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Sodium dodecyl sulfate-modified carbon paste electrodes for selective determination of dopamine in the presence of ascorbic acid

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Abstract

A carbon paste electrode (CPE) modified by a monolayer film of sodium dodecyl sulfate (SDS) was used for detection of dopamine (DA). Cyclic voltammetry demonstrated improved response of the DA sensor. This suggests the effectivity of surface modification of CPE by SDS. Impedance spectroscopy was used for the characterization of CPE surface properties. The effect of SDS concentration on the electrode quality also reveals that SDS formed a monolayer on CPE surface with a high density of negative-charged end directed outside the electrode. As a result, the carbon paste electrode modified with SDS (SDS/CPE) exerted discrimination against ascorbic acid in physiological circumstance. Thus, it can selectively determine dopamine even in the presence of 220-fold AA combined with differential pulse stripping voltammetry. In pH 7.40 phosphate buffer solution, the oxidation peak current on differential pulse voltammograms increases linearly with the concentration of DA in the range of 5.0×10^{-7} to 8.0×10^{-4} mol · L^{-1} with a detection limit of 5.0×10^{-8} mol · L^{-1}. Satisfying results are achieved when detecting the DA in injection and simulated biology sample.

Keywords: Dopamine; Modified carbon paste electrode; Sodium dodecyl sulfate; Cyclic voltammetry; Differential pulse voltammetry; Impedance spectroscopy

1. Introduction

Dopamine (DA) is one of important monoamine neurotransmitters in mammalian central nervous systems. The determination of dopamine is a subject of great significance for investigating its physiological functions and diagnosing nervous diseases resulting from dopamine abnormal metabolism, such as epilepsy, Parkinsonism and senile dementia [1]. The fact that DA and other catecholamines are easily oxidizable compounds makes their detection possible by electrochemical methods based on anodic oxidation [2]. Dopamine has been determined using various electrochemical methods [3–5]. A major problem of these analyses is the coexistence of ascorbic acid (AA) in high relative concentrations. Usually, the concentration of DA is 10^{-8} to 10^{-6} mol·L^{-1} while AA is as high as 10^{-4} mol·L^{-1} in biological systems [6]. Moreover, at almost all electrodes materials, DA and AA are oxidized at nearly the same potential, which results in overlapped voltammetric response [7].

The successful route to overcome the problems of selectivity is to modify the electrode surface, because the modified electrode could decrease the overpotential, improve the mass transfer velocity and effectively enrich the substance [8,9]. Various modified materials have been modified on various base electrodes to investigate and detect dopamine [10–14]. Zhang et al. [15] have modified the acid-treated multi-walled carbon nanotubes (MWNTs) on the surface of gold electrode for selective detection dopamine. Because of the high concentration of carboxylic acid group and subtle structure of acid-treated MWNTs, the modified electrode can detect DA in the presence of excess ascorbic acid. The limit of detection is 2×10^{-7}mol·L^{-1}. Yuan and Hu [16] have fabricated a Nafion/nano-TiO_2 bilayer-modified electrode which can give sensitive voltammetric response of DA regardless of the 200-fold excess AA. Many sensors were fabricated with negatively charged polymer films, self-assembled monolayer or cation exchange. The major consideration is based on the different ion forms of DA and AA at the physiological pH of 7.40. AA exists in the

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anionic form (pK_a=4.10) while DA is in the cationic form (pK_b=8.87) [6]. Surfactants, a kind of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other, have been widely applied in electrochemistry to improve the property of the electrode/solution interface [17,18]. The surfactant-modified electrodes have been reported previously. Krishnananda et al. [19] have carried out the direct electrochemical studies on horse heart myoglobin and horseradish peroxidase at neutral surfactant-modified glassy carbon electrode. Improved electron transfer rate was found between these proteins and the modified electrode. Lenys and Hermes [20] have gained a chemically modified glassy carbon electrodes by using surfactant/clay films, containing ferrocenecarboxylic or ferrocenedicarboxylic acid. The results show that the surfactant molecules incorporated into the clay could increase the permeability and the positive surface of the film. Svancara et al. [21] also reported a carbon paste electrode modified with cationic surfactants, which was used to determine chromate based on synergistic pre-concentration of the chromate anion at modified electrode. However, surfactants-modified electrodes have not been used to study the electrochemical behavior of dopamine. Wen et al. [22] have investigated the micellar effect on the electrochemistry of dopamine and found that the anodic peak current of dopamine is enhanced in sodium dodecyl sulfate micelle, but the interference coming from ascorbic acid cannot be eliminated.

To improve the selectivity, a sodium dodecyl sulfate (SDS) modified carbon paste electrode (SDS/CPE) was fabricated by the hydrophobic adsorption of SDS on the surface of CPE. Comparing with other chemically modified carbon electrodes, the SDS/CPE has some unique properties, such as a single-component surface, high density of negative charges covered on electrode surface, the ability to be further modified by common blending methods, and so on. The voltammetric response of DA on SDS/CPE was increased greatly compared with on CPE. After an open circuit accumulation, a further enhancement of the oxidation peak current was observed, and a high discrimination against AA was represented on SDS/CPE. Furthermore, the electrochemical characterization of SDS/CPE was investigated by electrochemical alternating current impedance technique. To sum up, this method for determination of DA has the following advantages: easy to prepare, easy renewal, low cost, high selectivity, and low detection limit.

2. Experimental

2.1. Apparatus and reagents

All electrochemical experiments were performed with a CHI660A electrochemical workstation (Shanghai Chenhua Co., China) controlled by a microcomputer with CHI660 software. A three electrode electrochemical cell was employed. A naked carbon paste electrode (NCPE), SDS/CPE or SDS/GCE was used as working electrodes, with a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. All potentials reported were versus the saturated calomel electrode.

Dopamine (Sigma) was used as received. Other chemicals were analytical grade and used without further purification. 0.1 mol·L^{-1} NaCl+Na_2HPO_4+KH_2PO_4 buffer solution (PBS) with various pH was employed as supporting electrolyte. Ultrapure water (R=18 MΩ) obtained from a Milli-Q system (Millipore Co. USA) was used for preparing all the solutions. High-purity nitrogen was used for deaeration.

2.2. Preparation of electrode

The naked carbon paste electrode was prepared as follows: 1.0 g graphite powder and 0.5 mL paraffin oil were mixed by hand to produce a homogenous carbon paste. The carbon paste was packed into the cave of a homemade carbon paste electrode (3 mm in diameter) and then smoothed on a weighing paper.

The glassy carbon electrode was previously polished, with alumina suspensions of difference grain size (1.0 and 0.05 μm) on a billiard cloth. After that, the electrodes were placed in 1:1 nitric acid, ethanol and water, and properly cleaned in a sonicator for 5 min, respectively.

The modified electrode was prepared by dipping a drop of 8.0×10^{-3} mol·L^{-1} SDS solution (10 μL) onto the surface of the bare carbon paste electrode or well-polished glassy carbon electrode by a microinjector. Two minutes later, the electrode was completely rinsed with water to remove unadsorbed modifier and dried in air at room temperature.

The carbon paste electrode surface was renewed by extrusion of approximately 0.5 mm carbon paste from the holder and smoothing with a weighing paper and repeated the above modification processes. Typically, such mechanical renewal of the carbon paste surface was made when starting a new series of measurements (e.g., prior to analysis of each sample).

2.3. Methodology

In cycling voltammetric measurements, the potential swept from −0.2 to 0.5 V or 0.6 V with a scan rate of 50 mV s^{-1}. The parameters in electrochemical impedance experiment were as follows: initial potential of 0.17 V, frequency range of 0.01–1000 Hz with amplitude of 5 mV. The differential pulse voltammograms (DPVs) were achieved at an initial potential of −0.2 V and a final potential of 0.5 V, with a pulse width of 5 s and amplitude of 5 mV. Except for the special mention, all experiments were carried out at the ambient temperature (approx. 25 °C) and nitrogen atmosphere, after modified electrode was accumulated in sample solution at open circuit for 10 min.

3. Results and discussion

3.1. The property of SDS-modified electrode

3.1.1. Optimization the electrode material and modifying method

Dopamine (DA) showed a quasi-reversible redox wave on NCPE in PBS (pH 7.40). Addition of the anionic surfactant SDS to the supporting electrolyte increased the reversibility of voltammetric response of DA and enhanced peaks currents, i_{pa} and i_{pc}, significantly (Fig. 1). The results were consistent with those obtained at the glassy carbon electrode [22]. But an interesting phenomenon was found that the peak current were increasing with the immersion time of the NCPE in SDS solution. The same effect also occurred at GCE, but not significantly. After 20 min enrichment, comparing with the original currents at micelles, anodic peaks currents of DA at NCPE enhanced 83%; at GCE, it enhanced 22%. As shown in Fig. 1, i_{pa} at NCPE reached the maximum after 4 h and increased almost 4-fold.

It is well established that surfactants can be adsorbed on solid surfaces to form surfactant films [23]. In the present case, significant influence upon addition of SDS can be rationalized by the adsorption of the surfactant at the electrode surface which may alter the overvoltage of the electrode and influence the rate of electron transfer. The increasing sensitivity with immersion time can also be rationalized by the increasing adsorbance of SDS on electrode surface.

In order to gain more sensitive sensor for DA and save preparing time, a novel SDS-modified electrode was fabricated by applying the surface modifying method. It can be seen from Fig. 2 that carbon paste electrode modified with SDS (SDS/CPE) showed higher sensitivity for DA than SDS/GCE. The experiments indicated that CPE was more suitable for our study, because the paraffin oil in CPE gave a more hydrophobic surface which was in favor of the adsorption of SDS on the electrode surface. Accordingly, carbon paste electrode was used as base electrode in this work.

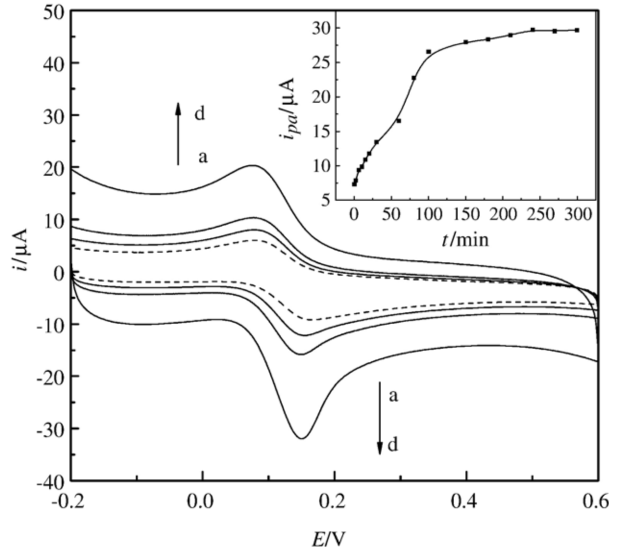


Fig. 1. Cyclic voltammograms of dopamine (0.15 mmol·L^{-1}) recorded at a naked carbon paste electrode in pH 7.4 PBS. The potential was scanned from −0.2 to 0.6 V with a scan rate of 50 mV s^{-1}: (a) in blank PBS, (b–d) in 8.0 mmol·L^{-1} SDS micelles, after 5 min, 20 min, and 80 min. The inset is the plot of dependence of DA oxidation peak current (i_{pa}) on enrichment time (t).

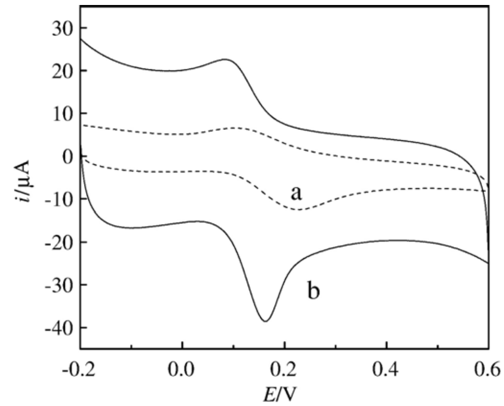


Fig. 2. Cyclic voltammograms of dopamine (0.15 mmol·L^{-1}) recorded at SDS/GCE (a) and SDS/CPE (b) in pH 7.40 PBS. Experiment conditions as Fig. 1.

The stability and reproducibility of the modified electrode were examined in eight parallel determinations. When we detect 1×10^{-5} mol·L^{-1} DA solution, the signal at the same electrode surface could be repeated with a relative standard deviation from ±3% to ±9%. For the different electrode made from the same carbon paste, the relative standard deviation varied from ±3% to ±12%. Such diversity might appear to be relatively significant; nevertheless, these values were being typical for complicated mechanisms involving accumulation of the analyte via ion-pairing and its subsequent re-release during the electrochemical detection [21]. When the modified electrode was stored dry and airtight at room temperature for 10 days, the same shape of the voltammetric curves of DA could be maintained and only a 10.1% decay of initial current could be observed. It indicated the high electrochemical stability of the SDS/CPE and the application potential. Because of the strong adsorption of DA on the SDS layer, for a different concentration of DA sample, a new modified electrode should be used. In order to eliminate system error, all experiments should be accomplished with the same batch of carbon paste electrode.

3.1.2. Electrochemical impedance spectroscopy (EIS) of SDS/CPE

It is well known that electrochemical alternating current impedance technique is a useful tool for studying the interface properties of surface-modified electrodes. So it was used to investigate the character of SDS/CPE surface. Fig. 3 shows the Nÿquist diagram of electrochemical impedance spectroscopy (Z'' versus Z') obtained at NCPE (Fig. 3A) and SDS/CPE (Fig. 3B). It is well established that for a diffusive species, the EIS includes a semicircle part and a linear part, of which the semicircle part at high frequencies corresponds to the electron transfer-limited process and the linear part at low frequencies corresponds to the diffusion process [24]. Fig. 3A indicates that the $[Fe(CN)_6]^{4-/3-}$ is a diffusive species at NPE. A well-shaped but incomplete semicircle is observed at bare CPE in the frequency range of 966.8–1.7 Hz. The charge transfer resistance (R_{ct}=3.60 kΩ) can be calculated by Eq. (1), which implies low electron transfer resistance of NPE to the redox probe. Furthermore, the electron-transfer resistance can be translated into the exchange current under equilibrium ($I_0=7.14\times10^{-6}$ A)

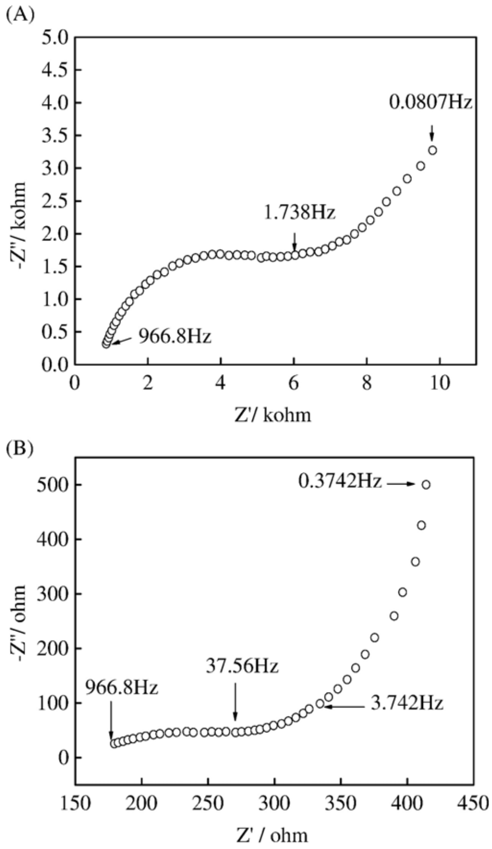


Fig. 3. Nyquist diagrams ($-Z''$ vs. Z') for the EIS measurements at NCPE (A) and SDS/CPE/CME (B). In the presence of 1.0 mmol·L^{-1} $[Fe(CN)_6]^{4-/3-}$ in 0.1 mol·L^{-1} KCl, amplitude: 5 mV, initial potential: 0.17 V, frequency range: 0.01–1000 Hz.

through Eq. (2) [25], which implies the high electron transfer velocity at NPE.

$$(Z' - R_{ct}/2)^2 + (-Z'')^2 = (R_{ct}/2)^2 \tag{1}$$

$$R_{ct} = RT(nFI_0)^{-1} \tag{2}$$

It can be seen from Fig. 3B that in the low-frequency region, the appearance of a nearly vertical line showed SDS/CPE like as a pure capacitor [24], and in the high-frequency region, the radius of the semicircle is so large that it is nearly parallel to the real part of impedance (Z'). All these show SDS/CPE has some characteristics of the high charge transfer resistance and low exchange current, which indicates that the SDS-modified layer obstructs the electron transfer of the electrochemical probe. The reason of these differences between NCPE and SDS/CPE may be the following: the SDS anions adsorbed on the electrode surface formed a negative electric field around electrode surface. Thus, the redox probe with negative charge ($[Fe(CN)_6]^{4-/3-}$) may more difficultly arrive at the electrode. Moreover, SDS can form a less electric conductive layer on the electrode to cause a much higher electron-transfer resistance.

After the fitting procedure, the specific capacitance (i.e., normalized to electrode area) of the modified layer, C_m (64.32 μF cm^{-2}) was determined. The thickness (d) of the membrane can be estimated according to the Eq. (3) [26]

$$C_m = \varepsilon_0 \kappa / d \tag{3}$$

where ε_0 is the permittivity of the free space ($\varepsilon_0 = 8.85 \times 10^{-14}$ F cm^{-1}) and κ, the membrane dielectric constant (estimated as 78.49) [27]. Under these assumptions, the thickness of the SDS membrane was estimated as 10.8 nm. This value is in good agreement with the distance of 9.4 nm from the polar head to the tail end of alkyl chains for SDS monolayer [28].

These results not only prove the validity of the surface-modifying method used in this study but also certify the adsorption characters of SDS on the CPE surface. SDS molecule forms a monolayer on the CPE surface with “stand” mode. A negative electric field exists around the modified electrode surface. The monolayer adsorption of SDS on the CPE surface is similar to the adsorption character of SDS on the graphite surface [29].

3.1.3. The influence of concentration of SDS on voltammetric response of dopamine on SDS/CPE

Falaras et al. [30] have reported that the preparation of the organoclay-modified glass carbon electrode was based on the formation of a second CTAB layer on the first one through the van der Waals interaction. In this work, the paraffin oil layer covered on the carbon particles had similar hydrophobic property to that of the first SDS layer of the organoclay-modified electrode. Thus, when CPE was immersed in 8.0 mmol·L^{-1} SDS solution, SDS might form a stable layer on the surface of CPE. To achieve further understanding of the adsorptive behaviors of SDS on CPE, the effects of SDS concentration on the responses of DA at SDS/CPE were investigated. Different concentrations of SDS were used to fabricate the different modified electrodes according to the method described in Section 2.2.

Fig. 4 shows the effects of SDS concentration on the reduction (dot curve) and the oxidation (solid curve) peak

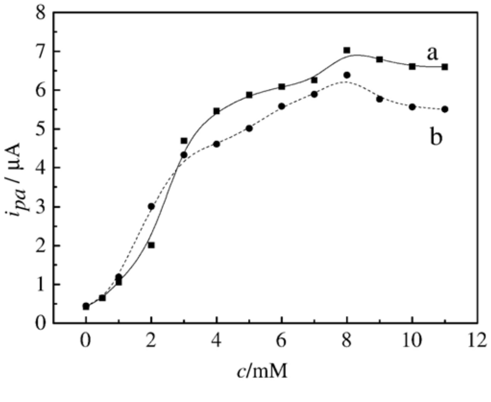


Fig. 4. Effects of SDS concentration on the redox peak current of 0.04 mmol·L^{-1} DA. The solid curve with squares (a) represent anodic peak (i_{pa}) and dot curve with dots (b) represent cathodic peak current (i_{pc}). Accumulation time: 10 min, experiment conditions as Fig. 1.

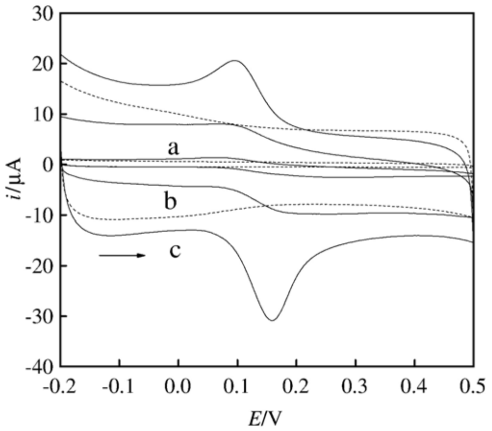


Fig. 5. Cyclic voltammograms (at 50 mV s^{-1}) of the naked (curve a and b) and the SDS-modified CPE (curves c) in pH 7.40 PBS in the presence (solid curves) and the absence (dot curves) of 0.15 mmol·L^{-1} DA. The curve b expresses the condition of directly adding SDS in DA solution to form 8.0 mmol·L^{-1} SDS solution. Accumulation time: 10 min.

currents of 4.0×10^{-5} mol·L^{-1} DA. When the SDS concentration is lower than the 8.0 mmol·L^{-1} the critical micelle concentration (CMC) of SDS at room temperature [31], both i_{pa} and i_{pc} increase rapidly with the increase of SDS concentration. However, the signals of DA apparently decrease in the range of 8.0–11.0 mmol·L^{-1}. This plot is very similar to the SDS adsorption isotherm on the graphite surface [29], which also has the maximum adsorption capacity about CMC. Surfactant molecules will form micelles at high concentration ($C_{SDS}>$ CMC), which causes the decrease of available dissociative SDS molecules and the SDS adsorbed on surface. It indicates the accumulation ability of SDS/CPE to DA has a direct proportion with SDS adsorbance on electrode surface. Based on the above discussions and the inference in Section 3.1.2, in the presence of SDS solution, multilayer or monolayer adsorption may occur at first. However, when these electrodes are thoroughly rinsed with water, the outer layer in the multilayer may be removed and an SDS monolayer-coated CPE may be obtained. Thus, it is rational to infer that the CPE modified by 8.0 mmol·L^{-1} SDS is covered by a compact SDS monolayer. The hydrophobic alkyl terminal group in the SDS molecule adsorbed at the hydrophobic electrode surface through Van der Waals interaction, and the hydrophilic sulfate terminal group oriented outside. The relevant report [27] has proved that the adsorbed SDS organized in a dense monolayer on a hydrophobic C_{18} surface near the CMC which also supported our inference.

3.2. Electrochemical behavior of dopamine at SDS/CPE

3.2.1. Cyclic voltammetric response of dopamine

Fig. 5 shows the cyclic voltammograms (CVs) of DA on SDS/CPE (c) and NCPE with (b) and without (a) adding SDS in the supporting electrolyte. In the potential range of −0.2–0.5 V, at SDS/CPE a pair of well-defined redox peaks of DA (c) appears at an $E^{0\prime}$ [$(E_{pa}+E_{pc})/2$] value of 127 mV, with ΔE_p only 64 mV, which is much smaller than on NPE (a) (ΔE_p = 217 mV). The smaller peak potential difference (ΔE_p) and the higher redox peaks (i_p) indicate the accumulation ability of the SDS/CPE to DA. The curve b shows CVs of 8.0 mmol·L^{-1} SDS and 3.0×10^{-5} mol·L^{-1} DA mixture on NPE. There is also a certain accumulating effect, because of the spontaneous adsorption of SDS on the electrode surface, but not obviously as the SDS/CPE (curve c), indicating that the accumulating effect is due to the modified SDS layer on the electrode surface not the SDS in solution.

With the increase of the immersion time, the reduction peak current (i_{pc}) and the oxidation peak current (i_{pa}) both increase correspondingly. In order to quantify the relationship between the peak current and the concentration of dopamine, every experiment was carried out after SDS/CPE was immersed in the analyte solution for 10 min.

3.2.2. The effect of scan rate on the peak current and peak potential of dopamine

The scan rate has a great influence on the peak current of DA on SDS/CPE. The anodic and cathodic peak currents are directly proportional to the scan rate (v) in the range of 20–170 mV s^{-1} with correlation coefficient of 0.996 and 0.994, respectively. The linear regression equations are expressed as $i_{pa}(\mu A)=2.052–0.0590v$ (mV s^{-1}); $i_{pc}(\mu A)=1.446+0.0664\ v$ (mV s^{-1}). Moreover, i_{pa} is not equal to i_{pc} ($i_{pa}/i_{pc}=1.33$). The difference between the anodic peak potential and the cathodic peak potential, ΔE_p, is increasing with the scan rate in the same scan range. The results indicate that the electron transfer reaction is controlled by the adsorption of DA on the electrode surface and the electrode process is irreversible.

3.2.3. The effect of pH on the peak current and peak potential of dopamine

Fig. 6 shows that peak potential difference increases with the acidity in pH 6.00–7.40. Every point in the figure was present in the average value of five measurement. There is an abrupt stop at pH 6.00 due to the totally disappearance of cathodic peak current. While supporting electrolyte at pH 7.40–8.40, ΔE_p reaches a minimum and remains constant. The effect of pH on

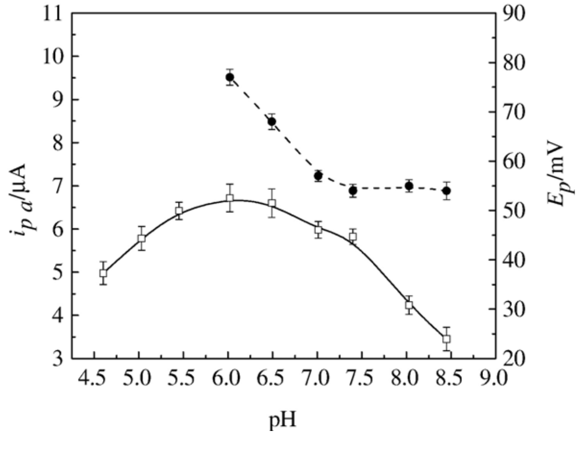


Fig. 6. Dependence of DA oxidation peak current (i_{pa}) (solid curve and squares) and peak potential difference (ΔE_p) (dashed curve and dots) on solution pH. The plot is the average of the data obtained from five recordings performed with different electrode. Accumulation time: 10 min, experiment conditions as Fig. 1.

ΔE_p reveals that the proton participate in the oxidation process of DA, which is in accord with the well-known oxidation mechanism of DA shown at Scheme 1.

Fig. 6 also reveals the anodic peak current of DA in PBS has a relative stability region from pH 4.50 to 7.40 and decreased rapidly in alkaline solution. More sensitive response achieves at acidic solution also can be well explained by the proton participating in the oxidation process of DA, and acidic solution making SDS molecule ionize easily. In order to simulate the biological environment and to get the higher selectivity (the optimum condition to avoid the inference of AA was discussed in Section 3.3.), pH 7.40 PBS was used as optimum in this study.

3.3. The response of DA in the presence of ascorbic acid (AA)

It is well known that AA widely coexists with DA in real biological matrices. So, avoiding AA interference is an important target for any DA analytical methods. The interference of AA to DA detection arises from two aspects: one is the very similar oxidation potential of AA and DA at ordinary electrode; the other is the electrocatalytic oxidation of dopamine by ascorbic acid [32]. Namely, oxidized dopamine, i.e., dopamine-*o*-quinone, is chemically reduced by ascorbic acid. Thus, one would anticipate that the oxidation wave of DA will be affected by the concentration of AA. The steady-state current of DA at SDS/CPE in the presence of increasing concentration of AA was carefully examined at various pHs by differential pulse voltammetry, which has a higher selectivity and sensitivity compared with cyclic voltammetry.

At neutral solution, the SDS/CPE shows more discrimination against AA. The endurable concentration of AA is 4.0×10^{-3} mol·L^{-1} at pH 7.40 compared with 1.0×10^{-3} mol·L^{-1} at pH 6.00. Considering pK_a (8.87) of DA and first pK_a (4.10) of AA [6], these can be easily comprehended. At neutral pH, DA exists in the cationic form while AA is completely in the anionic form. Therefore, physiological pH (7.40) is the optimum selection in this work.

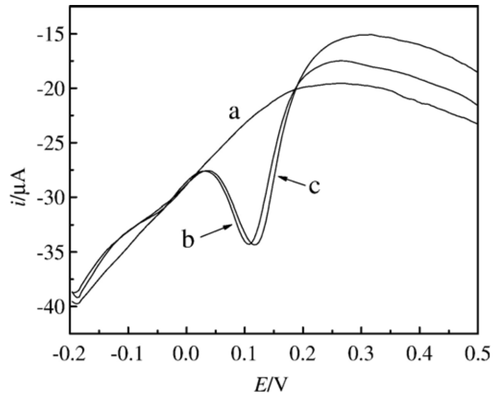
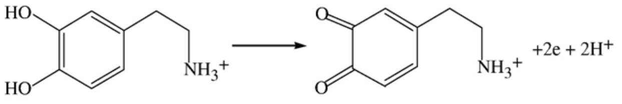


Fig. 7. Differential pulse voltammograms of 4.0 mmol·L^{-1}AA (a), 0.040 mmol·L^{-1}DA (b) and 4.0 mmol·L^{-1} AA+0.040 mmol·L^{-1} DA (c) at SDS/CPE. The potential was scanned from −0.2 to 0.5 V with a pulse width of 5 s and amplitude of 5 mV. Supporting electrolyte: 0.1 mol·L^{-1} PBS (pH=7.40).

Curve a in Fig. 7 is the differential pulse voltammogram of AA at SDS/CPE. It is clear that AA has no electrochemical response on SDS/CPE surfaces. So the interference induced from the overlapping of AA oxidation wave can be well avoided. Moreover, Fig. 7c shows the differential pulse voltammogram of mixed solution of 4.0×10^{-5} mol·L^{-1} DA and 4.0×10^{-3} mol·L^{-1} AA which AA is 100-fold higher than DA. In this situation, the peak potential of DA has a little shift from 0.108 to 0.112 V, and the peak current has a little rise from 9.99 to 10.25 μA. The corresponding DA concentration only changes 2.6%, which indicates that the determination error of DA concentration was in the permission region (±5.0%). The experiment shows the electrocatalytic oxidation effect of AA also can be eliminated at SDS/CPE, which was not realized in SDS micelles added to DA solution [22].



Scheme 1. The oxidation reaction of dopamine on electrode.

At experimental pH, the amine group in DA molecule is electropositive, whereas the hydroxyl next to the carbonyl group in AA molecule is electronegative [6], and the SDS monolayer on the electrode surface is electronegative due to its ionization. Therefore, on the one hand, electropositive DA is attracted electrostatically to the monolayer and can be oxidized at relatively low potentials. On the other hand, electronegative AA is repelled from the electrode due to the electronegative monolayer and has no electrochemical response. Moreover, the SDS/CPE has the selective response to DA in the mixture of DA and 100-fold AA also can be explained by the small thickness of the diffusion layer of oxidation reaction of DA [33]. After 10 min enrichment, DA electrode reaction is completely controlled by the adsorption. The oxidized DA has still been attracted around the electrode and cannot have change to be reduced by ascorbic acid in solution. Further experiments which has shown higher sensitivity can be achieved if other electrochemical methods, such as differential pulse stripping voltammetry, is used. In such experiments, after open circuit enrichment in sample solution, SDS/CPE is transferred to blank supporting electrolyte for differential pulse voltammetry. The interference coming from AA can be eliminated thoroughly for no AA is adsorbed on SDS/

Table 1

Determination of DA in injection of dopamine hydrochloride ($n=10$, $t_{0.05,9}=2.26$)

Number	Nominal content ($\times10^{-5}$ mol·L^{-1})	Found by standard method[a] ($\times10^{-5}$ mol·L^{-1})	Found by the method in article ($\times10^{-5}$ mol·L^{-1})	RSD (%)
1	2.11	2.11	2.09±0.05	3.3
2	4.22	4.25	4.23±0.09	3.0
3	10.5	10.5	10.7±0.21	2.8

[a] The standard methods for detect dopamine on *Pharmacopoeia of China* (Part II).

Table 2
Recovery data for synthesized biology solution[a] spiked with various amounts of DA

Number	Added ($\times 10^{-5}$ mol·L^{-1})	Found ($\times 10^{-5}$ mol·L^{-1})	Recovery (%)
1	4.00	4.10	102.8
2	8.00	8.06	100.7
3	20.0	21.4	107.0

[a] 1.0×10^{-3} mol·L^{-1} AA in diluted 50-fold fresh urine sample from the healthy volunteers.

CPE and no AA exists in electrolyte. 1.0×10^{-5} mol·L^{-1} DA can be detected in the presence of 2.2×10^{-3} mol·L^{-1}AA (220-fold of DA concentrations).

3.4. Analytical applications

In 0.1 mol·L^{-1} pH 7.40 PBS, the anodic pulse peak currents are measured and plotted against the bulk concentrations of DA. The oxidative peak currents increased linearly with the concentrations of DA in the range of 5.0×10^{-7}–8.0×10^{-4} mol·L^{-1} with a correlation coefficient of 0.996. The linear regression equation is expressed as $i_p(\mu A) = 5.003 + 6.63 \times 10^4 c$ (mol·L^{-1}). When the signal–noise ratio (SNR) is 3, the detection limit (3σ), taken as the concentration that gave a signal equal three times of standard deviation of blank signal calculated from the analytical graph [34], is 5.0×10^{-8} mol·L^{-1}.

The sample of an injection of DA was determined after suitable dilution. Table 1 showed the results of the sample determination. Every sample was parallel detected by SDS/CPE for 10 times, the relative standard deviation was given to indicate the precision of this method. The average value of 10 determinations by applying a calibration plot correspond with the value obtained by standard methods on Pharmacopoeia of China (Part II) [35]. Recovery was studied in the synthesized sample. The acceptable recovery was obtained as shown in Table 2.

Synthesized sample was prepared as follows: The supporting electrolyte was fresh urine sample from healthy volunteer 50-fold diluted by pH 7.40 PBS. AA was dissolved in supporting electrolyte to gain 1.0×10^{-3} mol·L^{-1} synthesized biology solution. Various amounts of DA reserve solution were spiked into it to get different synthesized biology sample.

4. Conclusion

A carbon paste electrode modified with sodium dodecyl sulfate was developed in this work based on the surface-modifying method. The modified electrode had a regular surface covered by a compact monolayer of SDS with high density of positive charges directed outside, which was characterized by electrochemical impedance spectroscopy and the effect of SDS concentration on electrode capability. This electrode exhibited strong enrichment ability towards dopamine and discrimination against ascorbic acid. This is attributed to the cation preconcentration ability and anionic repellency of SDS film. SDS/CPE was used to determine the dopamine in injection and simulated sample with high concentration of AA, and a satisfying result was achieved. The application of this electrode creates a new approach to determine the importance neurotransmitter dopamine sensitively and selectively.

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