



A facile method to anchor reduced graphene oxide polymer nanocomposite on the glassy carbon surface and its application in the voltammetric estimation of tryptophan in presence of 5-hydroxytryptamine



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ABSTRACT

A 4-amino-3-hydroxy-1-naphthalenesulfonic acid (AHNSA) and reduced graphene oxide (rGO) based polymer nanocomposite (PNC) has been electrodeposited directly on the surface of glassy carbon electrode (GCE) using cyclic voltammetry. The electrochemical reduction of graphene oxide (GO) to rGO and the synthesis of PNC have been inspected using FE-SEM, TEM and Raman spectroscopy. The modified GCE was further used for the voltammetric quantification of Tryptophan (Trp) in the presence and absence of 5-hydroxytryptamine. The PNC modified sensor exhibited improved sensing and electrocatalytic properties in comparison to unmodified GCE, rGO modified GCE and AHNSA modified GCE. The fabricated sensor showed a linear calibration plot in the range of 0.5–200 μM with sensitivity and limit of detection (L.O.D.) of 0.0451 $\mu\text{A } \mu\text{M}^{-1}$ and 316 nM ($n = 3$) respectively in comparison to 0.19 $\mu\text{A } \mu\text{M}^{-1}$ and 2.54 μM ($n = 3$) respectively for unmodified GCE. The proposed method was also successfully applied for the determination of Trp in commercially available pharmaceutical formulations, human urine and plasma samples.

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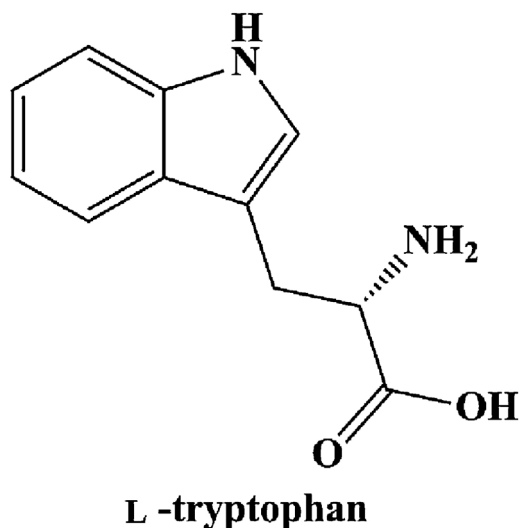
1. Introduction

Graphene has been a topic of intense research during last decade due to its compendium of properties, like its high mechanical strength [1], tunable band gap [2,3], and astonishing electron mobility at room temperature [4,5]. Graphene is an example of material, where a pool of properties can be found and thus is a potential candidate for a plethora of applications including biosensors [6,7], fuel cells [8], capacitors [9], electrocatalysis [10], and many more. However, its high cost limits its practical application in the real world and thus many researchers are working towards finding a cost effective, environment friendly and efficient route for the synthesis of graphene. At present, the major method employed for graphene synthesis includes epitaxial growth, mechanical exfoliation and chemical reduction of graphene oxide (GO) [11,12]. Out of the three methods, the chemical reduction of GO is most widely used for the synthesis of graphene (reduced graphene oxide; rGO), however, the use of toxic chemicals like hydrazine or hydro-

quinone for carrying out reduction makes it a less suitable method [12,13]. The electrochemical reduction of GO can serve as an alternative technique for synthesizing electrochemically reduced GO (ErGO) as it provides a fast, green and inexpensive means for the reduction of materials [13]. As the ErGO has the propensity to agglomerate and revert back to graphite, conducting polymer 4-amino-3-hydroxy-1-naphthalenesulfonic acid (AHNSA) has been used to overcome the problem of aggregation and to confer stability to the rGO sheets formed [14]. The oxygenated functional moieties at the surface of ErGO provides increased number of active sites for the electrodeposition of poly AHNSA, whereas, AHNSA prevents the aggregation of rGO sheets. Thus both rGO and AHNSA provide the synergistic effect, where both strengthens each other and results in a polymer nanocomposite (PNC) with superior properties [14]. The use of conducting polymer further enhances the conductivity of the PNC, whereas the synergistic interaction between AHNSA and rGO results in shorter ion diffusion paths and π - π interaction that fosters the electron transport [15]. Thus, the superior electron transport properties of AHNSA:ErGO PNC has been exploited and the resulting composite has been employed for developing a voltammetric sensor for the quantification of tryptophan (Trp) or L-2-amino-3-(indole-3-yl) propionic acid (Scheme 1); an essen-

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L -tryptophan

Scheme 1. Trp structure.

tial amino acid required by the human system for the synthesis of proteins and some specialized molecules, such as serotonin, NAD and ATP [16,17]. Many studies in the recent times have shown the direct effect of Trp concentration on the functioning of endocrine system. [16,18]. However, acute changes in Trp levels have also been found associated with the basic behavioral and psychological nature of mammals. Trp levels are monitored to investigate and diagnose symptoms like mood swings, insomnia, seasonal affective disorder, Schizophrenia, Bipolar Disorder, Bulimia Nervosa, Obsessive Compulsive Disorder, Panic Disorder, Premenstrual Syndrome etc. [16,19]. Thus, in alternative medicine, L-tryptophan has been employed for the treatment of large number of physiological conditions, such as depression and mental disorders, anxiety, premenstrual dysphoric disorder (PMDD), grinding teeth, attention deficit- hyperactivity disorder (ADHD), smoking cessation and many more [20].

Various methods for the determination of Trp have been reported in the recent literature, such as, flow injection chemiluminescence [21], high pressure liquid chromatography [22], colorimetry [23], chromatography-spectrophotometry [24], electroanalytical methods [25], however, electrochemical detection has been found more attractive technique for the determination of electroactive compounds because of its sensitivity, fast operation, reproducibility, accuracy, low-cost, negligible sample and solvent consumption and recently it has been developed as a potentially useful technique for pharmaceutical applications [26]. Many electrodes with different type of surface modifications have been practically extended for the determination of Trp in the last few years, such as, Co₃O₄ nanoparticles-decorated graphene composite modified glassy carbon electrode (GCE) [27], GCE in the presence of electrochemical catalyst, 4-chlorocatechol [28], 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one modified multiwall carbon nanotubes paste electrode (DMBQMCNTPE) [29], gold nanoparticles modified carbon paste electrode (CPE) [30], multi-walled carbon nanotubes bridged mesocellular graphene foam nanocomposite (MWNts/MGF) modified GCE [31], gold nanoparticles/overoxidized-polyimidazole composite modified GCE [32], p-phenylenediamine, glutaraldehyde linked cysteamine capped cadmium sulfide quantum dots modified screen-printed carbon electrodes (SPCEs) [33] and many more.

In the present study, a facile, single step polymer modification of ErGO has been carried out. The surface modified glassy carbon electrode (GCE) thus obtained has been characterized using Field Emission Scanning Electron Microscopy (FE-SEM), Transmission

Electron Microscopy (TEM), Raman Spectroscopy and electrochemical Impedance Spectroscopy (EIS). The electron transport properties and sensing ability of PNC have been analyzed using AHNSA:ErGO modified glassy carbon electrode for the determination of Trp.

2. Experimental

2.1. Instrumentation

Bio-analytical system (BAS, West Lafayette, USA) CV-50W voltammetric analyzer was used to carry out electrochemical experiments. A three electrode system consisting of a glassy carbon electrode as working electrode, Ag/AgCl (3 M NaCl; BAS Model MF-2052 RB-5B) as a reference electrode and Pt wire as auxiliary electrode was used. The pH measurements were carried out using a digital pH meter (Eutech Instruments, model pH 700). The morphology of the surface was characterized by using the Field Emission Scanning Electron Microscopy (FE-SEM, model; Zeiss ultra plus 55), Transmission Electron Microscopy (TEM, model; Technai G² 20S-TWIN) and Raman Spectroscopy were performed using Renishaw inVia Raman microscopy at 540 nm. Electrochemical impedance spectroscopy (EIS) experiments were carried out using VersaSTAT 3 (PAR, USA) instrument.

2.2. Chemicals and reagents

Tryptophan (Trp), AHNSA, ascorbic acid (AA), uric acid (UA), 5-hydroxytryptamine (5-HT), hypoxanthine (HX), graphite powder (<20 nm), and sulphuric acid were purchased from Sigma-Aldrich (USA) and were used as received without any further purification. Phosphate buffers of pH ranging from 2.4–10.0 were prepared according to the previously reported method [34]. All other solvents and chemicals used in the measurement throughout the experiment were of analytical grade.

2.3. Preparation of graphene oxide

Graphene oxide (GO) was synthesized following previously reported procedure [11]. Briefly, GO was synthesized by reacting graphite powder with KMnO₄ in the presence of H₃PO₄ and H₂SO₄ (20:180) mixture. The mixture was then heated at 50 °C for 12 h, after which a brown colored suspension was observed that changed its colour to yellow on the addition of water followed by H₂O₂ (30%). The final mixture thus obtained was centrifuged and the sediment was washed successively with water, HCl and ethanol to get GO. The GO was dried in vacuum and characterized using XRD, FE-SEM and Raman spectroscopy.

2.4. Fabrication of modified sensors

In order to fabricate the modified sensors, the surface of the glassy carbon electrode was first polished to a mirror like finish using the paste of alumina powder (grade I) and ZnO on a micro cloth pad and then rinsed with double distilled water. In order to fabricate AHNSA modified GCE sensor, the electropolymerization of AHNSA has been performed directly on the pre cleaned surface of GCE by scanning the potential between –800 mV to +2000 mV in a 2 mM AHNSA solution (prepared in 0.1 M nitric acid) at a sweep rate of 100 mV s⁻¹ for 15 scans. After the completion of 15 scans, the polymer modified surface was rinsed with double distilled water and stabilized by scanning in 0.5 M H₂SO₄ between –1000 and +1000 mV at the scan rate of 100 mV s⁻¹ until the overlapping voltammetric response was not obtained. The fabricated sensor was then termed as AHNSA/GCE and was characterized using voltammetry and FE-SEM.

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