

The Electro-analytical Effect of Poly (L-aspartic acid) Modified Glassy Carbon Electrode on Dopamine

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We detect dopamine (DA) by the poly (L-aspartic acid) modified carbon electrode (PL-ASP/GCE). The results show that DA can be electro-catalyzed by PL-ASP/GCE effectively. Carrying out the cyclic voltammetry (CV) scan, we get the optimum condition for the detection of DA: the acidity value is pH=5.0, scan rate is 100 mV/s, and the stirring time is 125 s. By using PL-ASP/GCE, the interference of ascorbic acid (AA) and uric acid (UA) on the detection of DA can be removed. The electrooxidation process for DA at PL-ASP/GCE is controlled by the diffusion in high concentration and the corresponding process is controlled by the adsorption in low concentration. In the optimum condition, the anodic peak current is well correlated with the concentration of DA in the range of $1.325 \times 10^{-5} \sim 1.18 \times 10^{-8}$ mol/L and the detection limit can reach 1.02×10^{-9} mol/L.

Keywords: PL-ASP/GCE, Dopamine, CV

1. INTRODUCTION

Dopamine (DA) is an important neurotransmitter in the brain and can be used to synthesize norepinephrine. DA belongs to a group of compounds known as catecholamines that plays a particularly important role in the regulation of physiological process in living systems [1-4]. The changes of the content of DA will induce some serious disease, such as Schizophrenia, Parkinson's disease, neuromuscular disorders, and so on [5-7]. Therefore, the study on the determination of DA is very important in the clinical application. Though there are many reports [8-12] on the detection of DA using modified electrode, to the best of our knowledge, the study on DA with the poly (L-aspartic acid) modified carbon electrode has not been disclosed until to date.

In this paper, we will detect DA by the poly (L-aspartic acid) modified carbon electrode (PL-ASP/GCE), which has good electro-catalysis to DA and can remove the interference of ascorbic acid

(AA) and uric acid (UA) effectively. The detection limit of DA at the modified electrode can arrive at 1.0×10^{-9} mol/L, so the modified electrode can be used to detect DA.

2. EXPERIMENTAL

The reagent of DA, L-Aspartic acid, ascorbic acid, and uric acid were supplied by China Pharmaceutical Biological Products Analysis Institute. Other employed solutions were prepared with analytic grade reagents and doubly distilled water.

Cyclic voltammetry (CV) was performed on an EG&G PAR M398 electrochemical impedance system with an M283 potentiostat/galvanostat. The three-electrode-system was used to carry out electrochemical tests. A glass carbon electrode (GCE) and PL-ASP/GCE served as a working electrode, respectively, a platinum wire served as a counter electrode, and a saturation calomel electrode (SCE) served as reference electrode. A Luggin capillary was used to connect the reference and working electrodes. Highly pure nitrogen gas was passed through the solution for 10 min to remove oxygen dissolved in solution before measurements, and all measurements were carried out under nitrogen atmosphere at room temperature ($25.0 \pm 0.1^\circ\text{C}$).

The basal electrode was pretreated as follow: GCE was polished using 6[#] grade Al_2O_3 polishing paper, ultrasonically washed with double distilled water for 10 min, dried by highly pure nitrogen gas, then scan in the potential range of $-0.5 \sim 1.80$ V in 0.5 mol/L H_2SO_4 solution with the scan rate of 100 mV/s until the CV curves were stable (about 10 circles).

The basal GCE served as a working electrode, a platinum wire served as a counter electrode, and a SCE served as reference electrode. The basal GCE scan for 8 circles in the potential range of $-0.8 \sim 2.5$ V in the phosphate buffer solution ($\text{pH}=5.0$, and the content of L-ASP was 2.0×10^{-3} mol/L) with the scan rate of 100 mV/s. The pretreated electrode was called PL-ASP/GCE after the electrode surface was drip washed by doubly distilled water.

3. RESULTS AND DISCUSSION

3.1. CV of DA at PL-ASP/GCE

The CV curves of GCE and PL-ASP/GCE in the DA solution and phosphate buffer solution ($\text{pH}=5.0$) are shown in Figure 1. There is no obvious redox peaks for GCE in 1.0×10^{-5} mol/L DA solution (curve c) and PL-ASP/GCE in phosphate buffer solution (curve b). However, there is a pair of sensitive redox peaks for PL-ASP/GCE in 1.0×10^{-5} mol/L DA and phosphate buffer solution (curve a). From curve a, we can get the corresponding electrochemical parameters as follow: anodic peak potential (E_{pa}) is 0.306 V, cathodic peak potential (E_{pc}) is 0.226 V, the peak-to-peak potential separation between anodic and cathodic peak potential (ΔE) is 80 mV, anodic peak current (i_{pa}) is -7.552×10^{-5} A, cathodic peak current (i_{pc}) is 7.617×10^{-5} A, and the ratio of $i_{\text{pa}}/i_{\text{pc}} \approx 1$. The experimental results show the redox reaction of PL-ASP/GCE in 1.0×10^{-5} mol/L DA solution is reversible and PL-

ASP/GCE can electro-catalyzed DA effectively. The fast electron transfer rate of DA at PL-ASP/GCE can contribute the three-dimensional space of PL-ASP/GCE, which can supply more space potential field. The carboxyl of PL-ASP can form hydrogen bond with the hydroxyl of DA. The formed hydrogen bonds will weaken the bond energy of hydroxyl in DA. In addition, the hydrogen bonds can enrich DA and cause the concentration of DA increasing at the electrode surface, so the peak current increase obviously.

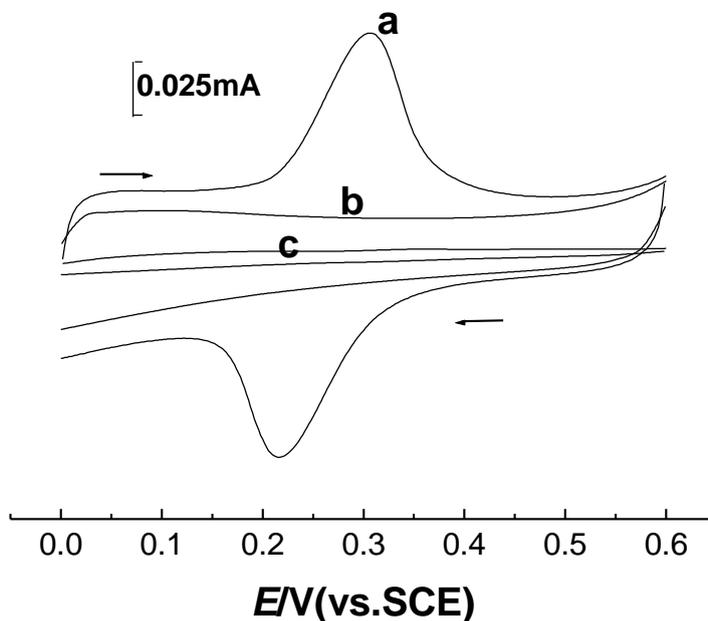


Figure 1. CV curves of PL-ASP/GCE in 1.0×10^{-5} mol/L DA and phosphate buffer solution (a), PL-ASP/GCE in the phosphate buffer solution (b), and GCE in 1.0×10^{-5} mol/L DA solution (c). Scan rate: 100 mV/s.

3.2. The choice of the condition of determination of DA

3.2.1. The effect of pH values of the base solution

The different acidity phosphate buffer solution is composed with 2.0 mol/L Na_2HPO_4 and 0.1 mol/L $\text{C}_6\text{H}_8\text{O}_7$, and the pH values are from 2.2 to 8.0. Then 1.05×10^{-5} mol/L DA solution is configured with the different acidity phosphate buffer solution. Figure 2 shows the CV curves of PL-ASP/GCE in 1.0×10^{-5} mol/L DA with different pH values. From which, we can find that the redox peak potentials of DA shift negatively with the pH values increasing. The relationship ($E_{\text{pa}} = -0.069 \text{ pH} + 0.6548$) between the redox peak potential of DA and the pH values are shown in Figure 3. The correlation coefficient is 0.9985 and the slope is -69.0 mV/pH . Therefore, we can conclude that the reaction of DA at PL-ASP/GCE is the proton participated redox reaction. As shown in Figure 3, the peak currents of DA increase in the range of pH 2.2~8.0 and reach the maximum at pH=5.0, so pH=5.0 is the best acidity value for the determination of DA with PL-ASP/GCE.

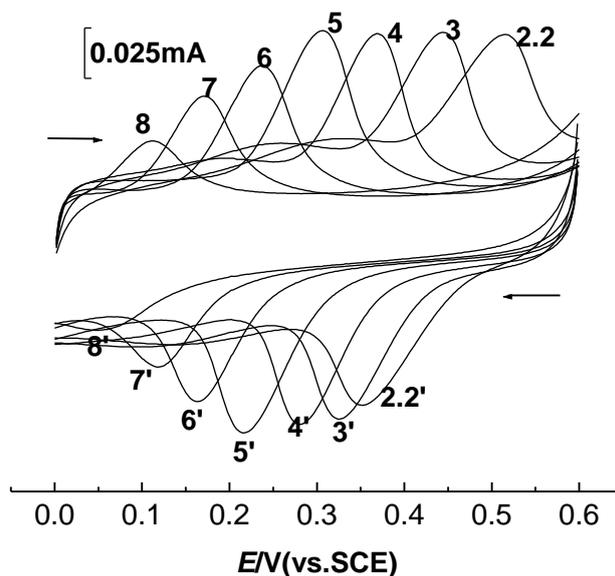


Figure 2. CV curves of PL-ASP/GCE in 1.0×10^{-5} mol/L DA with different pH values. Scan rate: 100 mV/s

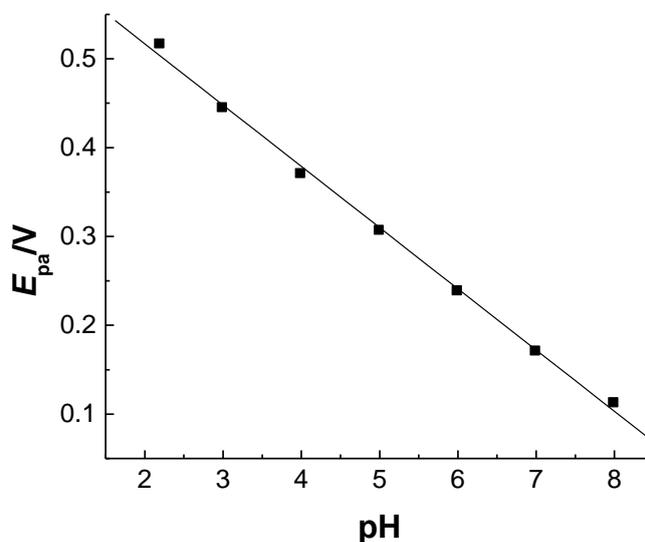


Figure 3. The relationships between the redox peak potential of DA and the pH values.

3.2.2. The effect of the scan rate

Figure 4 list the CV curves of PL-ASP/GCE in 1.0×10^{-5} mol/L DA with different scan rates. With the increasing of the scan rate in the range of 60~240 mV, the peak current increases accordingly. Nevertheless, E_{pa} will shift positively, E_{pc} will shift negatively, and ΔE will increase with the increasing of the scan rate, which will lead to the reversibility of the reaction of DA at PL-ASP/GCE decrease. Comprehensive consideration suggests that the scan rate to determine DA is 100 mV/s.

To investigate the control model of DA at PL-ASP/GCE surface, we carried the CV scan in the DA solution with different concentrations at the scan rate of 60~240 mV/s. The relationships between -

$\lg i_{pa}$ and $-\lg v$ in DA solution with different concentrations are shown in Figure 5. In the high concentration solution, the slope is close to 0.5, which demonstrates that DA at PL-ASP/GCE in the high concentration solution is controlled by diffusion. On the other hand, the slope is about 1 in low concentration solution, so the corresponding control model is controlled by adsorption. As the current is influenced by the gathering time in the low concentration solution of DA, therefore, we will take the stir step to determine DA.

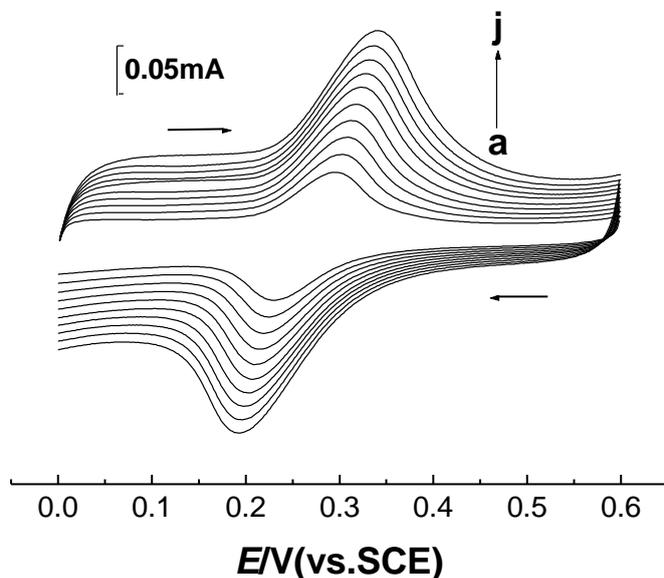


Figure 4. CV curves of 1.0×10^{-5} mol/L DA at PL-ASP/GCE. Scan rate (v): (a) 60; (b) 80; (c) 100; (d) 120; (e) 140; (f) 160; (g) 180; (h) 200; (i) 220; (j) 240 mV/s

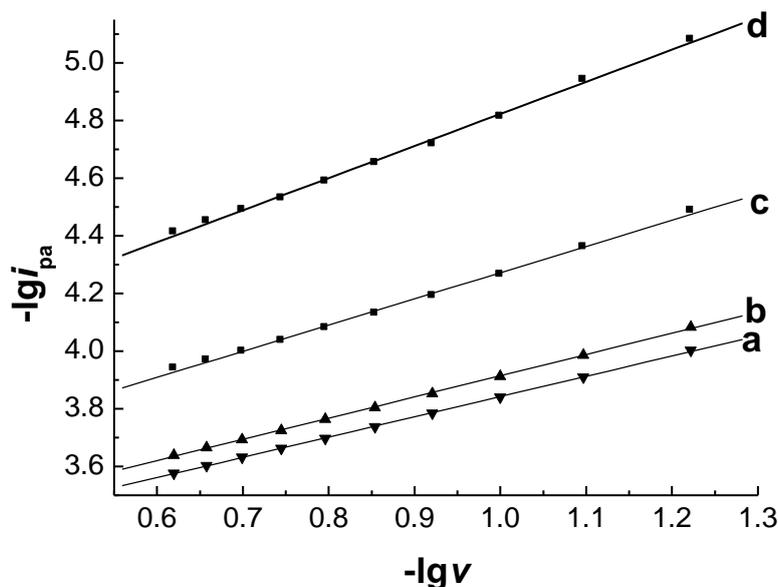


Figure 5. The relationships between $-\lg i_{pa}$ and $-\lg v$ in different concentrations solution of DA. Concentration of DA: (a) 100; (b) 10; (c) 1.0; (d) 0.1; (e) 0.01 ($\times 10^{-5}$ mol/L). Scan rate (v) range: 60~240 mV/s

3.2.3. The effect of the gathering time

As we stated above, the gathering time will influence the peak current obviously. Table 1 shows the influence of the stirring time on the peak potentials and currents of DA. We can find from Table 1 that i_{pa} increases with the stirring time extending and reaches the maximum for the stirring time of 125 s. To extend the stirring time, the peak current change a little, which suggests that DA is saturated the electrode surface for the stirring time of 125 s. Therefore, the best stirring time is 125 s for the experiment.

Table 1. Influence of the stirring time on the peak potentials and peak currents of DA^a.

t/s	E_{pa}/V	E_{pc}/V	$i_{pa}/10^{-5}A$	$i_{pc}/10^{-5}A$
60	0.286	0.236	-1.768	2.051
70	0.292	0.228	-3.349	4.011
80	0.298	0.224	-5.065	5.681
90	0.304	0.220	-6.262	6.908
100	0.308	0.218	-6.632	7.623
110	0.310	0.218	-7.005	7.794
120	0.310	0.218	-7.328	7.925
125	0.310	0.216	-7.633	7.986
130	0.310	0.216	-7.636	7.983
135	0.310	0.218	-7.703	7.994

^a $C_{DA}=1.05\times 10^{-5}$ mol/L. Scan rate: 100 mV/s

3.3. The working curves and detection limit

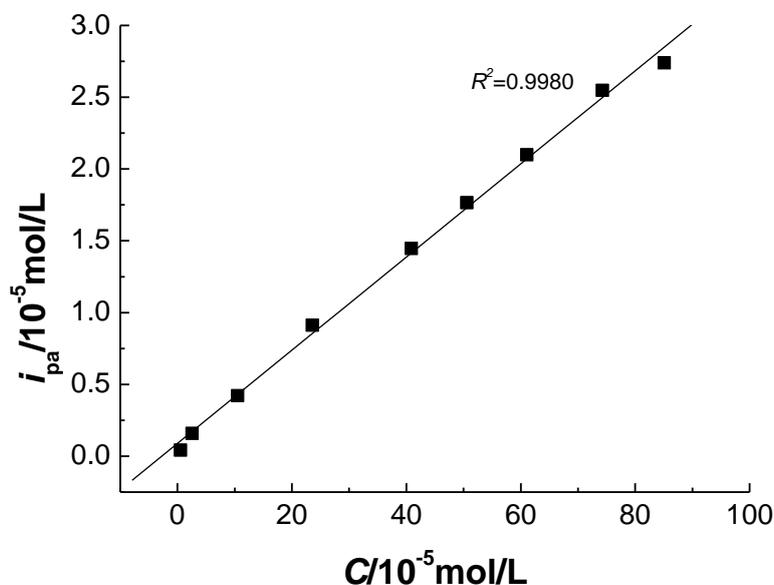


Figure 6. The relationships between i_{pa} and the concentrations of DA at GCE in phosphate buffer solution (pH=5.0).

The relationships between i_{pa} and the concentrations of DA at GCE in phosphate buffer solution are shown in Figure 6. i_{pa} is well correlated with the concentration of DA in the range of $5.15 \times 10^{-6} \sim 8.51 \times 10^{-4}$ mol/L. The equation of linear regression is $i_{pa}(A) = 0.0325 C + 8.94 \times 10^{-7}$, the correlation coefficient is 0.9980, and the detection limit is 1.02×10^{-6} mol/L.

The relationships between i_{pa} and the concentrations of DA at PL-ASP/GCE in phosphate buffer solution are shown in Figure 7 (A) (the concentration of DA is $1.06 \times 10^{-4} \sim 1.325 \times 10^{-5}$ mol/L) and Figure 7 (B) (the concentration of DA is $1.325 \times 10^{-5} \sim 1.18 \times 10^{-8}$ mol/L). As shown in Figure 7 (A) and (B), i_{pa} is well correlated with the concentration of DA in the range of $1.06 \times 10^{-4} \sim 1.325 \times 10^{-5}$ mol/L and $1.325 \times 10^{-5} \sim 1.18 \times 10^{-8}$ mol/L. The correlation coefficients are 0.9972 and 0.9985, respectively, and the detection limit is 1.02×10^{-9} mol/L. The sectional linear relation is attribute the different control model at PL-ASP/GCE in the different concentration solution of DA.

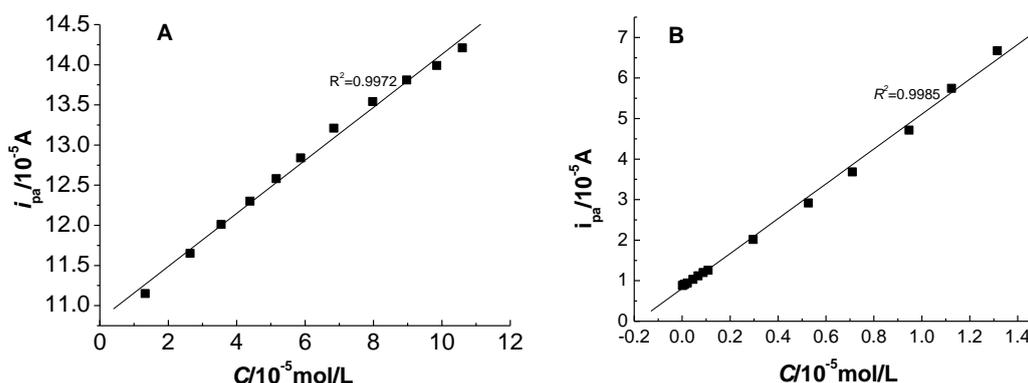


Figure 7. The relationships between i_{pa} and the concentrations of DA at PL-ASP/GCE in phosphate buffer solution. (A): the concentration of DA is $1.06 \times 10^{-4} \sim 1.325 \times 10^{-5}$ mol/L; (B): the concentration of DA is $1.325 \times 10^{-5} \sim 1.18 \times 10^{-8}$ mol/L.

3.4. The interference experiment

Ascorbic acid (AA) and uric acid (UA) can coexist with DA in the brain and body fluid, and the E_{pa} of them is very close at the solid electrode, which will interfere the detection of DA seriously [13]. PL-ASP/GCE can remove the interference of AA and UA effectively. The CV curves of DA in the presence of AA and UA at PL-ASP/GCE in phosphate buffer solution (pH=5.0) are shown in Figure 8. There is a pair of anodic peak (peak b) and cathodic peak (peak d) for DA (see Figure 8). The anodic peak c for AA and anodic peak a for UA are both demonstrate irreversible. The anodic peak potential difference between peak c and b is 191 mV, and the corresponding value is 157 mV between peak a and b. The results above suggest that presence of AA and UA will not interfere the detection of DA at PL-ASP/GCE.

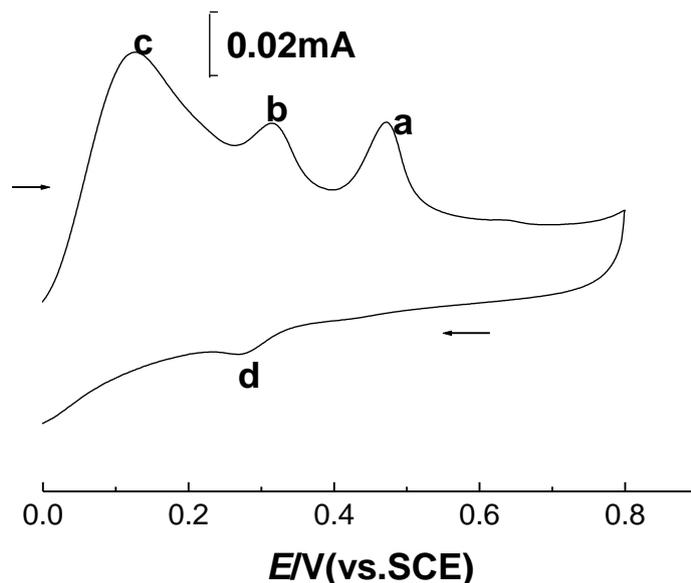


Figure 8. CV curves of DA in the presence of AA and UA at PL-ASP/GCE in phosphate buffer solution (pH=5.0).

4. CONCLUSIONS

PL-ASP/GCE can electro-catalyze DA effectively. From the CV scan, we get the optimum condition to detect DA: the acidity value is pH=5.0, scan rate is 100 mV/s, and the stirring time is 125 s. By using PL-ASP/GCE, the interference of AA and UA on the detection of DA can be removed.

The electrooxidation process for DA at PL-ASP/GCE is controlled by the diffusion in high concentration and controlled by the adsorption in low concentration. In the optimum condition, i_{pa} is well correlated with the concentration of DA in the range of $1.325 \times 10^{-5} \sim 1.18 \times 10^{-8}$ mol/L and the detection limit is 1.02×10^{-9} mol/L.

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