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An electrochemical method for selective detection of dopamine by depleting ascorbic acid in diffusion layer

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ABSTRACT

A facile method for selective detection based on the concept of electrochemical depletion of interfering species in diffusion layer was established. The feasibility of the method was verified by detecting dopamine in the presence of ascorbic acid. By applying a proper step potential to working electrode, at which interfering species, ascorbic acid, is oxidized while dopamine is kept unconsumed, an interferent-depleted region is thus created in the diffusion layer of the working electrode. Then the target analyte is detected by applying a follow-up linear sweep voltammetry with faster sweep rate to ensure the amount of the interfering species that diffuses to the electrode surface is negligible. The influence of step potential, step duration and sweep rate on dopamine detection has been systematically investigated. Since the proposed method only requires easily achievable potential control and commonly used electrode without modification, it is facile and thus high reproducibility is expected.

1. Introduction

In recent years, Xia's group proposed and developed a concept of electrochemical depletion of electroactive species in diffusion layer for selective detection [1–4]. The depletion of interfering reactive species in the diffusion layer is a simple and reproducible method, which opens a new direction for interferent-depleted electrochemical sensors. In their approach, two working electrodes are required, which should be positioned close enough so that their diffusion layers can overlap. During the detection, one electrode is used to deplete the electroactive interfering species, the other is used to detect target analyte.

Xia's concept was first established with selective glucose detection in the presence of AA by adopting an SECM configuration of the two working electrodes to achieve overlapping of the diffusion layer [1,2]. The substrate electrode was served as an interferent-depleted micro-circumstance, while the tip electrode was used for detecting glucose by sensing hydrogen peroxide formed during the process of the oxidization of glucose on the glucose oxidase layer-coated substrate electrode. In order to avoid the complexity of Pt tip electrode localization in the SECM configuration, a probe-in-tube microdevice was then designed and proved by selective determination of hydrogen peroxide in solution [3]. In the microdevice, a probe electrode is inserted into a cylindrical tube electrode, the former is used to detect the target analyte and the latter is used to deplete the electroactive interfering species. A further work on a highly selective amperometric glucose biosensor was achieved by coating a gold tube with a conductive layer of glucose oxidase/nafion/graphite and using a Pt probe electrode in the diffusion layer of the modified gold tube to selectively detect hydrogen peroxide from the enzyme catalytic oxidation of glucose [4].

Different from dual-electrode strategy from Xia's group, Einaga' group controls the diffusion layers by proper design of composite electrodes [5,6]. A Cu-implanted boron-doped diamond electrode (BDD) and a Ni-arrayed BDD electrode were designed and fabricated by ion implantation or photolithography. With the metal-modified electrodes, non-enzymatic glucose detection was successfully performed based on the different diffusion length scale at metal microstructures and the BDD macrostructures. Due to the surface inertness of BDD to glucose, glucose can only be oxidized at the metal microstructure with hemispherical diffusion, while the interfering species can be oxidized at both the metal and BDD surfaces in a linear diffusion process. The electrochemical properties of BDD with low background current, extremely high stability, and inactivity toward the oxidation of glucose benefit the electrochemical depletion of interfering species in the diffusion layer by the composite electrodes. It is also worthy to mention that Liu et al. [7] performed nitrobenzene analysis in water by combining triple potential step amperometry with electrode modified by didodecyldimethylammonium bromide and nitroreductase.

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The above diffusion layer-based detection approaches are diverse from traditional strategies for selectivity improvement, and therefore may become promising electrochemical sensing methods. However, the applications of these methods are still restricted because of the complexity of electrode design. For example, it is an unavoidable problem to locate two electrodes in the dual-electrode system, or to employ expensive equipments to prepare the metal-arrayed boron-doped diamond electrodes. Therefore, developing diffusion layer-based detection using conventional and unmodified electrode is still a desirable and challenging task.

This paper proposes a novel method based on single-electrode and combined potential step and follow-up linear sweep voltammetry (LSV) for selective detection in the diffusion layer.

The determination of dopamine (DA) attracts increasing attention of researchers due to its important role as a neurotransmitter. Electrochemical method has been used for determining DA because of its advantages of simplicity and sensitivity. However, the interference of ascorbic acid (AA) must be circumvented in order to detect DA precisely. Many works have been carried out to improve the selectivity by modifying electrodes using different materials including polymer films [8–16], carbon materials [17–20], self-assembled monolayers [21,22], boron-doped diamond [23], nanoparticle [24–26], and composite film [27–29]. In addition, Zen et al. [30] reported selective detection of DA and UA in the presence of AA by controlling environment temperatures. Fast-scan cyclic voltammetry has also been used for DA Detection [31,32]. Luczak investigated the electrochemical reactivity of DA in the presence of morpholine as nucleophile for detecting DA [33].

In order to verify the feasibility of the proposed method, DA was detected in the presence of AA. As shown in Fig. 1, interfering species AA can be depleted in the diffusion layer upon application of an appropriate step to potential in the diffusion controlled region where DA cannot be oxidized yet; then a linear sweep voltammetry with faster scan rate is applied to detect the DA. With the present approach, only simple and easily realizable potential control and commonly used electrodes such as unmodified glassy carbon electrodes are needed. Precisely locating of two electrodes in the above-mentioned approaches is avoided. Therefore, high reproducibility is expected with the present approach. Systematic investigation of the influence of step potential, step duration and scan rate on DA determination will be given.

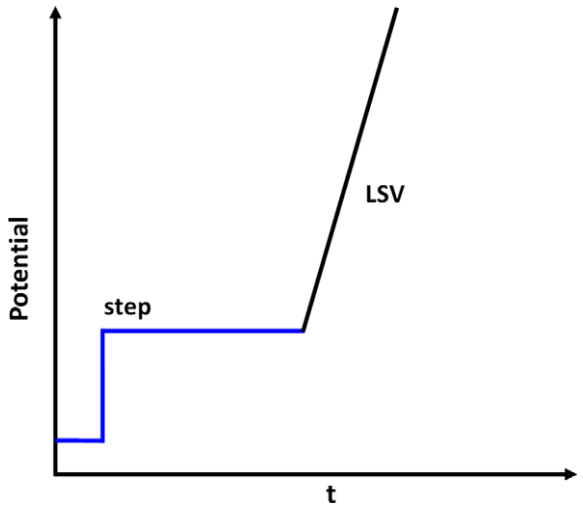

Fig. 1. Potential sequence applied to the working electrode. The potential step is used to deplete interfering species in the diffusion layer while the target analyte does not oxidize or reduce. The linear sweep voltammetry (LSV) is used to detect the analyte.

2. Experimental

Dopamine was purchased from Sigma. Ascorbic acid was obtained from Sinopharm Chemical Reagent Co., KCl, NaH_2PO_4, K_2HPO_4 and H_3PO_4 (85%) from Shanghai Reagent Co., were of analytical grade. All solutions were prepared with Milli-Q water (18.2 MΩ cm, Millipore). A buffer solution was made of 0.1 M K_2HPO_4, 0.1 M NaH_2PO_4 and 0.1 M KCl. The pH was adjusted to 3 with H_3PO_4 (85%) and was measured by a pH meter.

Electrochemical measurements were performed using an electrochemical workstation (CHI660c, Chenhua Corp., Shanghai, China). A conventional three-electrode system was employed in which a glassy carbon electrode (GCE, 1 mm in diameter, Aida Corp., Tianjin, China) was used as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The GCE was successively polished with 0.3 μm and 0.05 μm alumina, followed by ultrasonication in Milli-Q water to remove residual alumina. All solutions under investigation were deaerated by blowing nitrogen prior to measurements. A continuous flow of nitrogen was maintained over the solution during the experiment. The measurements were conducted at room temperature.

3. Results and discussion

3.1. The voltammetric behavior of DA and AA

pH will influence the electrochemical behaviors of both DA and AA. Alarcon-Angeles et al. investigated the influence of pH on the oxidation peak potentials of DA and AA [34]. The results demonstrated that as the pH increases, both the peak potential and the peak current diminished, and that the best current response for DA oxidation was obtained at pH 3. They also mentioned that pH 3 benefits the separation of the peak potentials of DA and AA. Therefore, we selected pH 3 as the most appropriate parameter for verifying the feasibility of the presented method.

The electrochemical behaviors of DA and AA will be influenced not only by pH of the solution, but also by the electrode material and surface conditions. Therefore, we must select appropriate conditions to ensure the separation of the peak potentials of DA and AA. For electrochemical detection of biological species, carbonaceous materials are the extensively used electrode materials. Among them, glassy carbon electrode is commercially available, cheaper, and commonly used. So we select GCE as working electrode. In order to ensure the reproducibility of electrode surface conditions, the electrodes were treated prior to each experiment by the same procedure as described in experimental section. The cyclic voltammograms of the treated GCE in PBS solutions were nearly the same, which indicated the reproducibility.

As shown in Fig. 2, the oxidative peaks of DA and AA in a mixed solution of 0.1 mM DA and 0.4 mM AA at pH 3 overlap each other at sweep rate of 0.1 V/s, i.e., the oxidation of AA shows obvious interference on the determination of DA. Therefore it is difficult to detect DA in the presence of AA by conventional cyclic voltammetry. In the present approach, it is crucial to select a proper step potential, where AA can be oxidized in diffusion controlled region while the target DA is not oxidized yet. For this purpose, cyclic voltammograms (CVs) of the target analyte and the interfering species at slow sweep rate were also measured, respectively, shown as the inset of Fig. 2. It is shown that the oxidation of interfering electroactive species AA starts at more negative potentials than the oxidation of target analyte DA. At potentials positive than 0.19 V, the oxidation rate of AA reaches a diffusion-limited level. On the other hand, the oxidation of DA starts at about 0.35 V. If we apply a step potential of 0.19–0.35 V to the working electrode, the interfering