Amperometric Determination of Dopamine Using Activated Screen-Printed Carbon Electrodes

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ABSTRACT

In this paper, we determined dopamine using screen-printed carbon electrodes (SPCEs) which was activated by 0.1 mol L⁻¹ NaOH solution to determine the electrode to improve the capability of detection. Cyclic voltammetry and differential pulse voltammetry were used to investigate the electrochemical behavior of dopamine. Cyclic voltammetry studies indicated that electrochemical oxidation of dopamine at the surface of SPCEs was decided by pH value. Different pulse voltammetry for dopamine oxidation at the SPCEs yielded a well-defined oxidation peak at 0.2 V in 0.1 mol L⁻¹ phosphate buffer (pH 5.0). The proposed electrodes showed great selectivity for dopamine and a good linear relationship between dopamine concentration and oxidation current was obtained within the range of 2.0 × 10⁻⁷ mol L⁻¹–300.0 × 10⁻⁶ mol L⁻¹ with a detection limit of 6.7 × 10⁻⁸ mol L⁻¹ (S/N = 3). In addition, the results showed that the precision in terms of reproducibility was 2.8% in the case of the activated SPCEs. The recovery rates of this technology were 95.40 to 103.4% with a relative standard deviation (RSD) of 2.7%.

Keywords: Screen-printed Carbon Electrodes, Activated, Dopamine, Electrochemical Detection

1. Introduction

Dopamine (DA), as one of the most important excitatory chemical neurotransmitter, secretes by the hypothalamus and pituitary gland that can directly affect people’s emotions. The concentration of DA in the central nervous system and psychological factors affected. DA is used to help cells transmit pulse and mainly responsible for the brain’s desire, feel the excitement and fun of information transmission, but also with addiction-related and plays an important role in the function of human metabolism, cardiovascular, renal, central nervous and hormonal systems. However, abnormal levels of DA may be related to Schizophrenia, Huntington’s disease, and Parkinson’s disease, the latter of which has symptoms of tremor, rigid posture, slow movements, and a shuffling unbalanced walk. So it is essential to develop methods to detect DA in biological fluids.

In addition, several approaches have been used to detect DA, such as Spectrophotometry, Chromatographic analysis, Electrochemical luminescence, electrophoresis, electrochemical method. Among them, the electrochemical method is the most widely used now, because of its fast detection time, simplicity, low cost, and no sample pre-treatment.

SPCEs are disposable microelectrodes realized by printing layers of different electroconductive and insulating inks with controlled their electrochemical performances on a substrate material and an insulating substrate. SPCEs have been successfully used as inexpensive disposable sensors and applied to a variety of monitoring and analysis. With the development of screen-printed electrode preparation technology, SPCEs have already been quantitative production owing to its low price and excellent performance. Using the SPCEs can further promote the development of sensors towards miniature, automation and commercialization.

In order to build the simpler sensor without reducing its detection performance, even more better than ever before for detecting of DA, we used SPCEs activated by 0.1 mol L⁻¹ NaOH solution rather than modified some materials which could improve the electrochemical performance of electrodes to detect DA and evaluated the influence of different electrochemical parameters in this paper. The electrochemical behaviors of DA at the SPCEs were investigated. It was found that DA yielded a pair of sharp peak type, well-defined reversible redox peaks at this electrode. In addition, SPCEs showed high stability and excellent reproducibility in the process of determining DA.

2. Experimental

2.1 Apparatus and reagents

Electrochemical measurements were carried out on a CHI660A electrochemical analytical instrument (CH Instrument Company, Shanghai, China). A three-electrode system was used, including SPCE or activated SPCEs as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter-electrode. The pH of solutions was measured with a pH meter (Precision Instrument Co., Ltd, Shanghai, China). Dopamine,
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Figure 1. Electrochemical Impedance Spectroscopy in 0.1 mol L\(^{-1}\) phosphate buffer (pH 5.0) containing 5 mmol L\(^{-1}\) [Fe(CN)\(_6\)]\(^{3-}/4-\) and 0.1 mol L\(^{-1}\) KCl for the bare electrode (a) and the activated electrode (b). The frequency range is between 0.05 and 10\(^4\) Hz.

Figure 2. Cyclic voltammograms at the bare electrode (solid lines a) and the activated electrode (dashed lines b) in of 1.0 \times 10^{-7} \text{mol L}^{-1}\) DA in phosphate buffer (pH 5.0); scan rate: 0.1 V s\(^{-1}\).

uric acid, ascorbic acid, portugal sugar were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ferricyanide, potassium ferrocyanide, NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All solutions were prepared with doubly distilled water.

2.2 Preparation of the activated screen-printed carbon electrode
20 µL of 0.1 mol L\(^{-1}\) NaOH solution was dropped on the surface of the SPCEs, and then the activated screen-printed electrode was obtained by scanning 20 s under constant potential of −1.2 V. Finally, the electrode was washed with double distilled water and dried by N\(_2\).

3. Results and Discussion

3.1 Characterization of the activated electrode
Electrochemical Impedance Spectroscopy (EIS) was used to study the surface of the electrode electrochemical reaction kinetics and the main parameter was the change of charge transfer resistance.\(^{18}\) Figure 1 showed the EIS of the bare electrode (a) and the activated SPCE (b) in 0.1 mol L\(^{-1}\) phosphate buffer (pH 5.0) containing 5 mmol L\(^{-1}\) [Fe(CN)\(_6\)]\(^{3-}/4-\) and 0.1 mol L\(^{-1}\) KCl. The result indicated that when the SPCE was activated, its \(R_{\text{on}}\) was the diameter of the semicircle at high frequency and the electrode was clearly greater than that of untreated electrode. This was because that a portion of the insulation material on the surface of SPCE was dissolved in NaOH solution and more conductive points were exposed, so the conductivity of SPCE has been well improved.

3.2 Electrochemical behavior of DA on the activated SPCE
Figure 2 showed cyclic voltammograms (CVs) of DA under the potential windows between −0.1 and 0.7 V (vs. Ag/AgCl) at the bare electrode and the activated electrode in phosphate buffer (pH 5.0). There was a pair of blunt, poorly reversible reduction oxidation peaks. Compared with the untreated electrode, DA showed a pair of well-defined waves which were more negative than that at bare electrode. Furthermore, the peak current increased, the difference of peak potential got smaller. It can be inferred that DA can effectively accumulate on the activated SPCEs surface and its electrochemical oxidation is promoted. The activated SPCEs offers a huge surface area and a large numbers of active sites, which is why activated electrodes are more active for DA and greatly increase the oxidation peak current.

3.3 Effects of activated potential on the peak current of DA
The activated potential was an important factor in the activated process. We investigated the peak current varies with the change of the activated potential in 50 µmol L\(^{-1}\) DA solution (Phosphate Buffer Diluted, pH 5.0). The results just as shown in Fig. 3, it is found that the peak current increased with decreasing activated potential up to −0.6 to −1.2 V. As the activated potential continuously reduce, the peak current decreased. The reason might be that a short anodization removed polishing debris and exposed a very clean pyrolytic carbon film in basic solution which could be used to microfabricate reactive sites on carbon surfaces, which was consistent with previous literature.\(^{19}\) In addition, as the activated potential was too high, the SPCEs were not fully activated, there are some the conductive carbon particles were not exposed. Therefore, the activated potential of −1.2 V was selected for further studies.

3.4 Effects of activated time on the peak current of DA
In the activated process, the length of the activated time played a crucial role in the activated electrode effect. To investigate the electrochemical behavior of DA on the activated electrode in 50 µmol L\(^{-1}\) DA solution (Phosphate Buffer Diluted, pH 5.0), cyclic voltammograms were recorded at different activated time (Fig. 4). The results showed that the peak current of DA reaches the maximum value when the activated time was activated at −1.2 V for 20 s. It was because that when the activated time was too short, some active sites were not exposed and SPCEs were not fully activated; meanwhile, as the activated time was too long, the SPCEs was destroyed. Thus, the activated time of 20 s was selected for further studies.

3.5 Effects of pH on the peak current of DA
The solution pH was an important factor in the electrochemical reaction for the detection of DA. Different pulse voltammetry was used to investigate the solution pH effects on the electrochemical behavior of DA at the activated electrode. Figure 5 showed that the peak current was the maximum at a pH was 5.0. The peak current decreased when the pH increased from 3 to 5. After that, the peak current decreased. There was a relationship between the peak potential of DA and solution pH, which can be described by the following equation: \(E_p = -0.0509 \text{pH} + 0.4737\) (\(R^2 = 0.9914\)). The redox process involved proton and electron transfer in the oxidation reduction reaction, which agrees with previous reports.\(^{20-22}\) Thus, the solution pH of 5.0 was selected for further studies.

3.6 Effects of the scan rate on the peak current of DA
In the case of other conditions being the same, sweep speed from low to high were measured respectively including 0.01 V s\(^{-1}\), 0.02 V s\(^{-1}\), 0.05 V s\(^{-1}\), 0.10 V s\(^{-1}\), 0.20 V s\(^{-1}\), 0.40 V s\(^{-1}\), 0.60 V s\(^{-1}\), 0.80 V s\(^{-1}\) and 1.00 V s\(^{-1}\). Then, we investigated the effect of the
scan rate on the electrochemical response in 0.1 M phosphate buffer (pH 5.0) containing 1.0 × 10⁻⁴ mol L⁻¹ DA by CV and the results were shown in Fig. 6. The current response was linearly increasing as the scan speed increasing, and the peak current were linearly a function of the square root of the scan rates with linear coefficients of 0.9948 and 0.9997, indicating that the electrochemical reaction of DA on the activated electrode was controlled by diffusion process.²³,²⁴

Figure 3. (A): CVs of different activated potentials to the response current of SPCE. (B): effect of activated potentials on oxidation peak current of 50 μmol L⁻¹ DA (Phosphate Buffer Diluted, pH 5.0). Scan rate: 0.1 V s⁻¹. (a-f): −0.6, −0.8, −1.2, −1.4, −1.6 V.

Figure 4. (A): CVs of different activated time to the response current of screen-printed electrode. (B): effect of activated times on oxidation peak current of 50 μmol L⁻¹ DA (Phosphate Buffer Diluted, pH 5.0). Scan rate: 0.1 V s⁻¹. (a-c): 10, 15, 20, 25, 30 s.

Figure 5. Effects of pH on the anodic peak current (A) and peak potential (B) in phosphate buffer. The base solution: 0.1 M phosphate buffer (pH 5.0) containing 1.0 × 10⁻⁴ mol L⁻¹ DA. Scan rate: 0.1 V s⁻¹.
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Figure 6. Cyclic voltammograms of ASPCE at different scan rates in 0.1 mol L\(^{-1}\) phosphate buffer (pH 5.0) containing 1.0 \times 10^{-4}\text{mol L}^{-1} DA (A) and linear relationship of redox peak current \((I_p)\) and \(v^{1/2}\) (B) scan rate (a-i): 0.01, 0.02, 0.05, 0.10, 0.20, 0.40, 0.60, 0.80, 1.00 V s\(^{-1}\).

Table 1. Comparison with different methods for detection of DA.

<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>Linear range (mol L(^{-1}))</th>
<th>Detection limit (mol L(^{-1}))</th>
<th>References</th>
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<tbody>
<tr>
<td>Poly-glutamic acid patterned carbon nanotube</td>
<td>(3.3 \times 10^{-5} - 2.66 \times 10^{-5})</td>
<td>(3.8 \times 10^{-7})</td>
<td>14</td>
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<tr>
<td>Polypyrrole-graphene</td>
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<td>(1.0 \times 10^{-7})</td>
<td>25</td>
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<tr>
<td>Multi-walled carbon nanotubes with methylene blue composite film</td>
<td>(4.0 \times 10^{-7} - 1.0 \times 10^{-5})</td>
<td>(2.0 \times 10^{-7})</td>
<td>26</td>
</tr>
<tr>
<td>Carbon nanotube-modified ionic liquid-nanozeolite</td>
<td>(8.12 \times 10^{-7} - 3.01 \times 10^{-4})</td>
<td>(1.16 \times 10^{-7})</td>
<td>27</td>
</tr>
<tr>
<td>Flower-like gold nanostructure</td>
<td>(1.0 \times 10^{-6} - 1.50 \times 10^{-4})</td>
<td>(2.0 \times 10^{-7})</td>
<td>28</td>
</tr>
<tr>
<td>Exfoliated graphite paper electrode</td>
<td>(5.0 \times 10^{-7} - 3.5 \times 10^{-6})</td>
<td>(1.0 \times 10^{-8})</td>
<td>29</td>
</tr>
<tr>
<td>Activated screen printing electrode</td>
<td>(2.0 \times 10^{-7} - 3.0 \times 10^{-4})</td>
<td>(6.7 \times 10^{-8})</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 7. DPVs of different concentrations of DA in phosphate buffer of pH 5.0. Concentration of DA. (a-i): 0.2, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0, 200.0, 300.0 \mu\text{mol L}^{-1}. Inset: the calibration curve of DA concentrations at the activated electrode. Scan rate: 0.1 V s\(^{-1}\).

3.7 Dopamine detection by the activated electrode

Because it had good resolution capability and high sensitivity than cyclic voltammetry, different pulse voltammetry was used to detect DA in phosphate buffer (pH 5.0). Activated Screen-Printed sensor for measuring DA had a good response effect. Figure 7 showed that the peak current of DA increases gradually. The peak current of DA was increased gradually with increasing its concentration apparently, however, the peak potentials remained unchanged. Furthermore, the peak current was linear from DA concentrations of \(2.0 \times 10^{-7}\) to \(300 \times 10^{-6}\text{mol L}^{-1}\) with a Linear regression equation of \(I_p\) (\(\mu\text{A}\)) = 0.114c (\(\mu\text{M}\)) + 0.4837 (R\(^2\) = 0.9988). The detection limit of this method was \(6.7 \times 10^{-8}\text{mol L}^{-1}\) (S/N = 3), which was better than that at most of modified electrodes (in Table 1). But, the activated electrodes had the advantage of low cost, simple preparation, mass production and cheap instrument. What’s more, this method helped to achieve the commercialization of sensor for detection of DA.

3.8 Reproducibility

In this experiment, reproducibility experiment of this method was carried out in 0.1 M Phosphate Buffer (pH 5.0). The same DA (100 \mu\text{mol L}^{-1}) solution was determined for seven times using seven electrodes, the relative standard deviation (RSD) of the peak current was 2.8% (n = 7). The results indicated that the activated screen-printed electrode had good reproducibility.

3.9 Interference experiment

The selectivity of the electrode had to be investigated before a new electrochemical sensor was built because of the oxidation potential of uric acid closed to that of DA. UA was the main interference for the determination of DA. In addition, the possible interference for DA determination was investigated including ascorbic acid, epinephrine, acetaminophen, Cl\(^{-}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), SO\(_4^{2-}\), NO\(_3^{-}\), and NO\(_2^{-}\). As can be seen from Fig. 8, for example, in the presence of 10-fold of uric acid, the peak current of DA decreased by 6.1%. In the presence of 10-fold of ascorbic acid, it decreased by 9.6%. In the presence of 20-fold of acetaminophen, it decreased by 8.3%. In the presence of 2000-fold of various ions, it decreases by 3.6%. The experimental results indicated that those chaff interferences had no effect on the determination of DA owing to the peak current change were below 10%, indicating the activated SPCEs had excellent selectivity for DA determination.
performed the activated pretreatment by sodium hydroxide solution. Finally, we developed a new convenient and sensitive screen-printed sensor for the determination of DA. The sensor had the advantages of simple, rapid, accurate and can detect the actual sample application, providing a new method for the future commercial development of DA sensor.

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References