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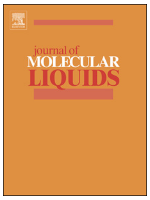

Highly selective and sensitive dopamine and uric acid electrochemical sensor fabricated with poly (orotic acid)

Haiyan Zhang [a], Yuanzhen Zhou [a,*], Juncai Zhang [b,c], Long Gou [a], Jianbin Zheng [b]

[a] School of Science, Xi'an University of Architecture and Technology, Xi'an 710055, China
[b] Institute of Analytical Science/Shaanxi Provincial Key Lab of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, China
[c] Chemistry and Chemical Engineering College, Xianyang Normal University, Xianyang, Shaanxi 712000, China

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ABSTRACT

A novel dopamine (DA) and uric acid (UA) electrochemical sensor (poly-OA/CPE) was fabricated by electrochemical polymerization of orotic acid (OA) on a carbon paste electrode (CPE). The sensor was characterized by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) and the electrochemical behaviors of dopamine (DA) and uric acid (UA) were investigated. The experimental results illustrated that the sensor has an excellent electrocatalytic activity towards the oxidation of DA and UA. By using DPV method, low detection limits ($S/N = 3$) of 0.08 μM and 0.28 μM for DA and UA were obtained, with the linear calibration curves over the concentration range of 0.31–15.21 μM and 17.71–141.01 μM for DA and 0.82–11.32 μM and 13.62–200.62 μM for UA, respectively. Moreover, the sensor exhibits good selectivity and sensitivity toward simultaneous determination of DA and UA. The practical analytical utility is illustrated by the determination of DA in pharmaceutical samples without any preliminary treatment.

1. Introduction

Dopamine (DA) has been demonstrated to be a critical catecholamine neurotransmitter that broadly consists in the central nervous system of mammals. It influences a variety of motivated behaviors, attention span, and neuronal plasticity and exhibits potent physiological functions and pharmacological characters by playing very significant roles in contacting the nervous systems. Thus, low levels of DA have been implicated in pathogenesis of neurological disorders such as Parkinson's disease, schizophrenia [1–3] and HIV infection [4]. Uric acid (UA), the final product of purine metabolism, is present in blood and urine. The detection of UA is a subject of great importance because extreme abnormalities of UA levels in a human body have been linked with leukemia, gout, pneumonia and Lesch–Nyhan syndrome [5,6]. Thus, the determination of these two molecules is important not only in the field of biomedical chemistry and neurochemistry but also for diagnostic and pathological research [7,8].

In the past years, various detection methods have been used to determine DA and UA, such as liquid chromatography [9,10], capillary electrophoresis [11], and fluorescence [12]. The methods based on electrochemical measurements offer advantages in that they are simple, rapid, easy operation, and low-cost still providing enough sensitivity to detect submicromolar concentrations of analytes, while these methods require expensive and sophisticated instrumentation. However, due to the fouling of the electrode surface by the oxidation products, as well as the irreversibility of DA's electrochemistry, using conventional electrodes to detect DA generally gives poor results. Also, ascorbic acid (AA) exist in physiological samples at high concentrations and can be easily oxidized at potentials close to that of DA and UA, which results in overlapped voltammetric response making their discrimination highly difficult. Therefore, the determination of these molecules is an important topic not only in the field of biomedical chemistry and neurochemistry but also for diagnostic and pathological research. In order to overcome these problems, a variety of chemically modified electrodes have been constructed. There are reports about self-assembled monolayer [13,14], polymer film [15], nanoparticles [16,17], metal oxides [18] and composite material [19] modified electrodes that have been used for the simultaneous determination of DA and UA.

Among them, polymer modified electrodes (PMEs) prepared by electropolymerization have been drawn extensive attention due to its high selectivity, sensitivity and homogeneity in electrochemical deposition, and strong adherence to electrode surface [20,21]. Various PMEs were studied towards the electrocatalytic oxidation of DA and UA. Ensafi et al. reported on glassy carbon electrode modification with poly (sulfonazo III) film and studied the electrocatalytic activities toward oxidation of DA and UA [22]. Chitravathi et al. has reported electrochemical behavior of poly (naphthol green B)-film modified CPE, and simultaneous determination of DA and UA was carried out [23]. Lin et al. modified the glassy carbon electrode with poly (Evans Blue), thus, simultaneous determination of DA, AA and UA was carried

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* Corresponding author at: School of Science, Xi'an University of Architecture and Technology, No. 13, Yanta Road, Xi'an, Shaanxi Province, China. Tel./fax: +86 29 82201498 8619.
E-mail address: zyz1289@126.com (Y. Zhou).

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out [24]. Lin et al. modified the glassy carbon electrode with poly (p-nitrobenzenazo resorcinol), thus DA was successfully distinguished in the presence of AA and UA [25]. Chandra et al. modified the graphite pencil electrode using poly (amaranth), and the modified electrode was used for the detection of DA in the presence of UA [26]. Atta et al. reported that the negatively charged poly (4-amino-1-1′-azobenzene-3,4′-disulfonic acid) modified glassy carbon electrode could response selectively to DA oxidation and eliminates the interference of AA and UA [27]. The result of the reports above showed that polymer with negatively charged groups is one of the key factors to enhance the enrichment capabilities of the electrode.

Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid, OA) (Scheme 1) is a well-known pyrimidinecarboxylic acid, which exhibits important physiological functions and pharmacological characteristics. It has been widely used as anti-anemia, nutritional tonic and common drug. In this study, we report a polymer of OA modified CPE and the electrochemical behaviors of DA and UA were carefully investigated. Electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) were used for surface characterization of poly-OA/CPE. The electrochemical behaviors of DA and UA at the poly-OA/CPE were carefully studied.

2. Experimental

2.1. Apparatus

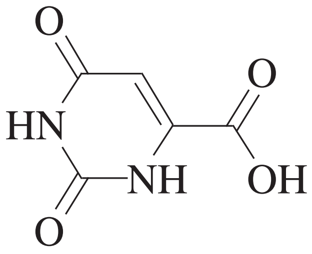
A CHI 832 Electrochemical Workstation (Chenhua Instruments in Shanghai, China) was used for electrochemical measurements. A conventional three-electrode system was used, where an Ag/AgCl (3.0 M KCl) electrode served as the reference electrode, a platinum wire electrode as the auxiliary electrode and a modified CPE as the working electrode. All the electrochemical experiments were carried out at room temperature of 25 °C. The surface morphology of sensor was analyzed by scanning electron microscope (SEM, Quanta 200).

2.2. Reagents and solutions

Dopamine hydrochloride injection was obtained from Shanghai He Feng Pharmaceutical Co., Ltd., China. AA and UA were purchased from China National Medicine Corporation. OA was purchased from Shanghai crystal pure industrial Co., Ltd., China. $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KCl, Na_2HPO_4, NaH_2PO_4, H_3PO_4, and NaOH were obtained from China National Medicine Corporation. All the chemicals were of analytical reagent grade and used without further purification. 0.1 M phosphate buffer solutions (PBS) with different pH values (from 2.0 to 9.0) were prepared by mixing the stock solutions of Na_2HPO_4 and NaH_2PO_4, and adjusting the pH with 0.1 M H_3PO_4 or 0.1 M NaOH. All solutions were made up with doubly distilled water.

2.3. Preparation of the modified electrodes

Before modifying, the bare CPE was prepared by mixing graphite powder and paraffin at the ratio of 5:0.7 (w/w) in an agate mortar, and then the paste was packed into a plastic tube (∅ = 3.0 mm). The electrical contact was provided by a copper wire connected to the paste in the inner hole of the tube. The CPE was first polished mechanically with weighing paper, ultrasonically cleaned by distilled water, and then treated in pH 7.0 PBS by repetitive scanning in the potential range from −0.4 V to 0.8 V at a scan rate of 100 mV s^{-1} until reproducible background was obtained before modification. Then, the poly-OA was electrochemically deposited on the CPE by cyclic sweeping from −2.0 to 2.0 V at scan rate of 100 mV s^{-1} for nine cyclic times in 0.1 M PBS (pH 8.0) containing 0.06 mM OA. After the electropolymerization, the modified electrode was rinsed thoroughly with distilled water for further application.



Scheme 1. Chemical structural formula of orotic acid.

2.4. Procedure

A standard three-electrode cell connected to the CHI 832 was used for electrochemical measurements. Electrochemical determination of DA and UA was carried out in a voltammetric cell with 50 mL of supporting electrolyte solution. EIS measurements were carried out in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) mixture containing 0.1 M KCl, while the applied perturbation amplitude was 0.005 V, the frequencies swept from 50 mHz to 100 kHz. CV measurements were recorded by cycling the potential between −0.4 V and 0.8 V at a scan rate of 100 mV s^{-1}. Differential pulse voltammetry (DPV) measurements were performed from −0.2 to 0.7 V at pulse amplitude of 0.05 V for the determination of DA and UA. Poly-OA/CPE could be used repeatedly after rinsed with doubly distilled water. The same procedure was applied for the samples analysis and all electrochemical measurements were carried out at room temperature.

3. Results and discussion

3.1. Electropolymerization of orotic acid on the CPE surface

Electrochemical polymerization on the CPE surface was carried out using 0.06 mM OA in a pH 8.0 PBS by applying potential cycling between −2.0 and 2.0 V at a scan rate of 100 mV s^{-1}. The CVs during the electro-polymerization process up to the 9th cycle is shown in Fig. 1. During the polymerized process, it is clear that a cathodic peak at ca. −0.6 V corresponding to the oxidation of OA increased gradually with cyclic time increasing and trended to be stable after 4 scans, indicating additional electroactive poly-OA deposition for each cycle. The possible mechanism for the electropolymerization of OA was proposed as the reaction of Scheme 2. The electrode obtained a greatly enhanced background current in blank PBS solution after

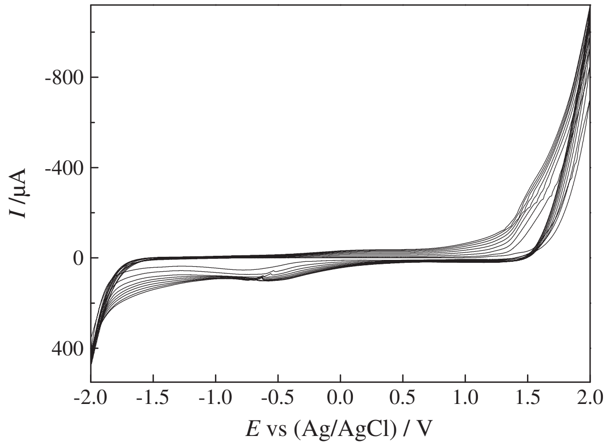


Fig. 1. CVs for electrochemically polymerization of OA (0.06 mM) in 0.1 M PBS (pH 8.0) on the CPE in the potential range from −2.0 to 2.0 V at a scan rate 100 mV s^{-1}. The cycling number is 9.

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