Electrochimica Acta 90 (2013) 317–325

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Nanomolar simultaneous determination of levodopa and serotonin at a novel carbon ionic liquid electrode modified with $Co(OH)_2$ nanoparticles and multi-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 30 July 2012
Received in revised form 31 October 2012
Accepted 17 November 2012
Available online 22 December 2012

Keywords:
Levodopa
Serotonin
Carbon ionic liquid electrode
Modified electrode
Electrochemical Sensor

ABSTRACT

A novel modified carbon ionic liquid electrode is prepared as an electrochemical sensor for simultaneous determination of levodopa (L-dopa) and serotonin (5-HT). The experimental results suggest that a carbon ionic liquid electrode modified with multi-walled carbon nanotubes and cobalt hydroxide nanoparticles, and coated with Nafion (Nafion/$Co(OH)_2$–MWCNTs/CILE), accelerates the electron transfer reactions of L-dopa and 5-HT. In addition it shows no significant interferences of uric acid and ascorbic acid as electroactive coexistent compounds with L-dopa and 5-HT in biological systems. The fabricated sensor revealed some advantages such as convenient preparation, good stability and high sensitivity toward 5-HT and L-dopa determination. The DPV data showed that the obtained anodic peak currents were linearly dependent on the L-dopa and 5-HT concentrations in the range of 0.25–225 and 0.05–75 μmol L^{-1}, respectively. The applicability of the modified electrode was demonstrated by simultaneous determination of 5-HT and L-dopa in human serum.

1. Introduction

Levodopa ((−)-3-(3,4-dihydroxyphenyl)-L-alanine, L-dopa) and 5-HT (5-hydroxytryptamine, serotonin) are important catecholamines in biological systems. L-Dopa is a naturally occurring dietary supplement and psychoactive drug found in certain kinds of food and herbs and is synthesized from the essential amino acids L-phenylalanine and L-tyrosine in the mammalian body and brain. Neurotransmitters play a significant role in the research of Parkinson's disease [1]. L-Dopa is currently the therapeutic drug in the treatment of Parkinson's disease and required by the brain to produce dopamine [2] which compensates the deficiency of dopamine in the organism and decreases the symptoms of Parkinson's disease. Various analytical methods have been developed for L-dopa determination, such as spectrophotometry [3,4], liquid chromatography [5,6], and capillary zone electrophoresis [7].

5-HT is another neurotransmitter of clinical interest which is synthesized in serotonergic neurons in the central nervous system and that plays a crucial role together with other monoamine transmitters in the emotional system such as regulation of mood, sleep, emesis (vomiting), sexuality and appetite. Low levels of 5-HT have been associated with several disorders, notably depression, migraine, bipolar disorder and anxiety [8,9].

The concentration of 5-HT in the animal brain is reported to be decreased with L-dopa injection. It has been pointed out that during L-dopa therapy, the content of 5-HT decreases in platelets of patients with Parkinson's disease. According to clinical evidence, L-dopa interferes with the metabolism of 5-HT in humans, which may be due to displacement of 5-HT with high doses of L-dopa as a false transmitter and inhibition of 5-HT synthesis [10,11]. In particular, various tumors of the sympatho-adrenal system are diagnosed by determination of the catecholamines and/or their metabolites in urine and blood [4] and hence, it is of great importance to develop a method for simultaneous determination of L-dopa and 5-HT.

Nafion is a commonly used film material in chemically modified electrodes for its unique ion-exchange, discrimination, chemical resistance and biocompatibility properties. As an ion-exchange polymer, Nafion films are highly permeable to cations but almost impermeable to anions [12–14]. In the pH range of 5.27–8.87, ascorbic acid (AA) (pK_a = 4.10) and uric acid (UA) (pK_a = 5.27) exist in anionic form, while L-dopa (pK_b = 8.72) and 5-HT (pK_b = 7.59) are in cationic form. Thus, a Nafion membrane strongly repulses anionic AA and UA and strongly attracts cationic species such as L-dopa, 5-HT or dopamine. Nagy et al. [12] demonstrated that negatively charged Nafion film could be used to determine some neurotransmitters. Nafion, due to its easy fabrication, good electrical conductivity, high chemical stability, good biocompatibility,

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http://dx.doi.org/10.1016/j.electacta.2012.11.121

and as a support for nanoparticles and enzyme has been widely used as a protective coating material.

Electrode modification with carbon nanotubes (CNTs) gives electrocatalytic activity toward the electro-oxidation of molecules. Furthermore, an increased electrode active surface area, which gives rise to enhanced electrochemical responses, and a demonstrated anti-fouling capability of electrode surfaces upon modification with CNTs, are other important practical advantages that have promoted a large number of significant applications in electroanalytical chemistry, including electrochemical sensors [15]. An important part of the impressive success of the use of CNTs for electroanalytical applications is probably due to the ability of this nanomaterial to promote electron transfer in electrochemical reactions [16].

Room temperature ionic liquids (RTILs) such as 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM)(PF_6), are compounds that composed of ions and exist in the liquid state below 298 K [17]. Because of their high stability, high electrical conductivity and very low vapor pressure, RTILs hold great promise for green chemistry applications in general and for electrochemical applications in particular [18]. In 2003, Fukushima et al. were the first to report that a thermally stable, highly conductive physical gel was formed with imidazolium ions and carbon nanotubes [19]. Recently, preparation of electrodes modified with a composite of room-temperature ionic liquids and carbon nanotubes have gained increasing attention for combining their desirable benefits to develop the performances of electrochemical sensing [20,21]. This new composite has several advantages compared to using graphite and other traditional carbon paste and composite electrodes, where it offers improved sensitivities toward a number of compounds, and at the same time lower detection potentials using a very small amount of MWCNTs [21].

Transition-metal nanoparticles, in different forms, have emerged as a novel family of catalysts able to promote more efficiently a variety of organic transformations because of their small size and extremely large surface-to-volume ratio [22,23]. Many nanoparticles have been successfully introduced onto CNTs, such as TiO_2 [24], CdTe [25], Au [26], Cu [27] and Ag [28]. Some electrodes such as platinum gauze [29], glassy carbon [30,31], and carbon paste [32,33] have been modified by Co and $Co(OH)_2$ particles and nanoparticles. Cobalt hydroxide with a low crystallinity and nano-flake network structure shows a high proton diffusion coefficient, giving excellent electrochemical performance. Various methods of preparation of cobalt hydroxide nanoparticles, ranging from spray pyrolysis [34], sonication [35], sputtering [36] and electrodeposition [30,37] to precipitate them at various pH values, have been considered. The method of precipitation is new and facile, needing no expensive raw materials or equipment. It is also easy for mass production and can be extended to synthesize other hydroxide or oxide nanocrystals [29].

To the best of our knowledge, there is only one report on the electrochemical determination of L-dopa and 5-HT using a glassy carbon electrode modified with a multi-walled carbon nanotube/chitosan composite [38]. Sun et al. used the paste of the RTIL and CNTs as the modifier on GCE for simultaneous determination of dopamine and 5-HT [39]. However these works suffers from the low sensitivity or narrow linear range of the proposed electrodes and interferences of uric acid and ascorbic acid during the determinations. In the present work an RTIL, (BMIM)(PF_6), is used as the binder for fabrication of a carbon ionic liquid electrode (CILE) then modified with a nanocomposite film which contains MWCNTs, $Co(OH)_2$ nanoparticles and Nafion, based on the idea that the MWCNTs with $Co(OH)_2$ nanoparticles could enhance the electron transfer rate for L-dopa and 5-HT, due to synergistic electrocatalysis which leads to increasing the sensitivity. Nafion as a cation-exchange polymer was used to reduce effects of some important interfering compounds like uric acid and ascorbic acid. The fabricated electrode was used as a new sensor for simultaneous determination of 5-HT and L-dopa.

2. Experimental

2.1. Reagents and solutions

L-dopa and 5-HT were obtained from Acros and Sigma chemical companies, respectively and Nafion (5 wt% solution in mixture of lower aliphatic alcohols and water) was obtained from Aldrich. (BMIM)(PF_6) was obtained from Hangzhou Kemer Chemical Limited Company. Spectrally pure graphite powder (average particle size 50 μm) from Merck was used as received. Multiwalled carbon nanotubes (MWCNTs) (>95 wt%, 5–20 nm) were purchased from PlasmaChem GmbH company. Other chemicals were obtained from Merck chemical company. Phosphate buffer 0.1 M solution (PBS) was prepared by dissolving appropriate amounts of sodium hydrogen phosphate and sodium dihydrogen phosphate in a 250 mL volumetric flask. The solution pH was adjusted to appropriate value by addition of 7.5 M sodium hydroxide solution. All electrochemical experiments were carried out in 0.1 M PBS at pH 7.5. The other chemicals were of analytical reagent grade purchased from Merck and used without further purification. Fresh human blood serum samples were available from Razi Institute of Vaccine and Serum Company (Tehran, Iran).

2.2. Synthesis of nanoscale $Co(OH)_2$

$Co(OH)_2$ nanoparticles (CHNPs) were synthesized according to a literature method [29]. Briefly, $Co(OH)_2$ materials were prepared by a simple precipitation method. The first step was the dissolving of cobalt chloride as aqueous solution (1 M, 25 mL) in a glass beaker, using a magnetic stir bar. The cobalt chloride solution was slowly adjusted to pH 9 by addition of 5 wt% $NH_3{\cdot}H_2O$ (30 mL) at a temperature around 10 °C. The $NH_3{\cdot}H_2O$ was added dropwise with a constant time interval of 5 s. The resulting suspension was stirred at this temperature for an additional 3 h. Then the solid was filtered, washed with a copious amount of distilled water several times. The obtained CHNP product was dried at 100 °C.

2.3. Instrumentation

All the voltammetric measurements were carried out using the Nafion/$Co(OH)_2$–MWCNTs/CILE electrode as the working electrode, Ag/AgCl 3 M KCl as the reference electrode and platinum wire as an auxiliary electrode at room temperature. A magnetic stirrer was used for the convective transport of the analyte. Cyclic voltammetry was scanned between −0.3 and 0.6 V at the scan rate of 0.1 V s^{-1}. Amperometric measurement was conducted under forced convection (stirring) by applying the appropriate potentials and allowing the transient currents to decay to a steady-state value. All experiments were done under a nitrogen atmosphere at room temperature by using an Autolab PGSTAT 30 Potentiostat Galvanostat (EcoChemie, The Netherlands) coupled with a 663 VA stand (Metrohm Switzerland). The pH measurements were performed with a Metrohm 744 pH meter using a combination glass electrode.

2.4. Electrode modification

The carbon ionic liquid electrode (CILE) was prepared by mixing graphite powder and $BMIMPF_6$ (w/w, 4:1) thoroughly in a mortar to form a carbon paste. A portion of the carbon paste was firmly filled into one end of a glass tube (ca. 1.8 mm i.d. and 10 cm long) and a copper wire was inserted through the opposite end to establish an electrical contact. The surface of