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Catalytic oxidation of dopamine at a microdisk platinum electrode modified by electrodeposition of nickel hexacyanoferrate and Nafion®

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Abstract

A chemically modified microelectrode has been prepared successfully by means of electrodepositing nickel hexacyanoferrate(II–III) on a microdisk platinum electrode. This modified electrode could catalyze the oxidation of dopamine and, moreover, eliminate the electrode poisoning caused by the electrochemical polymerization of dopamine at the bare platinum electrode. However, the oxidation of ascorbic acid could also be catalyzed at this modified electrode, thus interfering with the electrochemical response of dopamine. When the modified electrode was further covered with Nafion® membrane, the interference could be erased. The catalytic currents increased linearly with the concentration of dopamine in the range of 1.0×10^{-4} to 1.5×10^{-2} M. Such a microdisk modified platinum electrode could be used for the determination of dopamine. In addition, the reaction rate constant of dopamine at the modified electrode was evaluated by using a rotating disk electrode,

Keywords: Microelectrode; Double-film modified electrode; Dopamine; Nafion®, Rotating disk electrode

1. Introduction

Microelectrodes have been widely applied in low conductivity media, fast scan techniques and monitoring neurotransmitters in vivo because of their unique properties such as very small size, high mass transport and fast response time [1–3]. Recently, the modification of microelectrodes has caused extensive interest in bioelectrochemistry. In general, biomolecules are not easy to detect with the electrochemical method because of a poor electrochemical response even though their oxidation and reduction are thermodynamically favored. However, most of them, such as NADH, insulin, glucose, etc., could be detected at a chemically modified electrode [4–6].

Dopamine (3,4-dihydroxyphenyl ethylamine) is an important neurotransmitter in the mammalian central nervous system (CNS), and it could be detected electrochemically because of its electroactivity. The electrochemical oxidation of dopamine has been studied mostly on carbon base electrodes [7–11]. The results show that the electrochemical oxidation is a two-electron irreversible process with transfer of two proton. A carbon fiber microelectrode has been used successfully to determine dopamine in vivo by fast-scan cyclic voltammetry [12].

However, the electrochemical determination of dopamine was usually affected by the oxidation of ascorbic acid. So, it was necessary to solve the problem of the separation of the electrochemical responses of dopamine and ascorbic acid.

Chemically modified electrodes have been developed to separate the electrochemical response of dopamine and ascorbic acid. A greater separation of dopamine and ascorbic acid could be obtained when the electrode was pretreated electrochemically at high potentials [13–15]. Franck and Daniel [16] used self-assembled monolayers of ω-mercapto carboxylic acid, $HS(CH_2)_nCOOH$ ($n = 2, 5, 10$), on a gold electrode as a medium to induce electrochemical differentiation between dopamine and ascorbic acid. A modified graphite paste electrode was prepared by mixing the nujol oil paste with stearic acid. Electrostatic repulsion between the anionic carboxyl groups at the modified electrode retarded the electron transfer rate and shifted the oxidation potential region of ascorbic acid towards a more positive value so that the peak of dopamine can be separated from that of ascorbic acid [17].

Wightman et al. [18] and Rice et al. [19] took carbon fiber electrodes coated with the negatively charged poly-

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mer Nafion®, which repelled the ascorbic acid and other negatively charged species and attracted positively charged neurotransmitters such as dopamine and 5-hydroxytryptamine, to resolve the peak separation of dopamine and the interferents.

Although the interferance by ascorbic acid could be eliminated by electrochemical pretreatment at high potentials or by coating with nafion® [13,15,18], the fragility of carbon fiber makes the experimental processes rather difficult. Recently, intense research has been devoted to the preparation and the characterization of mixed-valent inorganic catalytic centers. Their major advantages are the efficient electrocatalysis and inherent stability as needed for practical analysis. Prussian blue (PB) and its analogues, such as nickel hexacyanoferrate, cobalt hexacyanoferrate, etc., have been constructed successfully and applied to the electrocatalysis and the determination of organic and inorganic species [20–27].

Lane and Hubbard [28] reported a poisoning effect on a platinum electrode from the oxidation of dopamine in physiological pH condition. Their conclusion was that the product of the ring closure and the aminochrome and so on can polymerize to form melanine-like compounds on the surface of the electrode, thus inhibiting the electron transfer reaction. Furthermore, because melanine formation occurs, and a free radical polymerization involving the semiquinone intermediate is involved, the concentration of dopamine–quinone at the surface of the electrode could vary from step to step in the experimental process, although each experiment was carried out under the same conditions.

Here, we report another type of modified electrode for the determination of dopamine depending on the electrodeposition of nickel hexacyanoferrate on a microdisk platinum electrode. A noticable catalytic oxidation for dopamine was observed. The poisoning effect on the electrode surface caused by the polymerization of dopamine is greatly reduced. When the modified electrode was furthur covered with Nafion® membrane, the electrode could eliminate the interference of ascorbic acid efficiently. This approach might be developed to prepare an amperometric sensor for the determination of dopamine and extend the study region in addition to carbon base electrodes.

2. Experimental

2.1. Reagents

Dopamine hydrochloride was purchased from Fluka AG (Switzerland). All other chemicals were of analytical grade. Nafion® (5 wt.% ethanol solution) was obtained from Aldrich Co. The phosphate buffer solutions were made up with 0.05 M NaH_2PO_4 and 0.05 M Na_2HPO_4. The dopamine hydrochloride and ascorbic acid solutions were prepared with phosphate buffer and the electrochemical experiments were kept under nitrogen atmosphere. All solutions were prepared with twice distilled water.

2.2. Apparatus

An M270 electrochemical system (EG&G, USA) as well as a three-electrode cell with a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and microdisk platinum electrodes ($\Phi = 30$ μm) as working electrode were used for the electrochemical experiments at 22 ± 0.1°C. A 5.0 mm platinum disk electrode was used to perform the measurement of the reaction rate constant with a PAR M636 ring-disk electrode system (EG&G, USA).

2.3. Construction of the modified electrode

Prior to modification, the microdisk platinum electrode was polished with sandpaper and 0.05 μm alumina slurry, and then cleaned by sonicating in twice distilled water for 5 min. After the electrode was pretreated by a continuous cyclic sweep from 0.0 to +1.4 V (SCE) at 50 mV s^{-1} in phosphate buffer solution (pH 7.0) until a constant background was observed, the nickel hexacyanoferrate film was electrodeposited on the surface of microdisk platinum electrode in a medium of 0.2 M $NaNO_3$ containing 1.0 mM $Ni(NO_3)_2$ and 1.0 mM $K_3Fe(CN)_6$ using a continuous sweep between −0.1 and 1.00 V at a scan rate of 40 mV s^{-1}. Obviously, the thickness of the film would increase with the cycle numbers of the sweep. When the film was formed with sufficient thickness, it was rinsed with twice distilled water. The cyclic voltammograms did not show any change when the modified electrode was swept repetitively, so it indicated that nickel hexacyanoferrate possesses a very robust adherence to the platinum electrode surface and this modified electrode had a good stability.

The Nafion® film modified electrode was prepared by putting a droplet of 0.5 μl of 5% Nafion® solution on the electrode surface, then drying under an infrared lamp.

3. Results and discussion

3.1. The electrochemical characteristics of the nickel hexacyanoferrate modified microelectrode

The cyclic voltammograms of nickel hexacyanoferrate film at different scan rates are shown in Fig. 1. A redox couple was observed and the peak currents increased linearly with the scan rate. The peak shape was almost symmetrical and the peak potential was at +350 mV. Thus, a surface process is involved. The modified electrode exhibited good stability whether stored in air or in a phosphate buffer for a few weeks. Its electroactivity was independent of the pH over the range of 5.0–8.0. These

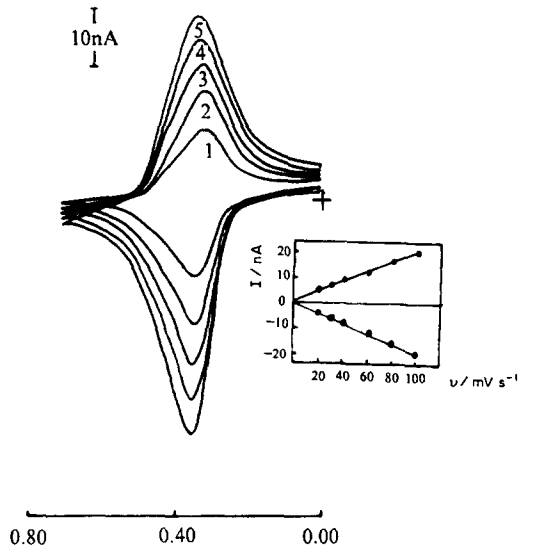

Fig. 1. Cyclic voltammograms of the nickel hexacyanoferrate modified electrode in phosphate buffer solution at scan rates of: (1) 20; (2) 40; (3) 60; (4) 80; (5) 100 mV s^{-1}. The inset shows the relation of the peak current and scan rate.

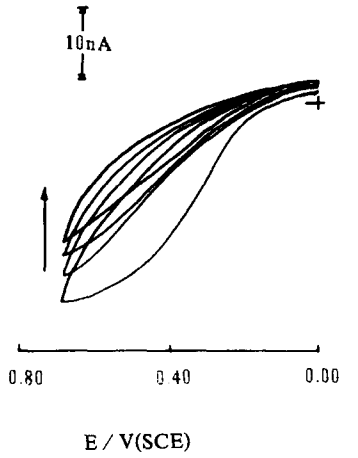

Fig. 2. Cyclic voltammogram of dopamine at a bare platinum electrode in pH 7.0 phosphate buffer at 20 mV s^{-1}.

results were consistent with those in Ref. [24]. The surface coverage calculated from the voltammograms using the equation of $I = n^2F^2A\Gamma v/4RT$ [24,29] or using the equation $Q = nFA\Gamma$ was about 1.0×10^{-9} mol cm^{-2}.

3.2. Electrochemical oxidation of dopamine at a bare microdisk platinum electrode

Owing to the pollution of a metal electrode surface by biomolecules, the measurement of dopamine was usually carried out with carbon substance electrodes [12,13]. Although microelectrodes usually possess high mass transport rate, the microdisk platinum electrode would still be polluted within several cycles when it is used in a solution of dopamine (see Fig. 2). The corresponding current decreased obviously with the increase in the number of cyclic sweeps. This could be due to the electrochemical polymerization of dopamine [28]. Moreover, this process produced melanine-like compounds on the surface of the electrode, thus inhibiting the electron transfer reaction. The anodic peak potential was at +450 mV at the bare platinum electrode. So, it is necessary to modify the electrode so as to reduce the pollution.

3.3. Catalytic oxidation of dopamine at the nickel hexacyanoferrate modified electrode

Fig. 3 showed the cyclic voltammograms of nickel hexacyanoferrate modified electrode in the absence (a) and presence (b) of dopamine. The increment of anodic current showed clearly that the modified electrode electrocatalyzed the oxidation of dopamine. This increasing oxidation current was due to the fact that the dopamine in solution diffused toward the electrode surface and reacted with $NaNiFe(CN)_6$ with the production of $Na_2NiFe(CN)_6$. The electrochemical process could be expressed as follows:

$$2Na_2NiFe(CN)_6 \rightarrow 2NaNiFe(CN)_6 + 2Na^+ + 2e^-$$

$$2NaNiFe(CN)_6 + 2Na^+ + DA_{red} \rightarrow 2Na_2NiFe(CN)_6 + DA_{ox}$$

Fig. 4 shows the voltammograms of dopamine at the $Na_2NiFe(CN)_6|NaNiFe(CN)_6$ modified electrode at the various scan rates. The catalytic currents of dopamine were proportional to the square root of scan rates. When this modified electrode was used in a solution of dopamine for a long time, no fouling of its surface was observed. These observations suggest dopamine does not adsorb or polymerize on the electrode surface.

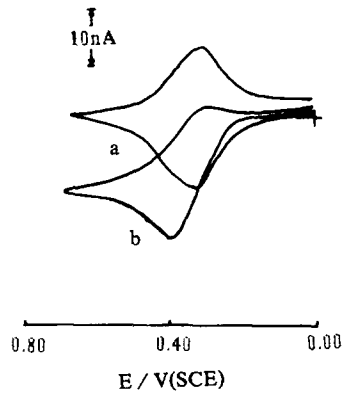

Fig. 3. Catalytic oxidation of dopamine at the $Na_2NiFe(CN)_6|NaNiFe(CN)_6|Pt$ modified electrode in pH 7.0 phosphate buffer at 20 mV s^{-1}. curve a: without dopamine; curve b: 2.0 mM dopamine; scan rate: 20 mV s^{-1}.

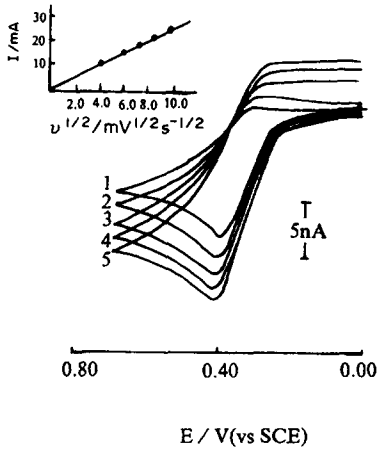

Fig. 4. Cyclic voltammograms of $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ | Pt modified electrode in pH 7.0 phosphate buffer containing 2.0 mM dopamine at scan rates of: (1) 20; (2) 40; (3) 60; (4) 80; (5) 100 mV s^{-1}. Inset: the corresponding plot of the catalytic current against the square root of scan rate.

The formal potential of the redox couple of $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ modified electrode is related to the concentration of Na^+ in solution. It obeys the Nernst equation. In addition, the film's catalytic activity is closely related to the scan rate during the preparation of the film because the scan rate would affect the structure of the electrodeposited film. A high catalytic efficiency could be obtained when it was prepared at a low scan rate.

3.4. Catalytic oxidation of dopamine at a rotating platinum disk electrode coated with $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$

With a rotating platinum disk electrode modified with $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$, the catalytic reaction dynamic of dopamine was studied. Fig. 5 shows the shape of the curves of the limiting current vs. $\omega^{1/2}$. At low rotation rate, the current was controlled by the transport of

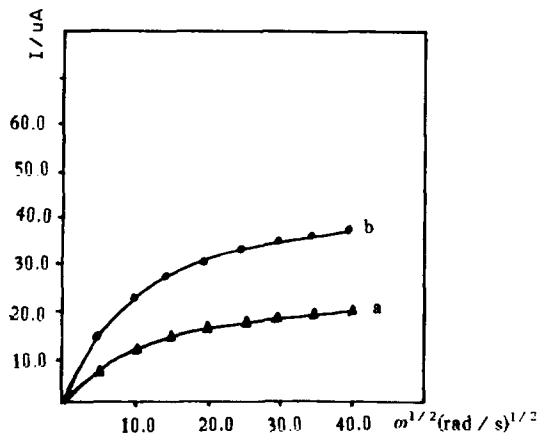

Fig. 5. Levich plot for the oxidation of dopamine at the $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ | Pt modified electrode in pH 7.0 phosphate buffer containing dopamine with a concentration of (a) 0.5 and (b) 1.0 mM.

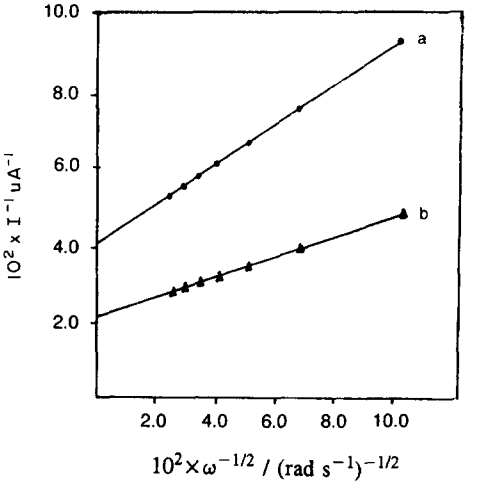

Fig. 6. Koutecky–Levich plots of the same data as in Fig. 5.

dopamine through the rather thick Levich layer so that the behavior of I_{lim} vs. $\omega^{1/2}$ appeared to be linear. At high values of ω, the thickness of a Levich layer decreased and the current was controlled by the rate-determining of dopamine with the $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$.

By means of plots of $(I_{lim})^{-1}$ vs. $\omega^{-1/2}$, the linear relation of Koutecky and Levich could be obtained (see Fig. 6). The linearity indicated that the system obeys the following equation: $1/I_{lim} = 1/I_{lev} + 1/I_{kin}$, where I_{lim} is the limiting current and I_{lev} is given by the Levich equation ($I_{lev} = 0.620nFAD^{2/3}\upsilon^{-1/6}c\omega^{1/2}$); the kinetic current I_{kin} is given by $I_{kin} = nFAk_s\Gamma_s c$. From the Koutecky–Levich plot the heterogeneous charge transfer rate constant (k_s) could be obtained. When the adsorbed quantity Γ_s was 1.49×10^{-9} mol cm^{-2}, $k_s = 8.5 \times 10^2$ l mol^{-1} s^{-1} at $c = 1.0$ mM and $k_s = 8.90 \times 10^2$ l mol^{-1} s^{-1} at $c = 0.5$ mM. The values of k_s increased with the decrease of the concentration of dopamine.

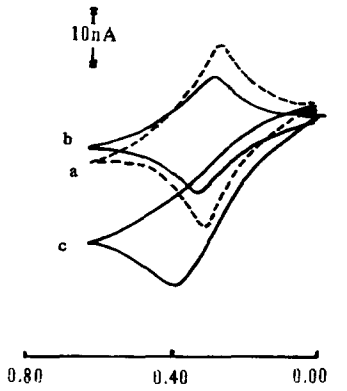

Fig. 7. Cyclic voltammograms in pH 7.0 phosphate buffer solution at $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ modified electrode (curve (a)) and further modified with nafion® (curve (b)); curve (c): (b) +2.0 mM dopamine; scan rate, 20 mV s^{-1}.

3.5. Elimination of the interference of ascorbic acid

Nafion®, a cation exchange polymer repels ascorbic acid and other negatively charged species and can provide a transport channel only for cations. Usually, ascorbic acid is a major interferent for the determination of dopamine. In order to reduce the interference, a Nafion®-coated $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ modified electrode was prepared. Figs. 7(b) and 7(c) show its cyclic voltammograms. These indicate that dopamine could also be catalyzed at the modified electrode coated with Nafion®. Compared with Fig. 7(a), the peak current decreased and the peak potential moved toward a somewhat more positive value. It was obvious that Nafion® film reduced the migration rate of Na^+ from solution to the membrane of $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$.

In general, the nickel-hexacyanoferrate film possesses a negative charge. This should decrease the response of ascorbic acid because of the electrostatic repulsion between the film and ascorbic acid. However, experimental results showed that the $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ could also catalyze the oxidation of ascorbic acid as well as dopamine (Fig. 8). While this modified electrode was further coated with Nafion®, no catalytic current was obtained for ascorbic acid. So the Nafion® | $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ modified electrode could be used for the determination of dopamine in the presence of an ascorbic acid concentration as large as 50-fold that of dopamine. A calibration curve of dopamine was obtained in the range of 1.0×10^{-4} to 1.5×10^{-2} M.

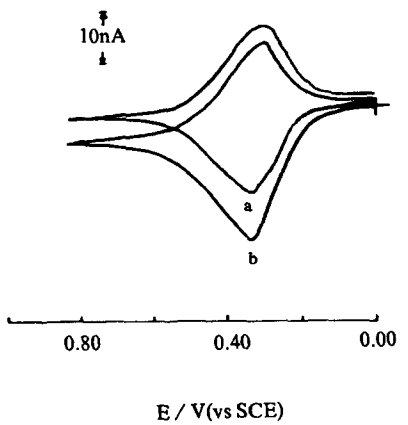

Fig. 8. Catalytic oxidation of ascorbic acid at $Na_2NiFe(CN)_6$ | $NaNiFe(CN)_6$ | Pt modified electrode in pH 7.0 phosphate buffer at 20 mV s^{-1}: curve (a) without ascorbic acid; curve (b) with 2.0 mM ascorbic acid.

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