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Biosensors and Bioelectronics

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

Electrosynthesis of an imidazole derivative and its application as a bifunctional electrocatalyst for simultaneous determination of ascorbic acid, adrenaline, acetaminophen, and tryptophan at a multi-wall carbon nanotubes modified electrode surface

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ARTICLE INFO

Article history:

Received 28 June 2012

Received in revised form

16 September 2012

Accepted 20 September 2012

Available online 27 September 2012

Keywords:

Electrosynthesis

Bifunctional

Ascorbic acid

Adrenaline

Simultaneous determination

ABSTRACT

In this research, the electrosynthesis of 4-(1*H*-benzo[*d*]imidazol-2-ylthio)-5-methylbenze-1,2-diol (as an imidazole derivative) is reported. An imidazole derivative multi-wall carbon nanotube modified glassy carbon electrode (IMWCNT-GCE) was constructed and used as an excellent bifunctional electrocatalyst for oxidation of ascorbic acid (AA) and adrenaline (AD). Cyclic voltammetry was used to calculate the surface electron transfer rate constant, k_s , and the electron transfer coefficient, α , for the electron transfer between MWCNT-GCE and the electrodeposited imidazole derivative. The kinetic parameters such as the electron transfer coefficient, α , and the heterogeneous rate constant, k' , for the oxidation of AA and AD at the IMWCNT-GCE surface were estimated. The modified electrode was found quite effective for the simultaneous determination of AA, AD, acetaminophen (AC), and tryptophan (Trp) in a mixture solution. The detection limits of AA and AD were calculated as 0.96 μM and 0.38 μM , respectively. Finally, IMWCNT-GCE was satisfactorily used for the determination of AA, AD, and AC in pharmaceutical samples.

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1. Introduction

Now a days, the development of voltammetric methods for simultaneous determination of biomolecules in human fluids has been fascinating to biologists and analytical researchers (Zare and Nasirizadeh, 2011; Shahrokhian et al., 2009; Zare et al., 2006; Zare and Nasirizadeh, 2009). Biochemical compounds such as ascorbic acid (AA), adrenaline (AD), acetaminophen (AC), and tryptophan (Trp) are oxidized at nearly the same potential with poor sensitivity at unmodified electrodes. The overlap of their voltammetric responses makes their simultaneous determination highly difficult (Noroozifar et al., 2011). To overcome this problem, various modified electrodes have been constructed (Zare et al., 2005; Babaei et al., 2008; Nasirizadeh and Zare, 2009; Alothman et al., 2010; Zare and Nasirizadeh, 2010; Habibi et al., 2011). AD and AA always exist together in biological fluids, at most solid

electrodes; AA is oxidized at a potential close to that of AD, resulting in an overlapping voltammetric response. Electroanalytical methods with modified electrodes have raised great interest in simultaneous determination of the two compounds (Chen et al., 2006; Ensafi et al., 2010; Lu et al., 2011). A complementary presence of AA intensifies the main favourable effect of AC and concomitantly compensates for the potential toxicity in the function of the liver (Grundmann et al., 2006). Moreover, much of the corresponding literature points to major interferences between AA and AC (Habibi et al., 2011). Therefore, determining AC and AA simultaneously promises to be of great importance for the illustration of their precise physiological functions.

Also, in the presence of AA, Trp can be converted into 5-hydroxytryptophan which forms serotonin, an important brain chemical in animals. Determining Trp and AA concentration in animal blood can help scientists control the production of serotonin in the body (Babaei et al., 2008). As widely known, the oxidation peaks of AA, AD, and AC are nearly at the same potential on a bare electrode, which results in overlapping voltammetric responses, hence making their distinction highly

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difficult. They usually coexist in the extra cellular fluid of the central nervous system and serum. Thus, determining the neurotransmitter AD and its coexisting species individually or simultaneously is an important issue not only in the field of biomedical chemistry but also in diagnostic and pathological research. To meet the purpose, it is necessary to make further efforts for the fabrication of simple, rapid, selective and sensitive electrochemical modified electrodes that can be used for simultaneously determination of the above-mentioned biomolecules in presence of each other.

Electrosynthesis is a safe and low-cost method that is widely used for the synthesis of organic compounds. Catechol and hydroquinone redox systems have been extensively studied because of their biological and environmental importance, as well as the classical fundamental importance of their redox chemistry. There has been a growing interest in the study of reactions involving quinones produced through the oxidation of catechols versus other nucleophiles. This is due to the mechanistic and synthetic importance of these reactions (Fakhari et al., 2007; Shayani-Jam and Nematollahi, 2010; Costentin, 2008; Varmaghani and Nematollahi, 2011). Therefore, we have allocated the present study to the synthesis of 4-(1*H*-benzo[d]imidazol-2-ylthio)-5-methylbenzene-1,2-diol (as an another imidazole derivative). The compound has been used to modify multi-wall-carbon nanotubes (MWCNT) deposited at a glassy carbon electrode (GCE) surface. In this study, an imidazole derivative and MWCNT modified glassy carbon electrode (IMWCNT-GCE), serving as an excellent bifunctional electrocatalyst, has been used for electrocatalytic oxidation of AA and AD individually and in the presence of AC and Trp. The literature review indicates that there are not any reports about chemically modified electrode that can be used for electrocatalytic oxidation of both species of AA and AD, and simultaneous determination of AA, AD, AC, and Trp.

2. Experimental

2.1. Apparatus and chemicals

A potentiostat (μ Autolab, Eco Chemie, Utrecht, Netherlands), was used for electrochemical measurements. The working electrode was IMWCNT-GCE, and the reference electrode was a saturated calomel electrode (SCE). Also, a platinum electrode (Azar Electrode Co, Iran) was used as the auxiliary one. The pH measurements were done with a Metrohm model 691 pH/mV meter.

The multi-wall carbon nanotubes (10–20 nm in diameter, 5–20 μ m long, and 95% pure) were purchased from NanoLab Inc. (Brighton, MA). 4-methylcatechol, 2-mercaptobenzimidazole, phosphate salts, silica gel 60 (0.2–0.5 mm), AA, AD, AC, Trp, and the other reagents were provided from Merck Company and used as received. An injection solution of AD and vitamin C, tablets of AC, and an oral solution of AC were purchased in a local drugstore.

2.2. Electro-organic synthesis of an imidazole derivative

In a typical procedure, a 100-mL mixture of water/acetonitrile (85/15) containing phosphates ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$) as the buffer and supporting electrolyte (pH 7.0, $C=0.15$ M) was pre-electrolyzed at a chosen potential (0.15 V) in an undivided cell. Subsequently, 2 mmol of catechol and 2 mmol of nucleophile were added to the cell, and electrolysis was performed at the same potentials. The electrolysis was terminated once and more than 95% of the primary current was decayed. The process was interrupted several times during the electrolysis, and the carbon anode was washed in acetone in order to reactivate it. At the end

of the electrolysis, the cell was kept in a refrigerator overnight. The precipitated solid was collected by filtration and washed thoroughly with distilled water. After checking the purity of the resulted material, the product was characterized using IR, ^1H NMR, ^{13}C NMR, and MS (see S1, Supplementary Information).

2.3. Preparation of IMGCE, MWCNT-GCE and IMWCNT-GCE

MWCNT-modified GCE was prepared as following: after mechanical polishing of GCE using 0.05 μm alumina in water slurry using a polishing cloth and rinsing it with double distilled water, the electrochemical activation of the electrode was performed by a continuous potential cycling from -1.45 to 1.7 V at scan rate potential of 100 mV s^{-1} in a sodium bicarbonate (0.1 M) solution. 3 μL of a homogenized DMF-MWCNT mixture (1 mg/5 mL) was placed directly onto the activated GCE surface and dried at room temperature to form a MWCNT film at the GCE surface. IMWCNT-GCE was prepared by modifying the MWCNT-GCE in 0.15 M phosphate buffer solution (pH 7.0) containing 0.10 mM of the imidazole derivative by 16 cycles of scan rate potentials between -100 mV and 500 mV at 20 mV s^{-1} . To fabricate the imidazole modified GCE (IMGCE), the activated GCE was placed in a 0.15 M phosphate buffer (pH 7.0) containing 0.10 mM of the imidazole derivative. It was modified with the same procedure described for IMWCNT-GCE.

3. Results and discussion

3.1. Electrosynthesis of 4-(1*H*-benzo[d]imidazol-2-ylthio)-5-methylbenzene-1,2-diol

The cyclic voltammogram of 1.0 mM 4-methylcatechol in a water/acetonitrile (85/15) solution containing a 0.15 M phosphate buffer (pH 7.0) shows an anodic and a corresponding cathodic peak, which correspond to the redox reaction of 4-methylcatechol, the corresponding *o*-benzoquinone, and vice versa through a quasi-reversible two-electron process (Fig. 1, curve a). A ratio of the cathodic peak current to the anodic peak current (I_{pc}/I_{pa}) is near to 1, particularly during the repetitive recycling of the potential. It can be considered as a criterion

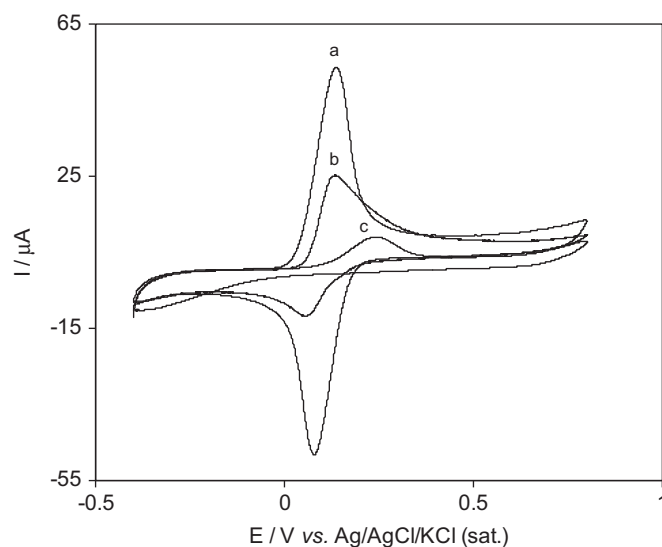


Fig. 1. Cyclic voltammograms of (a) 1 mM of 4-methylcatechol, (b) 1 mM of 4-methylcatechol in the presence of 1 mM of 2-mercaptobenzimidazole and (c) 1 mM of 2-mercaptobenzimidazole at a glassy carbon electrode in phosphate buffer (pH 7.0, 0.15 M); scan rate potential of 100 mV s^{-1} and room temperature.

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