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Electrochemical determination of dopamine using a poly(2-picolinic acid) modified glassy carbon electrode

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A poly(2-picolinic acid) chemically modified electrode (CME) for the determination of dopamine (DA) by cyclic voltammetry is described. Compared with a bare glassy carbon electrode, the CME exhibits a 200 mV shift of the oxidation potential of DA in the cathodic direction and a marked enhancement of the current response. In pH 7.0 buffer solution, a linear calibration graph is obtained over the range from 2.5 $\times 10^{-7}$ to 1.0 $\times$ 10^{-5} mol dm^{-3} with a correlation coefficient of 0.998. The detection limit is 3.0 $\times$ 10^{-8} mol dm^{-3}. The modified electrode eliminated efficiently the interference from ascorbic acid (AA) when present in a 150-fold concentration ratio. It also showed excellent stability and reproducibility.

Dopamine (DA) is one of the naturally occurring catecholamines. It is an important compound for message transfer in the mammalian central nervous system. Changes in its concentration may lead to serious diseases such as Parkinson's. Hence, much research work on the determination of DA has been carried out.[1–7] However, a major problem encountered in the detection is the interference from ascorbic acid (AA),[8] which has an overlapping oxidation potential with DA on the solid electrodes. Chemically modified electrodes (CMEs) can be used to solve this problem. CMEs have attracted many investigators since the pioneering work in the mid-1970s.[9–12] One such electrode is the surface modified electrode. Methods of surface modification include adsorption, covalent bonding, attachment of polymer films, *etc*.[13–17] One common way is to cover the electrode surface with Nafion,[16,17] which has cation exchange properties. It is well known that DA exists in its protonated form at physiological pH (7.4), while AA exists as an anion. Hence, AA is repelled by the SO_3^- of the Nafion film and the interference of AA is eliminated. The other method is to cover the electrode surface with a self-assembled monolayer.[18,19] This kind of modified electrode does not block the fast reactions at the electrode surface. It can be used for fast sweep voltammetric analysis.[20] Another approach is to cover the electrode surface with electropolymerized films,[21–23] which have an electrocatalytic effect on DA. Polymer film modified electrodes can be differentiated from other modification methods such as adsorption and covalent bonding because they commonly involve multilayer adsorption, which can provide more 'active sites' resulting in obvious analytical signals. Together with its ease of preparation, good stability and reproducibility, the polymer modified electrode is particularly advantageous for electroanalytical research.

Noble metal electrodes are easily contaminated. Therefore, graphite and glassy carbon are the main base materials of CMEs. In this paper, we present the preparation of poly(2-picolinic acid) modified glassy carbon electrodes (GCEs). The modified electrodes showed an electrocatalytic activity for the oxidation of DA. There was no obvious response for AA at these modified electrodes. Even when its concentration was as high as 2 mmol dm^{-3}, only a very weak peak appeared at 0.005 V. However, this did not interfere with the determination of DA, *i.e.*, the interference of AA could be eliminated. Hence, the modified electrode has good selectivity for the determination of DA in the presence of AA.

Experimental

Reagents

2-Picolinic acid was obtained from Fluka (Buchs, Switzerland). Dopamine hydrochloride was purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Ascorbic acid was from Beijing Chemical Factory (China). These and all other chemical reagents (analytical-reagent grade, Beijing Chemical Reagent Company, China) were used without further purification. All aqueous solutions were prepared in doubly distilled, de-ionized water.

Apparatus

A CHI 660A Electrochemical Workstation (CHI Instruments, Austin, TX, USA) was used for electrochemical measurements. A conventional three-electrode system was employed with a bare or poly(2-picolinic acid) modified GCE (2.0 mm in diameter) as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All potentials reported in this paper were referenced to the SCE.

Procedures

The bare GCE was polished successively with 0.3 and 0.05 μm Al_2O_3 slurry on emery paper. It was then rinsed with doubly distilled water, and sonicated in 1 + 1 HNO_3, acetone and doubly distilled water for 10 min, respectively. After being cleaned, the electrode was immersed in 0.1 mol dm^{-3} NaCl solution containing 1.0 mmol dm^{-3} 2-picolinic acid and was conditioned by cyclic sweeping between −1.5 and 2.5 V at 100 mV s^{-1} for 15 scans. The modified electrode was then electroactivated by cyclic voltammetry from −0.4 to +0.6 V in PBS of pH 7.0.

All measurements were conducted at room temperature. The electrochemical experiments were performed in a 25 cm^3 electrolytic cell with 10 cm^3 solutions, from which oxygen was removed by purging with high-purity nitrogen. All measurements were carried out under a nitrogen atmosphere.

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Results and discussion

Electrochemical modification of 2-picolinic acid at the GCE surface

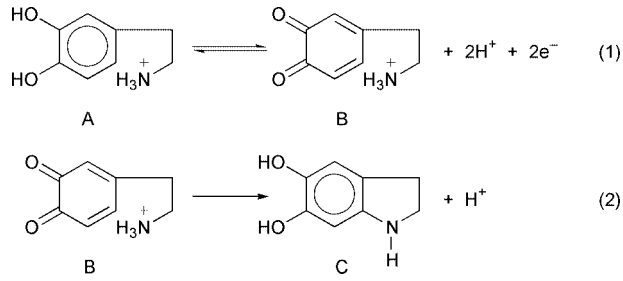
Fig. 1 shows the cyclic voltammograms of a 1.0 mmol dm^{-3} solution of 2-picolinic acid in 0.1 mol dm^{-3} NaCl. In the first cycle, there were no oxidation or reduction peaks. However, from the second cycle, two chemically irreversible cathodic peaks were observed, with cathodic peak potentials of −0.42 and −1.03 V, respectively, which might be attributed to the irreversible reduction of the pyridine ring of the 2-picolinic acid molecule. Moreover, during the polymerization, the cathodic peak currents increased continuously with repeated scans, which demonstrated that the 2-picolinic acid was not desorbed after the electrode reactions.

After modification, the electrode was carefully rinsed with doubly distilled water, and allowed to air-dry. It was then stored for later use.

Voltammetric behavior of dopamine at poly(2-picolinic acid) film CME

Fig. 2 shows the cyclic voltammograms of the poly(2-picolinic acid) film modified GCE in PBS of pH 7.0. No peaks were observed at the electrode over the potential range from −0.4 to +1.5 V.

Fig. 3 illustrates the cyclic voltammograms of DA on a bare GCE and CME in PBS of pH 7.0. It could be observed that the oxidation peak potential of DA shifted negatively from 0.40 to 0.20 V, *i.e.*, the overpotential decreased by 200 mV. Combined with the increase in the anodic peak current, these results indicated that the poly(2-picolinic acid) film exerts an electrocatalytic effect on DA. In addition, two reduction peaks appeared (see Fig. 3). The cationic current of peak 2 is large, while that of peak 3 is small. To establish the existence of peak 3, we successively repeated the cyclic voltammetric behavior of 0.1 mmol dm^{-3} DA in PBS of pH 7.0. From Fig. 4 it was found that peak 3 still appeared. The reasons for this are as follows [eqn. (1) and (2)]: DA (**A**) can be oxidized to dopaminequinone (**B**), which can undergo a ring closure reaction, resulting in leucodopaminechrome (**C**).[24,25]



Hence, we could conclude that peak 1 of Fig. 3 corresponded to the oxidation of DA (**A**) to dopaminequinone (**B**), peak 2 corresponded to the reduction of dopaminequinone (**B**) to DA (**A**), and peak 3 corresponded to leucodopaminechrome (**C**).

The effect of scan rate on the anodic peak current of DA was studied. As the scan rate increased, the oxidation peak current increased. The I_{pa} was proportional to the square root of the scan rate over the range 10–150 mV. The appropriate regression equation was: $I_{pa}(\mu A) = -3.3603 + 2.0885C$ (mol dm^{-3}), with a coefficient of 0.9988, which illustrates a diffusion-controlled process in the solution.

The effect of pH was complicated. Since it is near to physiological conditions, pH 7.0 was chosen in this work.

Analytical characterization

The poly(2-picolinic) acid modified GCE can be applied to the detection of the concentration of DA. Cyclic voltammetry was

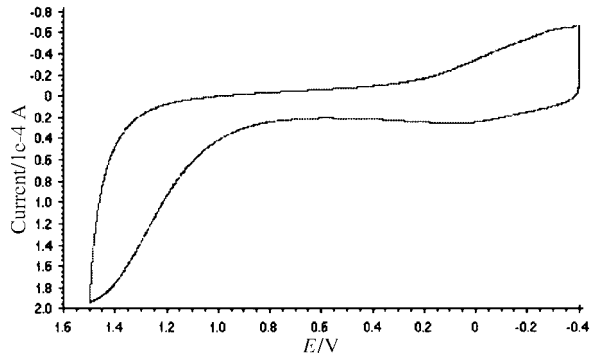


Fig. 1 Cyclic voltammogram of 2-picolinic acid in 0.1 mol dm^{-3} NaCl solution. Scan rate: 100 mV s^{-1}.

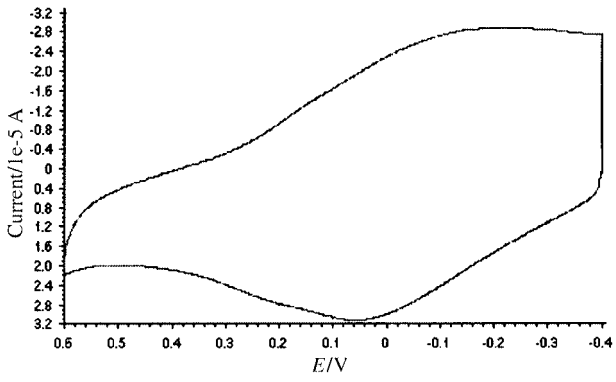


Fig. 2 Cyclic voltammogram of poly(2-picolinic acid) modified electrode in PBS of pH 7.0. Scan rate: 100 mV s^{-1}.

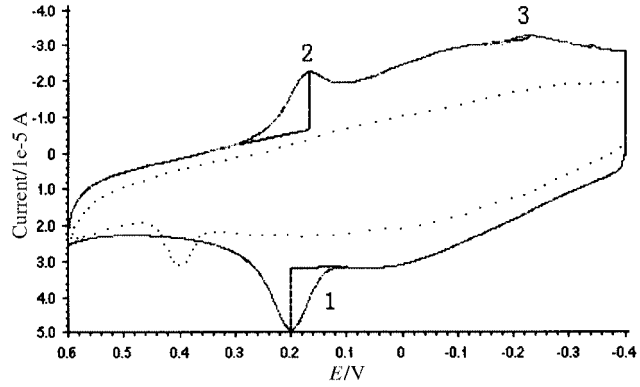


Fig. 3 Cyclic voltammograms of 0.1 mmol dm^{-3} DA in PBS pH of 7.0 at bare (·····) and poly(2-picolinic acid) film CME. Scan rate: 100 mV s^{-1}.

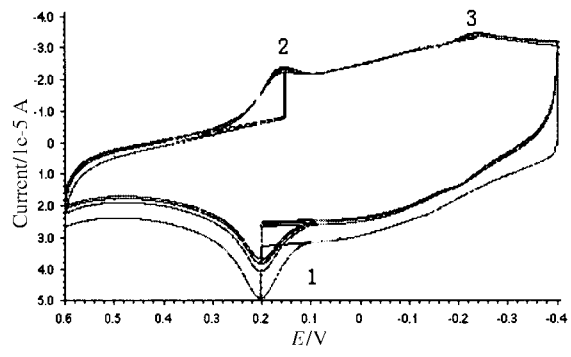


Fig. 4 Repeated cyclic voltammograms (five scans) of 0.1 mmol dm^{-3} DA in PBS of pH 7.0 at poly(2-picolinic acid) film CME. Scan rate: 100 mV s^{-1}.

employed in the experiments and the oxidation peak current of DA was used as the analytical signal. Experiments indicated that there was a linear relationship between the oxidation peak current of DA and its concentration over the range from 2.5×10^{-7} to 1.0×10^{-5} mol dm^{-3}. The detection limit for DA was 3.0×10^{-8} mol dm^{-3}. A DA concentration level of 1.0×10^{-5} mol dm^{-3} was used to examine the reproducibility of the poly(2-picolinic acid) CME. The relative standard deviation (RSD) of ten determinations was 2.7%, which showed that the poly(2-picolinic acid) CME has a good reproducibility.

Interference studies

In order to assess the possible analytical applications of the method described above, the effect of AA, organic acids and inorganic ions on the determination of DA was studied.

There was no obvious current response of AA at the poly(2-picolinic acid) CME. Even when its concentration was as high as 2 mmol dm^{-3}, only a very weak peak appeared at 0.005 V (see Fig. 5). However, this did not interfere with the determination of DA (see Fig. 6). Fig. 6 shows the cyclic voltammograms obtained at the polymer modified electrode. Fig. 6(b) was recorded in 0.1 mmol dm^{-3} DA solution. Fig. 6(c) was recorded in a solution containing 0.1 mmol dm^{-3} DA and 2 mmol dm^{-3} AA. The difference between them was very small, which indicated that 2 mmol dm^{-3} AA did not interfere with the determination of 0.1 mmol dm^{-3} DA. The reason for this is as follows: in PBS solution of pH 7.0, DA exists in the cationic form. Hence, the surface-active group COO^- of poly(2-picolinic acid) can attract DA into the polymer film. Also, through hydrogen bonding the polymer film can enhance the electron-transfer kinetics, *i.e.*, the permselective transport of DA; therefore, the selectivity, sensitivity, and reproducibility for DA are increased. In contrast, AA exists in the anionic form in PBS solution of pH 7.0. It is repelled by the surface functional group COO^-. Hence, it cannot enter the polymer film to the same extent as DA, and the interference with the determination of DA is diminished.

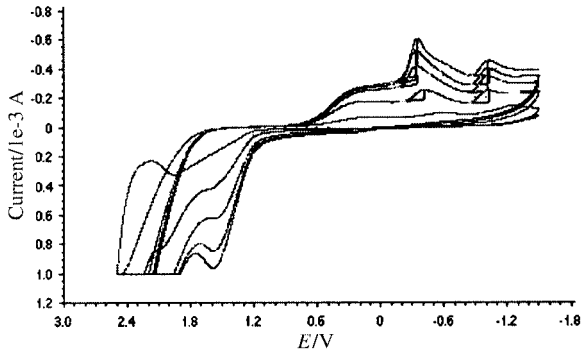


Fig. 5 Cyclic voltammograms of 2 mmol dm^{-3} AA in PBS of pH 7.0 at poly(2-picolinic acid) film CME. Scan rate: 100 mV s^{-1}.

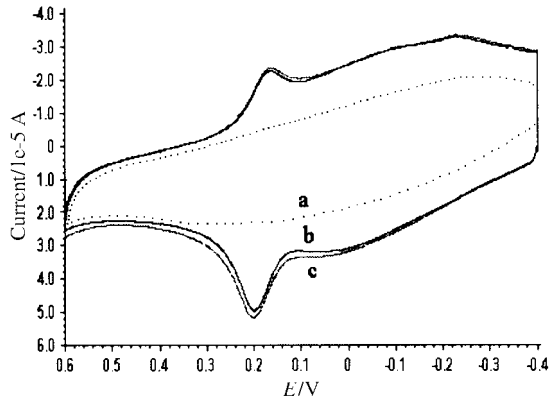


Fig. 6 Cyclic voltammograms recorded in (a): PBS of pH 7.0; (b): (a) + 0.1 mmol dm^{-3} DA; (c) (b) + 2 mmol dm^{-3} AA at the polymer modified electrode. Scan rate: 100 mV s^{-1}.

Table 1 Results of determination of DA in injections (n = 10)

Sample	Content/ mg l^{-1}	Proposed method/ mg l^{-1}	RSD (%)	Recovery (%)	Pharmacopeia method[26]/mg l^{-1}
1	10.0	9.97	3.2	99.7	10.32
2	10.0	10.05	2.4	100.5	10.44
3	10.0	10.43	2.6	104.3	10.71
4	10.0	9.95	3.6	99.5	10.27
5	10.0	9.89	3.0	98.9	10.25

Keeping the concentration of DA at a level of 1.0×10^{-5} mol dm^{-3}, no significant interference was observed from the following species: AA (150), NaCl (200), KCl (200), $Ca(NO_3)_2$ (200), glucose (10), citric acid (10) and tartaric acid (10), where the values in parentheses are the concentration ratios.

Analysis of samples

The proposed method can be efficiently used for the determination of DA in injections. The results are shown in Table 1, and are acceptable when compared with those given by the classical method.[26]

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References

1 A. Akiyama, T. Kato, K. Ishli and E. Yasydy, *Anal. Chem.*, 1985, **57**, 1518.
2 J. Ponchon, R. Cespuglio, J. M. Gonon and J. Pujol, *Anal. Chem.*, 1979, **51**, 1483.
3 P. Heiduschka and J. Dittrich, *Electroanalysis*, 1992, **4**, 223.
4 Z. Gao and A. Ivaska, *Anal. Chim. Acta*, 1993, **284**, 393.
5 M. R. Deakin, P. M. Kovach, K. J. Stutts and R. M. Wightman, *Anal. Chem.*, 1986, **58**, 1474.
6 A. C. Michael and J. B. Justile, Jr., *Anal. Chem.*, 1987, **59**, 405.
7 J. Wang and A. Walcarius, *J. Electroanal. Chem.*,1995, **407**, 183.
8 F. G. Gonon, M. J. Buda, R. Cespuglio, M. Jouvert and J. Pajol, *Nature (London)*, 1980, **286**, 902.
9 B. F. Watkins, J. R. Behling, E. Kariv and L. L. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 3549.
10 R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, 1973, **77**, 1401.
11 P. R. Moses, L. M. Wier and R. W. Murry, *Anal. Chem.*, 1975, **47**, 1882.
12 R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, 1973, **77**, 1411.
13 R. W. Murry, *Anal. Chem.*, 1987, **59**, 379A.
14 D. W. Abruna, *Coord. Chem. Rev.*, 1988, **86**, 135.
15 D. W. Arrigan, *Analyst*, 1994, **119**, 1953.
16 G. Nagy, G. A. Gerhardt, A. F. Oke, M. E. Rice and R. N. Adams, *J. Electroanal. Chem.*, 1985, **188**, 85.
17 J. M. Zen, G. Iiangovan and J. J. Jou, *Anal. Chem.*, 1999, **71**, 2797.
18 A. Dalmla, C. C. Liu and R. F. Savinell, *J. Electroanal. Chem.*, 1997, **430**, 20.
19 F. Malem and D. A. Mandler, *Anal. Chem.*, 1993, **65**, 37.
20 I. Lötzbeyer, W. Schuhmann and H. L. Schmidt, *J. Electroanal. Chem.*, 1995, **395**, 341.
21 G. Erdogdu, H. B. Mark, Jr. and E. Karagozler, *Anal. Lett.*, 1996, **29**, 221.
22 H. T. Xu, F. Kitamara, T. Ohsaka and K. Tokuda, *Anal. Sci.*, 1994, **10**, 399.
23 A. Ciszewski and G. Milczarek, *Anal. Chem.*, 1999, **71**, 1055.
24 M. D. Hawley, S. V. Tatawawadi, S. Piekarski and R. N. Adams, *J. Chem. Soc.*, 1967, **89**, 447.
25 M. Zhu, X. M. Huang, J. Li and H. X. Shen, *Anal. Chim. Acta*, 1997, **357**, 261.
26 Editorial Committee of the Ministry of Health of P. R. China, *Pharmacopeia of P. R. China, Part 2*, Chemical Industry Press, Beijing, 1995, p. 609.