

# Electrocatalytic boost up of epinephrine and its simultaneous resolution in the presence of serotonin and folic acid at poly(serine)/multi-walled carbon nanotubes composite modified electrode: A voltammetric study

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## ABSTRACT

The present paper describes the new strategy for the development of nanosensor based on dropcasting of multi-walled carbon nanotubes (MWCNTs) followed by electropolymerization of serine (ser) onto the glassy carbon electrode (GCE). The developed nanocomposite sensor was abbreviated as poly(ser)/MWCNTs/GCE and was characterized by using electrochemical impedance spectroscopy (EIS) technique. The EIS results confirmed the fast electron transfer rate at the surface of poly(ser)/MWCNTs/GCE. The proposed sensor exhibited good catalytic activity towards the sensing of epinephrine (EP) individually and simultaneously in the presence of serotonin (5-HT) and folic acid (FA) in 0.1 M phosphate buffer solution (PBS) at pH 7.0. The limit of detection (LOD) and limit of quantification (LOQ) of EP was found to be  $6 \times 10^{-7}$  M and  $2 \times 10^{-6}$  M respectively. The fabricated sensor showed excellent precision and accuracy with a relative standard deviation (RSD) of 4.86%. The proposed composite sensor was effectively applied towards the determination of EP in human blood serum and pharmaceutical injection sample.

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## 1. Introduction

Epinephrine (EP) (1-(3,4-dihydroxyphenyl)-2-methylamino-ethanol) (also known as adrenaline) is an important catecholamine neurotransmitter in the mammalian central nervous system for transporting the information among the biological cells [1], which exists in the nervous tissue and body fluids as a large organic cation. It plays significant role in the function of the central nervous, hormonal and cardiovascular systems. Many life phenomena are connected to the concentration of EP in blood. Changes of its concentration in blood show the way to many diseases [2]. Medically, EP has been used as a common emergency healthcare medicine [3]. These catecholamine drugs are used to treat hypertension, sepsis, bronchial asthma, cardiac surgery and myocardial infarction [4,5]. EP is not only healthcare medicine but also a powerful doping agent, thus, it is banned by the World Anti Doping Agency (WADA) in taking during sports competition [6]. Therefore, the determination of EP in human body fluids has attracted much attention to the researchers. Serotonin (5-hydroxy tryptamine, 5-HT) is a monoamine neurotransmitter synthesized in serotonergic neurons in the central nervous system (CNS) and plays a crucial role in the emotional system together with EP in the brain [7,8]. Folic acid (FA) (vitamin B<sub>9</sub>) works principally in the brain and CNS. Thus, it is necessary

for the production of EP and 5-HT in the nervous system. Therefore, simultaneous determination of EP, 5-HT and FA has acquired great importance.

Carbon nanotubes (CNTs) are considered as a novel material due to their unique properties and extensive applications since its discovery by Iijima [9]. Recently, CNTs are considered for the fabrication of electrochemical sensors because of their unequal properties such as anti-surface fouling, high sensitivity, a large edge plane/basal plane ratio, high surface-to-volume ratio [10], high ability to promote electron transfer [11], good electrical conductivity, and high chemical stability and tubular structure. Previously, different types of electrochemical sensors based on CNTs have been reported to detect the biological analytes such as paracetamol [12], neurotransmitters [13–15], proteins [16], cytochrome c [17], ascorbic acid [18], NADH [19] and hydrazine compounds [20,21]. Thus, CNTs are suitable materials for the development of electrochemical sensors.

Numerous analytical methods have been developed for the determination of EP. These methods consist of chemiluminescence [22], chromatographic methods [23], capillary electrophoresis [24], flow injection analysis [25] and spectroscopic methods [26]. However, these methods need more complicated procedures, costly instrumentation and over analysis time when compared to electroanalytical methods. Electroanalytical techniques have several advantages such as good sensitivity and selectivity, low cost, low background current, wide range of potential ranges, quick surface renewal, easy fabrication, and

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trouble-free operation. In electroanalytical techniques, the redox course of the analyte occurs at high over potential owing to the slow electron transfer rate at conventional electrodes (such as GCE, Au and Pt). The electrochemical determination of EP in the presence of ascorbic acid (AA), uric acid (UA), FA and 5-HT at the conventional electrodes is of poor result, to overcome this problem, the modification of the electrode surface is of great interest. The concept of electrode surface modification is one of the advanced methods in the field of electroanalytical chemistry. The modifications onto the surface of electrode lead to considerable diminish of over potentials and enhance the electron transfer rate for system of redox reactions. Various materials have been used for the modification of electrode surfaces such as polymer films [27–29], nanoparticles [30,31], surfactants [32–34], organic compounds [35,36], metals [37], and metal oxide nanoparticles [38] including MWCNTs [39,40]. Nevertheless, when compared to the above materials, polymer layer-MWCNTs composite based electrodes show high sensitivity and boost up the electro-redox reaction of analytes. A poly(serine) film onto the electrode surfaces offer extraordinary surface area, thereby, exhibits good catalytic activity towards the electrochemical determination of analyte. In this connection, in our present study, a facile and simple nanocomposite sensor (poly(ser)/MWCNTs/GCE) was synthesized for the determination of EP individually and simultaneously in the presence of FA and 5-HT.

## 2. Experimental

### 2.1. Instrumentation

CHI 660D electrochemical work station was used for the measurements of cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). A conventional three electrode system was employed, which consists of a modified/unmodified GCE as working electrode; saturated calomel electrode (SCE) as reference electrode to measure cell potentials and glassy carbon rod as an auxiliary electrode to measure the current. Elico U 120 pH meter combined with pH CL 51 B was used to measure pH values. IR spectra were recorded on Bruker Alpha-Eco ATR-FTIR (Attenuated total reflection-Fourier transform infrared) interferometer with single reflection sampling module equipped with ZnSe crystal.

### 2.2. Reagents

Epinephrine was from HiMedia Laboratories Pvt. Limited, Mumbai. Serotonin and folic acid serine were from Sigma.  $K_3[Fe(CN)_6]$  was from Merck Specialities Pvt. Limited, Mumbai.  $K_4[Fe(CN)_6]$  and KCl were from Qualigens fine chemicals, Mumbai. Multi-walled carbon nanotubes (Dropsens, Edificio CEEI, Llanera (SPAIN)) were used as received. The stock solution of 10 mM EP was prepared and stored in a refrigerator. The working solution was prepared by diluting the stock solution with buffer solution. 0.1 M PBS was prepared from  $NaH_2PO_4 \cdot 2H_2O$  and  $Na_2HPO_4$ . Adrenaline® was taken as epinephrine injection. All chemicals were of analytical grade and were used without further purification.

### 2.3. Preparation of MWCNTs/GCE

The GCE was polished to a mirror finished on polish pads with 0.3 and 0.05  $\mu\text{m}$  alumina slurry and cleaned thoroughly with distilled water successively. MWCNTs were solubilized in ethanol (1 mg/ml) and then ultrasonicated for 5 min to get MWCNTs dispersion. Immobilization of MWCNTs was achieved by drop casting of 5  $\mu\text{L}$  onto the surface of GCE and dried at room temperature in the air. Hereafter the resultant electrode was abbreviated as MWCNTs/GCE and was used as working electrode.

### 2.4. Preparation of poly(ser)/GCE and poly(ser)/MWCNTs/GCE

Fig. 1 shows the uninterrupted 5 CV cycles at MWCNTs/GCE and GCE in 1 mM serine aqueous solution (pH 7.0). Initially, the scan was run from  $-0.5$  to  $1.0$  V, it was observed that no polymer film was formed on the MWCNTs/GCE and GCE surface. However, when the window was extended from  $-0.5$  to  $2.0$  V the effective polymerization was achieved. On the other hand, when the potential window was extended in negative direction, the polymerization was not observed. Therefore, the window  $-0.5$  to  $2.0$  V was considered for the successful polymerization process. The film coated electrode was washed with distilled water to remove the physically adsorbed material. Hereafter the resulted electrodes were abbreviated as poly(ser)/GCE and poly(ser)/MWCNTs/GCE respectively and were used as working electrodes. The steps involved towards the fabrication of poly(ser)/MWCNTs/GCE was illustrated in Fig. 2.

## 3. Result and discussion

### 3.1. Characterization of poly(ser)/MWCNTs composite

FT-IR spectrum (Fig. S1) of the poly(ser)/MWCNTs composite gives a confirmative evidence for the presence of poly(ser) molecule and the MWCNTs. The asymmetric stretching of the CH group of the poly(ser) molecule was found as a prominent band at  $2926\text{ cm}^{-1}$ . A strong and characteristic band at  $1744\text{ cm}^{-1}$  is due to stretching vibration of carbonyl group. Appearance of a band at  $3438\text{ cm}^{-1}$  confirms the stretching vibrations of the NH and OH functions. Strong stretching bands are evident in the region  $1600\text{--}1400\text{ cm}^{-1}$  particularly at  $1403$ ,  $1465$ ,  $1580\text{ cm}^{-1}$  for MWCNTs [41].

### 3.2. Electrochemical impedance study of poly(ser)/MWCNTs/GCE

Electrochemical impedance spectroscopy (EIS) technique is a powerful and emerging tool for the study of interfacial electron transfer properties and is used to identify the impedance changes of the electrode surface during the modification process. By using EIS, the impedance spectral data was recorded for bare GCE, poly(ser)/GCE, MWCNTs/GCE and poly(ser)/MWCNTs/GCE (in the form of Nyquist plots) in 1 M KCl containing  $2.5\text{ mM } [Fe(CN)_6]^{3-/4-}$  as a redox probe at the initial potential of  $0.209\text{ V}$  with the range from  $1$  to  $10^5\text{ Hz}$  (Fig. 3). Primarily, the semicircle portion at high frequencies in the Nyquist plots corresponds to the magnitude of the charge transfer resistance ( $R_{ct}$ ) in the equivalent circuit. This value extensively varies based on the modification of the electrode surfaces [42]. In order to work out the  $R_{ct}$  values, the impedance values were fitted to Randles equivalent circuit (Fig. 3

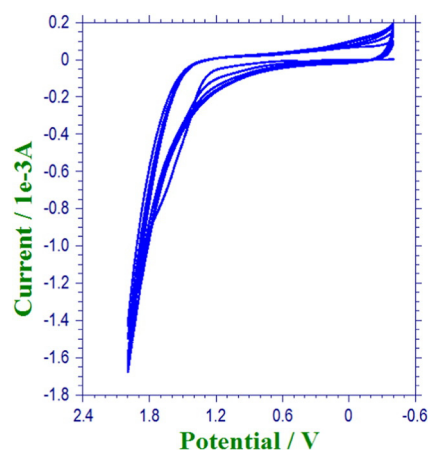


Fig. 1. Five continuous cyclic voltammograms for the electrochemical polymerization of serine onto the surface of MWCNTs/GCE.

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