



Poly-dopamine thin film for voltammetric sensing of atenolol



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ABSTRACT

In this paper, a novel and highly sensitive atenolol sensor based on a poly-dopamine (PDA) is presented. PDA has been synthesized using a facile electro-deposition method. The polymer has been characterized with different techniques such as scanning electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. The glassy carbon modified with PDA has been applied for extraction and electrochemical sensing of atenolol. The extraction parameters such as pH, extraction time, and agitation rate were optimized. Differential pulse voltammetry has been used for quantitative determination of atenolol. The PDA thin film-based sensing platform exhibits high selectivity and sensitivity with a detection limit of 2.7×10^{-8} M. Determination of atenolol in real samples has been demonstrated. The results suggested that the PDA modification of electrodes may provide a new strategy for atenolol concentration determination in physiological solutions.

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1. Introduction

The presence of active pharmaceutical ingredients in commercial and clinical samples is of vital concern in today's industrial environment and provides a new challenge in sample analysis. Tremendous increase in the use of antihypertensive medications such as β -blockers points toward an increasing number of hypertension cases in last decade. Atenolol (Scheme 1) is one of the most widely used β -blockers. It is a hydrophilic β_1 -receptor blocking agent, which is of immense therapeutic use in the treatment of various cardiovascular disorders, such as angina pectoris, cardiac arrhythmia, and hypertension [1]. Due to the clinical importance of atenolol; it would be worthwhile to vital that a simple and sensitive method for its determination in commercial and clinical samples is established.

To date, numerous analytical methods have been elaborated and used for determination of atenolol, such as: spectrophotometry [2], high performance liquid chromatography with UV detection [3,4], gas chromatography–mass spectrometry [5], high performance thin layer chromatography [6], solid-phase extraction and liquid chromatography–tandem mass spectrometry [7,8], molecular imprinted polymer extraction followed by liquid chromatography–mass spectrometry [9], flow-injection chemiluminescence [10], room temperature phosphorescence [11],

capillary electrophoresis with electrochemiluminescence [12], and capillary zone electrophoresis with UV detection [13,14].

However, most techniques reported are plagued by lack of adequate sensitivity, cost-effectiveness or feasibility as a consequence of interferences, low stability at some operational conditions, and cumbersome sample preparation steps, which restricts their use or reusability in many applications especially in sample analysis.

Nonetheless, among the aforementioned techniques, electrochemical methods are more attractive as a means for determining many biological and pharmaceutical compounds. Their appeal stems from their reasonable equipment and simple principle, which have made them promising technique for sample analysis. Some of the electrochemical methods which have been used to determine of atenolol are summarized in Table 1 [15–19].

Electropolymerization is a common method to modify glassy carbon electrode (GCE) because of its simplicity, strong adherence of polymer thin film to electrode surface, broad potential window, chemical stability, and ability to provide larger surface area by forming homogeneous film [20].

Among different monomers, bio-inspired research has found that dopamine (3,4-dihydroxy phenethylamine) is able to undergo an oxidative polymerization reaction in marine condition (i.e. alkaline solution) and form strong adhesion on the substrate on which it is grown [21]. In contrast to other well established techniques, such as mono-layer self-assembly, surface modification by polydopamine (PDA) is carried out in an *in-situ* process [22,23]. The PDA coating on the surface of substrates is typically thin and offers highly robust structure at a wide range of pH [24–26]. Intrigued by the dormant potential of PDA, thus far it has been implemented

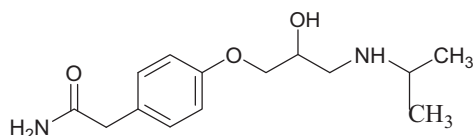
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Table 1
Some electrochemical methods which previously used for determination of atenolol.

Electrode	Modifier	Method	LR ^a (μM)	LOD ^b (μM)	Ref.
Glassy carbon	C ₆₀	DVP	250–1500	160	[15]
Glassy carbon	–	CV	2500–10,000	–	[16]
Carbon paste	Copper-oxide	DPV	12–96	1.12	[17]
Carbon paste	MWCNT	DPV	3–210	0.29	[18]
Glassy carbon	Au nanoparticles and MWCNT	DPV	1–60	0.5	[19]
Glassy carbon	Polydopamine	DPV	0.1–1	0.027	This work

^a Linear range.

^b Limit of detection.



Scheme 1. Chemical structure of atenolol.

as an electrochemical sensing platform for a myriad of substances. Recently, PDA reduced graphene oxide nanocomposite has been applied for electrochemical application in simultaneous determination of hydroquinone and catechol [27]. Chronocoulometric DNA biosensor based on a GCE modified with gold nanoparticles, PDA and carbon nanotubes has been reported, lately [28]. A phenolic biosensor based on magnetic PDA has been introduced, as well [29].

In this report, a facile and universal approach was developed to prepare a uniform layer of PDA at the surface of GCE by using electrochemical method. The thin film was characterized using scanning electron microscopy and electrochemical techniques. The glassy carbon modified with PDA has been employed for extraction and electrochemical sensing of atenolol. The influential parameters affecting the adsorption of atenolol such as pH, adsorption time, and agitation rate were optimized. In the optimum condition, the various concentrations of atenolol were adsorbed at the surface of the modified electrode. Furthermore, differential pulse voltammetry was used for quantitative determination of atenolol.

2. Experimental

2.1. Apparatus

Voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer model 797 VA. A conventional three-electrode system was used with a glassy carbon disk electrode (2 mm diameter GCE), a KCl-saturated calomel reference electrode (SCE), and a Pt wire as the counter electrode. A digital pH/mV/Ion meter (Metrohm) was employed for the preparation of the buffer solutions which were used as the supporting electrolyte in voltammetric experiments. The scanning electron microscope images were obtained using LEO 1430VP. Electrochemical impedance spectroscopic measurements were performed using a Galvanostat/Potentiostat microAuto-lab 3, with a three-electrode system same as voltammetric experiments.

2.2. Reagents

All chemicals were of analytical reagent grade from Merck. All aqueous solutions were prepared with doubly distilled deionized water, deionized and filtered water was taken from a millipore water purification system.

2.3. Electrochemical synthesis of PDA

In this work, PDA thin film was constructed on GCE surface by electropolymerization method. Pretreatment of GCE was performed using 2500 Emery paper (MATADOR, Germany) rinsing thoroughly with doubly distilled deionized water. Dopamine (DA) was then electropolymerized on the surface of the GCE by repetitive cyclic potential scan for 10 cycles between -0.4 and $+1.5$ V at 50 mV s^{-1} in acetate buffer (0.1 M, pH 5.0) containing 5.0 mM DA [30]. The modified electrode was denoted as GCE/PDA. The electrode has been washed with distilled deionized water prior use.

2.4. Adsorption of atenolol on the surface of GCE/PDA and cyclic voltammetry studies

The stock standard solution of 1 mM atenolol was prepared by dissolving 0.67 mg of atenolol in phosphate buffer (pH 5.6) and diluting with the buffer for preparation of various concentrations. The adsorption process was performed onto the modified electrode within 3 min under stirring. The electrode was taken out of the adsorption cell and was then transferred into voltammetric cell. Voltammogram was recorded by applying potential from -0.25 to $+0.75$ V.

3. Results and discussion

3.1. Characterization of PDA thin film

3.1.1. Scanning electron microscopy studies of PDA/GCE

Surface morphology of the (a) bare GCE and (b) GCE/PDA (10 cycles) is shown in Fig. 1A and B, respectively. Formation of PDA layer on the GCE surface can be confirmed by the deposited PDA clusters on the surface.

3.1.2. Electrochemical impedance spectroscopy (EIS) studies of GCE/PDA

EIS is an effective technique for providing useful information about the impedance changes on the electrode surface during the fabrication process. The Nyquist plot of the EIS includes a semicircular portion and a linear portion. The semicircular portion at higher frequencies corresponds to the electron-transfer-limited process and its diameter is equal to the charge transfer resistance (R_{ct}), which controls the charge-transfer kinetics of the redox probe at the electrode interface. Meanwhile, the linear part at lower frequencies corresponds to the diffusion process [31]. Fig. 2 shows the Nyquist plots of the EIS of (a) bare GCE, (b) GCE/PDA (5 cycles), and (c) GCE/PDA (10 cycles) in 5.0 mM $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ (1:1) containing 0.1 M KCl (Some frequencies have been shown at the top of points). However, the diameter of the semicircle is increased with the polymerization of dopamine at the surface of electrode. Compared with the bare GCE, in the electropolymerization process of PDA, with increasing the number of the cycles the PDA thin film thickness increases and blocks the charge transfer of the redox probe. Changes of the impedance spectra are observed in the course

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