Journal of Electroanalytical Chemistry 636 (2009) 40–46

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Electrochemical determination of L-dopa in the presence of ascorbic acid on the surface of the glassy carbon electrode modified by a bilayer of multi-walled carbon nanotube and poly-pyrrole doped with tiron

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ARTICLE INFO

Article history:
Received 17 May 2009
Received in revised form 14 August 2009
Accepted 2 September 2009
Available online 6 September 2009

Keywords:
Multi-walled carbon nanotube
Poly-pyrrole
Electro-polymerization
Tiron
L-dopa
Electrochemical determination

ABSTRACT

There are high attractions in the development of conducting polymer (CP) coatings to improve the electrochemical properties and biocompatibility of electrodes in the area of biosensors. A new type of the modified electrodes is prepared in a layer-by-layer process by using multi-walled carbon nanotube (MWCNT) and poly-pyrrole. In this procedure, the glassy carbon electrode is casted by a drop suspension of MWCNT, which leads to form a thin film of nanotube on its surface. In the second step, electrochemical polymerization of pyrrole in the presence of tiron (used as doping anion) is performed on the surface of the MWCNT pre-coated electrode. The modification procedure led to fabrication of a modified electrode that can be used as a sensitive and selective sensor for voltammetric determination of L-dopa. The electrochemical behavior of L-dopa is investigated on the surface of the modified electrode using cyclic voltammetry (CV) in various potential sweep rates and pHs of the buffer solution. The effect of drop size of MWCNT suspension and the number of cycles in the electro-polymerization process on the electrode response toward L-dopa has been optimized. The results of CV and DPV investigations showed a considerable enhancement in the anodic peak current of L-dopa (up to seven times) associated with decreasing about 180 mV in the corresponding peak potential. Furthermore, high reproducibility as well as low detection limit of the electrode responses can be considered as significant features of the prepared modified electrode.

1. Introduction

Parkinson's disease (PD) is believed to be related to low levels of dopamine in certain parts of the brain. Levodopa (L-dopa) is considered the most effective treatment available for Parkinson's disease. When L-dopa is taken orally, it crosses through the "blood–brain barrier". Once it crosses, it is converted to dopamine. The resulting increase in brain dopamine concentrations is believed to improve nerve conduction and assist the movement disorders in PD. Therefore the success of dopamine replacement therapy by its precursor, L-dopa, is a major landmark in the field of neurology. Chronic L-dopa treatment in PD patients is frequently associated with some side effects such as nausea and vomiting results from the increases of plasma L-dopa level. Clearly the process of L-dopa detection and its concentration determination is an important feature in pharmaceutical and clinical procedures [1–3].

Several methods for the determination of L-dopa have been described in literature including high performance liquid chromatography (HPLC) [4,5], flow injection system [6] and capillary zone electrophoresis [7–9]. Beside the fact that the methods based on electrochemical sensors have many advantages over the other methods, there are few papers on the determination of L-dopa in pharmaceutical formulations using the modified electrodes [10–12].

Carbon nanotubes (CNTs) are new kinds of carbon nanostructure materials which have been widely used because of their fascinating electronic, chemical and mechanical properties such as high electrical conductivity, high surface area and chemical stability [13–16]. They also exhibit extraordinary mechanical strength and unique electrical properties that make them potentially useful in many applications [17–20]. As a result of their electronic properties, they have been exploited as a means to promote the electron transfer reaction for a wide range of molecules and biological species in electrochemical investigations [21–24].

On the other hand, in the recent years, conducting polymers (CPs) which exhibit several interesting properties such as, significant electrical conductivity and reversible convertibility between

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doi:10.1016/j.jelechem.2009.09.010

redox states, have received considerable attention in the development of sensors and biosensors [25–27]. The electrical conductivities of CPs are known to be strong functions of their oxidation states and doping anion used in the electro-polymerization process [28,29]. In the case of poly-pyrrole (ppy), the results of cyclic voltammetry showed that the oxidized polymer is highly conducting, while the reduced form is not. Consequently, among the CPs, ppy have been of great interest both from a fundamental point of view and for broad potential applications in the area of biosensors [30–34].

In fact, composites of CPs and CNTs could be synthesized by either chemical or electrochemical polymerization in the presence of CNTs [26]. Nanocomposites of CPs are found to have superior performance relative to the conventional materials due to their much larger exposed surface area. These nanomaterials can be used in a variety of electrochemical biosensing schemes thereby enhancing the performance of these devices and opening new horizons in their applications [35]. In the present work, the modified electrode was fabricated via an electrochemical polymerization of ppy on the surface of a GC electrode pre-coated by a thin layer of MWCNT. This has numerous advantages over those of chemically prepared ones. The electrochemical polymerization of pyrrole on the surface of glassy carbon electrode coated with a nanotube film is described in the presence of tiron as doping anion. This process leads to fabrication of a modified electrode which can be applied as a sensitive and selective sensor for voltammetric determination of L-dopa. The electrochemical behavior of L-dopa on the surface of the modified electrode is investigated by means of cyclic and differential pulse voltammetry (CV and DPV). The modified electrode showed important electrochemical advantages, such as considerable enhancement in peak current (up to 7 times) associated with significant decrease in peak potential, high selectivity and sensitivity, low detection limit, excellent reproducibility and relatively wide linear dynamic range. Also, the thickness and morphology of the bilayer of CNT and polymeric films coated on the electrode surface were characterized using atomic force microscopy (AFM). The results of AFM images showed a highly porous surface in which, the microscopic surface area is increased dramatically.

2. Experimental

2.1. Chemicals

Multi-walled carbon nanotubes (purity >95%) with outer diameter less than 10 nm and tubes length of 5–15 μm was prepared from Nanostructured and Amorphous Materials (USA). Levodopa (L-dopa) was from Aldrich. Tiron was purchased from Fluka and used as dopant counter anion in the electro-polymerization procedure. Pyrrole and dimethylformamide (DMF) were purchased from Merck. Stock solutions of L-dopa were freshly prepared as required in 0.1 M of appropriate buffer solutions. In these experiments 0.1 M acetate was used for preparation of pHs 4 and 5, and 0.1 M phosphate for pHs 3, 6 and 7. Aqueous solutions were prepared using doubled distilled water, which is prepared over the alkaline dilute permanganate solution. All solutions were deaerated by purging with nitrogen gas (99,999%) prior to each experiment. During the experiments, nitrogen gas was passed over the surface of the test solutions in order to avoid entrance of oxygen into the solution.

2.2. Apparatus

All electrochemical measurements were performed using a Metrohm Computrace Voltammetric Analyzer (model 797 VA) instrument. An electrochemical cell with a three-electrode configuration was used with a glassy carbon electrode (unmodified and/or modified) as working electrode. Counter and reference electrodes were a pt wire and saturated Ag/AgCl electrode, respectively.

A digital pH/mV/Ion meter (CyberScan, model 2500) was utilized for preparation of the buffer solutions, which were used as supporting electrolyte in the voltammetric experiments. The AFM images were taken by a Thermomicroscopes Autoprobe, CP Research (Veeco) in contact mode.

2.3. Preparation of the modified electrode

Beside the fact that conducting polymers exhibit interesting properties, the rate of their inter-conversion is usually slow. This is due to the slow transport of counter ions into the polymer layer to maintain the charge balance. It is found that nanotubular structures are good candidates for realizing rapid switching between redox states. For this purpose, the appropriate amount of pure MWCNTs was functionalized under nitric acid treatment process in order to obtain better nanotube dispersion [36]. After functionalization procedure, 1 mg of the functionalized MWCNTs (CNT-COOH) was dispersed in 1 mL of DMF solvent under ultrasonic agitation for 1 h prior to use. Then a desired μL of the dispersed CNTs was taken with a microsyringe and after casting on the electrode surface, the electrode was heated in oven at 50 °C for 15 min. The electrode was then kept in room temperature for 1 h (named as CNT-GC electrode). The electro-deposition of the ppy film on the surface of GC electrode pre-coated with CNT was carried out from an aqueous solution containing 0.02 M tiron and 0.01 M pyrrole by potential cycling between 0.0 V and +0.8 V (*versus* Ag/AgCl) at scan rates of 50 mV s^{-1} for a total of five scans (Fig. 4). After the electro-polymerization procedure, the electrode was rinsed thoroughly with doubled distilled water and used as a modified electrode without further treatment. This electrode recognized as ppy-CNT-GC electrode in the following parts.

3. Results and discussion

3.1. Surface characterization of the modified electrode

The morphology of the modifier films on the surface of GC electrode was studied by atomic force microscopy. Fig. 1 presents the topography images acquired in contact mode from the surface of CNT-GC and ppy-CNT-GC electrodes. From these images it can be seen that the surface morphology is considerably changed in the presence of ppy on the surface of the CNT-coated electrode. It is noteworthy to mention that the entire electrode surface was densely covered by polymer films in a homogenous way. The highly uniform microporous structure of ppy/CNT films, which are formed via layer-by-layer deposition, suggests much larger surface area that affects the electrode surface properties toward diffusing electroactive species. From these measurements, the thickness of the bilayer obtained by 5 cycles of electro-deposition on the surface of GCE pre-coated with 10 μL of CNT suspension is estimated to be 300 nm.

3.2. Electrochemical investigations on the surface of the modified electrode

The electrochemical behavior of L-dopa was investigated by means of cyclic (CV) and differential pulse voltammetry (DPV) on the surface of different electrodes including bare glassy carbon electrode (GC), glassy carbon electrode coated with CNT (CNT-GC) and layer-by-layer modified electrode (ppy-CNT-GC), respectively. The results of CV and DPV studies of 1 mM L-dopa in