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Short communication

Selective response of dopamine in the presence of ascorbic acid on L-cysteine self-assembled gold electrode

Guangzhi Hu, Yunchun Liu, Jun Zhao, Shiqiang Cui, Zhousheng Yang *, Yuzhong Zhang

School of Chemistry and Materials Science, Anhui Key Laboratory of Functional Molecular Solids, Anhui Normal University,Wuhu 241000, PR China

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Abstract

A L-cysteine (L-Cys) self-assembled modified gold electrode was used to detect dopamine (DA) by chronoamperometric method (CE) in the presence of ascorbic acid (AA). The defective limit is 2.0×10^{-8} mol L^{-1} ($S/N=3$). The proposed method was applied to detect DA in the samples with satisfied result.

Keywords: L-Cysteine; Modified electrode; Dopamine; Chronoamperometric method

1. Introduction

DA is one of the most significant catecholamine, which belongs to the family of excitatory chemical neurotransmitters [1,2] and plays a very important role in the function of the central nervous, renal, hormonal and cardiovascular system [3,4], which is a symptom of several diseases such as schizophrenia and Parkinsonism and to the HIV infection [5,6]. Hence, the determination of the concentration of this neurochemical is important. Various methods have been applied to detect DA, such as spectrophotometry [7], HPLC method [8], ion chromatography [9] and so on.

As well known, electrochemical approach is also used to detect DA. But, a major problem encountered with the detection of DA is the interference from AA (10^3 times higher than DA) that largely coexists with DA in the brain [10]. The irreversibility of its electrochemical property results in a large overpotential for oxidation at the conventional electrode [11]. In order to solve this problem, some modified electrodes such as pretreated carbon fiber electrode [12], nano-materials modified electrode [13,14], and polymer modified electrode [15,16], ion-exchange membrane electrodes [17,18] were applied to determine DA by their electrocatalytic oxidation. Ion-exchange membranes are mainly based on adsorption and electrostatic interaction, but a pre-concentration process is often needed before measurement, and these electrodes suffer from a memory effect, which will result in poor reproducibility.

Self-assembled monolayer (SAM) modified electrode have received much interest due to their simple preparation method and nicer stability [19–22]. Self-assembled monolayer of v-mercapto carboxylic acids HS–$(CH_2)_n$COOH on gold electrodes [23] have been reported to be used to determine DA by its electrocatalytic oxidation. The oxidation wave of DA shifts to less positive potential and AA is oxidized at more positive potentials ascribed to the negatively charged monolayer as compared to the bare gold electrode. Raj et al. [24] reported a cationic self-assembled modified electrode for the square-wave voltammetric detection of DA in the presence of AA. Zhang et al. [25] reported a DL-homocysteine self-assembled gold electrode, which has a good electrochemical response to DA in HAc-NaAc (pH 4.3) buffer solution.

In this paper, we reported a L-cysteine self-assembled gold electrode for amperometric sensor of DA in the presence of AA, which showed an electrocatalytic activity for the oxidation of DA. The redox reaction of DA on the modified electrode occurs at less potential. No redox signal of AA was found on L-Cys/Au electrode at window potential of DA, the modified electrode selective response to DA could be applied to determine dopamine under DA coexisting with AA condition.

* Corresponding author. Fax: +86 553 3869303.
E-mail address: yzhoushe@mail.ahnu.edu.cn (Z. Yang).

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2. Experimental

Electrochemical measurements were carried out on a CHI660A electrochemical workstation (CHI Instruments, Chenhua Corp., Shanghai, China). A conventional three-electrode system was employed with a bare electrode or L-Cys/Au (2.0 mm in diameter) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode.

L-cysteine (from Sigma) and DA (from Aldrich) were used as received. Other reagents used were of analytical grade. The L-Cys/Au electrode was prepared as in the following way: the surface of gold electrode was polished by 0.36 μm Al_2O_3, then sonicated in water for 5 min. The polished electrodes were electrochemically cleaned by cycling the potential scan between −0.20 and 1.70 V in 0.50 mol L^{-1} H_2SO_4 until the CV characteristics for a clean gold electrode [26]. The clean gold electrode was immersed into the deaerated solution containing 1.0×10^{-3} mol L^{-1} L-Cys for a certain time at room temperature, and then washed with triply distilled water and stored in 0.10 mol L^{-1} PBS (pH 7.0) at 4 °C for use. All aqueous solutions were prepared with triply distilled water from an all-quartz still. Prior to the experiment, solutions were purged with nitrogen for 15 min to remove oxygen. All the measurements were performed at room temperature.

3. Results and discussion

The cyclic voltammograms of 4.0×10^{-5} mol·L^{-1} DA in 0.1 mol·L^{-1} PBS (pH 7.0) on bare and L-Cys modified gold electrode were shown in Fig. 1. There is a pair of weak redox peaks observed on the bare gold electrode (see Fig. 1a). The difference between the anodic peak (E_{pa}) and the cathodic peak potential (E_{pc}) is 296 mV. However, a well-defined redox wave of DA was obtained on the L-Cys/Au electrode at E_{pa}=204 mV and E_{pc}=153 mV (as Fig. 1b), respectively. The E_{pa} shifts 186 mV negatively and the E_{pc} shifts 57 mV positively. The

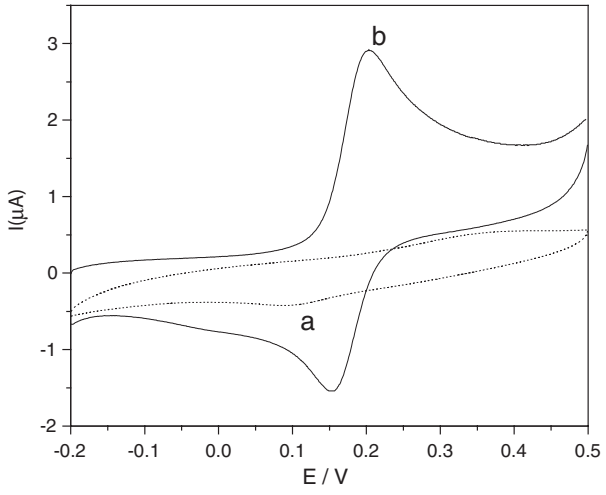

Fig. 1. Cyclic voltammograms of 4.0×10^{-5} mol·L^{-1} DA in 0.1 mol L^{-1} PBS (pH 7.0), scan rate: 50 mV/s, (a) on the bare Au electrode, (b) on the L-Cys/Au electrode.

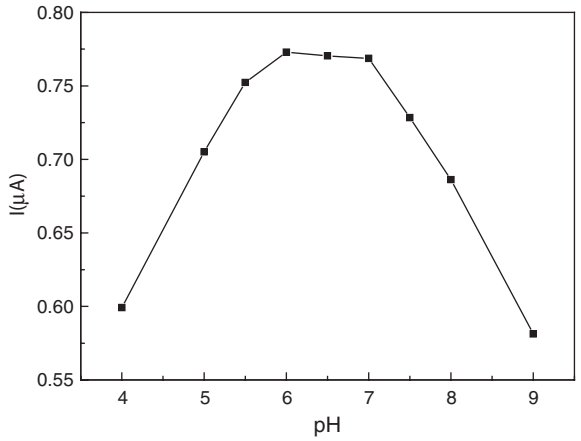

Fig. 2. The dependence of the anodic current of 4.0×10^{-5} mol·L^{-1} DA on solution pH in 0.1 mol·L^{-1} PBS on the L-Cys/Au electrode. Scan rate: 50 mV/s.

difference (ΔE_p) between E_{pa} and E_{pc} is 51 mV. The anodic peak current is 16 fold to the bare electrode. The above results suggested that there was an electrocatalytic response to dopamine on the L-Cys/Au electrode. The peak currents of DA solution on the L-Cys/Au electrode remained to be unchanged by continuous cyclic scanning. After the L-Cys/Au being immersed into the solution of 2.0×10^{-4} mol·L^{-1} DA for 5 min and then rinsed with distilled water, no response of DA was observed on the L-Cys modified electrode. Both of the results proved that DA was not adsorbed onto surface of the modified electrode.

The effect of solution pH on the response of DA was also examined in the range 4.0–9.0 (shown in Fig. 2). The anodic peak current (I_{pa}) enhanced with increasing solution pH until it reached 5.5. But when solution pH exceeds 7.0, the I_{pa} decreased with increment of pH. The probable reason was explained as follows: the negative carboxyl group of L-Cys molecule on electrode surface increased with increasing solution pH, thus, more positive DA molecules were attracted to the electrode surface. The I_{pa} increased with the increase of pH over the range 4.0–5.5. It trended to change slowly in the pH range from 5.5 to 7.0. Then, the protonation degree of DA decreased with the increasing pH. When solution pH is higher than 7.0, the negative carboxylic group of electrode surface is increased, but DA carrying positive charge decreased more. The static attraction interaction between DA and L-Cys mololayer decreased. Therefore, the anodic peak current of DA decreased with the increase of pH in the range 7.0–9.0. Since pH 7.0 is the physiological pH value, it was chosen for the electrochemical detection of DA. In addition, we explored the relationship between DA peak potential (E_{pa}) and pH. It can be found that peak potential shifted negatively with the increase in solution pH, indicating that protons take part in the redox reaction process of DA on the L-Cys modified electrode.

Scan rate has a great influence on the peak current (shown as Fig. 3). The peak current density is proportional to the square root of scan rate in the range 10–100 mV/s. It indicates that the electrode process is controlled by diffusion of DA [27]. The intercept of the plot of the peak current vs $v^{1/2}$ on the vertical axis is different from zero, which is due to the amount of DA

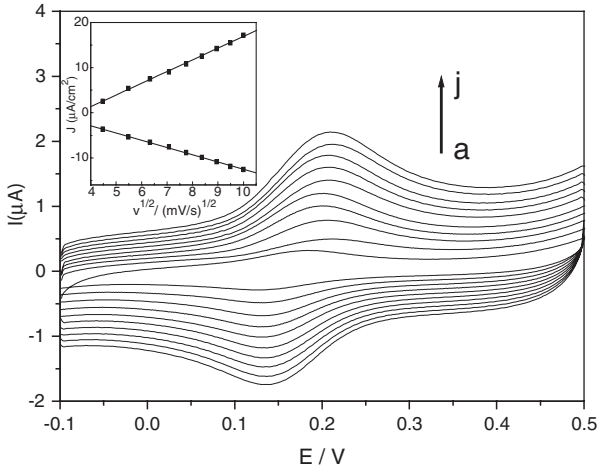

Fig. 3. Cyclic voltammograms of L-Cys/Au electrode in pH 7.0, 0.1 mol·L^{-1} PBS at different scan rates: a. 10, b. 20, c. 30, d. 40, e. 50, f. 60, g. 70, h. 80, i. 90, j. 100, (mV/s). (Inset) background-subtracted anodic and cathodic peak current density vs. square root of scan rate.

that is pre-adsorbed on the electrode surface and is electro-oxidized without diffusion.

Fig. 4 shows the differential pulse voltammograms (DPV) of DA in the presence of different concentrations of AA. It indicates that the peak current and peak potential of DA have no change at existing various concentration of AA. This is due to the electronegative carboxylic group of the electrode surface, which can selectively allure the positive DA and exclude the negative AA. So the self-assembled electrode can selectively detect the DA in the presence of AA. The peak at −0.22 V is caused by dopa acid, which is an electronegative group molecule. The peak current of dopa acid decreased with the increasing of AA. This result is accorded with a previous work [28]. We also investigated the influence of other substances and found that no interference in the presence of substance as the following: 80 fold uric acid, 100 fold dextrose, 100 fold citric acid, 150 fold NaCl and 150 fold KCl.

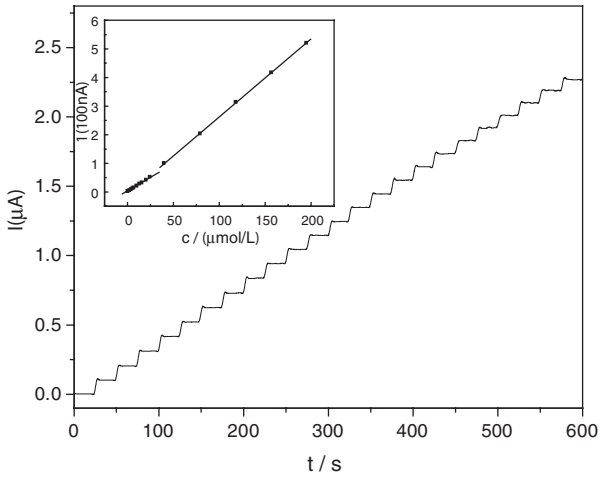

Fig. 4. Amperometric response of DA on the modified electrode in pH 7.0 PBS (at constant potential of 0.20 V modulated with 50 mV pulse in time intervals of 0.5 s, and stirring rate of 400 rpm), each addition of 4 μmol L^{-1} DA. (Inset) the relation between the anodic peak current and the DA concentration.

Chronoamperometric method (CE) can be used to detect biomolecules [29] and free radials [30]. The determination of DA applying the L-Cys/Au electrode was performed with CE. Fig. 5 showed oxidation currents amperometric current-time response caused by adding DA to the electrolyte solution under a constant potential. The amperometric response was obtained at +0.20 V for a successive addition of 4 μmol·L^{-1} DA to the stirring PBS. The nearly equal current steps for each addition of DA demonstrate a stable and efficient catalytic activity on the self-assembled monolayer. A linear relationship between DA oxidation peak currents and concentration was obtained in the range 1.0×10^{-7}–1.2×10^{-5} mol·L^{-1} and 4.0×10^{-5}–1.1×10^{-3} mol·L^{-1} with the correlation coefficients of 0.991 and 0.998, respectively. The detection limit is 2.0×10^{-8} mol·L^{-1} ($S/N=3$).

We also examined the response character of modified electrode to DA via this method. The modified electrode exhibited rapid response to the changes in the concentration of DA, producing steady-state signals less than 5 s. A low noise level accompanied the favorable signals. So the self-assembled electrode can be a highly selective DA amperometric sensor. The modified electrode was stored in PBS (pH 7.0) after every experiment. The cyclic voltammetric experiments were carried out using a modified electrode once a day at the same operation conditions. The redox peak currents of DA hardly change for a week and decreased with the storage time over a week.

Under the optimum conditions, the L-cysteine self-assembled electrode was applied to the determination of dopamine hydrochloride injection. Using the proposed method described above, the dopamine hydrochloride injection was analyzed by applying a calibration plot. In addition, a certain value of standard solution of DA was added into the corresponding injection for testing recovery. The results were shown in Table 1. The recovery and R.S.D. were acceptable. It shows that the proposed method could be efficiently used for the determination of DA injection.

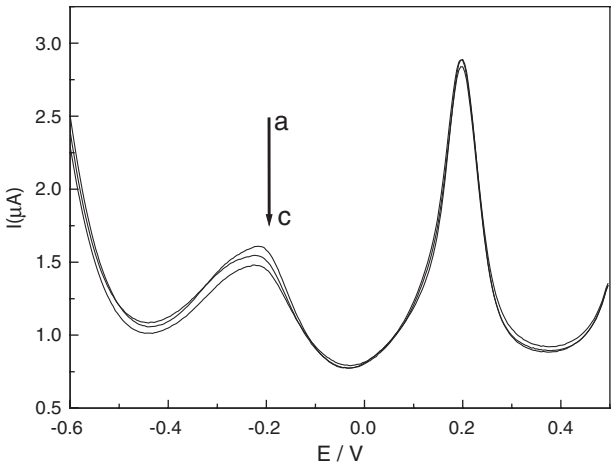

Fig. 5. DPV curves of 4.0×10^{-5} mol·L^{-1} DA in the presence of different concentration of AA in pH 7.0 PBS: (a) 5.0×10^{-5} mol·L^{-1}AA, (b) 1.0×10^{-4} mol·L^{-1} AA, (c) 1.5×10^{-4} mol·L^{-1} AA, scan rate: 50 mV/s.

Table 1
Determination results of DA concentration in injections ($n=5$)

Sample	Content ($\times 10^{-5}$ mol·L^{-1})	Found ($\times 10^{-5}$ mol·L^{-1})	R.S.D (%)	Added ($\times 10^{-5}$ mol·L^{-1})	Found ($\times 10^{-5}$ mol·L^{-1})	Recovery(%)
1	1.00	1.02	1.8	1.00	1.03	103
2	1.00	0.99	2.3	2.00	1.97	98.5
3	1.00	0.97	1.9	3.00	2.96	98.7

Acknowledgments

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