Sensors and Actuators B 183 (2013) 265–272

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Nanomolar simultaneous determination of levodopa and melatonin at a new cobalt hydroxide nanoparticles and multi-walled carbon nanotubes composite modified carbon ionic liquid electrode

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ARTICLE INFO

Article history:
Received 3 February 2013
Received in revised form 20 March 2013
Accepted 24 March 2013
Available online 1 April 2013

Keywords:
Levodopa
Melatonin
Carbon ionic liquid electrode
Modified electrode
Electrochemical sensor
Cobalt hydroxide nanoparticles

ABSTRACT

A novel modified carbon ionic liquid electrode (CILE) is prepared as an electrochemical sensor for simultaneous determination of levodopa (L-Dopa) and melatonin (Mel). The experimental results suggest that a carbon ionic liquid electrode modified with multi-walled carbon nanotubes and cobalt hydroxide nanoparticles accelerates the electron transfer reactions of L-Dopa and Mel. The fabricated sensor revealed some advantages such as convenient preparation, good stability and high sensitivity. The DPV data in 0.1 M phosphate buffer solution (PBS) (pH 7.5) allowed a method to be developed for the determination of L-Dopa and Mel concentrations in the ranges 0.1–300 and 0.01–50 μM, with the detection limits of 0.075 and 0.004 μM, respectively. The proposed method was successfully applied to determinations of these compounds in some pharmaceutical and human urine samples.

1. Introduction

Melatonin (Mel, N-acetyl-5-methoxytryptamine) is a lipophilic hormone, mainly produced and secreted at night by the pineal gland. The mechanisms that control its synthesis within the pineal gland have been well characterized [1] and the retinal and biological clock processes that modulate the circadian production of Mel in the pineal gland are rapidly being unraveled [2]. Main and best-known effect of Mel is restoring the natural cycle of organism functions [3]. It is safe and non-addictive sleep-inducing drug, which can eliminate disruptions in our circadian rhythm, in such situations as shift working, changing of time zones (during intercontinental air traveling) or insomnia. However, researchers also have shown that Mel has chronobiotic activities to resynchronize sleep and circadian rhythms disturbances and it is also involved in the regulation of seasonal reproduction, body weight and energy balance [4]. Mel can be detected in biological samples by several methods, such as HPLC [5], spectrofluorimetric and colorimetric methods [6,7] and electrochemical methods.

Levodopa (L-dopa) is a naturally occurring dietary supplement and psychoactive drug found in certain kinds of herbs and food and is synthesized from the essential amino acids L-phenylalanine and L-tyrosine in the brain and mammalian body. L-Dopa is currently the therapeutic drug in the treatment of Parkinson's disease and required by the brain to produce dopamine which compensates the deficiency of dopamine in the organism and decreases the symptoms of Parkinson's disease [8].

Carbon nanotubes (CNTs) are carbon materials that have a new kind of porous nanostructure, have been found to possess properties such as high surface area, high electrical conductivity, significant mechanical strength and chemical stability [9]. Multiwalled carbon nanotubes (MWCNTs) can be used to promote electron transfer reactions when used as electrode materials in electrochemical sensors [10].

Room temperature ionic liquids (RTILs) such as 1-butyl-3-methylimidazolium hexafluorophosphate, (BMIM)(PF_6), have been proposed to be very interesting and efficient pasting binder in place of non conductive organic binders such as Nujol or paraffin oil for the preparation of carbon ionic liquid electrodes (CILEs) [11]. This new composite has several advantages compared to other traditional carbon paste (CPEs) such as high electrical conductivity, high stability and very low vapor pressure [12], where it offers improved sensitivities toward a number of compounds, and at the same time

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http://dx.doi.org/10.1016/j.snb.2013.03.101

lower detection potentials using a very small amount of MWCNTs [13].

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 extremely large surface-to-volume ratio and small size [14]. Many nanoparticles have been successfully introduced onto CNTs, such as TiO_2 [15], Cu [16] and Ag [17]. Some electrodes such as glassy carbon electrode [18], and carbon paste electrode [19] have been modified by Co and $Co(OH)_2$ particles and nanoparticles. Cobalt hydroxide nanoparticles (CHNPs) with a low crystallinity and nano-flake network structure show a high proton diffusion coefficient, giving excellent electrochemical performance. Various methods of preparation of cobalt hydroxide nanoparticles, ranging from spray pyrolysis [20], sonication [21] and electrodeposition [18] 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 [22].

Simultaneous determination of L-Dopa and Mel is important, since numerous reports demonstrated that L-Dopa and Mel influence each other in their respective releasing [23–27] and also they coexist in a biological system. Lynch et al. [23] reported L-Dopa administration also causes profound increases in the pineal Mel content and its biosynthesis. This response is also potentiated by sympathetic denervation of the pineal. Srinivasan et al. [24] studied Mel secretion patterns in patients suffering from Parkinson disease. A phase advance of the nocturnal Mel maximum was noted in L-Dopa-treated but not in untreated patients. Under medication with L-Dopa, daytime Mel was additionally increased, a finding discussed in terms of an adaptive mechanism in response to the neurodegenerative process and possibly reflecting a neuroprotective property of Mel.

However, to the best of our knowledge no study has reported yet about the simultaneous determination of L-Dopa and Mel. In the present work an RTIL, (BMIM)(PF_6), is used as the binder for fabrication of a CILE and modified with a nanocomposite film which contains MWCNTs and CHNPs, based on the idea that the MWCNTs with CHNPs could enhance the electron transfer rate for L-Dopa and Mel, due to synergistic electrocatalysis which leads to increasing the sensitivity. The fabricated electrode was used as a new sensor for simultaneous determination of Mel and L-Dopa in some real samples.

2. Experimental

2.1. Reagents and solutions

L-Dopa and Mel were obtained from Acros and Sigma chemical companies, respectively. (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. 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 7.5 by addition of 1 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.

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

CHNPs were synthesized according to a literature method [22]. Briefly, $Co(OH)_2$ nanoparticles 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 drop wise 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 CHNPs product was dried at 100 °C.

2.3. Instrumentation

All the voltammetric measurements were carried out using the MWCNTs–CHNPs/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 −0.2 V and 1 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. X-ray diffraction (XRD) measurements were performed at a speed of 0.01° s^{-1} by a Bruker Axs diffractometer (Germany) with Cu Kα (λ = 1.5418 nm) operating at 40 kV, 30 mA. The morphology of the nanoscale CHNPs was investigated by scanning electron microscopy (SEM, Leica Cambridge, model S 360) and transmission electron microscopy (TEM, Philips CM10).

2.4. Electrode modification

The carbon ionic liquid electrode (CILE) was prepared by mixing graphite powder and (BMIM)(PF_6) (4:1, w/w) 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 the CILE was smoothened on a piece of weighing paper. The fabricated CILE was used as the basic solid electrode. A stock solution of MWCNTs–CHNPs in DMF was prepared by dispersing weighed amounts of MWCNTs and CHNPs (94/6%, w/w) in 1 mL DMF using ultrasonic bath until a homogeneous solution resulted, and 20 μL of the prepared suspension was casted on the CILE surface with a microsyring and dried at room temperature. During these procedures a small bottle was fitted tightly over the electrode so that the solvent could evaporate slowly and a uniform film was formed. The fabricated electrode was stored at 4 °C when not in use. For comparison, MWCNTs/CILE and CHNPs/CILE were prepared with similar procedures and used for further investigation.

2.5. General procedure

The electrode was first activated in PBS by cyclic voltammetric sweeps between −0.1 V and 1.1 V until stable cyclic voltammograms were obtained. Each sample solution (10 mL) containing 0.1 M PBS (pH 7.5) and appropriate amounts of L-Dopa and Mel were pipetted into a voltammetric cell. The open-circuit accumulation time was 90 s. Upon using the differential pulse voltammetric