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Electrocatalytic Oxidation of Dopamine and Ascorbic Acid at Poly (Eriochrome Black-T) Modified Carbon Paste Electrode

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A polymerized film of Eriochrome black T (EBT) was prepared on the surface of carbon paste electrode (CPE) in alkaline solution by cyclic voltammetry. The poly (EBT) film-coated CPE exhibited excellent electrocatalytic activity towards the oxidation of dopamine (DA) and ascorbic acid (AA) in 1 M potassium chloride solution (KCl). Favorable electrostatic interaction between the negatively charged poly (EBT) film and cationic species of DA or anionic species of AA at this electrode was observed. Compared with the bare CPE, the modified electrode enhanced peak currents of DA and AA respectively. The modified electrode was demonstrated to be electrocatalytically active for the oxidation DA in the presence of AA.

Keywords: Chemically modified electrode, Eriochrome black-T, Dopamine, Ascorbic acid, Electropolymerisation

1. INTRODUCTION

Dopamine (DA) is one of the naturally occurring catecholamines in the mammalian central nervous system, which plays a key role in neurotransmission. [1-3] Changes in the concentration of DA may lead to serious diseases such as Schizophrenia and Parkinson's. [4]. So DA is currently the subject of intense research focus to neuroscientist and chemists and it is essential to develop rapid and simple method for the determination of the concentration of DA. Methods for the detection of DA include chemiluminescence [5], flourimetry [6], ultraviolet spectroscopy [7], capillary electrophoresis [8], high performance liquid chromatography (HPLC) [9], and ion chromatography [10]. Since DA is electrochemically active compound it can also be determined by electrochemical methods [11-12]. Electrochemical techniques have attracted great interest in many cases and these techniques can be fast in detections, low costs and with merits of low detection limits and high accuracy [11]. However there

are two problems in the electrochemical detection of DA [13-14]. A major problem for the electrochemical detection of DA in real biological matrices is the coexistence of some interfering compounds. Among these ascorbic acid (AA) is of particular importance. Because AA exist at much higher concentration than that of DA and oxidizes at a near potential with DA on bare carbon electrode surface [6] which result in an overlap of their voltammetric response [15]. Another problem is the fouling of the electrode surface by the adsorption of oxidation products, which results in rather poor selectivity and reproducibility. Thus it is difficult to detect DA in the presence of high level of AA in real biological samples, hence it is important to construct suitable electrode and to establish a sensitive and selective detection method for DA.

Exploration of many kinds of chemically modified electrodes to detect DA selectively has occurred in past years. Several approaches based on polymer-modified electrode [16-25], carbon ionic liquid electrodes [26-28], nano materials modified electrodes [29-33] and self-assembled monolayers [34-38] have been tried to solving the problems. These films can carry negative charges and so they can selective detect the DA cation by electrostatic effect [39]. Because AA exists in its anionic forms (pKa 4.1) and DA in cationic (pKa 8.9) at the physiological pH 7.4, AA cannot enter the polymer film and interference with the determination of DA is diminished [40]. In recent years polymer modified electrodes have attracted great attention as polymeric film has good stability and reproducibility [41-42]. A number of researchers have employed polymeric film modified electrode to detect DA. So far different methodologies have been used for depositing polymeric films. Electropolymerisation is a good approach to immobilize polymers because adjusting the electrochemical parameters can control film thickners, permeation and charge transport characteristics [18]. Recently poly (Eriochrome Black T) modified glassy carbon electrode [43-45] have attracted more attention because of their novel electrode material which exhibits several excellent electrochemical properties and high electrochemical stability. These properties enable the poly (EBT) GC electrode to render good reproducibility.

As part of our research work on the development of new electrochemical sensors for the determination of DA [46-49]. Present work reports the voltammetric behavior of DA at bare and poly (EBT) film modified carbon paste electrode. The modified electrode showed an electrocatalytic activity for the oxidation of DA and AA.The results indicate that the modified electrode could be used to detect DA in the presence of AA

2. EXPERIMENTAL PART

2.1. Reagents

Dopamine (DA) in the hydrochloride form and ascorbic acid (AA) were analytical grade reagents from Fluka and were used as received. Graphite powder was obtained from Aldrich. All other chemicals such as perchloric acid, potassium chloride, eriochrome black –T, sulphuric acid and sodium hydroxide were of certified analytical grade and obtained from Merck, were used as received without any further purification. DA solution was prepared in 0.1M perchloric acid while AA was prepared in

doubly distilled water immediately prior to use. 1 M KCl was used as supporting electrolyte. All other solutions were prepared with doubly distilled water.

2.2. Apparatus

Cyclic voltammetric experiments were performed with a model EA-201 Electro Analyzer (chemilink systems), equipped with a personal computer was used for electrochemical measurement and treating of data. A conventional three electrode cell was employed throughout the experiments, with bare or poly (EBT) modified carbon paste electrode (3.0 mm diameter) as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum electrode as a counter electrode. All potentials in this paper are referred to SCE electrode.

2.3. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the cavity of homemade PVC (3 mm in diameter) and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.4. Preparation of Poly (EBT) modified carbon paste electrode

The modified electrode was prepared by electrochemically pre-treating the bare carbon paste electrode by cycling the potential scan between –400mV to 1400 mV in 0.05M sulphuric acid containing 1mM EBT at a scan rate of 100 mVs^{-1} for 20 times. Finally polymerization was carried out by immersing the electrode in 0.01M NaOH solution containing 1mM EBT and was conditioned by cyclic potential sweeping from –400 mV to 1400 mV for 20 cycles at 100 mV/s. After polymerizations the poly (EBT) film was rinsed sufficiently using doubly distilled water and was used for determination of DA in presence of AA.

3. RESULTS AND DISCUSSION

3.1. Electropolymerisation of Eriochrome black-T at CPE surface

Fig.1 shows cyclic voltammogram of 1mM eriochrome black-T in 0.01M sodium hydroxide solution at carbon paste electrode and its electrochemical polymerization potential was 1400 mV. The potential scan range especially the positive potential was the most important factor in preparing the poly (EBT) film .If the positive potential value for polymerization was below 1200 mV or if the negative potential was above -400 mV no polymer was formed. In the first cycle, with the potential scanning from –400 mV to 1400 mV the anodic peak was observed at 143 mV corresponding to the

oxidation of Eriochrome black-T monomer. The peak descended gradually with the increase in cyclic time; such decrease indicates the poly (EBT) membrane forming and depositing on the surface of the CPE by electropolymerisation. After polymerization the poly (EBT) modified CPE was carefully rinsed with water and was used for the determination of DA and AA.

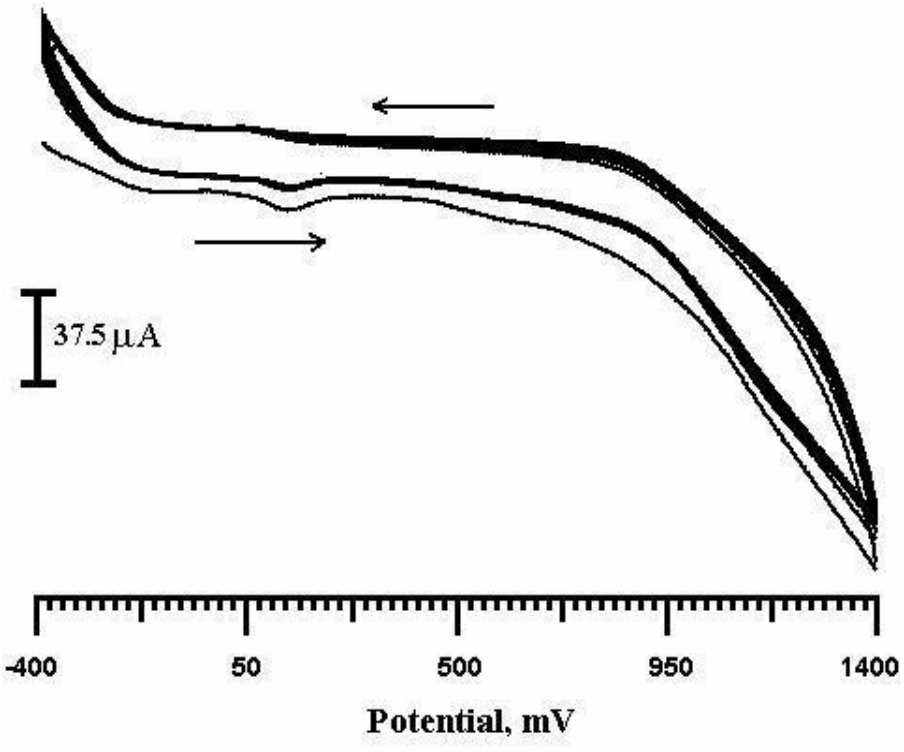

Figure 1. Repetitive cyclic voltammogram of 1mM Eriochrome black –T in 0.01M NaOH solution. Terminal potential 1400 mV; Initial potential - 400 mV. Scan rate: 50mV/s.

3.2. Electrochemical response of potassium ferrocyanide at poly (EBT) modified CPE

$K_4Fe(CN)_6$ was used as the electrochemical redox probe to investigate the electrochemical properties of poly (EBT) modified CPE. (fig.2). The cyclic voltammogram (CVs) of poly (EBT) modified CPE showed that the redox peak current increased than that of bare CPE. At the bare CPE the cyclic voltammogram of $K_4Fe(CN)_6$ (dashed line) showed a pair of redox peaks, with the anodic peak potential at 315 mV and the cathodic peak potential at 253 mV in 1M KCl. However for the poly (EBT) modified CPE a pair of redox waves of $K_4Fe(CN)_6$ were observed with greatly increase of the peak current (solid line). The anodic peak potential was located at 310 mV and the cathodic peak potential at 250 mV respectively. The results of the enhancement of peak current showed excellent catalytic ability of poly (EBT) modified CPE.

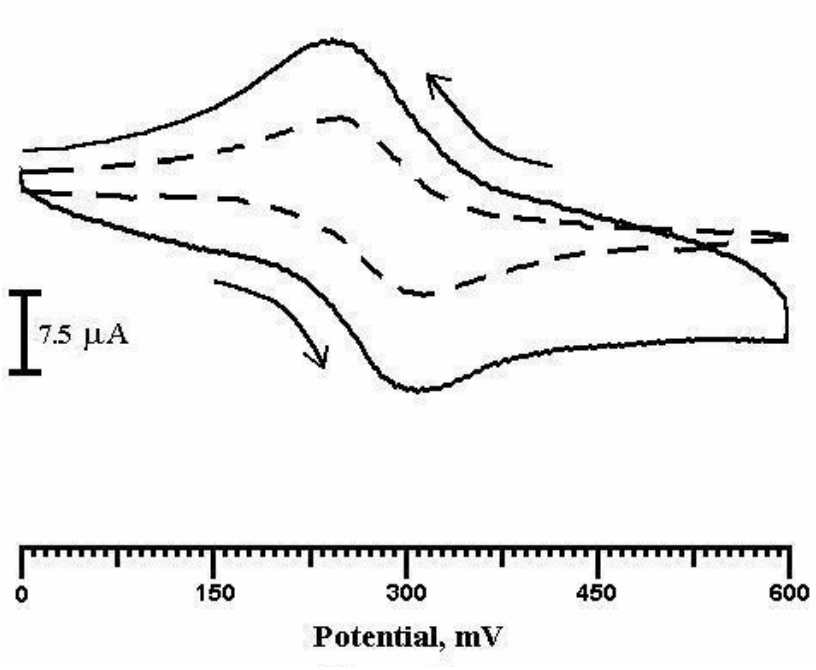

Figure 2. Cyclic voltammogram of 1mM potassium ferrocyanide in 1M KCl at bare electrode (dashed line) and modified electrode (solid line). Scan rate 50 mV/s.

3.3. Electrochemical response of dopamine at poly (EBT) modified CPE

Fig. 3. shows the CVs of 1 mM DA at bare and poly (EBT) modified CPE in 1M KCl at scan rate 50mV/s .The electrochemical response of DA shows great increase in peak current at the poly (EBT) modified CPE. At the bare CPE the cyclic voltammogram of DA (dashed line) shows an oxidation peak potential at 559 mV and reduction peak potential at 486 mV. The separation in peak potential (ΔE_p) is 73 mV and the ratio of redox peak current (i_{pa} /i_{pc}) was 1.41, which is the characteristic of a quasi-reversible electrode process. At the poly (EBT) modified CPE a pair of well-defined redox waves of DA was obtained with an increase of the redox peak current (solid line). The oxidation peak potential occurs at 545 mV and reduction peak potential at 480 mV respectively, with the peak potential separation (ΔE_p) 65 mV. The value of i_{pa} /i_{pc} was about 1, and no shift in the peak potential was observed in both bare and modified electrode which is the characteristics of the reversible nature of the electrode. It was observed that the peak currents enhanced greatly at the polymer modified CPE, which provides more evidence for asserting that the polymer on the surface of the CPE possessed high electrocatalytic activity to the electrochemical response of DA.

3.4. Effect of scan rate on the peak currents and peak potentials

The effect of scan rate on the peak currents at the poly (EBT) modified CPE in 1 M KCl was investigated by cyclic voltammetry in the presence of 1 mM DA (Fig.4a). As shown in fig. 4b. the anodic peak current increases linearly with the square root of scan rate in the range 50 mV/s to 350

mV/s (r = 0.99464) which indicates a diffusion controlled process occurring at the poly (EBT) modified CPE. Further the study showed that a good linear relationship between the anodic peak current (i_{pa}) was proportional to the scan rate (ν) over the range 50-350 mV/s which suggests a surface-controlled process in the solution (fig.4c). No shift in the oxidation peak potential of DA was observed with increasing scan rate. Also the slope of log i_{pa} vs. log ν (fig. 4d) was 0.83 which is larger than theoretical expected value 0.53 for purely diffusion controlled process [50] this indicates that the process is adsorption controlled. The plot of $ip/\nu^{1/2}$ vs log ν indicated an increase in the peak current with an increase in sweep rate (fig.4e) confirming that the reaction at the surface of electrode has adsorption complications. These results reveal that the anodic process is dominated by adsorption and diffusion of DA simultaneously.

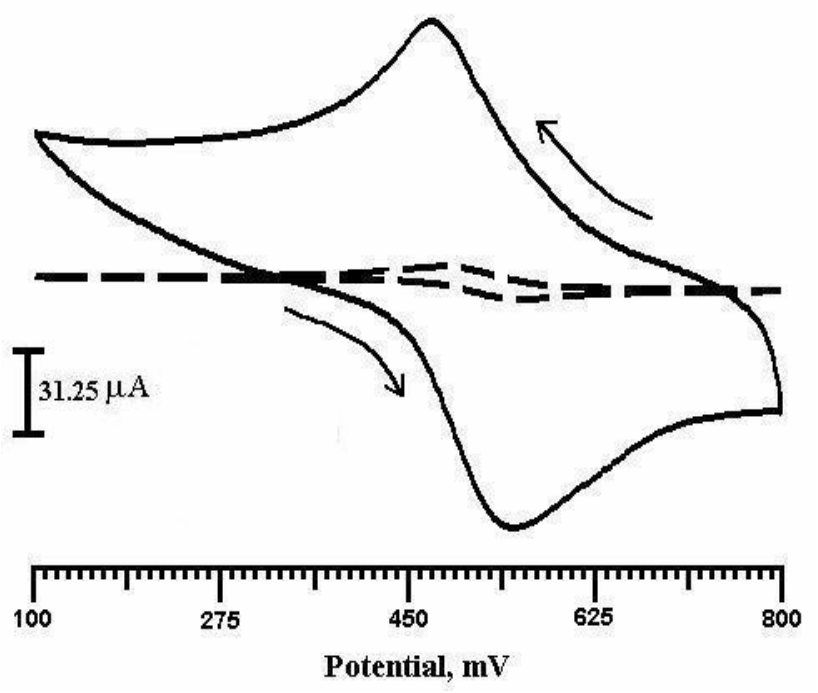

Figure 3. Cyclic voltammograms of 1 mM dopamine in 1 M KCl at the bare electrode (dashed line) and the modified (solid line). Scan rate 50 mV/s.

3.5. Electrochemical oxidation of dopamine and ascorbic acid at poly (EBT) modified CPE

The main objective of our work was the selective determination of AA and DA in 1 M KCl. Fig. 5. shows the cyclic voltammograms that were obtained for DA and AA coexisting in 1 M KCl solution at bare CPE and poly (EBT) modified CPE. The dashed line shows the cyclic voltammogram that was obtained for the solution containing 2 mM AA and 1 mM DA mixture in 1M KCl solution at bare CPE, where the cyclic voltammogram exhibited two oxidation peaks for both the analyte, which corresponds to AA and DA respectively. The oxidation peak for AA was obtained at 308 mV and that of DA at 508mV.

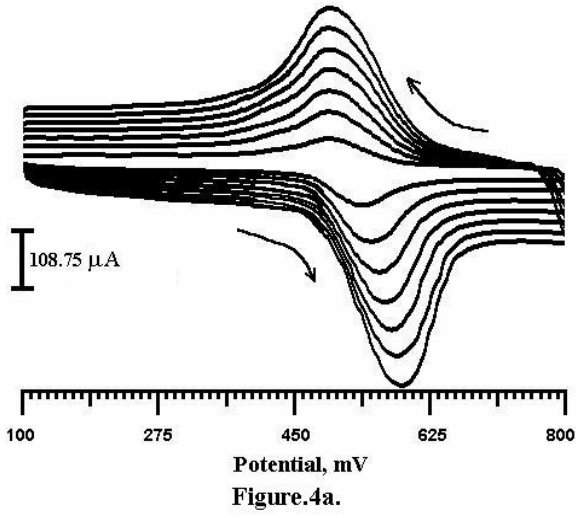

Figure.4a.

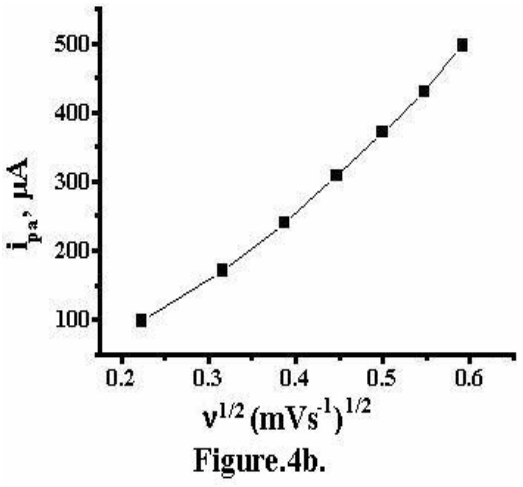

Figure.4b.

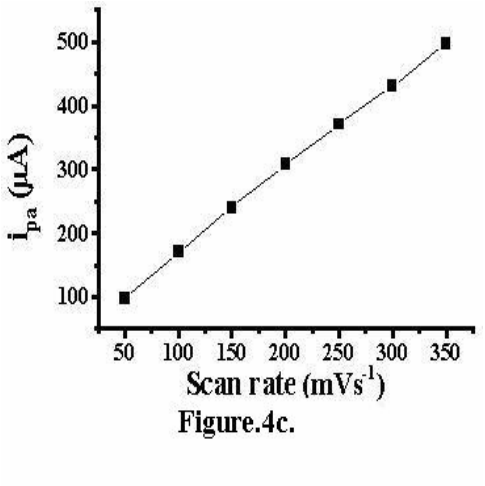

Figure.4c.

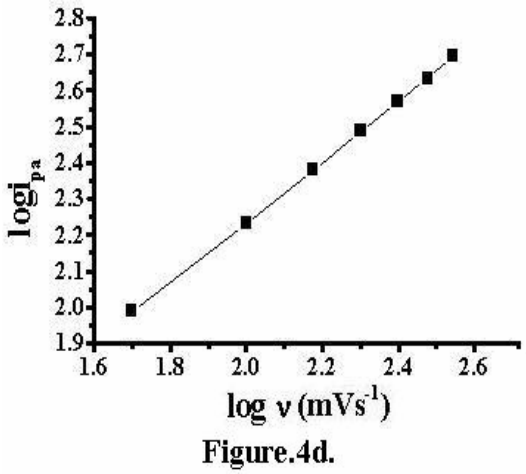

Figure.4d.

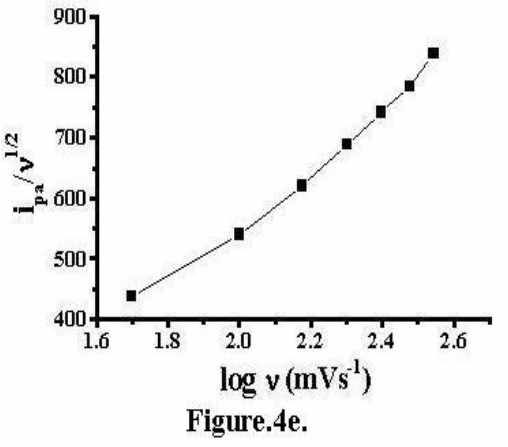

Figure.4e.

Figure 4. (a) Cyclic Voltammograms of poly (EBT) modified CPE in the presence of 1mM dopamine at different scan rates from (50, 100, 150,200,250,300,350) mV/s (b) Linear relationship between peak currents and the square root of scan rates. (c) Linear relationship between the peak current and the scan rate (d) Variation of the logarithm of peak current with the logarithm of the sweep rate (e) Plot of $i_p/v^{1/2}$ vs. log v.

These observations clearly indicate that the bare CPE effectively separated the voltammetric signal of AA and DA. The solid line shows the cyclic voltammogram for the oxidation of 1 mM DA and 2 mM AA in 1 M KCl at the poly (EBT) modified CPE. The modified electrode enhanced the oxidation peak current of both DA and AA. The oxidation peak potentials for AA and DA were obtained at 289 mV and 491 mV respectively. These gives clear evidence of the catalytic effect of the poly (EBT) modified CPE. The increase in the back ground current of poly (EBT) modified CPE implies that the sensitivity of the electrode increases after modification.

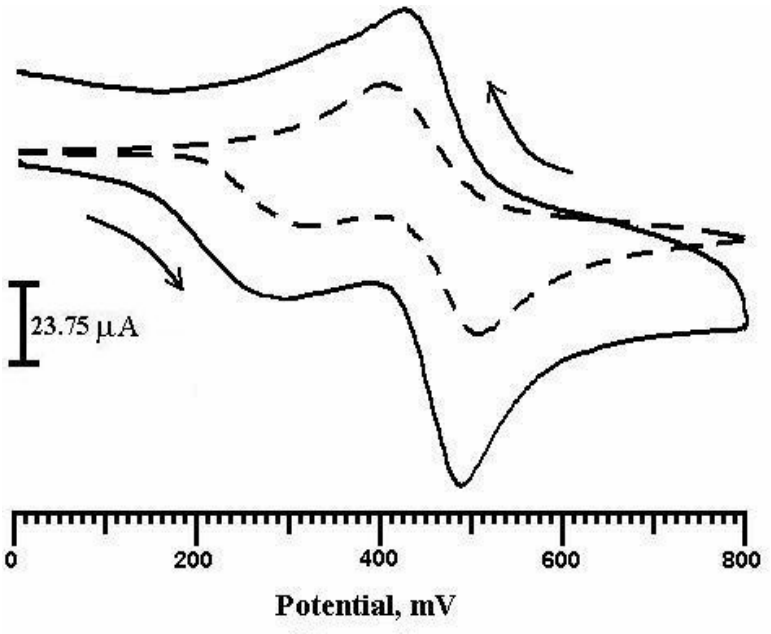

Figure 5. Cyclic voltammograms of 1mM dopamine and 2mM ascorbic acid using bare carbon paste electrode (dashed line) and poly (EBT) modified carbon paste electrode (solid line) in 1M KCl.

4. CONCLUSIONS

This report has shown that poly (EBT) modified CPE exhibits remarkable electrocatalytic effects towards the oxidation of dopamine and ascorbic acid. The results also indicated that the poly (EBT) modified CPE could be used for the determination of dopamine and ascorbic acid in their mixtures. The modified electrode enhanced the oxidation peak current of both DA and AA. The increase in the back ground current of poly (EBT) modified CPE shows that the sensitivity of the electrode increases after modification.

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