen that the voltammetric peak of UA appeared at about 0.45 V on bare GCE; the peak was rather broad, indicating a slow electron transfer kinetic. However, a sharp oxidation peak appeared at about 0.38 V on the nafion/SDBS composite film modified electrode, showing the modified electrode had strong electrocatalytic activity toward UA oxidation. The oxidation peak current of UA increased and the oxidation peak potential shifted toward less positive compared to that of the bare GCE, indicating that nafion/SDBS was able to accelerate the rate of UA electron transfer. Clearly, the modified electrode has strong electrocatalytical activity toward UA oxidation. This figure also shows that the peak currents of UA were proportion to its concentrations in the range from 4.0×10^{-6} to 8.0×10^{-4} M (Ip = 0.5674c + 0.0101, R = 0.9967).

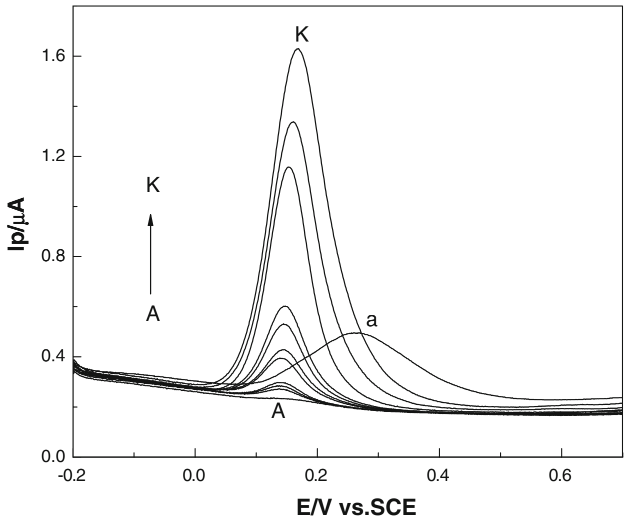

Fig. 3 DPV of the nafion/SDBS composite film modified electrode in 0.1 M PBS (pH 6.5) with different concentrations of DA: (A) 0.0; (B) 6.0×10^{-7}; (C) 8.0×10^{-7}; (D) 2.0×10^{-6}; (E) 4.0×10^{-6}; (F) 6.0×10^{-6}; (G) 8.0×10^{-6}; (H) 2.0×10^{-5}; (I) 4.0×10^{-5}; (J) 6.0×10^{-5}; (K) 8.0×10^{-5} M; (a) bare GCE, and the concentration of DA = 6.0×10^{-5} M

Figure 3 depicts the electro-catalytic behavior of DA at the nafion/SDBS composite film modified electrode (Fig. 3A–K) and bare GCE (Fig. 3a) in 0.1 M PBS (pH 6.5) that contained various concentrations of DA. As shown in Fig. 3, the oxidation of DA took place at 0.26 V on bare GCE, whereas the same occurred at about 0.16 V at the nafion/SDBS composite film modified electrode. The 0.10 V negative shift and enhanced peak current of the oxidation peak indicates that the nafion/SDBS composite film modified electrode plays an excellent catalytic effect on DA oxidation. The higher peak current may be attributed to the combination function of the surfactant and sulfonic groups of nafion. On one hand, anionic surfactant (SDBS), which absorbed at the electrode, attracted DA in neutral solution by electrostatic interaction, which changed the overpotential of the electrode and altered the electron transfer rate as well. On the other hand, the negatively charged nafion provided more exchanged site and transport channel for DA cations. Thus, significant advantages have been achieved by combining the electrocatalytic function of the SDBS with the charge-exclusion and preconcentration features of nafion. Figure 3 also indicates the peak currents of DA were proportional to its concentrations from 4.0×10^{-7} to 6.0×10^{-5} M (Ip = 0.0505c − 0.0012, R = 0.9956).

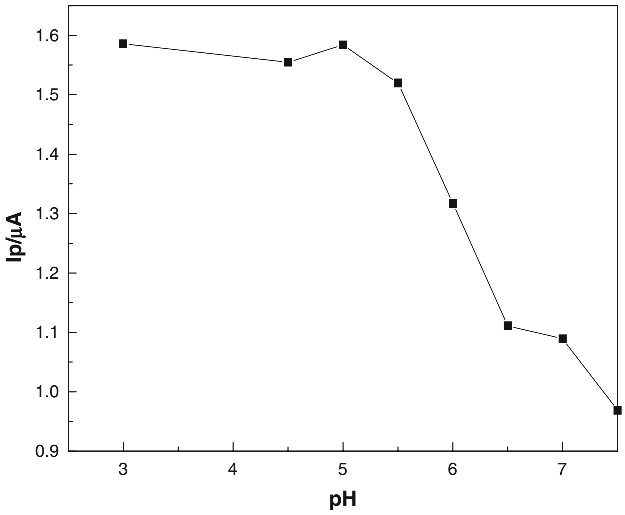

Fig. 4 Effect of solution pH on the DPV response of 2.0 × 10^{-4} M DA at the nafion/SDBS composite film modified electrode

3.3 Effect of pH on the oxidation of DA and UA in mixture

The effect of solution pH on the response of DA was studied in the range pH 3–7.5, as shown in Fig. 4. It can be observed from Fig. 4 that the peak current almost changed little between pH 3–5. Then, the oxidation peak current decreased as the pH increased from 5 to 7.5. The higher catalytic current at low pH could be partly explained on the basis of the dissociation ability of $–SO_3Na$ (H) group of SDBS/nafion film: at low pH, the $–SO_3Na$ group of SDBS/nafion film could dissociate favorably into a negative charge group $–SO_3^-$. Under this condition, the alkaline $–NH_2$ group of DA molecular (p*K*a = 8.9) could obtain a proton and form the positive ion of DA. Therefore, the negative charge group $–SO_3^-$ on the surface of modified electrode had a well affinity to the DA positive ions and could catalyze and promote the oxidation of DA in weak acidic mediator [12].

The effect of solution pH on the response of UA was also investigated in the pH range of 3–7.5. Figure 5 indicated that the oxidation peak current of UA deceased slowly in the range of pH 3–4.5, and then dropped greatly in the range of pH 4.5–7.5. Although the lower pH values were favorable to the determination of UA and DA, considering the physiological condition, pH 6.5 was chosen for studying the oxidation of UA and DA with the nafion/SDBS composite film modified electrode. Moreover, the separation between the oxidation peaks of these two compounds at pH 6.5 is better.

3.4 Electro-oxidation of DA and UA at the nafion/SDBS composite film modified electrode

In order to determine DA and UA simultaneously, the electrochemical behavior of mixture of DA and UA at the nafion/SDBS composite film modified electrode was studied.

Figure 6 exhibits the DPV voltammograms for the mixture of DA and UA at bare GCE, nafion-modified electrode and nafion/SDBS composite film modified electrode in 0.1 M PBS (pH 6.5). As it can be seen, at bare GCE, there exhibited two relatively well-defined oxidation peaks corresponding to DA and UA (curve a in Fig. 6), and the oxidation peaks potential were 0.20 and 0.47 V, respectively, with a peak potential separation of 0.27 V. At nafion-modified electrode, there exhibited two ill-defined

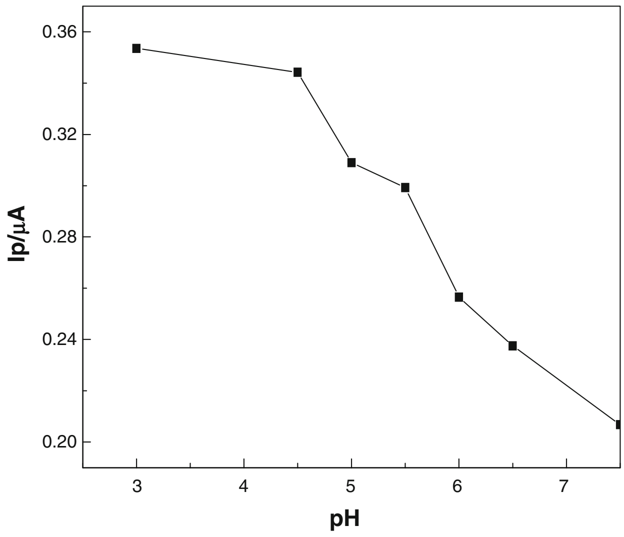

Fig. 5 Effect of solution pH on the DPV response of 1.0 × 10^{-4} M UA at the nafion/SDBS composite film modified electrode

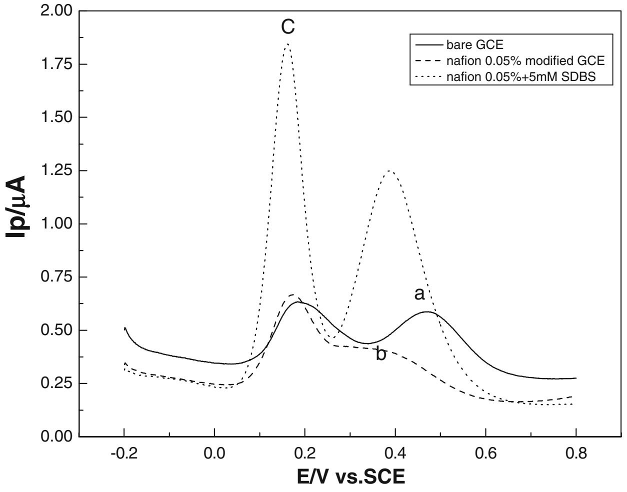

Fig. 6 DPV of 5.0 × 10^{-5} M DA and 1.0 × 10^{-4} M UA in 0.1 M PBS (pH 6.5). (a) bare GCE; (b) nafion-modified electrode; (c) nafion/SDBS composite film modified electrode

oxidation peaks corresponding to DA and UA (curve b in Fig. 6). However, at nafion/SDBS composite film modified electrode, there exhibited two well-defined oxidation peaks corresponding to DA and UA (curve c in Fig. 6), and the oxidation peaks potential were 0.15 and 0.38 V, respectively, with a peak potential separation of 0.23 V. What's more, the peak currents of DA and UA on nafion/SDBS composite film modified electrode are much larger than those at bare GCE or nafion-modified electrode. Meanwhile, the oxidation peak potentials of the two compounds at nafion/SDBS composite film modified electrode shifted to the negatively values, compared with that of bare GCE or nafion-modified electrode. This result also shows that the nafion/SDBS had good catalytic effects for the oxidation of DA and UA.

3.5 The DPV techniques for simultaneous determination of DA and UA

The electrooxidation processes of DA and UA in the mixture have been investigated. Figure 7 displays the DPV voltammograms that were obtained for DA and UA co-existing in 0.1 M PBS (pH 6.5) in various concentrations at the nafion/SDBS composite film modified electrode. The peak currents obtained increased linearly with increasing DA and UA concentrations in the range of 4.0×10^{-7}–8.0×10^{-5} M (Ip = 2.2834c + 0.0992) for DA and 4.0×10^{-6}–8.0×10^{-4} M (Ip = 0.4089c + 0.0798) for UA, with correlation coefficients of 0.9957 and 0.9968, respectively. The detection limit of DA and UA (signal-to-noise ration was 3) were 5.0×10^{-8} and 4.0×10^{-7} M, respectively. The oxidation peaks of DA and UA were well separated even in higher concentrations. Thus, simultaneous determination of DA and UA at physiological level was achieved by DPV techniques at the nafion/SDBS composite film modified electrode.

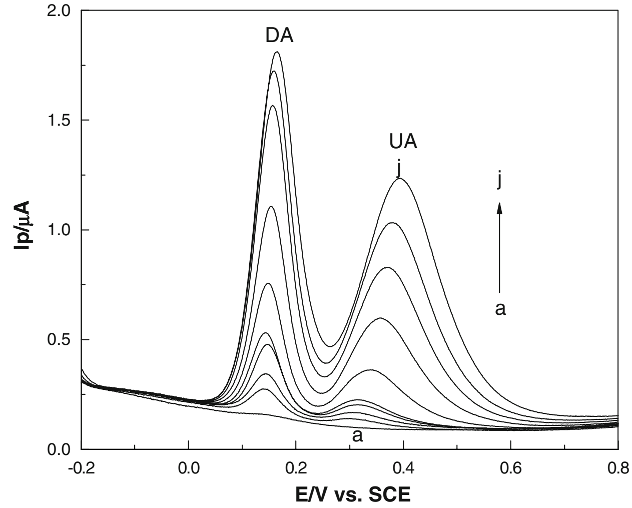

Fig. 7 DPV voltammograms of the nafion/SDBS composite film modified electrode in 0.1 M PBS (pH 6.5) with different concentrations of DA: (a) 0.0; (b) 2.0×10^{-6}; (c) 4.0×10^{-6}; (d) 6.0×10^{-6}; (e) 8.0×10^{-6}; (f) 2.0×10^{-5}; (g) 4.0×10^{-5}; (h) 6.0×10^{-5}; (i) 8.0×10^{-5}; (j) 1.0×10^{-4} M, and the UA concentrations were double of DA concentrations

4 Conclusion

A novel nafion/SDBS composite film modified electrode was fabricated and applied to determine UA and DA. The modified electrode shows excellent electrocatalytic activity for the oxidation of DA and UA. Moreover, the modified electrode presented wide linear range, low detection limit and high stability for simultaneous determination DA and UA, suggesting this electrode as a good and attractive candidate for practical applications.

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