Materials Science and Engineering B 185 (2014) 53–59

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Polyaniline–bismuth oxide nanocomposite sensor for quantification of anti-parkinson drug pramipexole in solubilized system

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ARTICLE INFO

Article history:
Received 9 September 2013
Received in revised form 25 January 2014
Accepted 8 February 2014
Available online 22 February 2014

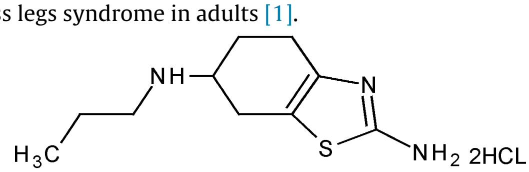
Keywords:
PANI
Bi_2O_3 nanopowder
PANI–Bi_2O_3/GCE
Pramipexole
Voltammetry

ABSTRACT

In this study, a new sensor polyaniline–bismuth oxide (PANI–Bi_2O_3) nanocomposite has been fabricated and characterized by cyclic voltammetry (CV), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). SEM was used to provide information about the morphology of the PANI–Bi_2O_3 nanocomposite. Cyclic voltammetric studies of electroactive species i.e. $K_3Fe(CN)_6$ demonstrate almost reversible electrochemical behaviour, with diffusion controlled mass transfer process in the double layer region of the electrode. EIS studies revealed that PANI–Bi_2O_3/GCE having lower charge transfer resistance which leads to higher electrocatalytic activity. This modified electrode was successfully used for the detection of pramipexole in pharmaceutical formulation in sodium lauryl sulphate (SLS) in Britton Robinson (BR) buffer at pH 4.5. The ease of fabrication, excellent electrochemical performance and high electroactive surface area are the promising features of the fabricated sensor.

1. Introduction

The anti-parkinson drug pramipexole, (*S*)-N^6-propyl-4,5,6,7-tetrahydro-1,3-benzothiazole-2,6-diamine [A] is an orally active, non-ergoline dopamine agonist, approved in the US and Europe for the treatment of early-stage Parkinson's disease and idiopathic restless legs syndrome in adults [1].



[A]

Electrochemical biosensors are appealing, as they have many potential applications in various fields, including medical diagnosis, pharmaceuticals and environmental control. Approaches for designing electrochemical biosensors now also include the incorporation of metallic nanoparticles in conducting polymer due to the strong electronic interaction between nanoparticles and polymer matrixes [2–6]. Many studies have reported the synthesis of PANI with different inorganic metal oxides viz., V_2O_5 [7], TiO_2 [8], SnO_2 [9], WO_3 [10], $LaFeO_3$ [11], and Fe_3O_4 [12].

The discovery of polymer nanocomposites by the Toyota Research Group has received a rapidly growing research interest in the field of materials science. Composites of conducting polymers and metal nanoparticles permit a facile flow of electronic charges across the polymer matrix during electrochemical processes. Inorganic–organic composite materials are important due to their extraordinary properties, which arise from the synergism between the properties of the components [3–6]. Amongst conducting polymers, polyaniline (PANI) is one of the most extensively studied polymers due to its environmental stability, interesting redox properties, high electrocatalytic activity and facile synthesis [13–16]. Among all the given metal oxides, bismuth oxide (Bi_2O_3) is recognized as one of the most promising electrode materials for electrochemical sensing devices due to its characteristic parameters such as energy band gap, large surface area, electrochemical stability and catalytic behaviour that are suitable for large range applications. Apart from the improvement in the sensitivity, its high electrical conductivity, chemical stability and mechanical strength proved a suitable electrochemical sensor for its application in voltammetric measurement [17–20]. Incorporation of this metal oxide into PANI can give rise to organic–inorganic hybrid material with improved physical, chemical and electrochemical properties. In this work, PANI–Bi_2O_3 nanocomposite is used as the signal enhancement element for the detection of pramipexole.

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http://dx.doi.org/10.1016/j.mseb.2014.02.007
0921-5107/© 2014 Published by Elsevier B.V.

Few analytical methods have been explored for the estimation of pramipexole viz., UV–visible spectrophotometric in pharmaceutical formulation [21–24], capillary electrophoresis with laser-induced fluorescence detector [25], high performance liquid chromatographic (HPLC), liquid chromatography–mass spectrometry (LCMS) [26–29], voltammetric [30] and chiral chromatographic method [31]. Modern electroanalytical techniques are becoming increasingly important for the determination of pharmaceutically significant compounds [32–35]. Electroanalytical techniques are time saving, cost effective, provide qualitative and quantitative information. In electroanalysis surfactants' influence, the electrochemical processes of electro-active species [36,37] and thus are widely used in electroanalytical chemistry to improve the sensitivity and selectivity. However, to the best of our knowledge, the application of PANI–Bi_2O_3 nanocomposite in electrochemistry has not been reported yet. In the present study, PANI–Bi_2O_3 nanocomposite synthesized by the interfacial polymerization method has been adopted to modify glassy carbon electrode. The modified electrode exhibited good electrocatalytic behaviour in the detection of pramipexole utilizing enhancement effect of surfactant. Charge transfer resistance was investigated using electrochemical impedance spectroscopy (EIS).

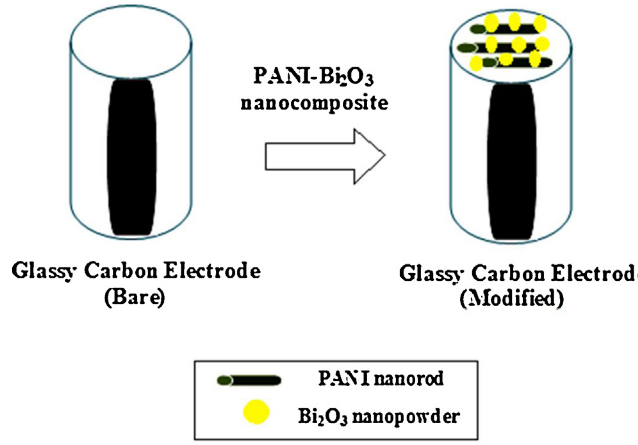
2. Experimental

2.1. Instrumentation

Electrochemical measurements were performed using a μ Autolab Type III (Eco-Chemie B.V., Utrecht, The Netherlands) potentiostat–galvanostat with 757 V A computrace software. A conventional three electrode system was used, consisting of an Ag/AgCl (3.0 mol/L KCl) as reference electrode, a bare or modified glassy carbon electrode as a working electrode, and a graphite electrode as an auxiliary electrode. All the solutions examined by an electrochemical technique were purged for 10 min with purified nitrogen gas, after which a continuous stream of nitrogen was passed over the solutions during measurements. All pH measurements were made on a Decible DB-1011 digital pH meter fitted with a glass electrode and a saturated calomel electrode as reference, which was previously standardized with buffers of known pH. The EIS study was carried out at Autolab 112 potentiostat–galvanostat 302N (The Netherlands) with software NOVA 1.8.

2.2. Chemicals and reagents

Bismuth(III) oxide nanopowder with 99.8% purity, 90–210 nm was obtained from Sigma Aldrich. All other chemicals used were of analytical reagent grade. Aniline was distilled under reduced pressure prior to use and other reagents were employed without further purification. Ultra pure water, obtained from Milli-Q purification system (Millipore Corp., Milford, MA, USA) and double distilled water from distillation assembly, was used for necessary detections. Pramipexole standard (98% purity) was received as a gift from Zydus Clinical Research Pvt. Ltd., Ahmedabad (India) and used as received. Tablet containing pramipexole (Pramipex) labelled 0.5 mg was obtained from commercial sources manufactured by Sun Pharmaceutical Industries. A KCl (1.0 mol/L) solution was prepared in double distilled water and used as supporting electrolyte. Stock solutions of pramipexole (1.0 mg/mL) were prepared in different solvent systems such as sodium lauryl sulphate (SLS), cetyltrimethyl ammonium bromide (CTAB), Tween 20, *N*,*N*-dimethylformamide (DMF), ethanol, methanol and water.



Scheme 1. The fabrication of sensor.

2.3. Preparation of PANI–Bi_2O_3 nanocomposite

The PANI–Bi_2O_3 nanocomposite was prepared by interfacial polymerization method using ammonium persulphate as an oxidizing agent. Typical synthesis consists the following steps: (1) 0.2 mL predistilled aniline was dissolved in 20 mL carbon tetra chloride and labelled it as solution A. (2) An amount of 450 mg ammonium persulphate was dissolved in 0.1 M camphor sulphonic acid and stirred until a homogenous solution is obtained and labelled it as solution B. (3) An amount of 60 mg Bi_2O_3 was added to solution B, and then solution A was added to the mixture B with vigorous stirring for 10 min by keeping it at temperature (4–5 °C) for 18–20 h. Polymerization reaction occurred at an interfacial layer between two immiscible solvents. (4) After that prepared nanocomposite (15 wt% Bi_2O_3 concentration) was extracted by centrifugation, washed with deionized water and ethyl alcohol for several times and left it for drying at room temperature overnight [38,39]. Similarly, other nanocomposites with respect to varied concentration of Bi_2O_3 were also synthesized.!!

2.4. Fabrication of PANI–Bi_2O_3 nanocomposite electrode

Before each measurement, the GCE was carefully polished with 0.5 μ alumina powder on a soft polishing cloth and thoroughly rinsed with double distilled water, ethanol and DMF, followed by sonication in an ultrasonic bath for 10 min. The electrode was then transferred to the supporting electrolyte and potential in the range of 0.2 to 1.5 V was applied in a regime of cyclic voltammetry for 20 cycles until a stable volammogram was achieved. Prepared PANI–Bi_2O_3 nanocomposite was dispersed in DMF with ultrasonication for 2 h to get homogenous suspension. 10 μL of the suspension was cast on the surface of freshly polished GCE. Scheme 1 shows the fabrication of the sensor.

2.5. Methodology

The method used for the analysis of pramipexole at PANI–Bi_2O_3 modified sensor is briefly described. Initially 20 tablets of pramipexole (0.5 mg/tab) were crushed to a fine powder and all contents were mixed thoroughly. A stock solution (1 mg/mL) was prepared by dissolving the sufficient amount of the crushed tablets equivalent to 10 mg of pramipexole into 10 mL aqueous solution of SLS. The solution was sonicated for 10 min to dissolve all contents of tablets properly and centrifuged at 3000 rpm for 5 min. After that, clear supernatant liquid of this solution was withdrawn and diluted to achieve the desired concentration. The square-wave