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Full Paper

Electroanalysis of Dopamine at Methionine Modified Carbon Paste Electrode by Cyclic Voltammetric Technique

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Abstract- The methionine modified carbon paste electrode exhibited good electrocatalytic properties towards dopamine (DA) oxidation in phosphate buffer (pH 7.0) than that of the bare electrode. The electrocatalytic response was evaluated by cyclic voltammetric technique. methionine modified carbon paste electrode has negative charge on its surface and in neutral solution DA exists as the positively charged species. In cyclic voltammetric measurements, favorable ionic interaction (i.e., electrostatic attraction) between DA and Methionine modified carbon paste electrode causes a negative shift of the oxidation potential for DA compared to that at the bare electrode. The electrode response was not affected by the oxidized product of DA. Several parameters such as scan rate variation, DA concentration and pH effect were investigated by cyclic voltammetric measurements. The peak currents were proportional to the concentration of DA with a detection limit of 1×10^{-6} M.

Keywords- Methionine, Modified Carbon Paste Electrode, Cyclic Voltammetry, Dopamine, PBS

1. INTRODUCTION

The electroanalytical techniques using chemically modified electrodes have been widely used as sensitive and selective analytical methods for the clinical and bio-technical analysis [1-6]. Dopamine (DA) is an important neurotransmitter of catecholamines released by neurons in a number of regions of the mammalian brain, and is thought to be important in the expression of a wide variety of behaviors [7,8]. DA in the basal ganglia is involved in motor control, and a causative link has been established between loss of DA in the dorsal striatum, due to neurodegeneration, and Parkinson's disease in humans [9]. In the prefrontal cortex, DA regulates cognitive functions [10]. DA imbalance in this region can lead to attention disorders and has been implicated in the path physiology of schizophrenia [11-13]. It possesses very strong electrochemical activity and is one of the main objects of study in the electroanalytical chemistry of neurotransmitters. There were many methods for the determination of DA, such as spectroscopy, chromatography and electrochemistry [14-16]. Because of its electrochemical activity, DA can also be determined with electrochemical method [17]. All of these methods require time-consuming and costly sample pretreatment. Thus, there is need for the development of selective, portable, inexpensive diagnostic tools for the determination of dopamine. Analytical methods based on eco-friendly techniques like potentiometric detection with chemically modified electrodes can be considered as an advantageous because they provides an easy construction and manipulation, good selectivity in a wide concentration range, a relatively low detection limit and show fast response perform analysis. This has led to increasing interest by our research group in the development and application of a chemically modified electrode using voltammetric techniques [18-20].

Amino acids have shown some advantages in electrochemical analysis [21]. So in the present study, methionine was used as a modifier. methionine contains of two sulfur-containing proteinogenic amino acids involves in the formation of peptides. In this paper, methionine was used to develop a modified electrode by a weight ratio calibration method in carbon paste electrode. This modified electrode showed an enhancement effects on the electrochemical oxidation of dopamine. The oxidation peak current increases remarkably and peak potential was shifted slightly to the positive value at this modified electrode. The experimental results show that the sensitivity for the determination of dopamine increases markedly at the methionine modified carbon paste electrode. Furthermore, some experimental parameters are optimized and an electrochemical method for the determination of dopamine is proposed.

2. EXPERIMENTAL SECTION

2.1. Reagents and Materials

Methionine, dopamine, perchloric acid, sodium dihydrogen phosphate, di-sodium hydrogen phosphate, graphite powder were obtained from Himedia, sodium dihydrogen phosphate, di-sodium hydrogen phosphate were used for the preparation of 0.1 M phosphate buffer solution. All chemicals and reagents were prepared with double distilled water. pH of the solution was monitored by a digital pH meter designed by systronics.

2.2. Apparatus and Procedure.

The electrochemical experiments were carried out using a Model CHI-660c Electrochemical work station. All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The carbon paste electrode was prepared as follows 70% graphite powder (particle size 50 mm and density is 20 mg/100 ml) and 30% silicone oil were mixed by hand to produce a homogeneous carbon paste electrode. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothened on a butter paper.

2.3. Electrode fabrication

Methionine modified carbon paste electrode was prepared by grinding the 6 mg of methionine with 70% graphite powder of 50 mm particle size and 30% silicon oil in an agate mortar by hand mixing for about 30 minute to get homogeneous methionine modified carbon paste. The paste was packed into the cavity of homemade CPE of 3 mm in diameter and smoothened on butter paper.

3. RESULTS AND DISCUSSION

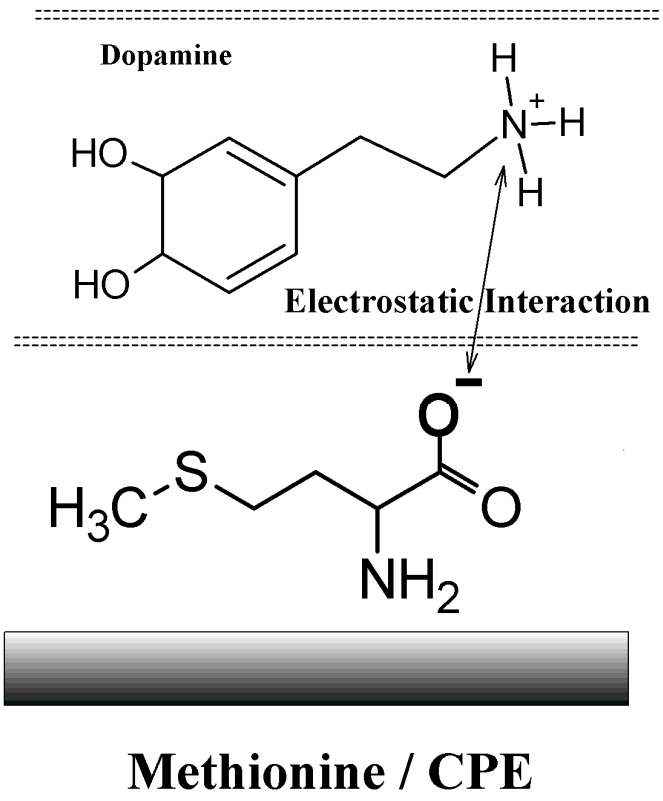
3.1. Calibration of electrode

Methionine was used as a modifier in the preparation of modified carbon paste electrode. Calibration of the sensor's detection parameter such as the working range was performed by the modifier concentration. It was prepared by adding the different amount of methionine into the carbon paste electrode. The characterization of methionine modified carbon paste electrode was investigated using cyclic voltammetric technique. By increasing the concentration of methionine in the carbon paste electrode, the electrochemical redox peak current of 1×10^{-4} M dopamine goes on increasing. Lower the concentration of the modifier lower was the DA oxidation peak current response, by increasing the concentration of methionine higher is the anodic peak of DA up-to 6 mg of methionine and above which the

background current increased with peak current. Hence 6mg of methionine was chosen for the preparation of modified electrode.

3.2. Electrocatalytic oxidation of dopamine at the methionine modified carbon paste electrode

The oxidation of dopamine at the bare and modified carbon paste electrodes was studied by cyclic voltammetric technique. As it is seen from Fig. 1, at the bare carbon paste electrode, the anodic peak current of dopamine was low, involving very slow electrode kinetics. In contrast, oxidation of dopamine at the methionine modified carbon paste electrode was associated with increasing anodic peak current. Interestingly the peak current for DA which was due to the electrostatic interaction between the negatively charged methionine modifier and the positively charged dopamine is shown in scheme 1. The results indicated that methionine modified carbon paste electrode can catalyze the electrooxidation of dopamine to dopamine hydroquinone.



Scheme 1. Mechanism of methionine modified carbon paste electrode

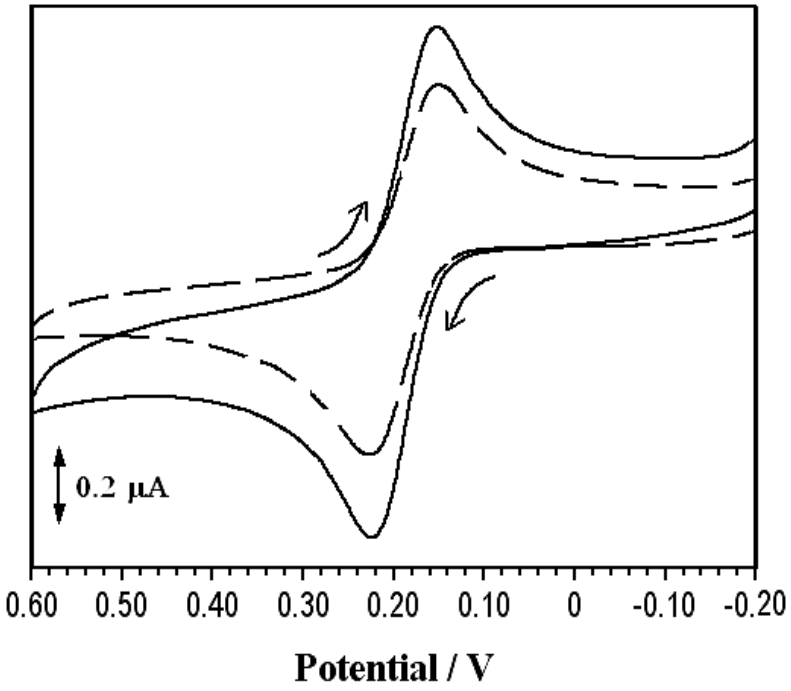


Fig. 1. Cyclic voltammograms obtained for bare carbon (dashed line) and methionine modified carbon paste electrode (solid line) in 0.1 M phosphate buffer solution of pH-7 containing 0.1 mM DA. Sweep rate 100 mV s^{-1}

3.3. Effect of scan rate

The effect of scan rate on the anodic peak current of DA was studied. It was found that with the increase in scan rate, the anodic peak current (I_{pa}) was increased, is shown in the Fig. 2A. The I_{pa} was directly proportional to the square root of scan rate over the range of 50-250 mV s^{-1} with correlation co-efficient was found to be 0.9998, which suggested that the electrode reaction was controlled by diffusion process. More types of evidence for the diffusion behavior were demonstrated by the following experiments. When methionine modified carbon paste electrode was switched into 0.1 M PBS (pH 7) after being used in DA, there was no peak signal at all which confirmed that the electrode process was diffusion controlled reaction.

3.4. Effect of concentration of DA

The cyclic voltammograms of different concentration of dopamine is shown in the Fig. 3A. Increase in concentration of dopamine from 1×10^{-4} M to 4.5×10^{-4} M both the anodic and cathodic peak current was increased. Fig. 3B shows the linear relationship between concentration of dopamine and anodic peak current. The correlation coefficient value was

found to be 0.9981. The detection limit was found to be 1×10^{-6} M at methionine modified carbon paste electrode.

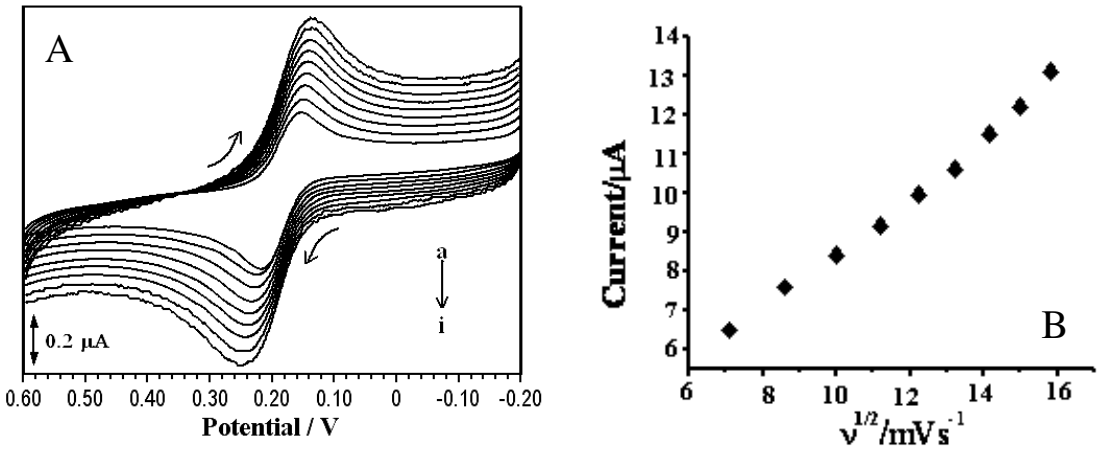


Fig. 2. (A) Cyclic voltammograms of a methionine modified carbon paste electrode in 0.1 M phosphate buffer (pH.7) containing 0.1 mM DA at different scan rates: (a) 50, (b)75 (c)100, (d) 125, (e) 150, (f) 175, (g) 200, (h) 225 (i) 250 mVs^{-1}. **(B)** Plot of square root of scan rate *vs*. current

3.5. Effect of pH on the oxidation of DA

The effect of solution pH on the electrochemical response of the methionine modified carbon paste electrode towards the determination of DA was studied in the pH range from 5.5 to 8.5. Cyclic voltammetric investigations at the extreme acidic and basic pH conditions were avoided due to less stability of the electrode. Fig. 4A shows the variation of peak potential with respect to changes in the pH of the buffer. It was observed that the peak potential of DA shifted negatively with the increase in pH of the phosphate buffer solution. The slope of the plot of pH versus anodic peak potential has revealed that the equal number of proton and electron were involved in the reaction (Fig. 4B). DA shows good electrochemical response at neutral pH conditions. Hence, the physiological pH 7.0 was chosen for the oxidation studies of DA using the methionine modified carbon paste electrode.

3.6. Stability and reproducibility

The stability of modified electrode, lifetime evaluation, maintenance and storage of the methionine modified carbon paste electrode has been studied by measuring its cyclic voltammetric response on storage for a longer duration at room temperature conditions. The electrode was stored in air and the current response for DA was noted every 2 days. It was observed that no apparent decrease in response for nearly 8 days. Such a good stability is

acceptable for most practical applications. No significant change in the peak potential and the current response between the new and renewed surface were observed, which indicated the uniform distribution of the methionine in the carbon paste electrode. The RSD of the cyclic voltammetric response for the oxidation of 1.0×10^{-4} M DA at eight successively regenerated methionine surfaces is 5.6%.

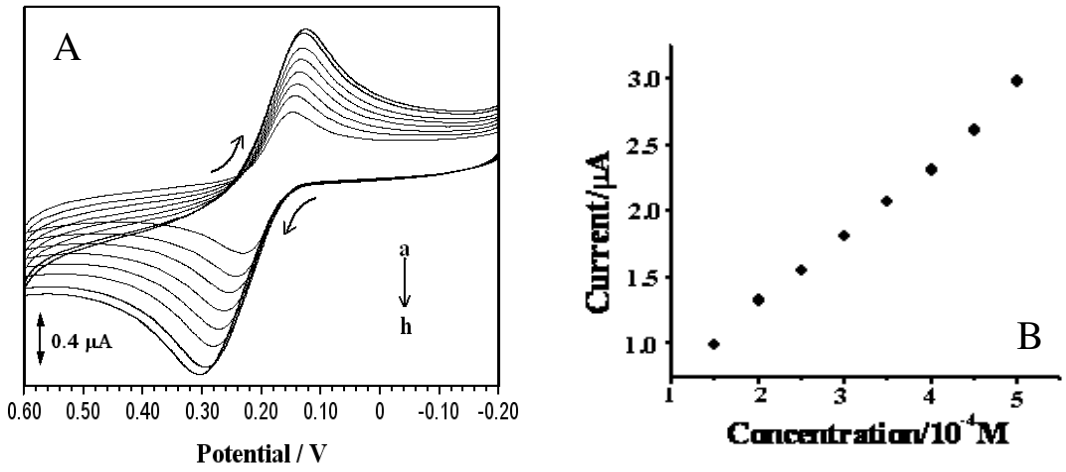


Fig. 3. (A) Cyclic voltammograms of the methionine modified carbon paste electrode in pH 7 PBS with different concentrations of DA: (a) 1×10^{-4} M (b) 1.5×10^{-4} M (c) 2×10^{-4} M (d) 2.5×10^{-4} M (e) 3×10^{-4} M (f) 3.5×10^{-4} M (g) 4×10^{-4} M (h) 4.5×10^{-4} M **(B)** Plot of concentration *vs*. current

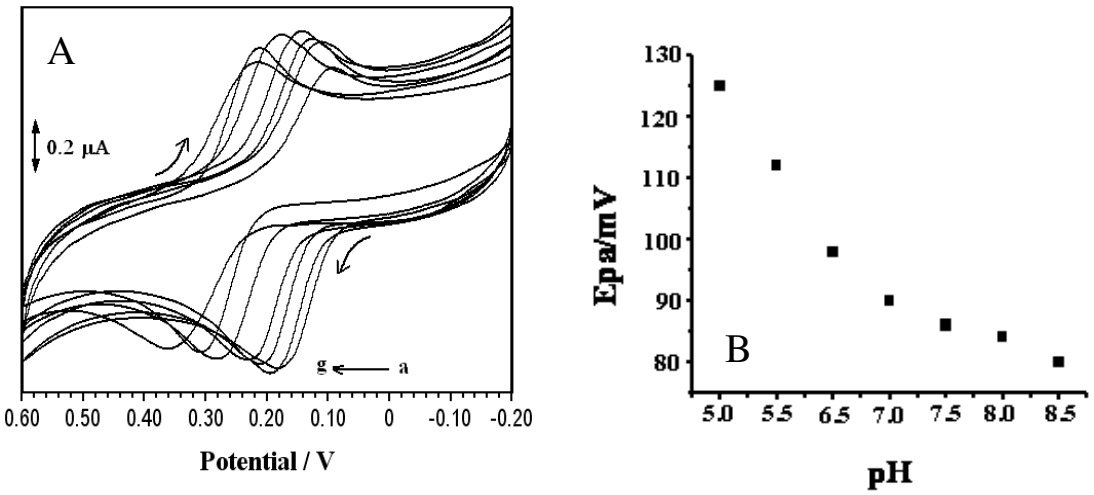


Fig. 4. (A) Cyclic voltammograms of 0.1 mM DA at methionine modified CPE at different pHs (a) 5.5, (b) 6.0, (c) 6.5, (d) 7.0, (e) 7.5, (f) 8.0, (g) 8.5 with scan rate of 100 mV s^{-1} **(B)** Graph of pH *vs*. E_{pa}

4. CONCLUSION

The methionine modified carbon paste electrode is a promising tool for direct determination of dopamine without any pretreatment. The electrostatic interaction between negatively charged methionine film and positively charged DA shifts its oxidation peak potential to less positive direction of potential. A good analytical performance has been demonstrated. The electrode shows a stable response without fouling of the electrode surface by the adsorption of the oxidized product of dopamine. The proposed method showed a low detection limit, electrode mechanism, good sensitivity and stability of the methionine modified carbon paste electrode. The results obtained have shown better results than those based on chemically grinding modified electrodes.

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