

Full Paper

Selective Determination of Dopamine in the Presence of Ascorbic Acid Using a Poly (Nicotinic Acid) Modified Carbon Paste Electrode

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Received: 5 November 2011 / Accepted: 30 May 2012 / Published online: 20 June 2012

Abstract- A carbon paste electrode (CPE) modified with poly (nicotinic acid) was used for the sensitive and selective voltammetric determination of dopamine (DA). The electrochemical response characteristics of the modified electrode toward DA, ascorbic acid (AA) were investigated by cyclic voltammetry (CV). The results show an efficient catalytic activity of the electrode for the electro-oxidation of DA, which leads to an improvement to the reversibility of the electrode response. The effect of pH and potential sweep rate on the mechanism of the electrode process was investigated. The modified electrode exhibits an efficient electron mediating behavior along with well-separated oxidation peaks for AA and DA. Under the optimum pH of 7.0 in 0.2 M phosphate buffer solution (PBS), the CV anodic peak current showed a linear relation *vs.* DA correlation coefficients. High sensitivity and selectivity, high reproducibility, along with ease of preparation and regeneration of the electrode surface by simple polishing make this method suitable for the determination of DA and AA in pharmaceutical and clinical preparations.

Keywords- Carbon Paste Electrode, Nicotinic Acid, Electropolymerisation, Dopamine, Ascorbic Acid, Cyclic Voltammetry

1. INTRODUCTION

Detection of biological molecules using chemically modified electrodes is more attractive strategy since electrochemical sensors combines the specificity of biological or chemical recognition layers with the inherent advantages (sensitivity, speed, miniaturization, linearity) of electrochemical transduction [1-3]. Polymer modified electrodes (PMEs) are received considerable attention among the researchers for sensing applications. Electropolymerisation is a good approach to prepare PME as adjusting electrochemical parameters can control film thickness, permeation and charge transport characteristics [3-5].

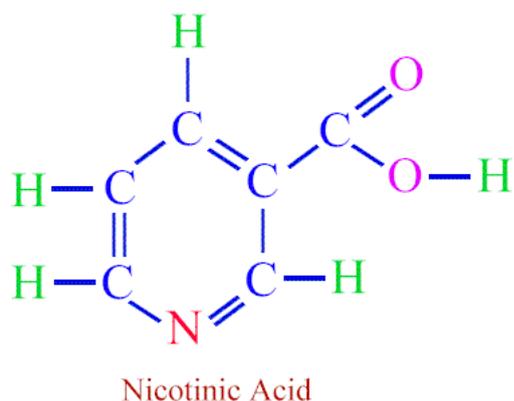
Simultaneous determination of dopamine (DA) and ascorbic acid (AA) has received considerable attention, due to their potential role in human metabolism. DA is an important neurotransmitter, and plays an important role in the function of mammalian central nervous system, renal, hormonal and cardiovascular systems [6]. In extracellular fluids, it is commonly known that the basal concentration of DA is approximately 50 nM [7]. Extreme abnormalities of DA levels are symptoms of several diseases such as epilepsy, senile dementia and Parkinsonism [8–10]. Similarly, AA is a needed compound of human body and it has been used for the prevention and treatment of common cold, mental illness, infertility and cancer. In mammalian tissue, AA, whose concentration is approximately 100 μ M, is present along with several neurotransmitters including DA [11]. Therefore, development of effective methods for resolution of responses and simultaneous determination of them is very important in analytical and clinical chemistry.

Exploration of many kinds of chemically modified electrodes to detect DA selectively has occurred in past years. Several approaches based on polymer-modified electrode [12-21], carbon ionic liquid electrodes [22-24], nano materials modified electrodes [25-29] and self-assembled monolayers [30-34] have been tried to solving the problems.

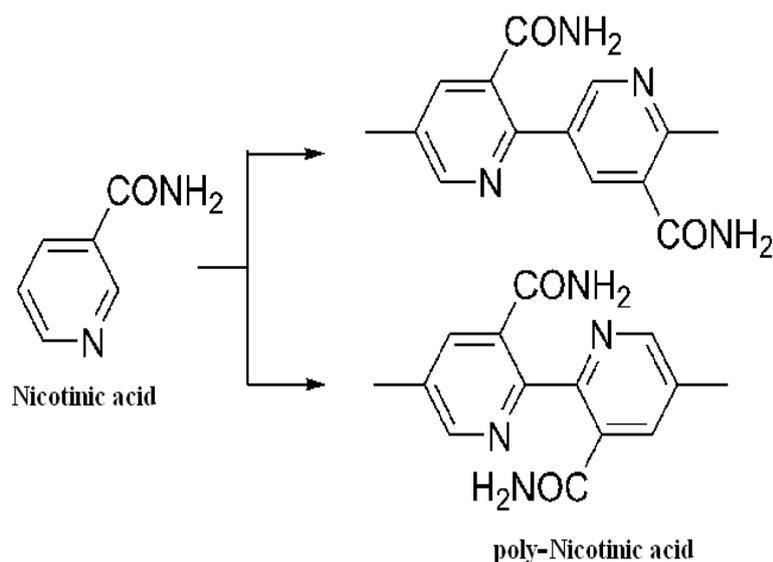
Recently poly (nicotonic acid) modified glassy carbon electrode [35] have attracted more attention because of their novel electrode material which exhibits several excellent electrochemical properties and high electrochemical stability. These properties enable the poly (nicotinic acid) GC electrode to render good reproducibility.

Vitamin pp, usually referred to as nicotinic acid (pyridine 3-carboxylic acid, NA), niacin or vitamin B₃ is shown in Fig. 1. It displays important biological activity and is one of the important water soluble vitamins that are easily lost when boiled in water, and it can't be stored in the human body. NA is usually found in urine.

As part of our research work on the development of new electrochemical sensors for the determination of DA [36-43]. Present work reports the voltammetric behavior of DA at bare and poly (nicotinic acid) 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



Scheme 1. Nicotinic acid



Scheme 2. The possible polymerization mechanism of nicotinic acid

2. EXPERIMENTAL

2.1. Apparatus and reagents

Cyclic voltammetric experiments were carried out with a model CHI (Model 680) connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare or poly(nicotinic acid) modified CPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were *vs.* the SCE.

Dopamine hydrochloride (DA), Nicotinic acid and Ascorbic acid (AA) were obtained from Himedia chemicals and were used as received. All other chemicals were of analytical grades. 0.2 M Phosphate buffer solution was prepared by mixing standard stock solutions of 0.2 M Na_2HPO_4 and 0.2 M $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Freshly prepared solutions of DA and AA were used in all experiments. All other the solutions were prepared with double distilled water.

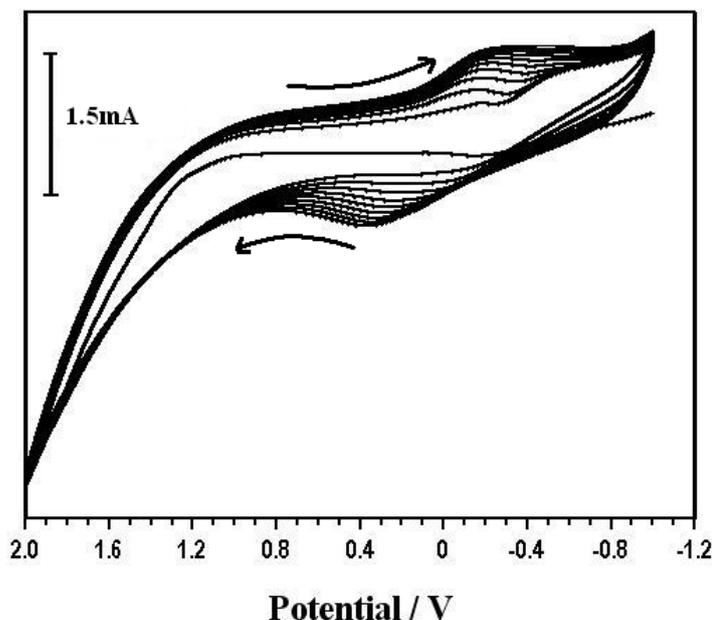


Fig. 1. Cyclic voltammogram of preparation of poly (nicotinic acid) film coated CPE. In 0.01 M NaOH, 1 mM nicotinic acid for 10 cycles at sweep rate of 100 mV s^{-1}

2.2. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder and silicon oil in the ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste at the end of the tube.

2.3. Preparation of pre treated and poly (nicotinic acid) modified CPE

The pretreated modified carbon paste electrode was prepared by scanning the bare CPE in the potential range from -1.0 V to 2.0 V . The peak heights of all these four peaks were all increased from cycle to cycle, indicating the accumulation of electroactive polymeric materials on the electrode surface. The possible polymerization mechanism is expressed in the Scheme 2 [35] containing 1 mM nicotinic acid at 100 mV s^{-1} for 10 times. After

polymerization the poly (nicotinic acid) modified CPE was rinsed with water and used for the determination of DA and AA.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical investigation of potassium ferrocyanide at poly(nicotinic acid) modified CPE

Fig. 2 depicts the CVs of bare carbon paste electrode and poly (nicotinic acid) modified electrode in the presence of standard $[K_4Fe(CN)_6]$ in 1 M KCl as supporting electrolyte. A pair of reduction and oxidation peaks was clearly observed. At a scan rate of 100 mV s^{-1} , the cathodic and anodic peak potentials were 0.093 and 0.278 V, at bare carbon paste electrode (dotted line) respectively. Comparing BCPE with MCPE, it could be observed that at the modified electrode, the anodic and cathodic peak potential were 0.270 and 0.061 V (solid line) and the peaks shift to a negative direction and the cathodic peak potential shifts to a positive one, and the difference between cathodic and anodic peak potentials at BCPE and MCPE 0.185, 0.209 V respectively. Meanwhile, the peak currents at modified CPE were increased significantly. These demonstrated that poly (nicotinic acid) could act as a promoter to enhance the electrochemical reaction and increase the rate of the heterogeneous electron transfer.

3.2. Electrochemical investigation of dopamine at the poly (nicotinic acid) modified CPE

Fig. 3 shows the cyclic voltammograms of DA at bare and poly (nicotinic acid) modified CPE. As can be seen, DA shows a sluggish and much smaller CV peak response with at the oxidation and reduction peak potentials occurred at 0.178 and 0.094 V, respectively at bare CPE. But at the poly(nicotinic acid) modified CPE, the peak current increased greatly and the peak potential shifted negatively. The voltammograms show a pair of reversible redox peaks with an oxidation and reduction peak potentials occurred at 0.265 and 0.082 V.

3.3. The effect of scan rate on the peak current and peak potential of dopamine

The effect of scan rate was studied by varying the scan rate from 100 to 400 mV s^{-1} at a concentration of 1 mM DA (Fig. 4A). The peak current values were plotted against the scan rate and resulted in a curved line. The plot of peak current vs. sweep rate resulted in a straight line with good correlation ($i_p = 7.0283v + 48.502$, $r^2 = 0.930$). These facts confirmed adsorption-controlled oxidation (Fig. 4B).

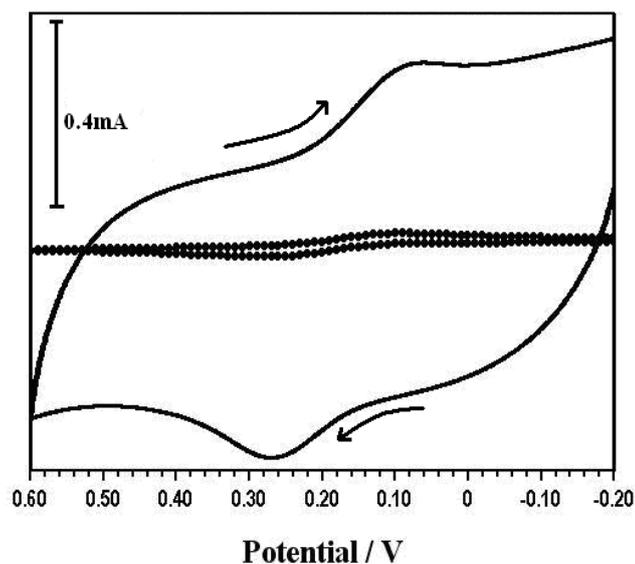


Fig. 2. Cyclic voltammograms for the electrochemical responses of $K_4[Fe(CN)_6]$ at bare (dotted line) and poly (nicotinic acid) modified CPE (solid line) in 1 M KCl containing 1 mM $K_4[Fe(CN)_6]$ at scan rate 100 mV s^{-1}

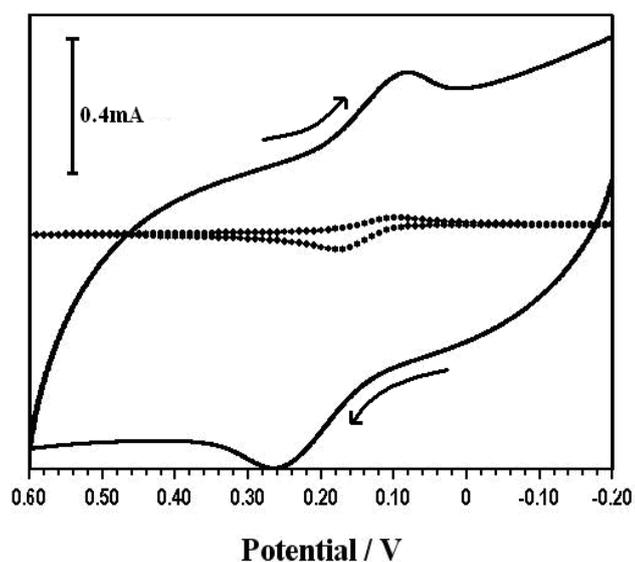


Fig. 3. Cyclic voltammogram of 1 mM DA in 0.2 M phosphate buffer solution of pH 7 at bare CPE (dotted line) and poly (nicotinic acid) film coated CPE (solid line)

3.4. The effect of pH on the peak current and peak potential of dopamine

The effect of pH on the electrode response and the oxidation potential was investigated by cyclic voltammetry in the solution containing 1 mM DA (Fig. 5A). The E_{pc} vs. pH graph

clearly indicates that the catalytic peak shifts to a more negative potential with increasing the pH. From Fig. 5B, it could also be seen that the current reached a maximum at pH 7. The reduction in current observed at lower pH values may correspond to the instability of DA under less acidic conditions.

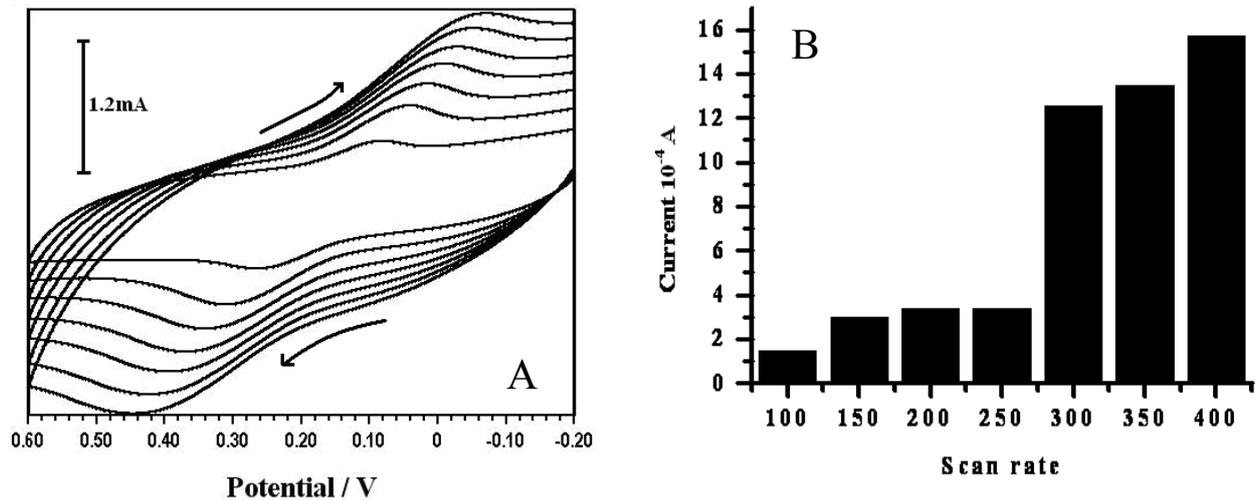


Fig. 4. A) Cyclic voltammograms of 1 mM DA on the poly (nicotinic acid) modified CPE at different scan rates (100, 150, 200, 250, 300, 350, 400 mV s^{-1}) in 0.2 M phosphate buffer solution pH 7.0 and B) The plot of the redox peak current vs. the scan rate

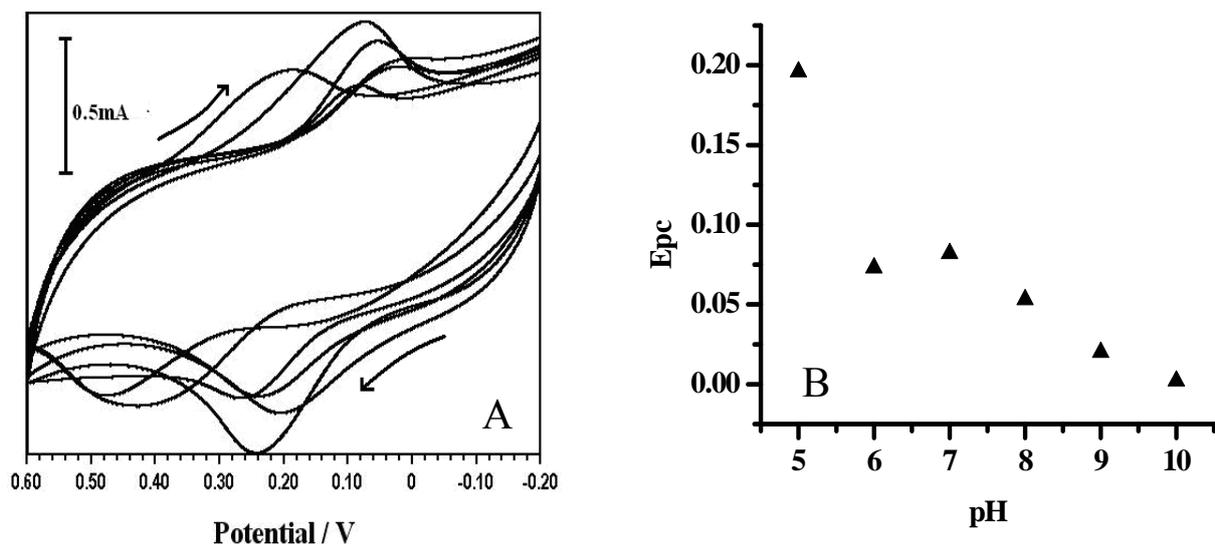


Fig. 5. A) Cyclic voltammograms obtained at the poly (nicotinic acid) modified CPE in 0.2 M phosphate buffer solutions in pH values 5,6,7,8,9 and containing 1 mM DA at scan rate of 100 mV s^{-1} and B) the plot of standard redox peak potential (E_{pa}) of DA on cyclic voltammograms vs. pH values

3. 5. The influence of concentration variation of DA

Electrocatalytic oxidation of dopamine was carried out by varying concentration at poly(nicotinic acid) from 1 to 3 mM as shown in Fig. 6A. By increasing the concentration of dopamine i_{pa} and i_{pc} goes on increasing with shifting E_{pa} towards positive and E_{pc} towards slight negative. The graph of current vs. concentration of DA shows increase in the anodic peak current with increase in the concentration of DA as shown in Fig. 6B.

3.6. Electrochemical response of ascorbic acid at the poly (nicotinic acid) modified CPE

Preliminary experiments were carried out to identify the general features, which characterize the behavior of AA on a carbon paste electrode modified with poly (nicotinic acid) Fig. 7 presents cyclic voltammograms of 2 mM AA in 0.2 M phosphate buffer (pH 7) at unmodified and poly(nicotinic acid)-modified carbon paste electrodes. A small peak was observed in the potential range of -0.2 to 0.6 V at the bare CPE. The cyclic voltammograms of AA at poly (nicotinic acid) modified CPE is also shown. The increase in anodic current at poly (nicotinic acid) modified CPE demonstrates that poly (nicotinic acid) modified carbon paste electrode plays an important role in the accumulation process of AA on the electrode surface.

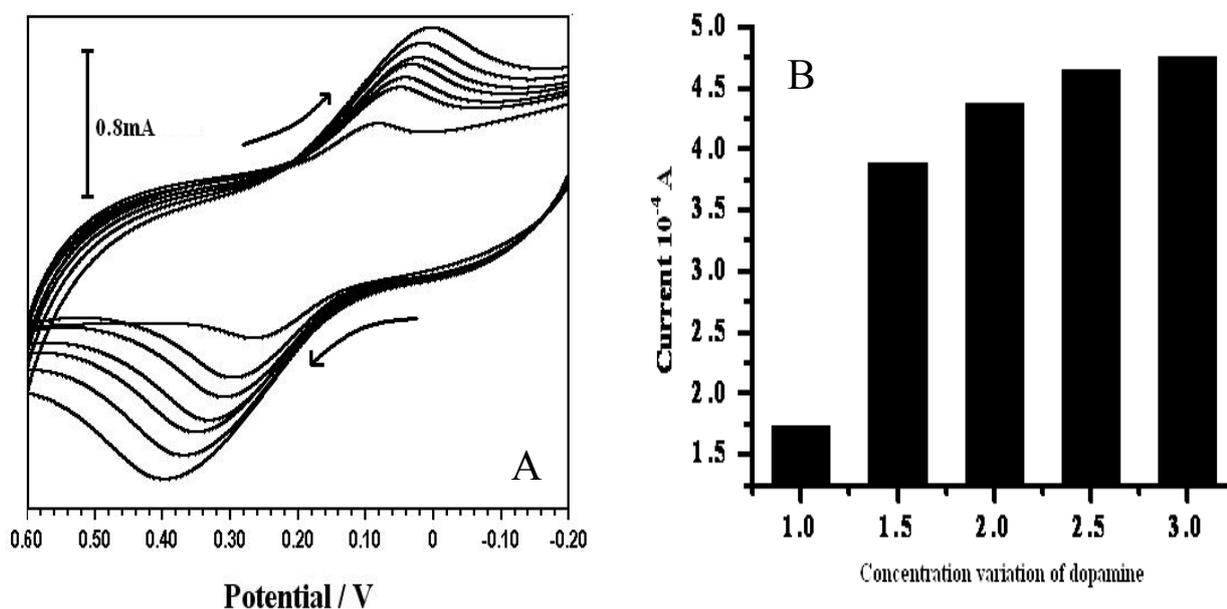


Fig. 6. A) Cyclic voltammogram of DA at different concentration (1-3.5 mM) B) Graph of current vs. concentration of DA

3.7. Effect of scan rate on the oxidation of AA

The effect of scan rate on the electrochemical response of ascorbic acid were examined in the 100–300 mV s^{-1} range. As it was shown in Fig. 8A there is a linear relationship between the peak current (i_p) and the scan rate within the range of 100–300 mV s^{-1} for AA. Results indicated that the electrode process is controlled by the adsorption of AA and there is a fast charge transfer on poly(nicotinic acid) modified carbon paste electrode(Fig. 8B).

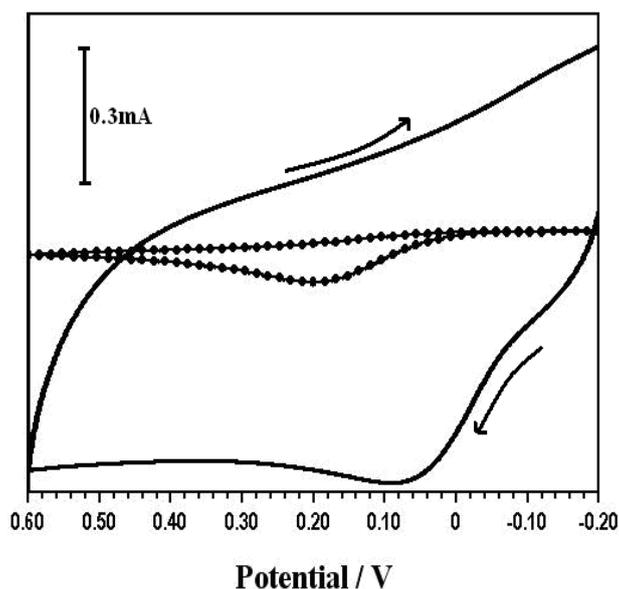


Fig. 7. Cyclic voltammograms obtained for the oxidation of 1 mM AA at poly (nicotinic acid) MCPE (solid line) and BCPE (dotted line) at scan rate 100 mV s^{-1}

3.8. Simultaneous determination of DA and AA at poly (nicotinic acid) modified carbon paste electrode

Since AA and DA coexist in the extra-cellular fluid of the central nervous system, both have a similar oxidation potential at most solid electrodes, and determination of these species is very difficult due to the overlapping signals. To evaluate the sensitivity and selectivity of the present system for the quantification of AA and DA. Fig. 9 displays the cyclic voltammograms of AA and DA in phosphate buffer at pH 7.0. As expected, at a bare CPE, it was verified interference in the AA and DA determination, which is indicated by an overlap of anodic peaks (dashed line), only one broad peak observed potential of 207 mV thus, disabling the simultaneous determination of AA and DA. However, as observed in this figure (solid line), Two well defined oxidation peaks at a potential of 0.227 and 0.107 V in phosphate buffer solution the measurement performed at the modified CPE allows a remarkable separation of AA and DA peaks. These results indicate that the poly(nicotinic

acid) modified carbon paste electrode exhibits excellent catalytic activity and well separated peak potentials for the determination of AA and DA.

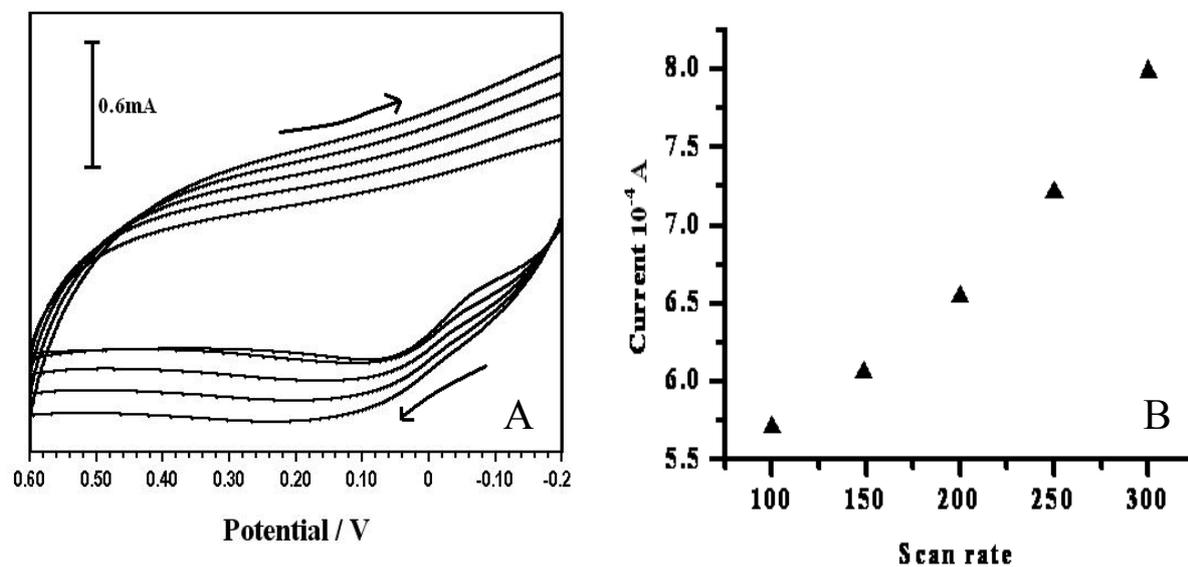


Fig. 8. A) Cyclic voltammograms for the oxidation of 1 mM AA at different scan rate 100, 150, 200, 250, 300 mV s⁻¹ in 0.2 M phosphate buffer solution (pH 7.0) and B) is the plot of anodic peak current vs. scan rate

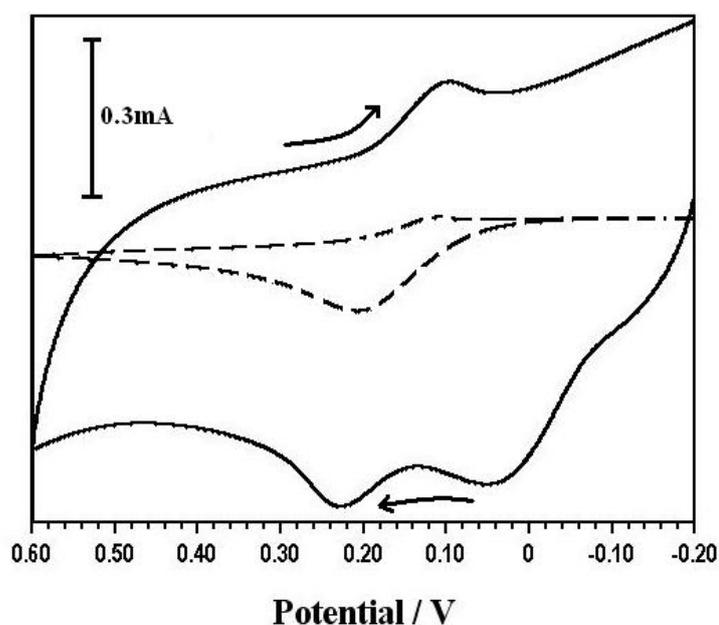


Fig. 9. Simultaneous determination of 0.5 mM DA, and 1 mM AA at bare CPE (dashed line) and at poly(nicotinic acid) film coated CPE (solid line)

3.9. Effect of DA concentration in the presence of AA at poly (nicotinic acid) MCPE

We carefully examined the oxidation current of AA at the poly (nicotinic acid) modified carbon paste electrode in the presence of increasing concentration of DA (Fig. 10A). No obvious change in the AA oxidation currents was observed while varying the concentration of DA, and the peak current of DA increased linearly with increasing DA concentration (1-3 mM) with a correlation coefficient of 0.95028 (Fig. 10B). Thus the homogeneous catalytic oxidation of DA by the oxidized AA is advantageously eliminated at the poly (nicotinic acid) modified carbon paste electrode.

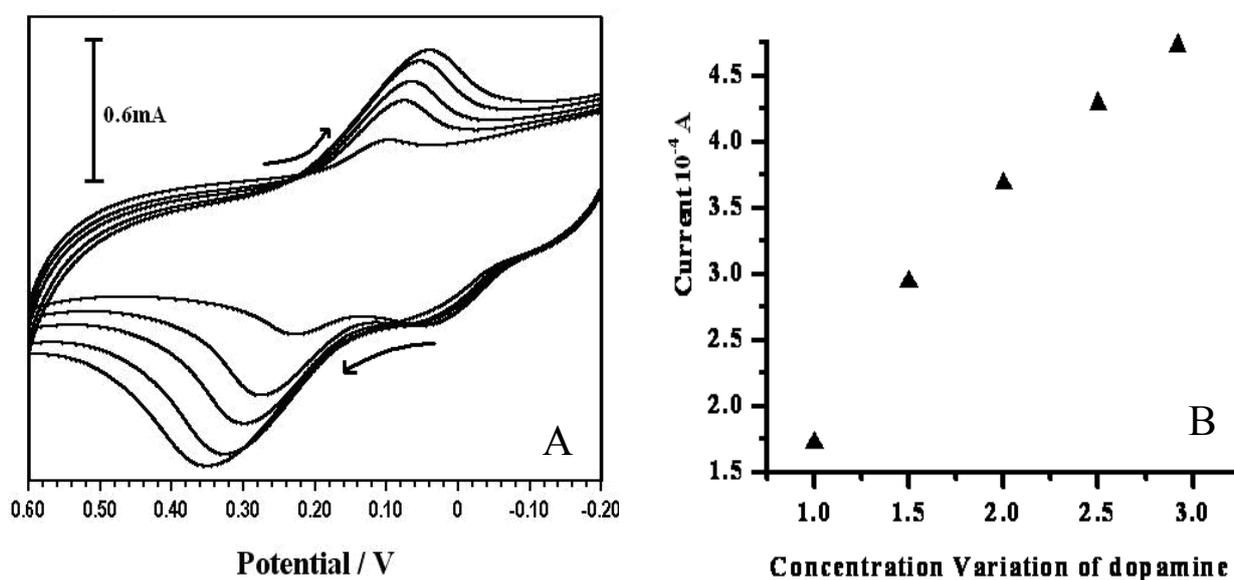


Fig. 10. A) Cyclic voltammograms obtained at the poly (nicotinic acid) MCPE in 0.2 M PBS pH 7.0 containing 1mM AA and DA with different concentrations (a) 1 (b) 1.5 (c) 2.0 (d) 2.5 (e) 3.0 mM at a scan rate of 100 mV s^{-1} B) plot of redox peak current of DA vs. concentration

4. CONCLUSION

This study has indicated that poly (nicotinic acid) modified carbon paste electrode exhibits highly electrocatalytic activity to DA oxidation. The redox response of the modified electrode is anticipated for a surface-immobilized redox couple. The electrochemical behavior of the modified electrode is strongly dependent on the solution pH. AA and DA coexist in a homogeneous solution and it can be simultaneously detected by this modified electrode since the separation of the oxidation peak potential for AA–DA about 120 mV. Therefore, simultaneous or independent measurements of the two analytes are possible by

using the modified electrode without any interference. The modified electrode acts as the electrochemical sensor for the determination of dopamine.

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