Materials Science and Engineering C 38 (2014) 197–205

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Electropolymerization of taurine on gold surface and its sensory application for determination of captopril in undiluted human serum

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ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form 30 December 2013
Accepted 29 January 2014
Available online 8 February 2014

Keywords:
Electropolymerization
Polytaurine
Captopril
Nanosensor
Biomedical
Human serum

ABSTRACT

Polytaurine film was electrodeposited on gold (Au) electrode through cyclic voltammetry from taurine and phosphate buffer solution. The electrocatalytic effect of polytaurine modified Au (PT/Au) electrode was investigated for electro-oxidation of captopril (CAP). Electrocatalytical activity of PT/Au electrode was studied using cyclic voltammetry (CV), chronoamperometry and differential pulse voltammetry (DPV). DPV was used to evaluate the analytical performance of CAP in the presence of phosphate buffer solution and good limit of detection was obtained by this sensor. The experimental conditions influencing the determination of CAP were optimized and under optimal conditions, the oxidation peak current was proportional to CAP concentration in the range of 0.06–0.2 μM, while the detection limit was 0.03 μM (S/N = 3). The results revealed that PT promotes the rate of oxidation by increasing the peak current. Finally, the applicability of the method to direct assay of human serum is described. The proposed sensor was successfully applied to determine cadaverine in fish samples, yielding satisfactory results. The spiked recoveries were in the range of 96.0–105.0%.

1. Introduction

Captopril (CAP) is an angiotensin-converting enzyme inhibitor (ACE inhibitor) and has been widely used as an antihypertensive drug [1,2]. CAP has been determined by several methods such as gas chromatography–mass spectrometry (GC–MS) [3], high performance liquid chromatography (HPLC) [4], photometry [5], fluorometry [6], chemiluminometry [7], and flow injection and sequential injection analysis [8]. Also CAP can be determined by electrochemical sensors to take the advantages of electrochemical methods [9–12]. Electrochemical sensors represent an important subclass of chemical sensors in which an electrode is used as the transduction element. Such devices hold a leading position among sensors presently available, have reached the commercial stage, and have found a vast range of important applications in the fields of pharmaceutical analysis.

The chemical modification of electrodes with a suitable reagent has been widely used for analytical applications. The resulting electrodes were designed to provide desired selective sites toward the analytes. Chemically modified electrodes have played an important role in the studies of electrocatalysis, electron transfer kinetics, membrane barriers, electroorganic synthesis, and the like [13–20]. One of the most important electrode modification techniques has involved the formation of an electrocatalytic system in which a redox species capable of undergoing a rapid and reversible electrode reaction is incorporated onto the electrode surface.

In recent decades, polymer film modified electrodes have been attracting great attentions due to their wide applications in the fields of electrochemical sensors [21]. Such modified films can significantly improve the electrocatalytic properties of analytes, raise the reaction rate and improve the stability of the electrode response [22–27]. Up to now, different methodologies have been used to prepare polymer film modified electrodes, including coating [28,29], covalent bonding [30] and electro-polymerization [31]. Among the methodologies, the electro-polymerization of organic molecules with favorable functional groups (– COOH, – NH_2, – OH, – SH etc.) has exhibited to be a very convenient means for preparing functionalized and electroactive polymers at electrodes, because the procedure can be conveniently controlled by adjusting the electrochemical parameters. Accordingly, the thickness, permeation and charge transport characteristics of the modified electrodes by polymers can be well defined [23], and the cost of sensors is also low due to the simple electro-deposition procedures. Moreover, the electro-polymerization of some organic molecules allows the production of novel biosensor electrodes [32–34].

In the present work, in continuation of our studies concerning the drug analysis [35,36], we used polytaurine as a new polymer film for electro-oxidation and determination of CAP. To the best of our

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http://dx.doi.org/10.1016/j.msec.2014.01.051

knowledge, this is the first report of the determination of CAP based on their direct electrochemical oxidation on polymer films. In addition this work is the first statement on the determination of CAP in undiluted human serum sample.

2. Experimental

2.1. Chemicals and reagents

All chemicals used in this work were of analytical reagent grade, from Merck (Germany). The CAP was kindly gifted by Sobhan Darou Co. (Rasht, Iran).

2.2. Apparatus

Electrochemical measurements were carried out in a conventional three-electrode cell (from Metrohm) powered by an electrochemical system comprising of AUTOLAB system with PGSTAT302N (Eco Chemie, Utrecht, The Netherlands). The system was run on a PC using NOVA software. The ac voltage amplitude used was 10 mV and the equilibrium time was 5 s. An Ag/AgCl-Sat'd KCl (from Metrohm) and a platinum wire were used as reference and counter electrodes, respectively. The working electrode was an Au electrode (from Azar electrode Co., Iran) and PT/Au electrode, exposing a geometric surface area of 0.0314 cm^2. For DPV measurements, a pulse width of 25 mV, a pulse time of 50 ms, and a scan rate of 50 mV s^{-1} were employed. The surface morphology of the modified electrodes was evaluated with a Vega-Tescan electron microscope (SEM, Hitachi Ltd., Tokyo, Japan).

2.3. Preparation of standard and real samples of CAP

Standard solution of CAP was prepared by dissolving an accurate mass of the bulk drug in an appropriate volume of 0.1 M phosphate buffer solution, pH 6.80 (PBS) (which was also used as supporting electrolyte), and then stored in the dark place at 4 °C. Additional dilute solutions were prepared daily by accurate dilution just before use. CAP solutions were stable and their concentrations did not change with time. Drug-free serum samples were obtained from healthy volunteers and stored frozen until the assay. The serum samples were mixed with the supporting electrolyte and directly analyzed by the calibration method, according to the proposed sensor.

2.4. Preparation of modified electrode

Au electrode (2 mm in diameter) was polished to a mirror-like finish with 0.3 and 0.05 μm alumina slurries (Beuhler, USA) followed by rinsing thoroughly with double distilled water. Then it was successively

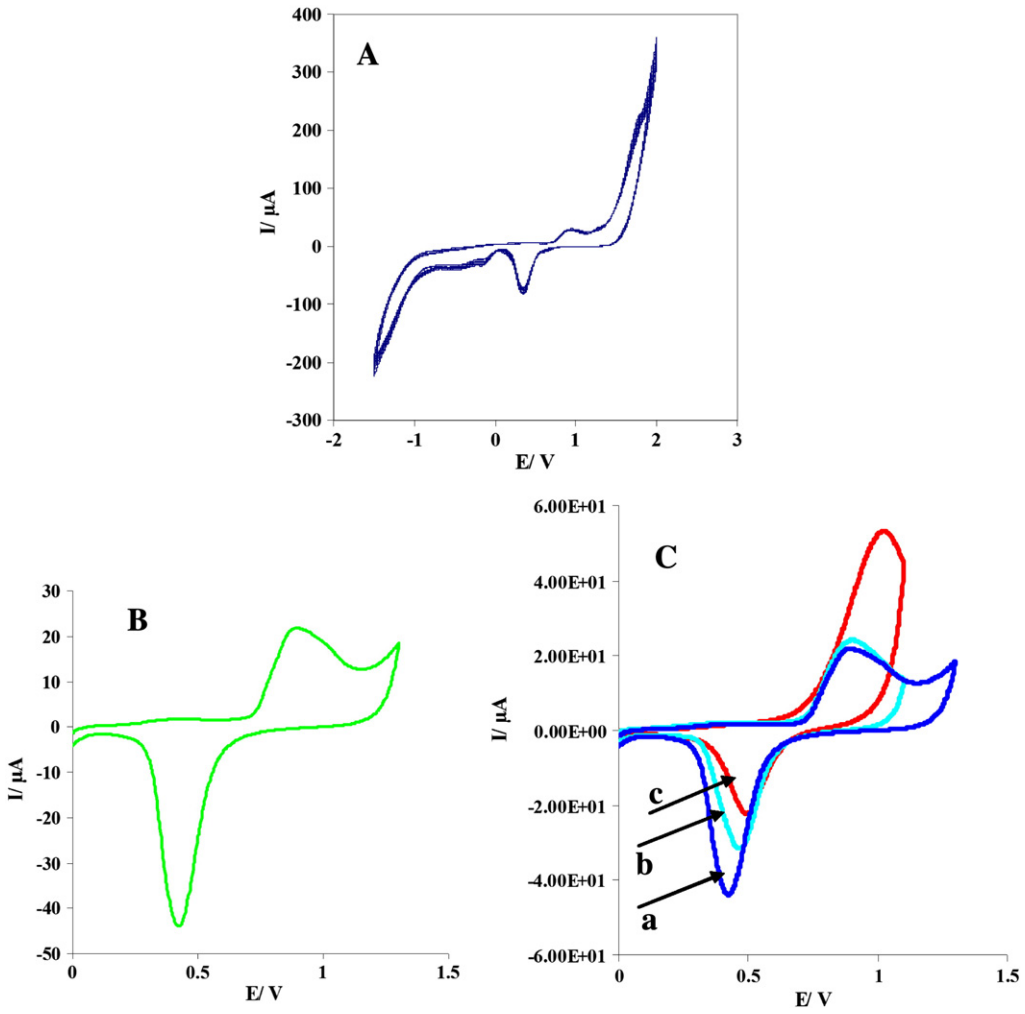

Fig. 1. A) CVs for 0.1 M taurine containing 0.1 M PBS using an Au electrode. The potential was scanned continuously at 100 mV s^{-1} between −1.5 and 2 V. B) CV obtained with bare Au electrode (curve a), (b) and (c) CVs of the PT/Au electrode in 0.1 M PBS in the absence (curve b) and the presence (curve c) of 0.1 mM of CAP.