



Simultaneous electrochemical determination of ascorbic acid and uric acid using poly(glyoxal-bis(2-hydroxyanil)) modified glassy carbon electrode

Eser Ergün^a, Şerife Kart^b, Derya Koyuncu Zeybek^b, Bülent Zeybek^{a,*}

^a Department of Chemistry, Faculty of Arts and Science, Dumlupınar University, Kütahya, Turkey

^b Department of Biochemistry, Faculty of Arts and Science, Dumlupınar University, Kütahya, Turkey

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ABSTRACT

In this paper, a novel polymer film of poly(glyoxal-bis(2-hydroxyanil)) P(GBHA), was prepared by electropolymerization of glyoxal-bis(2-hydroxyanil) (GBHA) on a glassy carbon electrode (GCE), and this electrode was utilized for the simultaneous detection of the ascorbic acid (AA) and uric acid (UA). The influences of electrochemical synthesis parameters on the electron transfer properties of P(GBHA) films were investigated, and the optimum synthesis conditions providing the lowest electron transfer resistance were determined. Scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) methods were employed for the characterization of the P(GBHA) film prepared under the optimum conditions. The electrochemical sensor exhibited high electrocatalytic activity toward the oxidation of AA and UA. The linear response ranges for the individual determination of AA and UA were 1.0–2000 and 1.0–200 $\mu\text{mol L}^{-1}$ with the detection limit of 0.26 and 0.3 $\mu\text{mol L}^{-1}$, respectively. These results present that the P(GBHA) is a promising substance for the production of electrochemical sensors with high sensitivity.

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1. Introduction

Ascorbic acid (AA, vitamin C) is one of the most significant water-soluble vitamins that is needed for biological metabolism and added in large quantities to food, drinks, cosmetics and pharmaceutical formulations due to the antioxidant properties of AA [1,2]. AA has important roles in the body, such as the amelioration of burns and injuries and the synthesis of collagen, blood vessels, cartilage, bones and tendons. In addition, AA has been employed for the prevention and healing of catarrh, sterility, mental disease, cancer and AIDS [3,4]. Hence, the fast and accurate analysis of AA with great selectivity and sensitivity is of considerable importance to food and pharmaceutical applications. Uric acid (UA, 2,6,8-trihydroxy purine) is the primary end product of purine metabolism and its concentration should be kept at a certain level in the body [5,6]. Anomalous concentration level of UA in the urine and serum is indicative of various illnesses, such as gout, hyperuricemia, and

Lesch–Nyhan syndrome [6,7]. Mostly, UA may be irreversibly oxidized in aqueous medium and the primary product is allantoin [6]. Because UA and AA coexist in biological liquids, such as blood and urine, it is essential to establish a method for selective detection of these biomolecules. Electrochemical methods have been frequently utilized for simultaneous analysis of AA and UA [8]. However, their simultaneous determination at traditional electrodes (carbon and metal) is highly difficult. Because the oxidation reactions of these compounds at the bare electrodes occur at almost the same potentials, and generally these electrodes experience a fouling effect by the oxidation product of AA, which causes relatively low selectivity and repeatability [9–11]. Hence, electrodes modified with conducting polymers have been employed to eliminate these problems [12–14].

The application of conducting polymers modified electrodes for the detection of biological compounds provides several advantages, such as enhanced peak current, lower overpotential, and high selectivity and sensitivity [15–18]. To prepare the modified electrodes, electropolymerization is a good approach to obtain an adherent film on the electrode surface. This method allows the control of the polymer growth process by adjusting such parameters as the electric charge, the electrochemical potential or the

* Corresponding author.

E-mail addresses: bzeybek43@hotmail.com, bulent.zeybek@dpu.edu.tr (B. Zeybek).

electric current. Electropolymerized conducting polymers have been extensively utilized for development and application of electrochemical sensors and for immobilization of biologically active species [15,17,19–21].

To the best of our knowledge, the electrochemical polymerization of glyoxal-bis(2-hydroxyanil) (GBHA) has not been reported in the literature. In this study, poly(glyoxal-bis(2-hydroxyanil)) (P(GBHA)) film has been deposited on a GCE for the first time. The P(GBHA) film was characterized by CV, EIS, SEM and ATR-FTIR spectroscopy techniques, and the P(GBHA) film modified GCE was effectively used for simultaneous analysis of AA and UA.

2. Experimental

2.1. Materials and reagents

GBHA, potassium hexacyanoferrate(II)trihydrate and potassium hexacyanoferrate(III) chemicals were supplied from Acros Organics (Thermo Fischer Scientific, USA). UA, AA, potassium chloride (KCl), disodium hydrogenphosphate dodecahydrate and sodium dihydrogenphosphate dihydrate were obtained from Merck (Merck KGaA, Germany). Sodium dodecylbenzenesulfonate (SDBS, Aldrich) (Sigma–Aldrich Co. LLC., Germany) was employed to increase solubility of GBHA. All chemicals were analytical grade and utilized without further purification. Stock standard solutions of UA (0.01 mol L^{-1}) and AA (0.1 mol L^{-1}) were freshly prepared by dissolving the required amount of reagent in ultra-pure water before experimental study.

2.2. Apparatus and procedures

Electrochemical studies were achieved by utilization of an Ivium CompactStat (Ivium Technologies B.V., The Netherlands) electrochemical instrument connected with a single compartment three-electrode cell stand (Bioanalytical Systems, BAS, Inc., USA). An Ag/AgCl (BAS MF-2052) and a platinum wire (BAS MW-1032) were utilized as the reference electrode and auxiliary electrode, respectively. The working electrode was a bare glassy carbon electrode (BGCE, BAS MF-2012, $d = 3 \text{ mm}$) or polymer modified GCE. Before each experiment, the surface of GCE was polished with $0.05 \mu\text{m}$ alumina suspension (Buehler). After the polishing process, the electrode surface was thoroughly washed with the ultra-pure water followed by ethanol in an ultrasonic bath to remove the alumina residue. Next, the surface was dried at room temperature.

A Bruker Alpha spectrometer with ATR attachment (Bruker Corporation Ltd., Germany) was used for Fourier transform infrared (FTIR) characterization of the powder GBHA monomer and P(GBHA) film. The spectrum of the polymer film was recorded directly by placing the P(GBHA) film coated GCE onto the DRIFT module. The spectra were collected from 400 cm^{-1} to 4000 cm^{-1} with spectral resolution of 4 cm^{-1} . Scanning electron micrographs of P(GBHA) film were recorded with a FEI Nova NanoSEM 650 Scanning Electron Microscopy (FEI, The Netherlands). The pH measurements were performed using a Mettler Toledo FE20 pH meter (Mettler Toledo, China). All solutions employed in the studies were prepared with the ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}$) obtained from Millipore Synergy device (Merck, France). All measurements were conducted at room temperature.

Electrochemical behaviors of P(GBHA) film modified GCE were studied by CV and EIS methods in 0.1 mol L^{-1} KCl and 5.0 mmol L^{-1} $\text{Fe}(\text{CN})_6^{3-/4-}$ solution. The cyclic voltammograms were recorded by scanning anodic direction in the potential window between -0.2 V and $+0.6 \text{ V}$ (vs. Ag/AgCl). The EIS studies were conducted in the frequency range of 10^5 – 0.01 Hz with 5 mV amplitude at open-circuit potential (E_{OCP}). Evaluation of impedance plots was accomplished

by fitting the experimental results to an equivalent circuit model by means of ZsimpWin (Version 3.50) software.

The DPV measurements were performed in the potential range from -0.2 to $+0.6 \text{ V}$ (vs. Ag/AgCl) in 0.1 mol L^{-1} phosphate buffer solution (PBS). The DPV parameters were as follows: step potential: 0.010 V ; pulse amplitude: 0.050 V ; pulse time: 0.200 s and scan rate: 0.010 V s^{-1} .

2.3. Sample preparation

For analysis of UA, urine samples were supplied from healthy volunteers and kept in a refrigerator following their collection. The urine samples were diluted 100-fold with PBS (pH 5.0) without any further pretreatment. Next, a certain volume of this solution was added into an electrochemical cell and the measurement process was performed. Then, a certain amount of UA standard solution was added to the electrochemical cell containing urine sample, and the DPV measurements were conducted.

The analysis of AA was achieved using two different samples. For the first, a tablet of vitamin C (labeled 1000 mg vitamin C per tablet) was fully ground into powder to be homogenized and dissolved in 25 mL of 0.1 mol L^{-1} PBS (pH 5.0) via ultrasonication. Afterwards, a certain amount of this solution was diluted to corresponding concentration with the PBS, and it was used for analysis. For the second sample, vitamin C injection solution (100 mg mL^{-1}) was diluted 10-fold with 0.1 mol L^{-1} PBS. A certain volume of the diluted solution was added into a volumetric flask, and the volume was brought up to 5.0 mL with the PBS (pH 5.0). The test solution was transferred into the electrochemical cell, and then the analysis process was performed. Furthermore, specific volumes of AA standard solution were transferred into the electrochemical cell, including the vitamin C sample; next, the analysis was performed according to the suggested procedure.

3. Results and discussion

3.1. Electrochemical synthesis of P(GBHA) on the GCE

Electrochemical synthesis of P(GBHA) was performed on a GCE surface using CV method in 0.1 mol L^{-1} PBS (pH 7), including 1.0 mmol L^{-1} GBHA and 0.1 mol L^{-1} SDBS. The influences of electrodeposition parameters (upper potential, sweep rate, and cycle number) on the electron transfer features of P(GBHA) films were systematically examined in 0.1 mol L^{-1} KCl solution including 5.0 mmol L^{-1} $\text{Fe}(\text{CN})_6^{3-/4-}$ by EIS method. The parameters were optimized to obtain a film with the lowest electron transfer resistance.

First, the potential interval was investigated for the electrosynthesis of P(GBHA) on the GCE. The P(GBHA) films were prepared between 0.0 V and various upper potentials (1.6 , 1.7 , 1.8 and 1.9 V vs. Ag/AgCl) at a 50 mV s^{-1} scan rate with 60 cycles. The electrochemical impedance spectra (Nyquist plots) of these electrodes were reported in Fig. S1(A). The smallest semicircle was observed at 1.7 V (vs. Ag/AgCl) potential and its diameter may be accepted to be equal to the electron transfer resistance (R_{et}) value. Table S1 shows the R_{et} values obtained from the EIS plots for parameters affecting the formation of P(GBHA) films. The P(GBHA) film synthesized at $+1.7 \text{ V}$ as the upper potential provides the best electron transfer property. Therefore, the potential range is determined to be between 0.0 and $+1.7 \text{ V}$ (vs. Ag/AgCl) for the electrodeposition of P(GBHA). When the upper potential applied during the electrosynthesis of the polymer film is higher than $+1.8 \text{ V}$ (vs. Ag/AgCl), the polymer film can be overoxidized, which can result in a decrease of electron transfer ability. In the case of upper potential's being lower than $+1.7 \text{ V}$ (vs. Ag/AgCl), the polymer film may not be deposited sufficiently on the surface of the electrode.

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