



# Multi-walled carbon nanotube/poly(glycine) modified carbon paste electrode for the determination of dopamine in biological fluids and pharmaceuticals



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## ABSTRACT

A modified carbon paste electrode (CPE) for the selective detection of dopamine (DA) in presence of large excess of ascorbic acid (AA) and uric acid (UA) at physiological pH has been fabricated by bulk modification of CPE with multi-walled carbon nanotubes (MWCNTs) followed by electropolymerization of glycine (Gly). The surface morphology is compared using SEM images. The presence of nitrogen was confirmed by the energy dispersion X-ray spectroscopy (EDS) indicating the polymerization of Gly on the surface of the modified electrode. The impedance study indicates a better charge transfer kinetics for DA at CPE modified with MWCNT/polyglycine electrode. The presence of MWCNTs in carbon paste matrix triggers the extent of electropolymerization of Gly and imparts more selectivity towards DA by electrochemically not sensing AA below a concentration of  $3.1 \times 10^{-4}$  M. Due to the exclusion of the signal for AA, the interference of AA in the determination of DA is totally ruled out by DPV method which is used for its detection at lower concentrations. Large peak separation, good sensitivity, reproducibility and stability allow this modified electrode to analyze DA individually and simultaneously along with AA and UA. Detection limit of DA was determined from differential pulse voltammetric (DPV) study and found to be  $1.2 \times 10^{-8}$  M with a linear dynamic range of  $5.0 \times 10^{-7}$  M to  $4.0 \times 10^{-5}$  M. The practical analytical application of this electrode was demonstrated by measurement of DA content in dopamine hydrochloride injection and human blood serum.

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## 1. Introduction

Carbon nanotubes (CNTs) are one-dimensional allotropes of carbon which have already proved their potential across wide areas of science and technology. Mass attention has been aroused towards CNTs since their discovery mainly because of their unusual electrical, thermal, optical, mechanical and structural properties. Moreover, they are ultra-light and biocompatible with excellent thermal and chemical stability [1–4]. Basically, there are two types of CNTs – single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are formed by seamlessly rolling a single graphene sheet with closed ends, in certain directions, while MWCNTs consist of arrays of such concentric graphitic layers separated by  $3.4 \text{ \AA}$  [5]. CNTs/CNT

composites/functionalized CNTs are used extensively as electrode materials or modifiers in electrode preparation because of their ability to improve sluggish electrode kinetics by facilitating the electron transfer rates between electro-active species and electrodes [6–8]. The major application of carbon nanotubes is in the field of medicine where it can be used for sensing molecules or species. It is evident from literature that CNTs can act as electro-catalysts towards various biologically important molecules. Hence, CNTs are suitable material for the development of electrochemical sensors [9–11].

DA is an important catecholamine neurotransmitter present in the mammalian central nervous system [12]. It plays a major role in the proper functioning of central nervous, renal, hormonal and cardiovascular systems [13]. The normal DA level in blood plasma is 0.04–4.50 nM [14]. Its deficiency can lead to various neurodegenerative diseases such as Parkinsonism, Schizophrenia, Huntington's disease, Senile dementia, Alzheimer's disease, and HIV [15–18]. Hence, the quantification of DA can lead to vital insights in the early diagnosis of several neurological disorders. DA being an

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electro-active compound, it is only natural that simple, rapid, cost effective, low power consuming and highly sensitive electroanalytical techniques are preferred to chromatographic, fluorimetric and chemiluminescence methods [19] for its determination. The major factor that hinders the electrochemical estimation of DA is that its redox potential is similar to coexisting molecules like ascorbic acid (AA) and uric acid (UA) at conventional working electrodes such as Au, Ag, Pt, glassy carbon (GC), graphite and carbon paste electrode (CPE) [20]. The adsorption of oxidation products of above molecules on electrode surface ends with fouling of electrode. High concentration of AA and UA leads to inaccurate estimation of DA. The homogeneous catalytic oxidation of AA by the oxidized product of DA also contributes ambiguity [21]. Substantial efforts have been devoted to surmount these problems. This prompted us to look for an electrode material with regard to the interferences such as those mentioned above will not affect the output signal of the neurotransmitter.

CNTs are promising material for the task of modifying the electrode. The use of CNT modified electrodes for analytical applications is well known. The relevant literature reports the use of different types of CNT modified electrodes in the study of catecholamine and related compounds. These are CNT-polymer nanocomposite electrodes, CNT-paste electrodes, CNT/sol-gel nanocomposite electrodes and layer-by-layer assembly of CNT film electrode [22–24].

Electro-polymerization has received enormous attention as a modification method because of its simplicity, selectivity and sensitivity towards analytes, strong adherence of the polymer film to the electrode surface, ability to provide larger surface area by forming homogeneous film and ability to promote electron transfer rates [25,26]. Electro-polymerization of numerous molecules on different electrodes has been used for the selective detection of DA [27–31]. CPE has been used as working electrode for many biosensor applications due to simplicity in preparation, easy renewability of surface, low background current, cost-effectiveness and above all, biocompatibility [32,33]. Poly(glycine) modified electrodes have already been used for the development of electrochemical sensors [34–36].

In continuation of our effort to use CPE and modified CPE for different applications [37–41], our objective in the present work was to develop a simple voltammetric method for the determination of DA in presence of large excess of AA and UA, by modifying CPE. The present work describes bulk modification of CPE with MWCNTs and followed by the electropolymerization of Gly onto its surface. The literature report confirms a better voltammetric response of DA at MWCNT modified electrodes as compared to its response under a similar condition of modification at CPE and this has been ascribed to the presence of a large number of edge plane defects at MWCNT modified electrodes [42]. This prompted us to use MWCNTs in the present study. With the combination of two modification techniques such as bulk modification using MWCNT and electro polymerization using glycine, we were able to fabricate an electrode in which we could incorporate the much desired properties such as low cost, increased sensitivity and selectivity, enhanced electrochemical response on account of increased electrode active surface area together with non interference of AA, which can otherwise lead to fouling of the electrode. The stability of the film obtained by casting was a matter of concern and therefore we opted for bulk modification in which a small amount of MWCNT used serves the purpose. As reported in our earlier work [43] the modification of CNT using MWCNT and the subsequent electropolymerisation using Patton and Reeder's reagent did not give an impressive result in the determination of acetaminophen due to resistance at the junction of the polymeric film and MWCNT modified CPE. In the present study, interestingly enough, the promotion of charge transfer at the poly(glycine) modified electrode was much smoother possibly on account of a lower resistance at

the junction of the poly(glycine) film and MWCNT modified CPE. This property of modified electrode material was utilized in the selective detection of DA in presence of large excess of AA and UA.

The importance of the present work lies in the 100% exclusion of AA signal at the modified electrode. Further, this research finds scope in the development of a bioelectronics device for commercial purpose since MWCNTs could be used for interfacing biological recognition event in combination with electrochemical transducer due to their biocompatibility and the elimination of interference by AA.

## 2. Experimental

### 2.1. Reagents

Dopamine hydrochloride (Aldrich), uric acid, ascorbic acid,  $\text{KH}_2\text{PO}_4$ ,  $\text{H}_3\text{PO}_4$ , NaOH pellets, glycine,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$  and  $\text{HClO}_4$  (all from Merck) were of analytical grade and used as received. All aqueous solutions were prepared with ultra pure water ( $>18.2\text{ M}\Omega\text{ cm}$ ) from Milli-Q Plus system (Millipore). Stock solutions of DA, UA and AA (25 mM) were prepared in 0.1 M  $\text{HClO}_4$ , 0.1 M NaOH and water respectively. Phosphate buffer solutions were prepared from  $\text{KH}_2\text{PO}_4$  and NaOH and acetate buffer was prepared from  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ . pH was adjusted using  $\text{H}_3\text{PO}_4$  or NaOH in the case of phosphate buffer while  $\text{CH}_3\text{COOH}$  or NaOH was used for acetate buffer. Graphite powder was obtained from Graphite India Ltd. The thin MWCNTs obtained from Nanocyl SA were synthesized by decomposition of ethylene using the combustion chemical vapor deposition method. The MWCNTs have an average diameter of 10 nm and length of several (0.1–10) micrometres.

### 2.2. Apparatus

All electrochemical experiments were performed using ChemiLink model EA-201 Electro Analyzer. A conventional three-electrode system was used for all electrochemical experiments, which comprises a bare or modified CPE as working electrode, a platinum wire as auxiliary electrode, while all potentials were measured and applied using saturated calomel electrode (SCE) as a reference electrode. The tip of the Lugin capillary was set approximately at a distance of 1 mm from the surface of the working electrode-bare and modified CPE- in order to minimize error due to IR drop in the electrolyte. The electrochemical experiments were performed in quiescent solution and voltammetric curves were recorded at room temperature ( $\sim 300\text{ K}$ ). The structural morphology of the electrodes was studied using a JEOL JSM-848 scanning electron microscope (SEM) and the energy dispersive X-ray spectroscopy (EDS) analysis. Electrochemical impedance spectroscopy (EIS) was performed using VersaSTAT 3. A digital pH/mV meter (ELICO LI 614) was employed to measure the pH of the prepared buffer solutions.

### 2.3. Generation of oxygen functionalities on MWCNTs

Since the oxygen functionalities on the surface of MWCNT improve their electrochemical properties, the same were generated by treating them with a mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (molar ratio 3:1). In a typical experiment, 75 ml of conc.  $\text{H}_2\text{SO}_4$  (97%) and 25 ml of conc.  $\text{HNO}_3$  (65%) were mixed and added to 1 g of MWCNTs in a round-bottomed flask and heated under constant agitation at  $50^\circ\text{C}$  for 8 h. It was allowed to cool down to room temperature after which an equal quantity of deionised water was added. It was filtered and the residue was washed several times

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