Measurement 90 (2016) 510–518

Contents lists available at ScienceDirect

Measurement

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

Application of L-DOPA modified carbon nanotubes as a bifunctional electrocatalyst for simultaneous determination of ascorbic acid, adrenaline, acetaminophen and tyrosine

Hamid R. Zare *, Behnaz Moradiyan, Zahra Shekari, Ali Benvidi

Department of Chemistry, Yazd University, Yazd 89195-741, Iran

ARTICLE INFO

Article history:
Received 16 April 2015
Received in revised form 5 May 2016
Accepted 7 May 2016
Available online 9 May 2016

Keywords:
Bifunctional electrocatalyst
Ascorbic acid
Adrenaline
Acetaminophen
Tyrosine
Simultaneous determination

ABSTRACT

L-DOPA multi-wall carbon nanotube modified glassy carbon electrode (DOPA-MWCNT-GCE) was used as a bifunctional electrocatalyst for simultaneous quantitative determination of ascorbic acid (AA) and adrenaline (AD). Electrochemical experiments show that the modified electrode plays the role of an excellent bifunctional electrocatalyst for the oxidation of AA and AD in two different potentials. The kinetic parameters such as the electron transfer coefficient, α, and the heterogeneous electron transfer rate constant, k', for the electrocatalytic oxidation of AA and AD at the DOPA-MWCNT-GCE surface were estimated. Through a different pulse voltammetric (DPV) method, the plot of the electrocatalytic current versus AA and AD concentrations emerged to be constituted of two linear segments with different sensitivities. In addition, detection limits of 1.5 μM for AA and 0.62 μM for AD were obtained. In DPV, the proposed bifunctional electrocatalyst could separate the oxidation peak potentials of AA, AD, acetaminophen (AC) and tyrosine (Tyr) present in a mixture though, at the bare GCE, the peak potentials overlap. Finally, DOPA-MWCNT-GCE was satisfactorily used for the determination of AA, AD, AC and Tyr in pharmaceutical preparations.

1. Introduction

Adrenaline, AD, (or epinephrine) is a hormone in the catecholamine family which acting as a neurotransmitter in mammalian central nervous system. AD maintaining normal physical activity of the body including heart rate, blood pressure and the reactions of the sympathetic nervous system [1–3]. Various analytical methods have been reported for the analysis of AD, such as high performance liquid chromatography [4,5], capillary electrophoresis [6,7], fluorimetry [8], spectrophotometry [9,10] and electrochemistry [11]. Among these methods, electrochemical techniques exhibit a higher selectivity and sensitivity than other commonly employed methods and have the inherent advantages of low cost and rapid sensing time [12]. The electrochemical detection of AD on the surface of bare (unmodified) electrodes has some fundamental problems, mainly, high overpotential and sluggishness of the kinetics of the electrode process. Moreover, the other problem of measuring this monoamine in vivo is the very low AD concentration and the large excesses of interfering substances, such as ascorbic acid (AA). AA acts as an antioxidant to prevent oxidative stress. Reducing AA intake leads to a lack of hydroxylation of prolines and lysines, causing a looser triple helix and resulting in scurvy [13]. AA is an essential vitamin with a recommended daily intake of about 70 mg. Due to the mentioned importance of AA, its determination in solutions has significant importance [14]. At the unmodified electrode surfaces, AA is oxidized at a potential close to that of AD, resulting in an overlapping voltammetric response. In order to resolve this problem, different modified electrodes have been used, which can eliminate the interference of these species to the AD determination [15]. Acetaminophen, AC, (or paracetamol) is widely used as an analgesic and anti-pyretic drug. AC is commonly used for the moderate of headaches, other minor aches and pains, and is a major ingredient in numerous cold and flu remedies [16]. Overdose ingestions of AC lead to accumulation of toxic metabolites, which may cause severe and sometimes fatal hepatotoxicity and nephrotoxicity [17]. In body cellular fluids there are high concentrations of AA together with AC. A major problem in the accuracy of AC determination in the electrochemical method is presence of some potentially interfering constituents, especially AA. Therefore, development of a method that could determine AC in pharmaceutical preparations and clinical samples without any interference has significant importance [18]. Tyrosine is a non-essential amino acid with a polar side group [19]. Tyrosine supplementation may be of great therapeutic importance in depression, hypertension, stress,

* Corresponding author.
E-mail address: hrzare@yazd.ac.ir (H.R. Zare).

http://dx.doi.org/10.1016/j.measurement.2016.05.024
0263-2241/

cognitive function and memory, Parkinson's disease, phenylketonuria, and narcolepsy. Also, tyrosine is a precursor of the thyroid. The thyroid hormones are tyrosine-based hormones produced by the thyroid gland that are primarily responsible for regulation of metabolism. Thyroxin and catecholamine neurotransmitters enhance mood and cognitive function especially under situations involving stress or when dopamine, adrenaline or noradrenaline levels require additional support [20]. In other words, AA, AD, AC and Tyr have effected on each other and therefore, simultaneous determination of these compounds is an important issue not only in the field of biomedical chemistry but also in diagnostic and pathological research. So far, various methods have been applied for the simultaneous determination of biomolecules [21]. The results show that the direct oxidation of AA, AD, AC and Tyr at bare conventional electrode surfaces requires high overpotentials and their oxidation peak potentials are close to one another. Although there are a lot of papers which have introduced new modifiers which are capable of electrocatalytic oxidation or reduction of various species, there are just a few reports regarding the introduction of a bifunctional electron transfer mediators for the simultaneous electrocatalytic oxidation of two analytical species at different potentials [21,22]. A bifunctional electrocatalyst is able to catalyze the redox reaction of two species simultaneously [22,23].

The aim of the present work is to fabricate and utilize a L-DOPA (L-3,4-dihydroxyphenylalanine) multiwall carbon nanotubes modified glassy carbon electrode (DOPA-MWCNT-GCE) as a bifunctional electrocatalyst for the electrocatalytic determination of AA and AD and also its application for the simultaneous determination of AA, AD, AC, and Tyr in a mixture. Finally, to evaluate the utility of DOPA-MWCNT-GCE for analytical applications, it was used for the determination of AA, AD, AC, and Tyr in pharmaceutical preparations.

2. Experimental

2.1. Apparatus and chemicals

Electrochemical measurements were performed with an Autolab/PGSTAT 101 (Eco-Chimie) with the powerful NOVA software. A three-electrode electrochemical cell was employed for all the electrochemical measurements. The working, counter and reference electrodes were a L-DOPA multiwall carbon nanotubes modified glassy carbon electrode (DOPA-MWCNT-GCE) with a diameter of 2 mm, a graphite electrode, and a saturated calomel electrode (SCE), respectively. All the potentials in the text were reported with respect to this reference electrode. The pH measurements were done with a Metrohm model 691 pH/mV meter. The scanning electron microscopic (SEM) measurements were carried out with a field emission microscope (FE-SEM), MIRA3 TESCAN at an acceleration voltage of 15.0 kV.

Ascorbic acid (AA) 99.7%, adrenaline (AD) 97%, acetaminophen (AC) 99%, tyrosine (Tyr) 99%, L-DOPA 99% and other chemicals with an analytical reagent grade were purchased from Merck Company. An injection solution of AD (1.0 mg AD per each 1 mL solution) from Darou Pakhsh Co., Iran and tablets of AA (250 mg AA per each tablet) from Darou Osveh Co., Iran; AC (500 mg AC per each tablet) from Darou Alborz Co., Iran and Tyr (0.1 mg per each Tyr tablet) from Merck KGaA, Germany were purchased from a local drugstore. The required phosphate buffer solutions (0.1 M) were prepared with H_3PO_4, and the pH was adjusted with 2.0 M NaOH. All the aqueous solutions were prepared with doubly distilled water.

2.2. Preparation of modified electrodes

L-DOPA (L-3,4-dihydroxyphenylalanine) multi-wall carbon nanotube modified glassy carbon electrode (DOPA-MWCNT-GCE) was prepared as follow: after mechanical polishing of GCE successively with alumina in water slurry using a polishing cloth and rinsing it with double distilled water, bare GCE (BGCE) was put in ultrasonic bath for 2 min. The electrochemical activation of GCE was performed by a continuous potential cycling from −1.0 to 1.6 V at a potential scan rate of 100 mV s^{-1} in a sodium bicarbonate solution (0.1 M). For modification of MWCNT-GCE, 2 μL of a MWCNT-DMF mixture (1 mg mL^{-1}) was placed directly onto the activated GCE surface and dried at room temperature to form a MWCNT film at the GCE surface. Then, MWCNT-GCE was immersed in a 0.1 M phosphate buffer solution (pH 5.0) containing 1.0 mM of the L-DOPA solution and DOPA-MWCNT-GCE was prepared by 20 cycles in the potential range of −400 mV to 800 mV at 25 mV s^{-1}. To fabricate the L-DOPA modified GCE (DOPA-GCE), the activated GCE was placed in a 0.1 M phosphate buffer solution (pH 5.0) containing 1.0 mM of the L-DOPA solution and it was modified with the same procedure described for preparation of DOPA-MWCNT-GCE.

3. Results and discussion

3.1. Surface morphology of the DOPA-MWCNT-GCE

The surface morphology of different electrodes was characterized using scanning electron microscopy. Scheme 1 shows the scanning electron micrographs (SEM) of the bare GCE (Scheme 1A), MWCNT-GCE (Scheme 1B), and DOPA-MWCNT-GCE (Scheme 1C). The SEM of the bare GCE (Scheme 1A) displays its own smooth surface. The distribution of MWCNT on the surface of GCE indicates in Scheme 1B. Furthermore, when the DOPA is electrodeposited on the MWWCNT-GCE, a thin film of DOPA has been adsorbed on the MWCNT-GCE (Scheme 1C).

3.2. Electrochemical characterization of DOPA-MWCNT-GCE

Inset of Fig. 1A shows the cyclic voltammograms of DOPA-MWCNT-GCE in a 0.1 M phosphate buffer solution (pH 5.0) at various potential scan rates, v. As it can be seen, two well defined confined redox couples appear when the potential scan is performed in the range of −280 to +510 mV. These redox couples correspond to the redox reactions of electrodeposited L-DOPA at the electrode surface. The anodic/cathodic peak potentials of the redox couples are measured about 155/−85 mV (redox couple I) and 345/265 mV (redox couple II). Based on above peak potentials, the formal potentials ($E^{0\prime}$) values of the two redox couples are calculated as 35 mV and 305 mV. The formal potentials have been estimated as midpoint of the anodic/cathodic peak potentials. In addition, $E^{0\prime}$ is almost independent of v when potential scan rate is lower than 170 mV s^{-1}, suggesting facile charge transfer kinetics over this range of potential scan rate. Furthermore, the plots of the anodic and cathodic peak currents versus the scan rate exhibit a linear relation as predicted theoretically for a surface-immobilized redox couple. Fig. 1A shows these variations for the redox couple I. The peak currents were measured by means of base-to-base method. Fig. 1B shows the variations of the anodic and cathodic peak potentials as a function of log ν for the potential scan rates of 50–2500 mV s^{-1}. Fig. 1C shows above variations are linear for the potential scan rates of 500–2500 mV s^{-1}. Based on the data of Fig. 1C, the charge transfer coefficient (α) and the apparent heterogeneous charge transfer rate constant (k_s) for the electron transfer between the electrode surface (MWCNT-GCE) and a surface confined redox couple of L-DOPA can estimate according to the theory that devised by Laviron [24]. Based on the Laviron theory, the kinetic parameters of α and k_s can obtain from the slope and intercept of linear plots E_p versus log v, when $n\Delta E_p \geqslant 200$ mV ($\Delta E_p = E_{pa} - E_{pc}$). Using these plots at pH 5.0, α value was obtained