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Full Paper

Fabrication, Characterization and Application of Poly (L-Cystine)/multi Walled Carbon Nanotubes Modified Glassy Carbon Electrode towards the Simultaneous Determination of Dopamine in presence of Uric Acid and Folic Acid

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Abstract- A sensitive electrochemical sensor was made by the electro polymerization of L-cystine (L-Cys) on the surface of a glassy carbon electrode (GCE) followed by drop casting of multi walled carbon nano tubes (MWCNTs). The sensor was characterized by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The sensor showed good electrocatalytic activity towards the sensing of dopamine (DA) and simultaneously discriminated DA in presence of uric acid (UA) and folic acid (FA). The kinetic parameters, such as heterogeneous rate constant, number of electrons transfer and charge transfer coefficient values were evaluated. The effect of concentration on the DA was studied and a linear relationship was observed between the concentration verses peak currents, with a limit of detection (LOD) and limit of quantification (LOQ) values as 2.8×10^{-6} M and 9.6×10^{-6} M, respectively. The present method was successfully applied toward the recovery of DA in injection sample.

Keywords- Dopamine (DA), L-Cystine (L-Cys), Multi-walled carbon nanotubes (MWCNTs), Voltammetry, Electrochemical impedance spectroscopy (EIS)

1. INTRODUCTION

Dopamine (DA) is one of the most important neurotransmitters and present in the mammalian central nervous system [1,2]. DA plays an important role in the control, motivation, arousal, cognition and a number of basic lower-level functions including lactation, sexual gratification and nausea [3]. DA is a metabolic precursor used in the treatment of Parkinson's disease. These concentrations have been linked with several neurological disorders, such as debilitating ailment Parkinson's disease, Alzheimer's, epilepsy and the mental disorder schizophrenia [4]. DA is available as an intravenous drug, which acts on sensitive nervous system to produce some effects such as increasing heart rates and blood pressure. DA is also believed to play a central role in Huntington's disease, a fatal genetic neurodegenerative movement disorder and has been associated with drug addiction and attention disorders [5]. Numerous methods have been employed for the detection of DA, such as chemiluminescence, flourimetry, ultraviolet visible spectroscopy, High performance liquid chromatography (HPLC), capillary electrophoresis and Ion chromatography techniques [6,7]. However these methods involve complicated procedures, costly instrumentation and expensive materials [8]. Among the all, electrochemical methods have proven to be the selective, sensitive and reliable for the determination of various drugs, pesticides, dyes, environmental pollutants and biologically important molecules [9,10]. Electro analytical techniques have several advantages such as simple preparation, good sensitivity and selectivity, low cost, low back ground current, wide potential ranges, surface renewal, and ease in handling [11-16]. However conventional electrodes such as GCE and carbon paste electrode (CPE) gives low sensitivity and low stability. To overcome these problems modification of surfaces with several materials have received considerable interest.

Several methods have been reported for the modification of electrode surfaces such as electrochemical polymerization of electrode with conducting polymers, modification with different nano-materials like carbon nanotubes, silver nanoparticles, gold nanoparticles, palladium nanoparticles and modification with bio molecules like enzymes, proteins and antibodies [17-20]. Many amino acids were used for the modification of electrode surface due to its conductivity properties. L-Cystine was used to modify the electrode surface due to its favorable redox activity in the thiol groups [21]. The polymerization of L-Cystine led to the formation of thioalcohol residues on the surface of the electrode there by enhancing the sensitivity and stability [22]. After the discovery of carbon nanotubes (CNTs) by Lijima in 1991 [23], they have emerged as effective materials for the fabrication of chemically modified electrodes [24,25]. This importance was due to the its good electrical conductivity, high chemical stability, film forming ability, large surface area, good biocompatibility and resisting interferences from biomolecules [26,27]. The CNTs have unique properties such as anti-surface fouling, high sensitivity, high surface to volume ratio and high ability to promote excellent electron transfer rate [28-30].

Uric acid (UA) is the final oxidation product of urine metabolism and is excreted through the urine [31,32]. Extreme abnormalities of UA levels are symphonic of several diseases, such as, cardiovascular disease, hyper uricaemia, uric acid stones, gout and Leseh-Nyhan syndrome [33,34]. Folic acid (FA) is a water-soluble vitamin -B [35] and was regularly removed from the urine, it is found in leafy vegetables, egg yolk, and legumes, liver and citrus fruits [36,37]. FA is an antioxidant for cancer prevention cells and several chronic diseases like gigantocytic anemia, leucopoenia, mentality devolution, psychosis, heart attack, and stroke [38,39]. The simultaneous discrimination of DA in the presence of FA and UA is of great interest, because of its overlapping oxidation peak potentials. The electroanalytical discrimination of DA at the conventional electrodes is of poor result, poor stability and low sensitivity to overcome these problems modification of the electrode surface is of great interest and challenge. In this connection, in our present investigation, a simple procedure was developed based on chemical sensor MWCNTs/Poly(L-Cys)/GCE for the simultaneous determination of DA in the presence of UA and FA.

2. EXPERIMENTAL

2.1. Instruments

A CH Instrument model number 1200A was used to carry out all the cyclic voltammetric (CV) measurements and CHI 660D (Texas, Austin, USA) electrochemical instruments was used for the study of electro chemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV) studies. The electrochemical cell consisted of three types of electrodes, a modified or bare GCE as a working electrode, a saturated calomel electrode (SCE) as a reference electrode to measure cell potential and a glassy carbon rod as an auxiliary electrode. By using Elico U 120 pH meter connected to pH CL 51 B electrode, the pH values of the buffer solution were measured. The multi walled nano carbon tubes of homogeneous solution was prepared with the help of Toshiba ultrasonication bath instrument, made in India.

2.2. Materials

All materials were obtained from commercial sources and used without further purification. Dopamine, Uric acid, Na_2HPO_4 and $K_3[Fe(CN)_6]$ were from Merck Specialties Pvt Limited, Mumbai, India. KCl was from Qualigens fine chemicals, Mumbai, India. $K_4[Fe(CN)_6]$ and NaH_2Po_4 was from Fisher Scientific Pvt Limited, Mumbai, India. Folic acid and L-cystine was form Sima-Alderich, India. Multi walled carbon nanotubes (MWCNTs) were from Dropsens, Edificio CEEI, Llanera (SPAIN). The stock solution of 10×10^{-3} M dopamine was prepared and working solution was prepared through diluting the stock solution with buffer solution. All reagents were of analytical grade.

2.3. Preparation of MWCNTs/Poly (L-Cys)/GCE

Prior to the modification of GCE, the GCE was polished on polishing pads with 1.0, 0.3 and 0.05 microns of alumina slurry to get a mirror shine and cleaned thoroughly with distilled water successively. Fig. 1 shows the electrochemical polymerization of GCE, which was carried by cyclic voltammetric studies with 5 successive cycles between the potential from 0.5 to 1.8 V. The film coated on the electrode surface (Poly(L-Cys)/GCE) was washed with distilled water to remove the physically adsorbed material. The Poly(L-Cys)/GCE was further modified with 5 µL of homogeneous suspension of 1 mg MWCNTs dispersed in 1ml ethanol by drop casting method. Here after the resulted electrode was denoted as MWCNTs/Poly(L-Cys)/GCE and used as a working electrode.

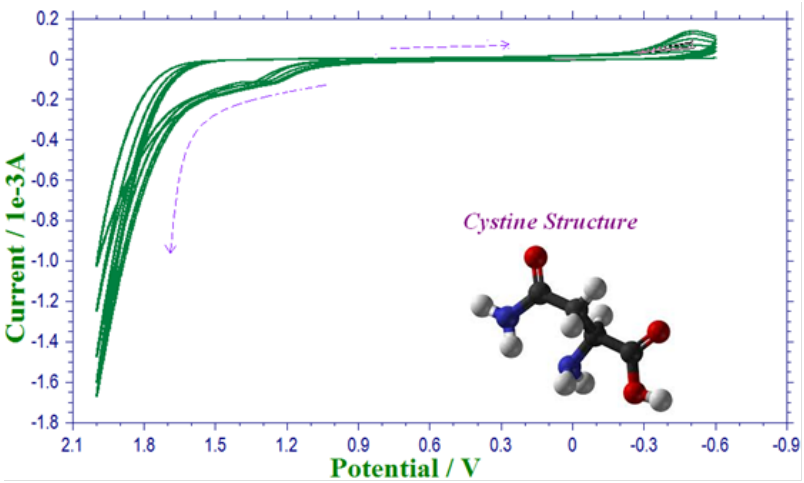


Fig. 1. Polymerization with L-Cystine at GCE (Scan rate 0.1 v/s and 0.1 m phosphate buffer solution of pH -7.0) inset structure of L-Cystine

2.4. Analytical procedure

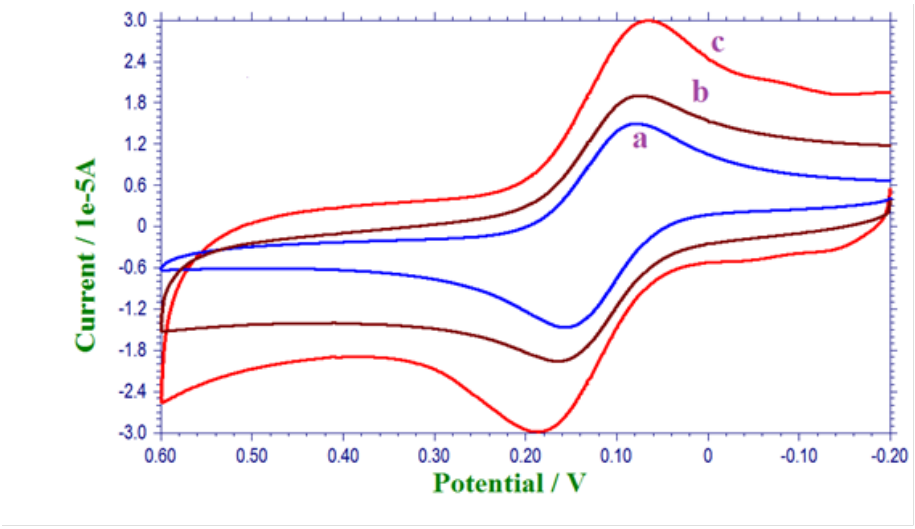
MWCNTs/Poly(L-Cys)/GCE was placed in phosphate buffer solution of pH 7.0 containing 1 mM DA solution. The electrolytic solution was stirred and then recorded CV and DPV measurements in the potential window -0.6 to 0.6 V at a potential scan rate of 0.1 V/sec. All the experiments were recorded at room temperature.

3. RESULTS AND DISCUSSIONS

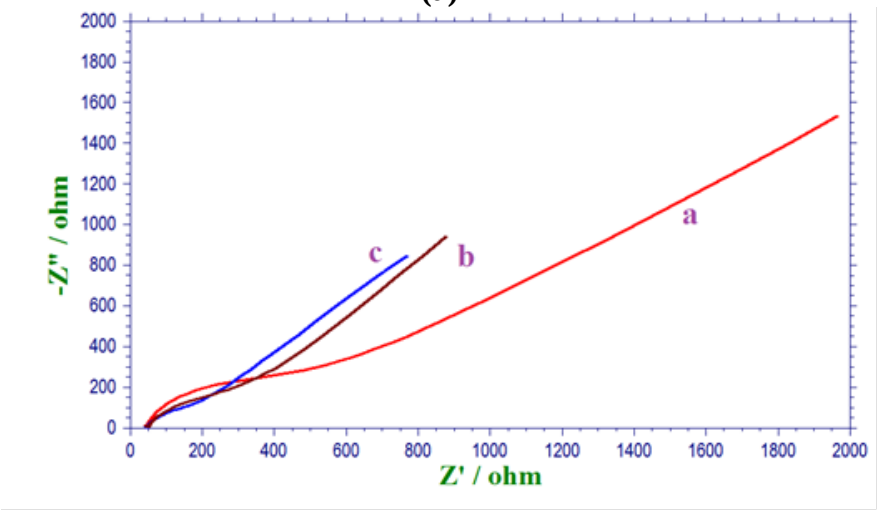
3.1. Electrochemical characterization of MWCNTs/Poly(L-Cys)/GCE with $[Fe(CN)_6]^{-3/-4}$

The electrochemical characterization of different electrodes was studied by using CV technique. The voltammetric behavior of 0.1 mM $[Fe(CN)_6]^{-3/-4}$ in 1 M KCl was examined at different electrodes and Fig. 2a shows the CV responses of $[Fe(CN)_6]^{-3/-4}$ at different electrodes with a scan rate of 0.1 V. The bare GCE showed a small current response (a) for

$[Fe(CN)_6]^{-3/-4}$, when the surface of the GCE was polymerized with L-Cystine, there was an increase in the current response for $[Fe\ (CN)_6]^{-3/-4}$ and this was due to the conductive nature of the L-Cystine. On further modification of Poly(L-Cys)/GCE with MWCNT's further enhancement in peak current response was observed, this was also due to the catalytic and conductive properties of MWCNT's [40,41]. The peak to peak separation (ΔEp) at the developed electrode was 0.176 V and the peak to peak current ratio was nearer to unity, this indicates the complete reversibility of $[Fe(CN)_6]^{-3/-4}$ at MWCNTs/Poly(L-Cys)/GCE [42].



(a)



(b)

Fig. 2. (a) Cyclic Voltammograms of 1 mM $[Fe(CN)_6]^{-3/-4}$ in 1 M KCl solution with a scan rate of 0.1V s^{-1} at a) bare/GCE b) Poly(L-Cys)/GCE c) MWCNTs/Poly(L-Cys)/GCE; **(b)** Nyquist plots for a) Bare/GCE b) Poly(L-Cys)/GCE c) MWCNTs/Poly(L-Cys)/GCE

The electrochemical impedance spectroscopy was widely used for the characterization of electrode surfaces. This technique provides unique information about the surface nature of the various materials. Here in, the EIS of different electrodes were observed by using 0.1 mM

$[Fe(CN)_6]^{-3/-4}$ in 1 M KCl. Fig. 2b shows Nyquist plots for bare GCE (a), Poly(L-Cys)/GCE (b) and MWCNTs/Poly(L-Cys)/GCE (c), it was evident that the bare GCE showed higher charge transfer resistance (R_{ct}) 289.2 Ω than the other two electrodes. After the modification of bare GCE surface with L-Cystine lead to the decrease in the charge transfer resistance to 99.32 Ω and on further modification with MWCNTs i.e. at MWCNTs/Poly(L-Cy)/GCE showed the least charge transfer resistance 46 Ω, indicating good electron transfer rate at the MWCNTs/Poly(L-Cys)/GCE [43].

3.2. Voltammetric investigation of DA at fabricated electrodes

The electrochemical behavior of 1 mM DA in PBS having pH 7.0 at bare GCE, MWCNTs/GCE, Poly(L-Cys)/GCE and MWCNTs/Poly(L-Cys)/GCE was examined with the help of DPV technique. From Fig. 3, at bare GCE, DA has shown very poor current response of 0.446×10^{-5} A (a) and on drop casting of MWCNTs on GCE an increase in the current response of DA to 1.153×10^{-5} A (b) was observed, when the GCE surface was polymerized with L-Cystine there was an increase in the current response of DA to 4.684×10^{-5} A (c) and this was due to the presence of thiol groups in the L-Cystine structure. This thiol groups easily transfer the electrons and increases the conductive nature. Further the modification of Poly(L-Cys)/GCE with MWCNTs, has shown the increase in the current response of DA to 6.871×10^{-5} A (d).

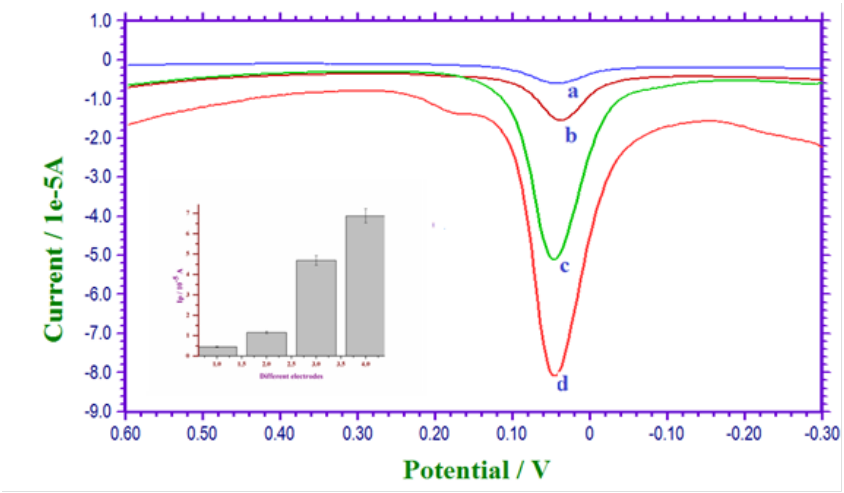


Fig. 3. Differential pulse voltammograms for the electrochemical response of 1 mM DA at a) bare/GCE b) MWCNTs/GCE c) Poly (L-Cys)/GCE d) MWCTs/Poly(L-Cys)GCE in a phosphate buffer solution of pH -7.Inset is the bar diagram illustrating different electrodes versus peak currents of 1 mM DA

The increase in the current of DA at MWCNTs/Poly(L-Cys)/GCE was due to the large surface area of MWCNTs, which shows good catalytic activity and conductivity properties.

The insert from Fig. 3 shows the bar diagram representing the response of DA at MWCNTs/Poly(L-Cys)/GCE, nearly tenfold increase in the current response of DA was observed in comparison with Poly(L-Cys)/GCE.

3.3. Electrochemical behavior of Dopamine at developed sensor

The electrochemical redox behavior of DA in PBS having pH-7.0 at MWCNTs/Poly(L-Cys)/GCE was examined by using the cyclic voltammetry technique (Fig. 4). In forward scan i.e., from -0.6 to 0.6 V, we have observed two oxidation peaks at potentials -0.305 V and 0.084 V the peak at 0.084 V was due to the oxidation of dopamine to dopamine-o-quinone and this undergoes Michael addition reaction to form the leucoaminochrome.

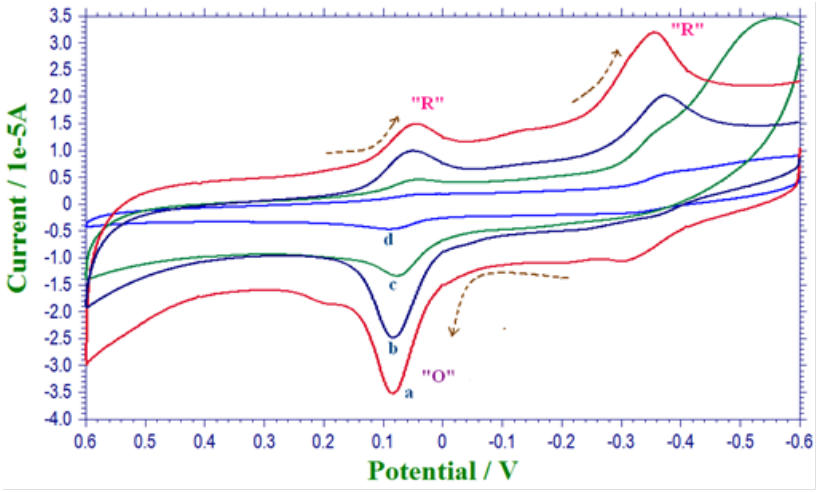
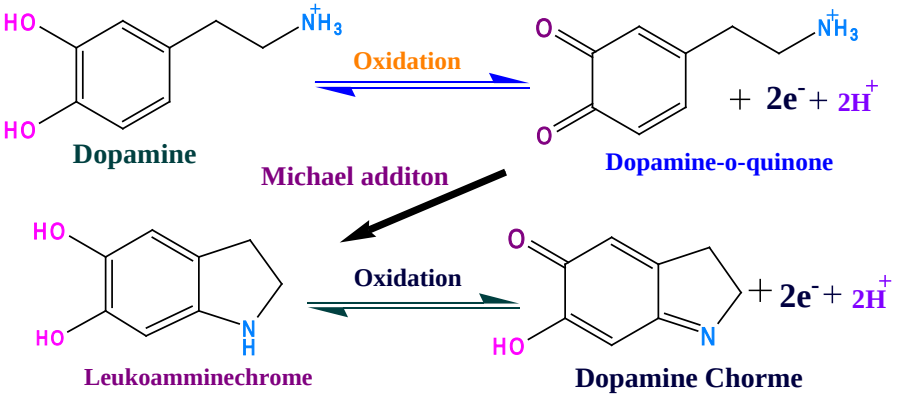
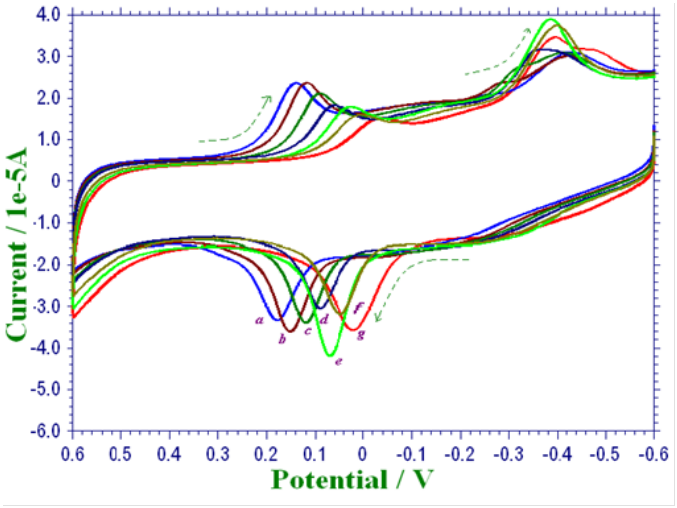


Fig. 4. Cyclic Voltammograms for the electrochemical response of DA at different electrodes in phosphate buffer solution of pH -7. a) bare GCE, b) MWCNTs/GCE, c) Poly(L-Cys)/GCE and d) MWCNTs/Poly(L-Cys)/GCE

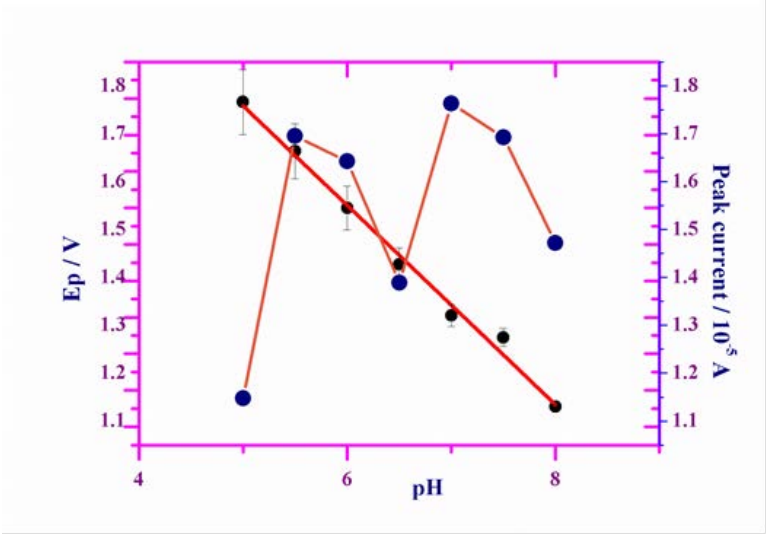


Scheme 1. Electrochemical redox mechanism of dopamine

In reverse scan i.e., from 0.6 to -0.6 V, we have observed two reduction peaks at potentials 0.044 V and -0.352 V. The peak at 0.044 V corresponds to the reduction of dopamine-o-quinone to dopamine and the reduction at -0.352 V corresponds to the reversible reduction of leucoaminochrome to dopamine chrome, further it undergoes reversible oxidation at 0.084 V. Based on the results obtained, we have proposed the electrochemical redox behavior of dopamine at the developed sensor and it was shown in scheme 1 [44].



(a)



(b)

Fig. 5. (a) Cyclic Voltammograms obtained for DA, at the MWCTs/poly(L-Cys)/GCE (1 mM DA) in phosphate buffer solution with a scan rate of 0.1 V/s^{-1} at different pH values [(a)-5.0 (b)-5.5 (c)-6.0 (d)-6.5 (e)-7.0 (f)-7.5 (g)-8.0]; **(b)** A plot between redox peak currents (10^{-5}A) and peak potentials (V) versus pH values of the PBS

3.4. Optimization of pH

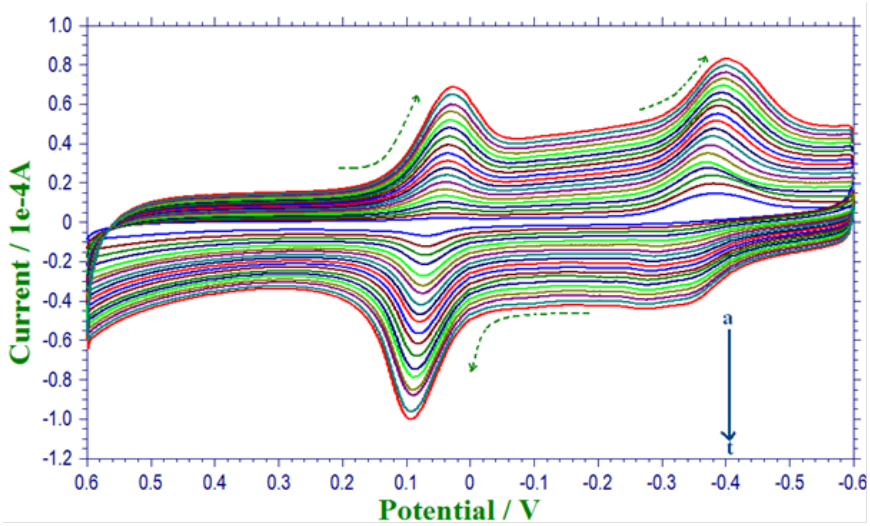
The effect of pH on the voltammetric response of DA at MWCNTs/Poly(L-Cys)/GCE surface was investigated by cyclic voltammetry using a 0.1 M phosphate buffer solution at various pH values, ranging from 5.0 to 8.0. The dependence of voltammetric behavior of DA at MWCNTs/Poly(L-Cys)/GCE was shown in Fig. 5a and the pH of the supporting electrolyte was greatly influencing the voltammetric response of DA. In acidic medium the peak currents of DA increased with increase in the pH up to 7.0, in basic medium it was observed that there was decrease in the peak currents of DA with increase in pH of supporting electrolyte. From Fig. 5a, the peak potentials of DA was shifted to less cathodic side with the increase in the pH of the buffer, indicating the involvement of protons in the oxidation process of DA. Fig. 5b shows the plot for peak current verses peak potentials response of DA, the maximum peak current was observed at pH 7.0 therefore, pH 7.0 was chosen as an optimal pH for all the subsequent electrochemical studies in this work. Furthermore, a good linear relationship was established between the anodic peak potential and electrolyte pH with a linear regression equation of Epa (V)=0.4486 (V)-0.05457 pH (R^2=0.99225). The slope of the regression equation was 0.05457 V/pH, which was very closer to the theoretical Nernst slop value of 0.059 V/pH, indicating the involvement of an equal number of protons and electrons in the oxidation of DA at MWCNTs/Poly(L-Cy)/GCE [45].

3.5. Effect of scan rate

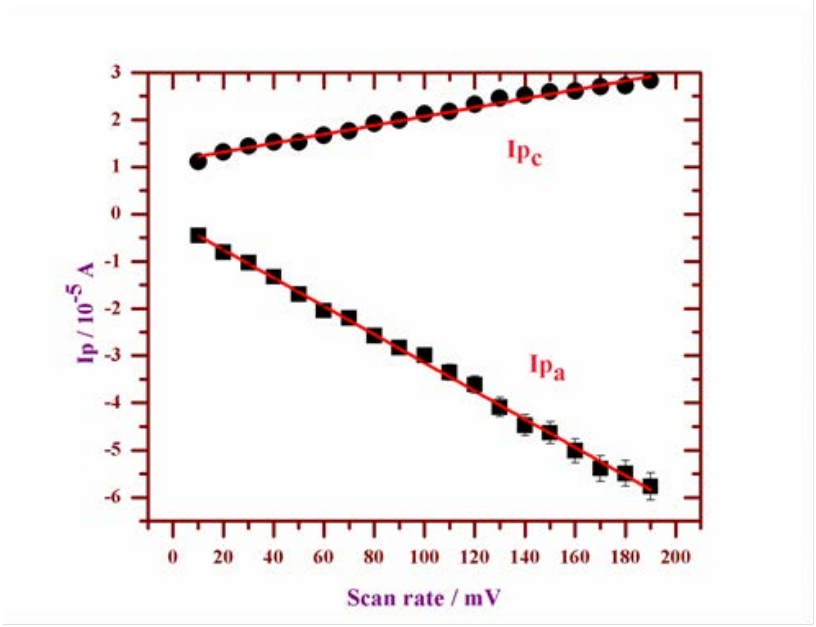
The CV response of 1 mM DA in 0.1 M PBS of pH 7.0 at MWCNTs/Poly (L-Cys)/GCE was examined with different scan rates ranging from 0.01 V to 0.18 V. The redox peak currents of DA increased linearly with increase in the scan rates. From Fig. 6a, a good linear relationship was observed for peak currents and scan rate with a correlation coefficient value (R=0.99767) indicating that the oxidation process of DA was under adsorption controlled process. The Fig. 6b, shows the plot for scan rates verses anodic and cathodic peak currents (I_{pa}, I_{pc}) these plots shows good anodic and cathodic linear equation of I_{pa} (10^{-5})A=1.388 (10^{-5})A–0.302 (Vs^{-1}) and I_{pc} (10^{-5})A=1.1264(10^{-5})A+0.00944 (Vs^{-1}). From the intercept of peak potential (E_p) verses logarithm of scan rate (log υ) and knowing the slop values from the equations 1 and 2, we have calculated the rate constant value as k_o=0.5317 and the number of electrons involved in the rate determining step as 0.9574≈1 [46].

$$E_p = E^o - m\,[0.78 + \ln (D^{1/2} / Ks) + (m/2)\,(\ln m)] + m / 2 \ln \upsilon \quad (1)$$

$$m=RT/(1-\alpha)\,nF \quad (2)$$



(a)



(b)

Fig. 6. (a) Cyclic Voltammograms for the electrochemical response of DA at a MWCTs/poly (L-Cys)/GCE in phosphate buffer solution having pH 7.0 and different Scan rates (a to t; 0.01 to 0.2 V/s^{-1}); **(b)** Calibration plots for the scan rate versus redox peak currents

3.6. Calibration curve, linear range, and detection limit

Differential pulse voltammetry (DPV) has much higher current sensitivity than that of cyclic voltammetry; hence it was used for the estimation of limit of detection and limit of quantification values [47]. DPV technique was employed to study the effect of DA concentration in 0.1 PBS (pH 7.0) at the surface of MWCNTs/Poly(L-Cys)/GCE. From Fig. 7 it was observed that there was an increase in the peak currents of DPVs with increase in the concentration of DA. A good linearity was observed for the concentration from 10µm to 200 µm of DA with a correlation coefficient value of R=0.9968 and the linear regression equation

of I_p (10^{-6}A) = -1.28576 + 0.08071(10^{-6}A). Based on the slop and standard deviation from the linear equation, the limit of detection and limit of quantification values were calculated as 2.8×10^{-6} M and 9.6×10^{-6} M respectively [48,49]. Table 1 displays the analytical performance of different electrochemical sensors with the present developed chemical sensor towards the detection of DA [50-53].

LOD=3S / m

LOQ=10S / m

Where 'S' is the standard deviation of the peak currents, m is the slope of the working curve.

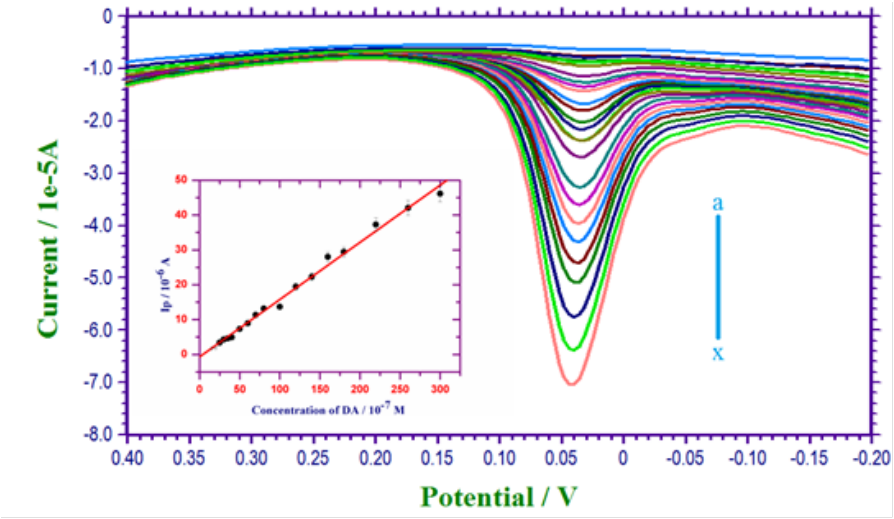


Fig. 7. a) DPVs for DA of different concentrations at MWCTs/poly (L-Cys)/GCE phosphate buffer solution having pH 7.0., 10 µm - (a) to 200 µm – (t); b) Inset figure - calibration plot for the peak currents versus different concentrations of DA

Table 1. Analytical performance of different electrochemical sensors with the present developed chemical sensor towards the detection of DA

Electrode Material	**Linearity range (mol L^{-1})**	**Limit of detection (µM)**	**Ref.**
nano-Au/SAMs/AU sensor	0.2×10^{-3} to 1.2×10^{-3}	90.0	[50]
Poly(TB)MCPE	4.0×10^{-5} to 3.2×10^{-3}	23.4	[1]
PA-MNPs/GCE	10×10^{-6} to 1.0×10^{-3}	14.1	[51]
Au/ ATP-ABA/GCE	1.5×10^{-5} to 1.3×10^{-4}	9.2	[52]
PPS/SAOS/MCPE	0.1×10^{-4} to 0.9×10^{-4}	4.43	[53]
MWCNTs/Poly(L-Cys)/GCE	10×10^{-6} to 40×10^{-5}	2.8	present work

3.7 Simultaneous determination of DA, UA and FA at MWCNTs/Poly(L-Cys)/GCE

UA and FA are common metabolites present in the human body with higher concentrations and the oxidation potentials of UA and FA are closer to the oxidation potential of DA. Due to this reason, the simultaneous determination of DA in the presence of UA and FA is of great importance. The simultaneous determination of DA in presence of UA and FA was examined by employing DPV technique. Fig. 8a shows the simultaneous response of DA, UA and FA.

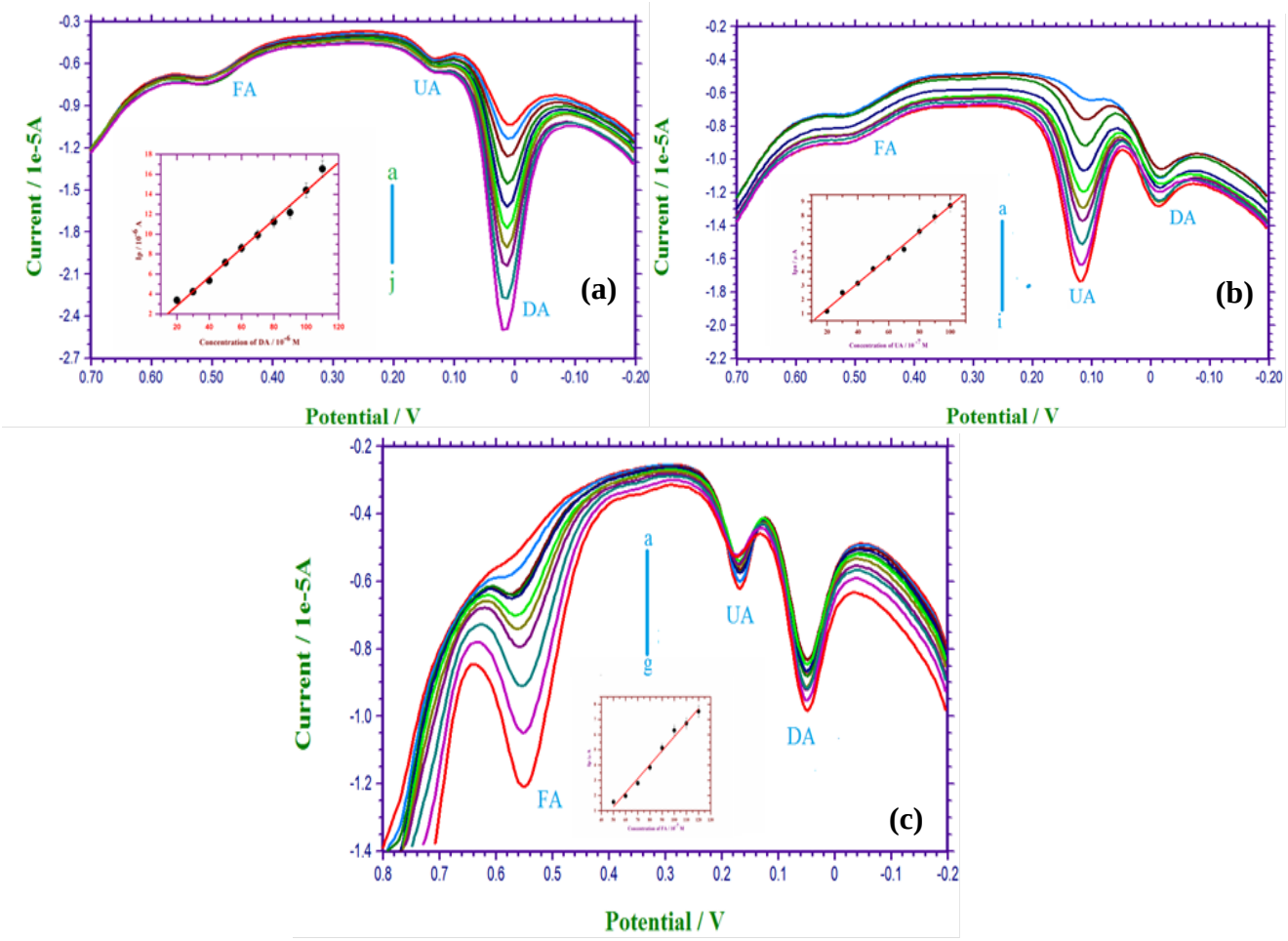


Fig. 8. (a) DPVs corresponding to the simultaneous determination of DA, in the presence of UA (100 µm) and FA (50 µm) with different concentrations of DA, i.e., 20 µm to 110 µm (a to j) at MWCNTs/poly (L-Cys)/GCE in PBS of pH 7.0; **(b)** DPVs corresponding to simultaneous determination of UA, in the presence of DA (30 µm) and FA (50 µm) with different concentrations of UA, i.e., 20 µm to 100 µm (a to i) at MWCNTs/poly (L-Cys)/GCE in PBS of pH 7.0; **(c)** DPVs corresponding to simultaneous determination of FA, in the presence of DA (30 µm) and UA (100 µm) with different concentrations of FA i.e., 30 µm to 130 µm (a to g) at a MWCNTs/poly (L-Cys)/GCE in PBS of pH 7.0

The concentrations of DA were increased regularly and the remaining two were set constant. The developed sensor was found to discrimination all the three compounds successfully and also reveals that, there was no influence of DA concentration on the peak currents and peak potentials of UA and FA. A good linearity was observed for the concentration of DA against peak currents with a linear relationship equation of I_pDA = -0.04936 + 0.14378 C_{DA}(mM) (R= 0.9953). Fig. 8b and 8c shows the simultaneous response of DA, UA and FA with regular increase in UA and FA concentrations and keeping remaining two constant. The linear equations for the increase in UA concentration and FA concentrations were found be as I_pUA = 0.51271 + 0.09218 C_{UA} (mM) (R = 0.99774) and $I_{p\ FA}$ = -3.57757 + 0.0856 C_{FA} (mM) (R = 0.97512). From the above results, it is evident that the developed sensor showed well separated peaks for DA, UA and FA and the concentrations doesn't influence the other peaks.

3.7. Repeatability, Reproducibility and stability of MWCNTs/Poly(L-Cys)/GCE

In order to elevate the practical utility of the developed sensor, we have studied the repeatability, reproducibility and stability of the developed method. The repeatability studies were carried out by scanning the number of CV's in the same day and the responses was found to be stable, indicating good repeatability of the MWCNTs/Poly(L-Cys)/GCE. To study the reproducibility of the MWCNTs/Poly(L-Cys)/GCE, we have fabricated a new electrode, new solutions and different analyst and recorded the CV's for the prepared sensors, the results showed low RSD value, indicating that the MWCNTs/Poly(L-Cys)/GCE has good reproducibility. Further the developed sensor was studied for its stability and the fabricated electrode was tested at different days with CV and the results showed good stability of the sensor.

3.8. Dopamine formulation studies from DA injection sample

The practical application of MWCNTs/Poly(L-Cys)/GCE was successfully used for the quantitative estimation of DA in dopamine injection sample with the help of DPV technique.

Table 2. Dopamine determinations in DA injection and blood serum samples

Medium	Added (µm)	Found (µm)	Recovery (%)	Bias (%)
Buffer	10	10.6	106	6
	20	21.5	107.7	7.7

The DA standard solution was prepared with a specified concentration (4 mg/1 ml) equivalent to DA injection and using standard addition method, we have estimated the

quantities of DA. The recoveries of DA in the formulations were shown in the given table-2. It can be seen from the obtained recoveries in table-2, that the developed sensor can be used for the monitoring of DA in pharmaceutical formulations.

4. CONCLUSION

The present work describes the development of MWCNTs/Poly(L-Cys)/GCE for the sensitive determination of DA. The developed sensor exhibited good catalytic activity towards the determination of DA. Based on the redox process of DA, the electrochemical oxidation and reduction mechanism was observed. The sensor was well characterized by CV and EIS techniques. Kinetic parameters such as charge transfer coefficient, heterogeneous rate constant values were evaluated. From the effect of concentration LOD and LOQ values were calculated. The simultaneous determination of DA in the presence of UA and FA was successfully carried out. The developed sensor has shown good repeatability, reproducibility and stability. Finally the developed sensor was tested successfully for the recovery of DA in pharmaceutical formulation.

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