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Materials Today: Proceedings 3 (2016) 1854–1863

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Recent Advances In Nano Science And Technology 2015 (RAINSAT2015)

Nanocomposite modified electrochemical sensor for sensitive and selective determination of noradrenaline

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Abstract

A glassy carbon electrode was modified with graphene-chitosan nanocomposite for the sensitive and selective determination of noradrenaline. The morphological characteristics of nanocomposite were studied by scanning electron microscope and atomic force microscopy. Electrochemical characterization of the modified sensor was done using cyclic voltammetry and electrochemical impedance spectroscopy. Enhancement in electron transfer process and reduction in charge transfer resistance was observed. The electrochemical behavior of noradrenaline at nanocomposite modified sensor was investigated in pH 7.4 phosphate buffer solution using cyclic voltammetry and square wave voltammetry. The modified sensor showed high sensitivity and selectivity for the determination of noradrenaline. The method was also successfully employed for determination of noradrenaline in a pharmaceutical formulation.

Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015.].

*Keywords:*Noradrenaline;Voltammetry;Graphene;Chitosan;Nanocomposite

1. Introduction

Noradrenaline (NA), a catecholamine derivative is secreted and released by adrenal glands. It plays important physiological roles in the central nervous system [1]. It is also commonly used as the drug of choice as a

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Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015.
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vasoconstrictor, cardiac stimulator and bronchodilator [2]. It stimulates arteriole contraction, affects muscle and tissue control, decreases peripheral circulation and activates lipolysis in adipose tissue. It is critically linked to mental diseases, heartfailure, DNA breaks in cardiac myoblast cells and diabetes [3]. Thus, it is important to determine its concentration in the biological fluids selectively.

Various methods have been explored for the determination of NA like spectrophotometry, capillary electrophoresis and high performance liquid chromatography [4-6]. NA being an electroactive compound, its electrochemical detection has been explored using various electrodes. Electrochemical detection is advantageous as offers fast, accurate, cheap and sensitive analysis of analytes undergoing redox reactions. The analysis is hindered at bare electrodes due to either interference or fouling effect [7]. Ascorbic acid and uric acid share similar redox potential as NA and thus interfere with its analysis [8]. Chemically modified electrodes using electron transfer mediators are thus being used to achieve sensitivity and selectivity in detection [3]. In this context, nanomaterials have gained much attention. Nanocomposites possess unique physical, chemical, optical, mechanical, magnetic and electrical properties as they combine materials with synergistic or complementary behaviors. Recently, various nanocomposites consisting of either metal-metal oxide, mixed metal oxides, polymers mixed with metal or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides have attracted attention as active materials for electrochemical sensing [9].

Graphene, a relatively new carbon-based nanomaterial has attracted interest in fundamental and applied sciences recently. It's unusual electrical conductivity, high specific surface area; high mechanical, thermal and chemical stabilities make it a suitable material for electrochemical catalysis and biosensing [10]. Chitosan, on the other hand possesses significant film-forming and adhesion properties. It is non-toxic, biocompatible and provides a hydrophilic environment to biomolecules as it has abundant amino and hydroxyl groups. Thus, it offers to improve hydrophilicity as well as biocompatibility via covalent grafting techniques [11-12]. In the present work we have used graphene-chitosan (GRP-CHIT) nanocomposite modified glassy carbon electrode (GCE) for the sensitive and selective electrochemical determination of NA using cyclic voltammetry (CV) and square wave voltammetry (SWV). Enhancement in current response was observed at the modified sensor (GRP-CHIT/GCE). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) was used to study the modifier surface. Electrochemical impedance spectroscopy (EIS) showed reduction in charge transfer resistance at the modified sensor. The effect of pH, scan rate and concentration on the electrochemical response was also studied. The applicability of the modified sensor was tested in human blood serum.

2. Experimental

2.1. Instrumentation

All electrochemical studies were performed on a PC-controlled AUTOLAB PGSTAT 302N (Eco-Chemie B.V., Utrecht, The Netherlands) potentiostat-galvanostat with IME663 and software NOVA 1.8. EIS was carried out using FRA 2 module. A standard three electrode electrochemical assembly was used in the study that contained GCE and GRP-CHIT/GCE as working electrode, platinum wire as counter and Ag│AgCl (3M KCl) as reference electrode that were fitted in one compartment cell connected with electrochemical workstation through Metrohm 663VA stand. The electrochemical cell was fitted with the nitrogen gas bubbler. All pH measurements were made on a Mettler Toledo pH meter fitted with a glass electrode and Ag│AgCl electrode as a reference which was pre-standardized with buffers of known pH. All measurements were carried out at room temperature. A DL-180 ultrasonic apparatus was used for sonicating the suspension of GRP-CHIT for modifying GCE. Atomic force microscopic (AFM) study was carried out at NanosurfEasyscan (Switzerland) with software Nanosurf 1.8. SEM was performed at Tescan (7718) involving the software, Mira TC.

2.2. Materials and Reagents

Chitosan was purchased from MP Biomedicals (India). GRP (12 nm) was procured from Graphene laboratories. Noradrenaline standard (≥99%) was obtained from the Sigma Aldrich. Ultra pure water (Milli-Q water with