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Review

A sensitive and selective sensor for dopamine determination based on a molecularly imprinted electropolymer of *o*-aminophenol

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ABSTRACT

A simple and reliable method was proposed for preparing a selective dopamine (DA) sensor based on a molecularly imprinted electropolymer of *o*-aminophenol. The sensor is selective for the determination of DA in the presence of high concentrations of ascorbic acid (AA), with a maximum molar ratio of 1/1000. The molecular imprinted (MIP) sensor was tested by cyclic voltammetry (CV) as well as differential pulse voltammetry (DPV) to verify the changes in oxidative currents of ferricyanide. In optimized conditions, DA at concentrations of 2×10^{-8} to 0.25×10^{-6} mol/L could be determined with a detection limit of 1.98×10^{-9} mol/L (S/N = 3). The MIP sensor showed high selectivity, sensitivity, and reproducibility. Determination of DA in simulated samples of dopamine hydrochloride showed good recovery.

Contents

1. Introduction

The natural neurotransmitter dopamine (DA) plays important roles in control of central nervous system, cardiovascular, renal, and hormonal functions. As well, it is involved in drug addiction and in Parkinson's disease [1–3]. The measurement of DA in biological systems is therefore important, but is complicated by the range of DA concentrations that are encountered in biological organisms, which can range from 10^{-7} to 10^{-3} mol/L. In recent years, a wide variety of techniques have been proposed for DA determination in biological samples.

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DA possesses very strong electrochemical activity, which make electrochemical techniques strong candidates as detection methods [4]. However, in biological tissues, electrochemical detection of DA is essentially prevented by the presence of high levels of ascorbic acid (AA) [5], which results in a large over-potential for oxidation with conventional electrodes [6]. Thus, electrochemical sensors for measuring DA in biological systems need to possess sensitivity but also a high degree of selectivity.

A number of modifications have been attempted for improvement of selective electrodes for determination of DA. The use of polymer modified [7–12] and ion-exchange membrane electrodes [13] designed to be used in conjunction with electrochemical methods [11,14–21] have shown promise. Zheng and Zhou [21] used a SDS-modified carbon paste electrode, formed by pre-adsorbing SDS, for selectively determining dopamine in the presence of ascorbic acid. They claimed that DA and AA signals could be separated using this system. However, this method required a prior 10 min concentration step and a high SDS concentration.

The methodology of molecular imprinting, first introduced by Anderson [22], has also been exploited [23–28], and has significant advantages. Firstly, molecular imprinting sensors (MIPs) have superior stability, low cost, and ease of preparation. Secondly, they may replace natural receptors as the detection component of selective electrodes. MIPs are made by synthesizing highly crosslinked polymers in the presence of "imprint" molecules (the template). After removal of the template, the polymer can be used as a selective binding medium for the print molecule or other structurally related compounds. MIPs that have complementary sites [29] (i.e., specific recognition sites [30] for the template molecules) can be prepared in various configurations that are adapted for the structure of target molecules. Over the past two decades, imprinted membranes have seen increasing use in analyte detection [31–46].

Molecular imprinting approaches for electrosynthesis of conducting polymers include galvanostatic, potentiostatic, and cyclic voltammetric methods. These provide simple and rapid techniques for controlling the thickness of the conductive polymer film, which can be easily grown and adhered to a transducer of any size and shape. Polymer thickness and deposition density, in turn, can be regulated by polymerization conditions [33]. Monomers that have been useful in the design of molecularly imprinted conducting polymers include polypyrrole [37,38], aniline, *o*-phenylenediamine [24,39] and *m*-aminophenol [40]. Recently, electropolymerization of *o*-aminophenol has been reported [41]; however, to our knowledge, *o*-aminophenol has not yet been used in the construction of a MIP sensor.

In this paper, the fabrication of a highly selective and sensitive DA sensor was investigated using an *o*-aminophenol MIP as an artificial recognition element. DA was chosen as a template molecule because of its prevalence and its electroactivity. The sensor reported here can be used for selective determination of DA even in the presence of high concentrations of AA.

2. Experimental

2.1. Materials

All chemicals were analytical grade and were used as supplied without further purification. Dopamine hydrochloride was purchased from Sigma–Aldrich, USA; *o*-aminophenol, ascorbic acid (AA), perchloric acid, sodium hydroxide, potassium ferricyanide, potassium dihydrogen phosphate, disodium phosphate and trichloroacetic acid were analytical grade and were purchased from Sinopharm Group Chemical Reagent Co., Ltd, China. Human serum was purchased from the Hospital of Guilin University of Technology, Guilin, China. Distilled water was used for preparation of all solutions and for washing.

2.2. Apparatus and electrodes

Electropolymerization was performed at 25 °C on a CHI660B electrochemical workstation (Shanghai Chenhua Instruments, Shanghai, China) connected to a personal computer. The classical three-electrode system consisted of a KCl saturated Ag/AgCl electrode as the reference electrode, a platinum electrode as the auxiliary electrode, and a MIP-modified gold electrode (d = 2 mm) as the working electrode.

2.3. Preparation of imprinted polymer (MIP) and non-imprinted polymer (nMIP) modified electrodes

The MIP was constructed by electropolymerization of *o*-aminophenol on the surface of the gold electrode, using cyclic voltammetry (CV) in the potential range between −0.20 and +1.20 V. Prior to the electropolymerization, the surface of gold electrodes were polished by 0.3 μm Al_2O_3, and then sonicated in distilled water for 5 min. The polished electrodes were electrochemically cleaned by cycling the potential scan between −0.20 and 1.50 V in 0.5 mol/L H_2SO_4 until the CV characteristics for a clean gold electrode were obtained [11]. Thirty cycles at 100 mV/s, in a solution of 0.01 mol/L DA, 0.02 mol/L *o*-aminophenol, and 0.1 mol/L $NaClO_4$ (pH 5.5, 25 °C) were used. An nMIP electrode was also prepared in every case, under the same experimental conditions, but without added DA.

After electropolymerization, the MIP and nMIP electrodes were washed with 0.5 mol/L H_2SO_4 for 12 h to remove the imprinting molecules. In strongly acidic conditions, DA molecules can escape from the stereo-cavity of the molecular imprinting membranes due to the destruction of the hydrogen bonds between DA and the molecular imprinting membranes. The end result is an electrode with a DA imprinted membrane. Electrosynthesis of poly *o*-aminophenol membrane and the imprinting of DA were illustrated in Scheme 1.

2.4. Electroanalytical measurements

A standard three-electrode cell connected to the CHI660B was used for electrochemical measurements, which were carried out in a supporting ferricyanide electrolyte (0.01 mol/L $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) solution) containing 0.2 mol/L NaCl. CV measurements were performed over a potential range from −0.1 to 0.5 V at a scan rate of 50 mV/s. PDV measurements were performed from −0.2 to 0.6 V at a scan rate of 50 mV/s and pulse amplitude of 50 mV. AC impedance was measured at a potential of 0.175 V over the frequency range from 100 mHz to 100 kHz, using an alternating voltage of 5 mV. All experiments were carried out at room temperature (25 °C).

3. Results and discussion

3.1. Cyclic voltammetry study of the MIPs–OAP electropolymerization

Electropolymerization of *o*-aminophenol was carried out by CV scanning in a 0.1 mol/L $NaClO_4$ solution (pH 5.5). When polymerized under acidic conditions, *o*-aminophenol molecular imprinted membranes acquired non-conductive properties. The cyclic voltammograms are shown in Fig. 1.

The currents decreased with increasing numbers of cycles and the highest current was obtained in the first scan. Oxidation of *o*-aminophenol was recorded as a distinct and irreversible peak at a peak potential of 0.44 V. When the number of cycles was increased to 30, the current density of the oxidation peak became