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Differential pulse voltammetric determination of dopamine with the coexistence of ascorbic acid on boron-doped diamond surface

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Abstract: Electrochemical determination of dopamine (DA) in the presence of ascorbic acid (AA) was achieved on boron-doped diamond (BDD) film electrode by differential pulse voltammetry. The experimental results indicated that the oxidative peaks of DA and AA could be separated completely on anodically-treated (BDD) electrode without further modification, although these two peaks can not be separated on glassy carbon electrode. The peak separation of DA and AA was developed to be 0.44 V. High sensitivity was obtained to determine DA selectively with the coexisting of a large excess of AA in acidic media by DPV. The detection limit of DA was achieved to be 1.1×10^{-6} M in the presence of AA with the concentration of 200 times more than DA. This technique was also applied to the determination of DA in real samples.

Keywords: Boron-Doped Diamond Electrode; DA; AA; Differential Pulse Voltammetry

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1 Introduction

Dopamine (DA) is a biologically important compound, which plays a key role in neurotransmission [1, 2]. Some diseases, such as schizophrenia and Parkinson's disease, are related to the loss of DA containing in neurons. Simple and fast detection of DA is necessary for study in the fields of neurophysiology and clinical medicine.

Due to its electrochemical activity, DA can be detected using electrochemical methods; however there are two problems in the electrochemical detection [3, 4]. A major problem for the electrochemical detection of DA in real biological matrixes is the coexistence of

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some interfering compounds. Among these AA is of particular importance. Because AA exists at much higher concentrations than that of DA, and oxidizes at similar potentials with DA on a conventional electrode surface, the result is an overlap of their voltammetric responses [5]. Another problem is the fouling of the electrode surface by the adsorption of oxidation products. Consequently it is important to construct suitable electrodes and to establish a sensitive and selective detection method for DA.

Exploration of many kinds of chemically modified electrodes to detect DA selectively has occurred in the past years. One classification of these modified electrodes is a polymer thin film or self-assembled film [6–12]. These films always carry negative charges and so they can selectively detect the DA cation by electrostatic effect. Another is carbon nanotube or carbon fiber modified electrodes [13–15].

Recently, BDD electrodes have attracted more attention because of their novel electrode materials, which exhibits several excellent electrochemical properties, including a wide electrochemical potential window in either aqueous or non-aqueous media, very low background current, and high electrochemical stability. These properties enable the BDD electrode to render good reproducibility [16–18]. Superior to glassy carbon electrodes, it is easy to refresh the BDD electrode surfaces so it can be applied to analyze biological samples without frequent surface refreshment [19–21]. In addition, BDD electrodes have recently been found to show high resistance to fouling and insensitivity to dissolved oxygen. These properties make the BDD electrode a promising material for electroanalytical applications. It was reported that anodic pretreatment of the BDD electrode makes it possible to determine NADH and other bio-molecules separately [22, 23].

In the present work, we firstly realized the complete separation of DA and AA on the BDD electrode, which was pretreated in a 1 M H_2SO_4 solution for only 10 s at the potential of 2.8V. Here, DA and AA were successfully separated on the BDD electrode with an oxidative peak separation of 0.44V. The detection limit of DA was developed to be 1.1×10^{-6} M. The present method was also evidenced to be available for the determination of real samples of DA.

2 Experimental

2.1 Reagents

DA (Fluka Chemika, Analytical grade) was prepared to 0.1 mM and AA (Aldrich, analytical grade) was to 1 mM, a 0.1 M $HclO_4$ solution was used as the supporting electrolyte. The actual sample was a commercial DA Hydrochloride Injection Solution (Shanghai HeFeng Pharmaceuticals CO., LTD, 10 mg DA/mL, 2 mL per dose). All the other reagents were of analytical grade. All water used was double distilled water activated within flasks made out of synthetic quartz. High purity nitrogen was used to remove all dissolved oxygen in the solution.

2.2 Electrode preparations

The diamond thin films were grown on a roughened n-type silicon substrate by a method of microwave plasma chemical vapor deposition (MWCVD) [24]. The surface area of the bare BDD electrode was 0.1 cm^2. The BDD electrode was ultrasonic rinsed with distilled water before measurement. The anodic pretreatment and refreshment of the BDD electrode is done by applying the potential of 2.8 V on the BDD electrode in a 1 M H_2SO_4 solution for just 10 s. The glassy carbon electrode (GC, 3 mm diameter, CHI) was polished on flat sheet glass with alumina powder of 1.0, 0.3, 0.05 μm grain size in turn, and then sonicated and rinsed in double distilled water.

2.3 Electrochemical Measurements

Electrochemical measurements were recorded using the CHI660 Electrochemical Workstation (CHI, USA). A three-electrode cell was used in electrochemical measurements, with the BDD or GC electrode as the working electrode, a Pt wire as the auxiliary electrode and Ag/AgCl (3 M KCl) electrode as the reference electrode. Both cyclic voltammetry and differential pulse voltammetry were adopted to study the electrochemical behavior of DA and AA. Electrochemical measurements were carried out at 25°C. All potentials in the paper were measured against the Ag/AgCl reference electrode. Unless otherwise specified, the sweep rate in CVs is 0.1 V s^{-1}, and the DPV parameters are as follows: the increment E of 0.004 V; Amplitude of 0.05 V; Pulse width of 0.05 s; Pulse period of 0.2 s.

3 Results and discussion

3.1 Separation of DA and AA on BDD electrode

Cyclic voltammetry was employed to investigate the electrochemical behavior of DA and AA on the GC electrode surface, as shown in Fig. 1. It can be seen that the oxidative peak potentials of DA and AA were at 0.545 V and 0.556 V, respectively. The peak potentials of these two substances were so close to each other that they overlapped in cyclic voltammograms obtained on the GC electrode.

For comparison, a similar experiment was performed on the BDD electrode. From Fig. 2, we can see that the oxidative peak potentials of DA and AA were at 0.64 V and 1.16 V respectively. Fig. 2 also shows CV of DA with the coexisting of AA obtained on the BDD electrode; the peak separation of DA and AA was achieved to be 0.44 V. From this figure, it can be assumed that DA and AA might be separated on a BDD electrode by means of cyclic voltammetry, but as shown in Fig. 2, with the coexistence of AA, the oxidative peak of DA becomes broad, flat, and steamed bread like. The peak potential of DA is indistinguishable and the value of the peak currents for DA is hard to read. From this we can conclude that CV is an unfavorable method for the separation of DA and AA and can not be used to determine DA which is interfered the presence of AA.

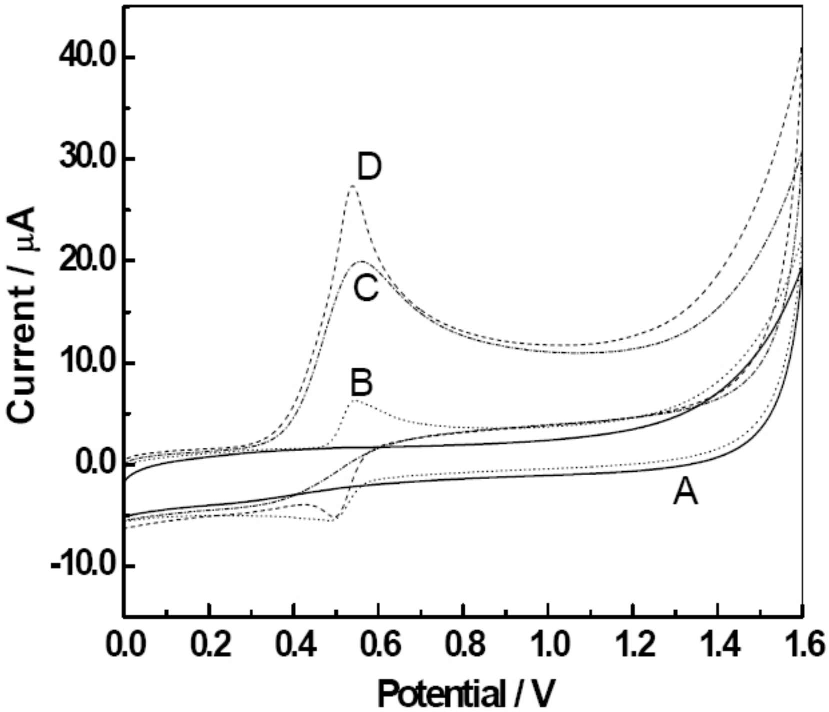

Fig. 1 CVs obtained on GC electrode in 0.1 M $HclO_4$ solution(A), A+ 1×10^{-4} M DA (B), A+1.0×10^{-3} M AA (C), and A+ 1×10^{-4} M DA +1.0×10^{-3} M AA (D) ; (Sweep rates 0.1 V s^{-1}).

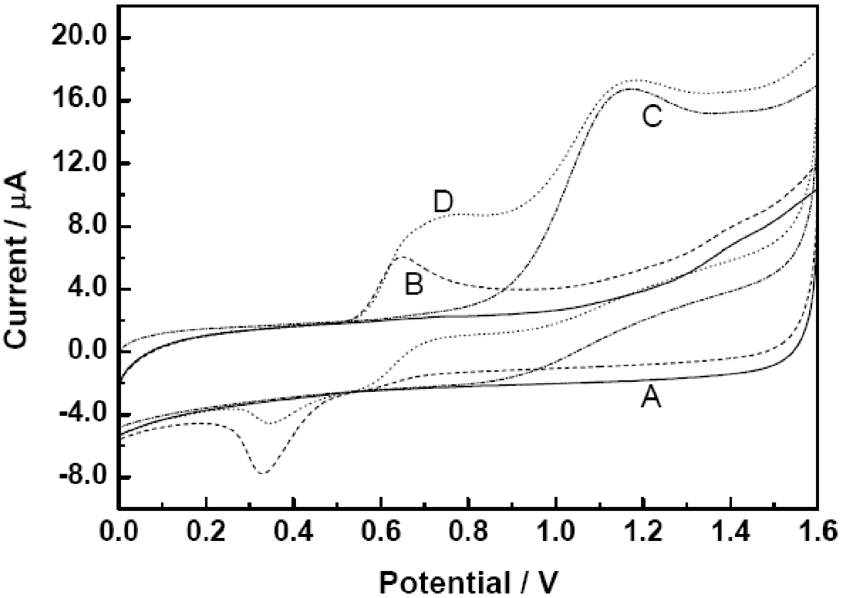

Fig. 2 CVs obtained on BDD electrode in 0.1 M $HClO_4$ solution(A), A+ 1×10^{-4} M DA (B), A+1.0×10^{-3} M AA (C), and A+ 1×10^{-4} M DA +1.0×10^{-3} M AA (D) ; (Sweep rates 0.1 V s^{-1}).

In order to clearly and more accurately determine DA in the presence of AA, we employed differential pulse voltammetry, a usual electroanalytical method with low non-faradic current, high sensitivity and good resolution. Fig. 3 depicts a differential pulse voltammogramm (DPV) of DA in the presence of AA on the GC electrode. We can see that the oxidation peaks from the separated solutions are at +0.495 V for DA and +0.444 for AA, respectively. The oxidation peaks of DA and AA in DA/AA binary mixture fully overlap. It is obvious that DA and AA can not be separated effectively on the GC electrode.

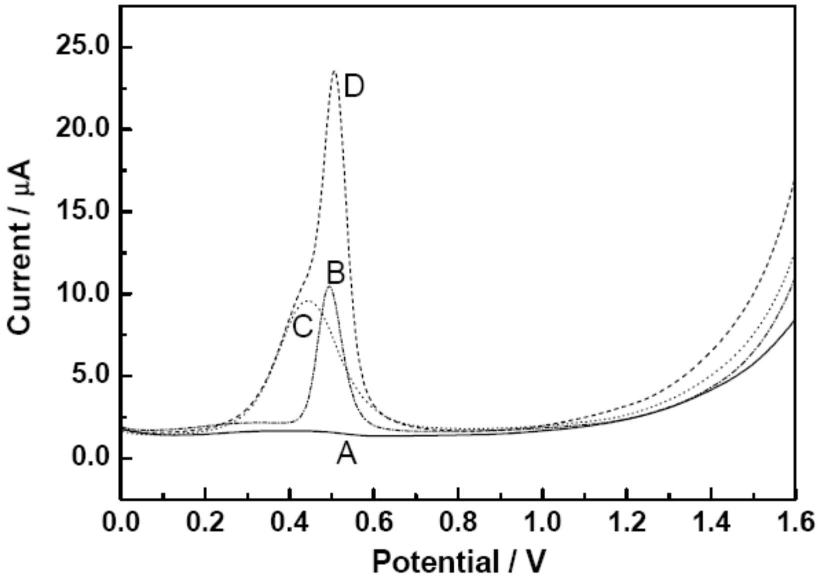

Fig. 3 DPVs obtained on GC electrode in 0.1 M $HclO_4$ solution(A), A+ 1×10^{-4} M DA (B), A+1.0×10^{-3} M AA (C), and A+ 1×10^{-4} M DA +1.0×10^{-3} M AA (D) (The increment E: 0.004 V; Amplitude: 0.05 V; Pulse width: 0.05 s; Pulse period: 0.2 s).

Compared to the response obtained on the BDD electrode, in DA/AA binary mixture, DA shows a well defined oxidation peak near +0.6 V, while that of AA is at +1.06 V (seen in Fig. 4). Thus the oxidation of DA is completely separated from AA by DPV on the anodic treated BDD electrode. Of particular interest is that the current response of DA increased from 4.78 μ A to 7.26 μA when 1 mM AA has been added into the same concentration of DA solution. It is assumed that the oxidation of DA may be accelerated by the coexistence of AA. Further study deserves to be performed to understand why this occurs.

As we know, the BDD surface is oxygen-terminated after anodic pretreatment in acidic solutions. The interaction between the ammonium group of protonated DA in 0.1 M $HclO_4$ and oxygen-terminated BDD is relatively strong; the adsorption of DA on the anodic pretreated BDD surface is much higher than that on GC and hydrogen-terminated BDD electrode surfaces. However, the oxygen-containing groups on AA attracted the C=O surface groups on the oxidized diamond much less strongly, so the oxygen-terminated BDD surface favors the separation of DA and AA oxidation peaks.

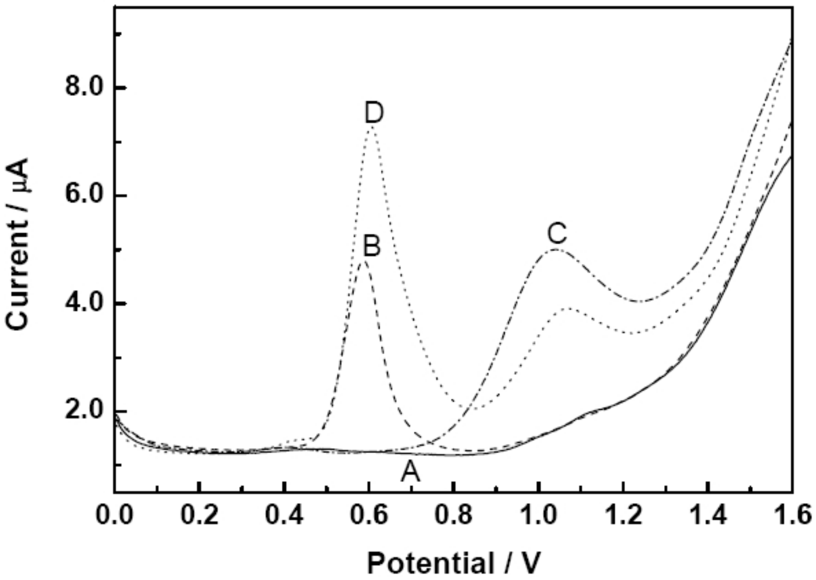

Fig. 4 DPVs obtained on BDD electrode in 0.1 M HclO$_4$ solution(A), A+ 1×10^{-4} M DA (B), A+1.0×10^{-3} M AA (C), and A+ 1×10^{-4} M DA +1.0×10^{-3} M AA (D) (The increment E: 0.004 V; Amplitude: 0.05 V; Pulse width: 0.05 s; Pulse period: 0.2 s).

3.2 Selective determination for DA in the presence of AA

As mentioned above, DA and AA were completely separated using the BDD electrode and differential pulse voltammetry. The calibration experiments for DA were firstly performed on the BDD electrode, and the DPV curves of different DA concentrations were shown in Fig. 5. The oxidation peak current of DA vs. its concentration was linear in the range from 5×10^{-6} M to 1×10^{-4} M, and the regression equation was $i_p(\mu\mathrm{A}) = 1.368 + 0.035C$ (μM) with a detection limit of 1.8×10^{-6} M at a signal to noise ratio of 3δ (where δ is the standard deviation of a blank solution, n = 10).

Next, the selective determination of DA and AA was carried out. Fig.6 shows the DPV of DA obtained on the BDD electrode in the presence of 1×10^{-3} M AA. The oxidation peak current (i_p) for DA was proportional to DA concentration in the range of 5×10^{-6} M to 1×10^{-4} M and the linear regression equation was $i_p(\mu\mathrm{A}) = 1.251 + 0.0585C$ (μM), and the correlative coefficient r was 0.9999. The detection limit was 1.1×10^{-6} M (3δ/S). Within this range, the maximum background concentration of AA was 200 times higher than the concentration of DA. Meanwhile, as demonstrated in Fig. 6, with a background concentration of AA maintained at 1×10^{-3} M, the oxidation peak current of AA decreased with the increasing concentration of DA. This may be due to the increased adsorption of oxidized DA on the BDD electrode with the increasing concentration of DA added into solution. So, the coexisting AA was more difficult to approach to the electrode with the increasing oxidation of DA, resulting in the decreasing peak current of AA.

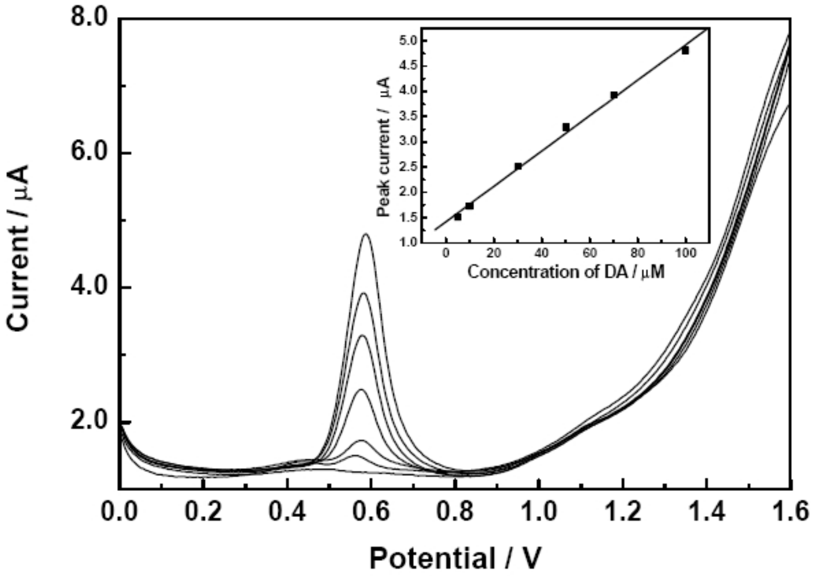

Fig. 5 DPVs of the DA in the absence of 1×10^{-3} M AA on BDD electrode; analytical concentration of DA , from bottom to top: 0.5×10^{-6}, 1×10^{-5}, 3×10^{-5}, 5×10^{-5}, 7×10^{-5}, 1×10^{-4} M. Inset figures is linear correlation between peak current and concentration of DA. (The increment E: 0.004 V; Amplitude: 0.05 V; Pulse width: 0.05 s; Pulse period: 0.2 s).

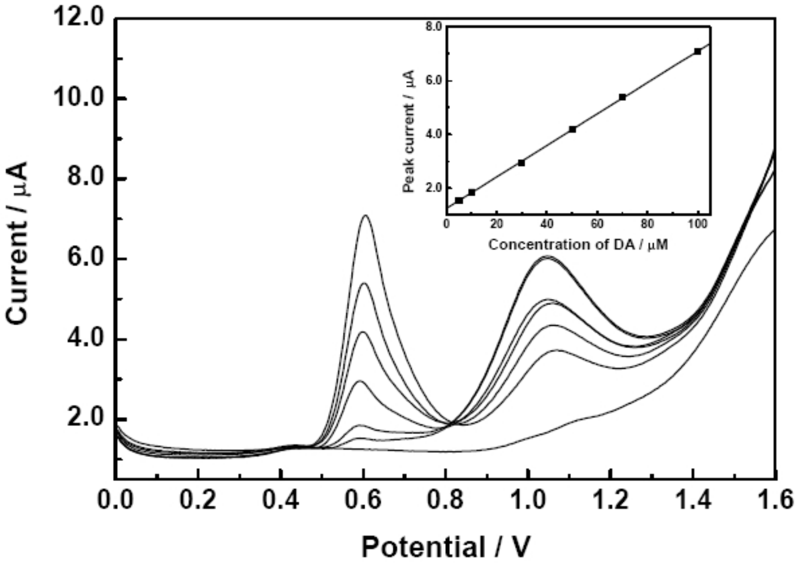

Fig. 6 DPVs of the DA in the presence of 1×10^{-3} M AA on BDD electrode; analytical concentration of DA , from bottom to top: 0.5×10^{-6}, 1×10^{-5}, 3×10^{-5}, 5×10^{-5}, 7×10^{-5}, 1×10^{-4} M. Inset figure is linear correlation between peak current and concentration of DA. (The increment E: 0.004 V; Amplitude: 0.05 V; Pulse width: 0.05 s; Pulse period: 0.2 s).

3.3 Measurement of Real Sample

Based on the above analytical method, the bare BDD electrode was employed to determine a real commercial sample of dopamine hydrochloride injection solution. The accuracy of the analytical method was validated by recovery measurement. The dopamine hydrochloride injection solution was diluted with double distilled water before measurements then five identical experiments were carried out for all the measurements. The identifiable concentration of DA in the commercial sample was 10 mg mL^{-1}. The determined average concentration of DA in the sample was 9.92 mg mL^{-1} (n=5) from which we can see that the results of analysis are in good agreement with the identifiable value of dopamine hydrochloride injection. The related standard difference (RSD) was 0.80%, and a relevant average recovery was 99.8% (n=5).

4 Conclusions

Selective determination of DA with the coexistence of AA was successfully developed on the BDD electrode by differential pulse voltammetry. The oxidation peaks of DA and AA were completely separated and the peak separation was developed to be 0.44 V. A good linear correlation between peak current and concentration of DA was obtained in a linear range from 5×10^{-6} M to 1×10^{-4} M in the presence of 1×10^{-3} M AA. The detection limit was achieved to be 1.1×10^{-6} M. Within this concentration range, the maximum background concentration of AA was 200 times higher than that of DA. This characteristic of the BDD electrode, together with our real sample analysis, provided a potential application of BDD electrodes in real biological determination.

Acknowledgements

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