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Electrocatalytic Oxidation of Dopamine at Chemically Modified Carbon Paste Electrode with 2,4-Dinitrophenyl Hydrazine

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Electrocatalytic oxidation of dopamine was investigated at 2,4-Dinitrophenyl hydrazine modified carbon paste electrode by using cyclic voltammetric technique. The 2,4-Dinitrophenyl hydrazine modified carbon paste electrode was prepared by grinding the mixture of 70% graphite powder and 30% silicon oil (as a binder) with 2mg of 2,4-Dinitrophenyl hydrazine. The modified carbon paste electrode was calibrated with standard potassium ferrocyanide solution in 1M KCl as supporting electrolyte. The modified carbon paste electrode shows good electrocatalytic activity towards dopamine when compare with unmodified carbon paste electrode in 0.2M pyrophosphate buffer solution of pH 7 at scan rate of 100mV/s. The effect of scan rate shows that the electrode process was diffusion controlled. Concentration effect and pH effect were studied.

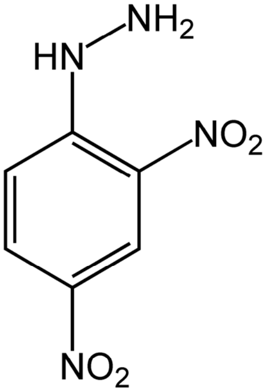
Keywords: Electrocatalytic oxidation, Dopamine, 2,4-Dinitrophenyl hydrazine, Modified carbon paste electrode, Cyclic voltammetry

1. INTRODUCTION

Dopamine (DA) is one of the most important neurotransmitters and plays a significant role in the functioning of central nervous system. A serious diseases such as Schizophrenia and Parkinsonism may result by loss of DA containing neurons [1,2]. Patient with this disease shows a low level of DA. Therefore it is significant to develop sensitive and simple methods for the determination of DA. Many methods were introduced to determine DA, such as spectroscopy, chromatography and electrochemistry [3-6]. Since DA is an oxidizable compound it can be easily detectable by electrochemistry methods based on anodic oxidation.

Carbon paste electrode has very much attracted towards the determination of biologically active molecules. Because of easy preparation of modified electrode, renewability, low background current and fast response. A number of modified carbon electrode was developed for the determination of DA by using voltammetric techniques [7-10]. Modified carbon paste electrode can be prepared by adding different types of modifiers. Modification can be done by grinding in an agate mortar [11-13], by electropolymerisation [14-16] and also by immobilization method [17, 18]. The modified electrode has good electrocatalytic activity such as sensitivity, selectivity and also low detection limit when compared to traditional carbon paste electrode.

In the present work the modification was done by adding 2,4-dinitrophenyl hydrazine for electrochemical investigation of DA by using cyclic voltammetry. 2,4-Dinitrophenylhydrazine (2,4-DNPH) is the chemical compound commonly known as Brady's reagent, having melting point 198 - 202 °C with a molar mass 198 and slightly soluble in water. It is a substituted hydrazine with a chemical structure (Scheme. 1). It is a wet red to orange crystalline solid substance. The hydrozone derivatives can also be used as evidence toward the identity of the original compound.



Scheme 1. Structure of 2,4- Dinitrophenyl hydrazine

2. EXPERIMENTAL PART

2.1. Reagent and Chemicals

2mg of 2,4-Dinitrophenylhydrazine was used as modifier. 25mM potassium ferrocyanide stock solution was prepared. DA was prepared by dissolving in 0.1N perchloric acid ($HClO_4$) solution. 1M potassium chloride was used as supporting electrolyte for potassium ferrocyanide. 0.2M pyrophosphate buffer solution (PPBS) of pH 7 was used as supporting electrolyte. Chemicals mentioned above were all purchased from Fluka and were analytical grade used without further purification. The solutions above mentioned were prepared by using double distilled water.

2.2. Apparatus and Procedure

The electrochemical experiments were carried out using a model-201 Electroanalyser (EA-201 Chemilink system). All experiments were carried out in a conventional three-electrode system. The electrode system contained a working carbon paste electrode, homemade cavity of 3mm diameter, a platinum wire as counter electrode and saturated calomel electrode as reference electrode. 2,4-dinitrophenyl hydrazine modified carbon paste electrode (2,4-DNPHMCPE) was prepared by grinding 2mg of silica gel with 70% graphite powder (Loba Chemie, 50mm particle size) and 30% silicon oil (Himedia) in an agate mortar by hand mixing for about 30 minute to get homogenous 2,4-DNPHMCPE. The paste was packed into the cavity CPE and smoothened on weighing paper. The bare CPE was prepared without adding modifier.

3. RESULTS AND DISCUSSION

3.1. Characterization of 2,4-DNPHMCPE using Potassium ferrocyanide

The 2,4-DNPHMCPE was characterized that 1mM potassium ferrocyanide in 1M KCl as supporting electrolyte at scan rate of 100 mV/s. The 2,4-DNPHMCPE was done by adding 2,4-DNPH from 2 to 10mg to the CPE the graph of current v/s different ratio of 2,4-DNPHMCPE was plotted in Fig 1a. From the graph we found that the 2,4-DNPHMCPE with 2mg 2,4-DNPH has highest sensitivity towards the potassium ferrocyanide.

Cyclic voltammogram for potassium ferrocyanide at BCPE (dashed line), with cathodic peak potential (E_{pc}) at 200mV and anodic peak potential (E_{pa}) 275mV (vs. SCE) in 1M KCl has supporting electrolyte (Fig.1b). The separation of redox potential peaks (ΔE_p) 75mV. However, for the 2,4-DNPHMCPE (solid line) pair of redox peak is obtained with strong enhancement in both anodic and cathodic peak current. The cathodic peak potential (E_{pc}) at 198mV and anodic peak potential at 275mV. From this result the ratio of 2,4-DNPHMCPE with 2mg 2,4-DNPH was kept constant for further analysis of DA.

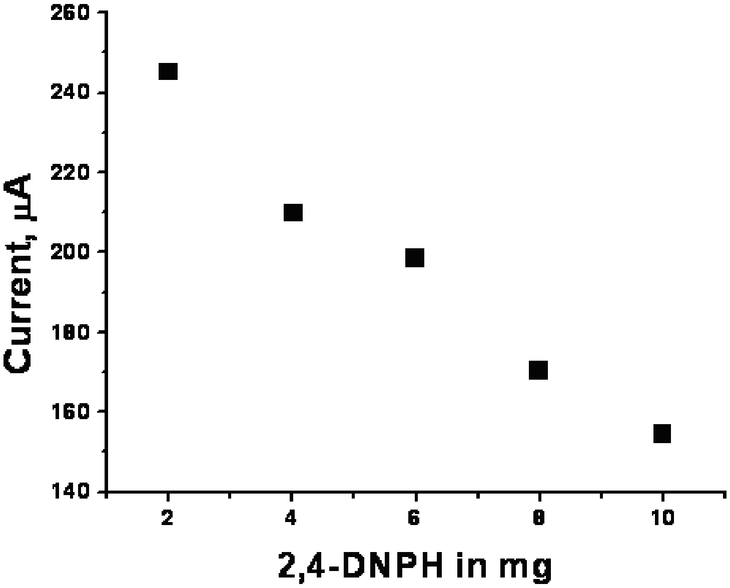


Figure 1a. Graph of current vs quantity of 2,4-DNPH in carbon paste electrode

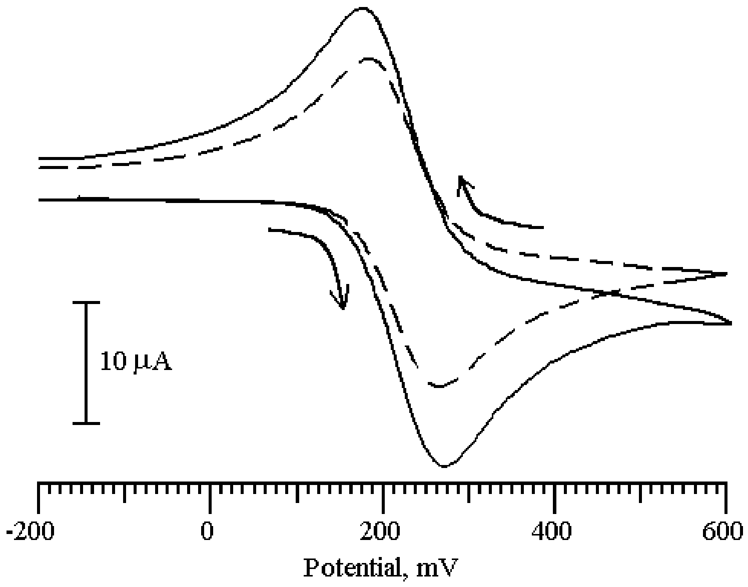


Figure 1b. Cyclic voltammogram of 1mM Potassium Ferrocyanide at BCPE (dashed line) and at 2,4-DNPHMCPE (solid line) at the scan rate of 100mV/s.

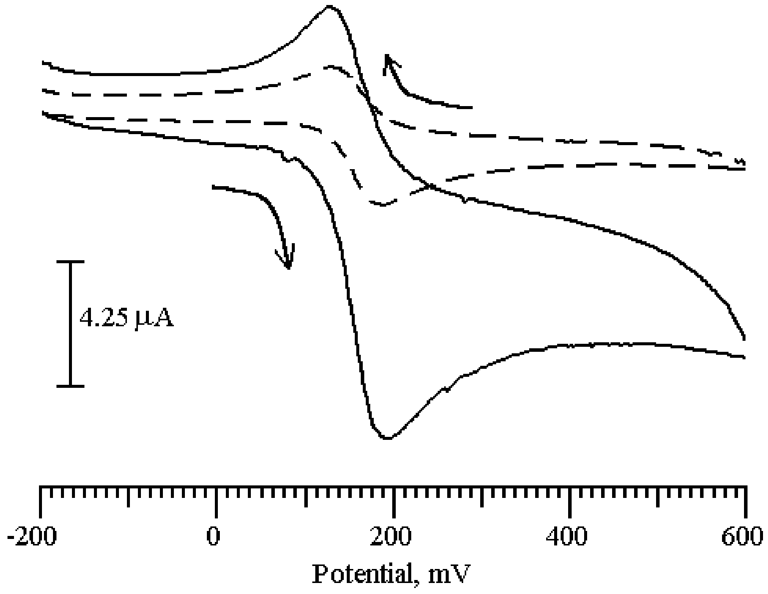


Figure 2. Cyclic voltammogram of 0.1mM DA at BCPE (dashed line) and at 2,4-DNPHMCPE (solid line) at scan rate of 50mV/s.

3.2. Electrocatalytic response of dopamine at 2,4-DNPH MCPE

DA being as easily oxidizable catecholamine which can be easily detectable by electrochemical method and shows reversible voltammogram with supporting electrolyte 0.2M pyrophosphate buffer solution pH 7 (Fig.2). Cyclic voltammogram for 1X10^{-4}M DA at BCPE (dashed line), with anodic peak potential (E_{pa}) 184mV and cathodic peak potential (E_{pc}) at 132mV (vs. SCE) in 0.2M pyrophosphate buffer solution pH 7. The separation of redox potential peaks (ΔE_p) 62mV. However, for the 2,4-DNPHMCPE pair of redox peak is obtained with strong increase in both anodic peak current. The anodic peak potential, 191mV and cathodic peak potential (E_{pc}) at 126mV. The separation of redox potential peaks (ΔE_p) was found to be 60mV which was characteristic of reversible voltammogram. The 2,4-DNPHMCPE showed good improvement of current signal for DA. The probable mechanism could be, due to the presence of hydrazine moiety in 2,4-Dinitrophenylhydrazine molecule could ready available for the electrocatalytic activity and hence, enhance the redox peak current of DA.

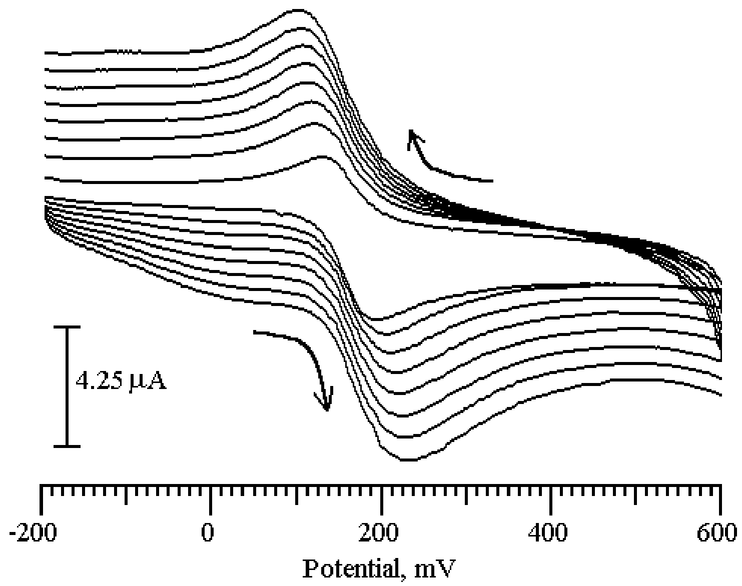


Figure 3a. Cyclic voltammogram of DA at different scan rate from 50mV/s to 400mV/s at 2,4-DNPHMCPE

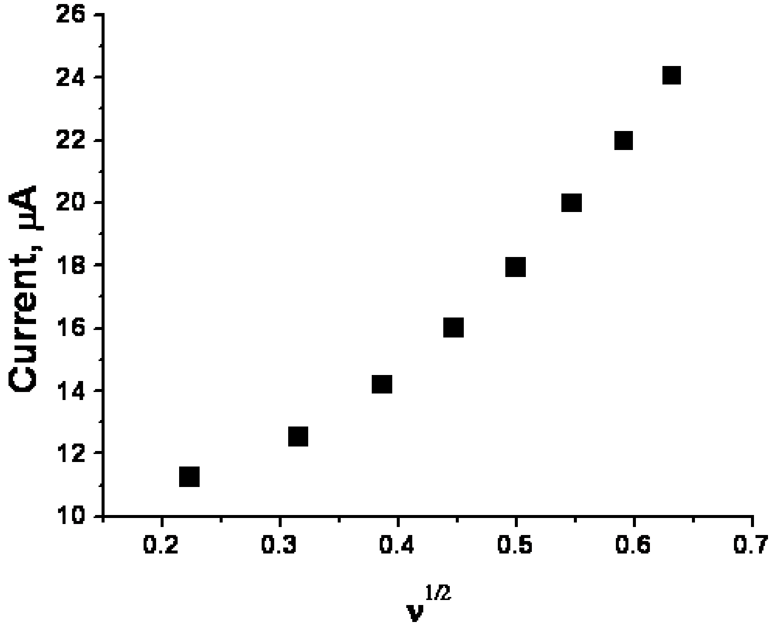


Figure 3b. Graph of current vs square root of scan rate

3.3. Effect of scan rate

Scan rate effect was performed by increase in the scan rate from 50mV/s to 400mV/s for $1X10^{-4}$M DA in 0.2M PPBS of pH 7. The 2,4-DNPHMCPE showed increase in the peak current with increase in scan rate (Fig. 3a). The graph of current Ipa vs square root of scan rate ($\nu^{1/2}$) were plotted (Fig. 3b). The graph obtained was straight line passing through the origin with correlation coefficient $r^2 = 0.9798$. This indicates that, the electron transfer reaction was diffusion controlled.

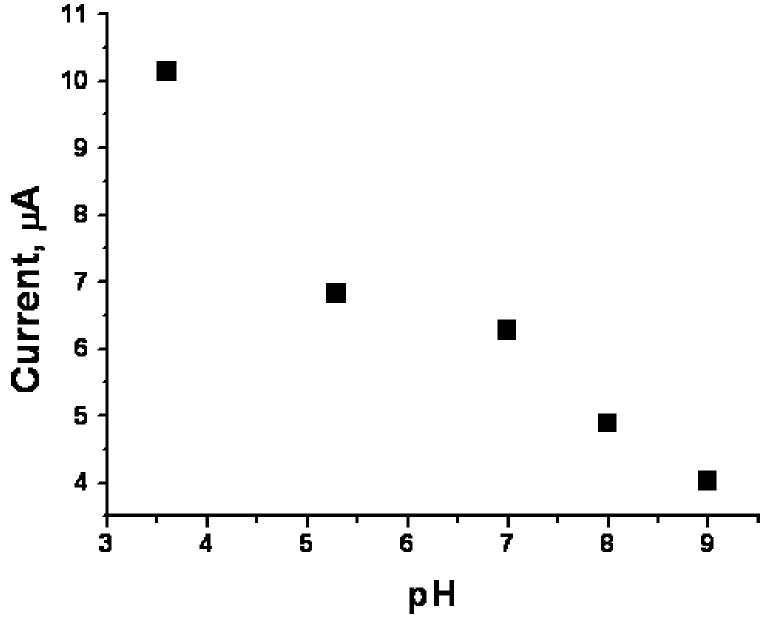


Figure 4a. Graph of current vs different pH

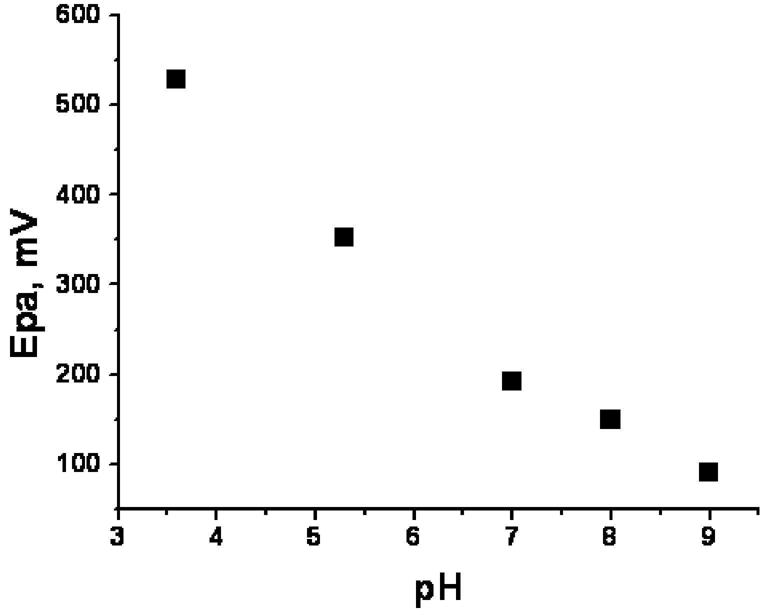


Figure 4b. Graph of Epa vs different pH

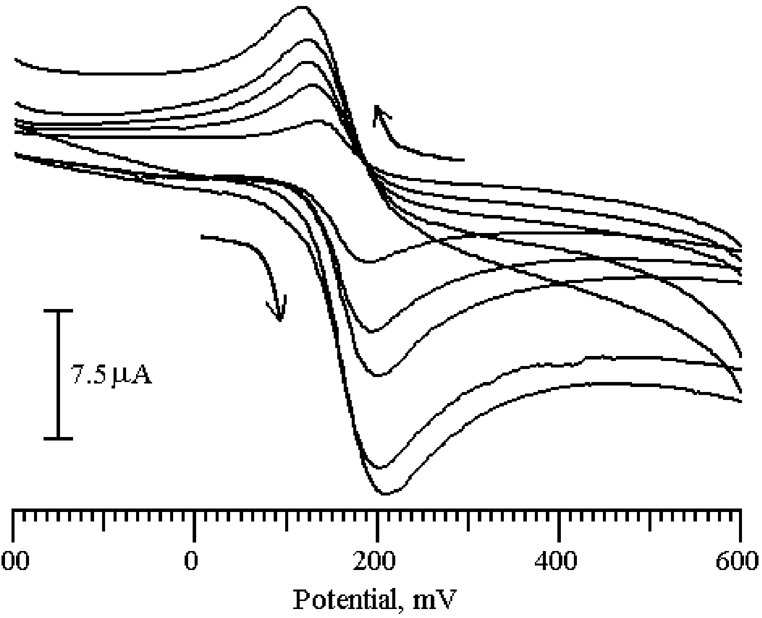


Figure 5a. Cyclic voltammogram for different concentration of DA at 2,4-DNPHMCPE

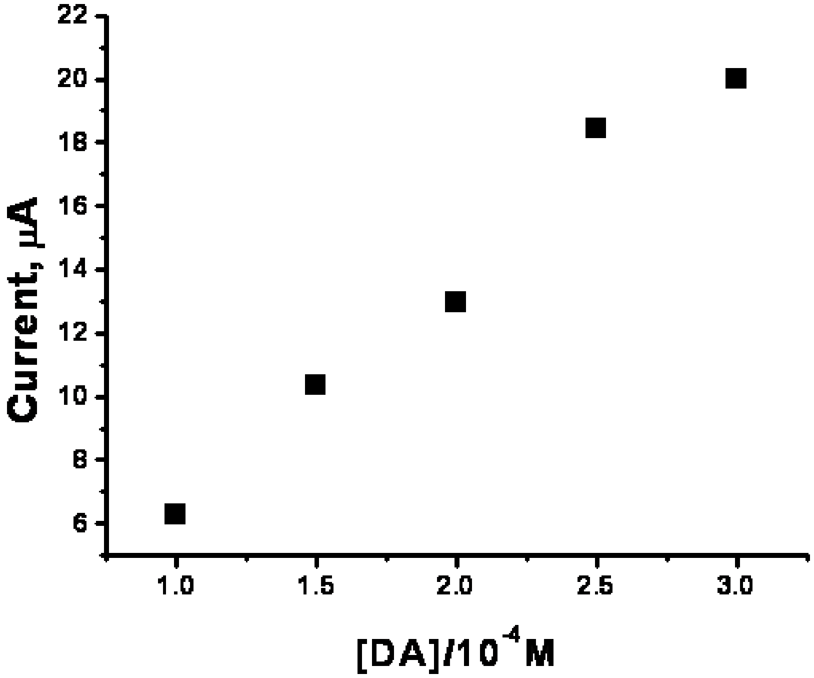


Figure 5b. Graph of current vs different concentration of DA

3.4. Effect of pH

Fig. 4a shows the effect of pH from 3.6 to 9 on the electrocatalytic oxidation of dopamine at 2,4-DNPHMCPE. The current signals obtained for DA were depend on pH. However the better shape of the voltammogram of the redox peak was obtained at pH 7 suggested it as optimal pH value. We further, studied the relationship between the anodic peak potential of dopamine and pH. The Fig.4b shows the graph of Epa vs pH. From the graph it was found that the anodic peak potential decreased with increase in pH with slope 62mV indicating that equal number of protons and electrons take part in the reactions [19].

3.5. Effect of Concentration of Dopamine

According to electrochemical response, the redox peak current increased with increasing the concentration of analyte (Fig. 5a). Concentration of dopamine was increased from $1.0\text{x}10^{-4}$M to $3.0\text{x}10^{-4}$M. The graph of anodic peak current against concentration of dopamine shows a linear relationship in the range $1.0\text{x}10^{-4}$M to $3.0\text{x}10^{-4}$M as shown in Fig. 5b.

4. CONCLUSIONS

In this work the modification of CPE was done by adding 2mg of DNPH. The characterization of MCPE was done for potassium ferrocyanide system. The MCPE has shown good electrochemical response for DA by increasing the current signal sufficiently. The scan rate effect was found to be diffusion-controlled electrode process. The concentration effect and pH effect was well investigated by using cyclic voltammetry. The modified electrode acts as a good sensor for DA and it can be further applied for the investigation of other neurotransmitter.

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