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Electrochemical Determination of Dopamine Using Banana-MWCNTs Modified Carbon Paste Electrode

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Abstract- A carbon paste electrode (CPE) modified by multiwalled carbon nanotubes (MWCNTs) and banana tissue was used for detection of dopamine (DA). The modified electrode show good selectivity toward DA in the presence of ascorbic acid (AA). The electrochemical determination of DA at the surface of modified electrode was investigated by differential pulse voltammetry (DPV). The linear curve was obtained in the range of 10-30 μM. The detection limit (3σ) was 2.09 μM for DA. Also the stability of modified electrode was investigated after 20 days, and results show that the modified has relatively good stability.

Keywords- Multiwalled Carbon Nanotubes, Banana Tissue, Carbon Paste, Dopamine, Differential Pulse Voltammetry

1. INTRODUCTION

Carbon paste electrodes, since their first introduction in 1958 by Adams [1], have been extensively employed in various electrochemical detection due to their simple and fast preparation, facile surface renewing, biocompatibility, non-toxic character, and relatively low-background characteristics [2]. Furthermore, carbon paste electrodes are extremely attractive

for their subsequent bulk modification with different modifiers, e.g. electrocatalysts and/or enzymes by mixing them into carbon paste matrix [3-6].

Dopamine (4-(2-aminoethyl) benzene-1, 2-diol (DA)) is a naturally occurring biogenic catecholamine formed by the decarboxylation of 3, 4-dihydroxyphenylalanine. It is a precursor to epinephrine and nor-epinephrine in a biosynthetic pathway [7], which functions as a neurotransmitter in the central and peripheral nervous systems. Insufficient DA concentration due to the loss of DA-producing cells may lead to a disease called Parkinson's disease [8] in which a person loses the ability to execute smooth and controlled movements [9-11]. DA can be supplied as a medicine; however its excess dosage may act on the sympathetic nervous system which cause an increase heart rate and blood pressure [12].

Thus, the investigation of electrochemical response of DA at the low concentration is necessary. Few methods based on the chemical modification of traditional electrode materials have been reported for the determination of DA (e.g., electrochemical determination of DA in the presence of ascorbic acid using sodiumdodecyl sulfate micelles as masking agent [13], poly-chromotrope 2B modified GC electrode [14], Nafion/carbon-coated iron nanoparticles–chitosan composite film modified electrode [15], Pt/Au hybrid film modified electrode [16], self-assembled gold nanoparticle films [17] and carbon paste electrode modified with polypyrrole/ferrocyanide films [18]). However, most of these methods face oxidation of biomolecule at electrode, fouling of electrode (due to adsorption of the oxidation products), unstable analytical signal [19], require high over potential, high detection limit, slow response and most of all are complex. The recent use of carbon nanotubes (CNTs) modified electrodes has revolutionized the electrochemical techniques for the determination of biomolecules. This is because of their exceptional properties [20-23] e.g. small dimensions, high mechanical strength [24], electric [25,26] and thermal behavior[27,28], biocompatibility, high stability, modifiable sidewalls [29-32], high surface area (creating a large interfacial region, which can have properties different from bulk material [33]). Therefore CNTs are best suited for almost any aspect of nanotechnology, including electronic and optoelectronic devices, biomedical, pharmaceutical, co smetic, automotive, aeronautic and aerospace industries, catalytic, and analytical chemistry [34,35]. Various types of biosensors for dopamine determination have been developed [36-39], biosensors seem promising tools for such analysis. A biosensor is described as a compact analytical device, incorporating a biological or biomimetic-sensing element. Biosensors offer great advantages over conventional analytical techniques [40].

Polyphenol oxidases are group of copper proteins that are widely distributed from bacteria to plant tissues. They catalyze the oxidation of hydroxyl phenols to their quinone derivatives. The enzyme catalyzes two distinct reactions involving molecular oxygen: the first involving hydroxylation of monophenols to o–dihydroxy phenols (cresolase activity) and the second one involving oxidation of o–dihydroxy compounds to quinones

(catecholase activity). The quinones formed are highly reactive and undergo spontaneous polymerization leading to the formation of brown pigments. This process is responsible for the browning of fruits and vegetables on their open surfaces. The use of animal and plant tissues provides numerous advantages for the fabrication of biosensors such as low cost and better life - time [41,42].

Whereas banana tissue is rich of polyphenol oxidase that catalyzes dopamine oxidation [43]. In this work, we fabricated MWCNTs-banana modified carbon paste electrode for voltammetric determination of dopamine. The electrochemical technique was differential pulse voltammetry.

2. EXPERIMENTAL

2.1. Instrumenttation

Electrochemical studies were carried out using a computer-controlled potentiostat / galvanostat (Autolab). Electrochemical measurements were performed in a three-electrode cell with a ban -MWCNTs-CPE, as working electrode, a Pt wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. Thus, all potential are referenced to the SCE.

2.2. Reagents and solutions

Banana was purchased at commercial maturity from a local store. Ascorbic (AA) acid and dopamine (DA) was purchased from Fluka. The solvent used for the electrochemical studies was twice distilled water. Buffer solution was prepared from orthophosphoric acid and its salts. High viscosity paraffin (density=0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter=0.1 mm) from Merck was used as the working electrode (WE) substrate. Multi - walled carbon nanotubes, MWCNTs (from Nanotab, USA, 95%), were added to solution containing sulfuric acid and nitric acid with ratio 3:1 (V/V) for 24 h with stirring. Then, the solution was filtered and the precipitate washed with distilled water, thoroughly. The precipitate was allowed to dry at room temperature. Sulfuric acid and nitric acid (from Merck) were used as received. All other reagents were of analytical grade.

2.3. Working electrode preparation

Banana-MWCNTs modified carbon paste electrode (ban-MWCNTs-CPE) was prepared in the following way. For preparation ban-MWCNTs-CPE (banana: 5%, MWCNTs: 10%), 0.01 g of banana and 0.02 g of MWCNTs were mixed with paraffin oil in a mortar followed by incorporation of graphite powder (0.2 g) with a subsequent mixing for 10 min. The resulting paste was then inserted in the bottom of a glass tube. The electric contact was established through a copper wire. The surface of the paste electrode was smoothed on a

weighing paper. Unmodified carbon paste electrode was prepared in a similar way, but without MWCNTs and banana.

3. RESULTS AND DISCUSSION

3.1. The electrochemical response of Da at the ban-MWCNTs-CPE

Electrochemical response of dopamine was investigated at the surface of ban-MWCNTs-CPE. Fig. 1 shows the differential pulse voltammograms of 10 μM DA in 0.1 M phosphate buffer +0.1 M KCl solution (pH=7.00) at the surface of bare CPE (curve a), ban-CPE (curve b), MWCNTs-CPE (curve c) and ban-MWCNTs-CPE (curve d). As can be seen, in the presence of MWCNTs and banana, electrooxidation current of DA was considerably increased. The second oxidation peak in the curve (d) of this figure seems to be related to polyphenol oxidase electrooxidation.

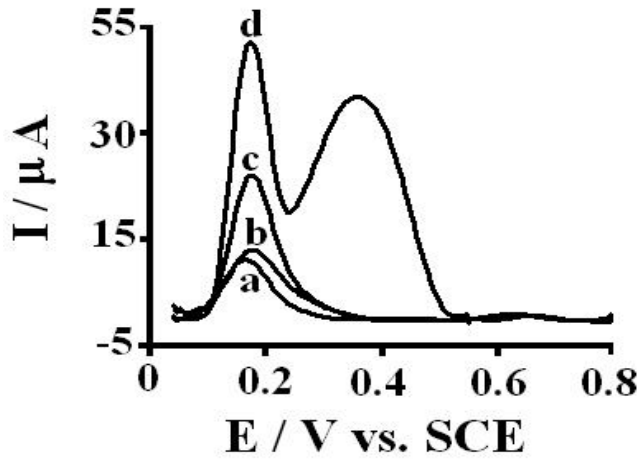

Fig. 1. Differential pulse voltammograms of 10 μM dopamine in 0.1M phosphate buffer +0.1 KCl solution (pH=7.00) at the surface of : a) bare CPE, b) ban-CPE, c) MWCNTs-CPE and d) ban-MCNTs-CPE. The scan rate of potential was 10 mV s^{-1}

3.2. Analytical performance of ban-MWCNTs-CPE for determination of Da

The electrooxidation peak current of DA at the surface of ban-MWCNTs-CPE can be used for determination of DA. Therefore, DPV experiment was performed using ban-MWCNTs-CPE in the phosphate buffer solution containing various concentration of DA. Fig. 2A shows the differential pulse voltammograms of increasing concentration of DA at ban-MWCNTs-CPE. Variation of oxidation peak current of DA *vs.* its concentration, (analytical plot) was linear in the range of 10-30 μM of DA concentration (Fig. 2B) with correlation coefficient (R^2) of 0.9931 (n=6). The detection limit (3σ) was 2.09 μM.

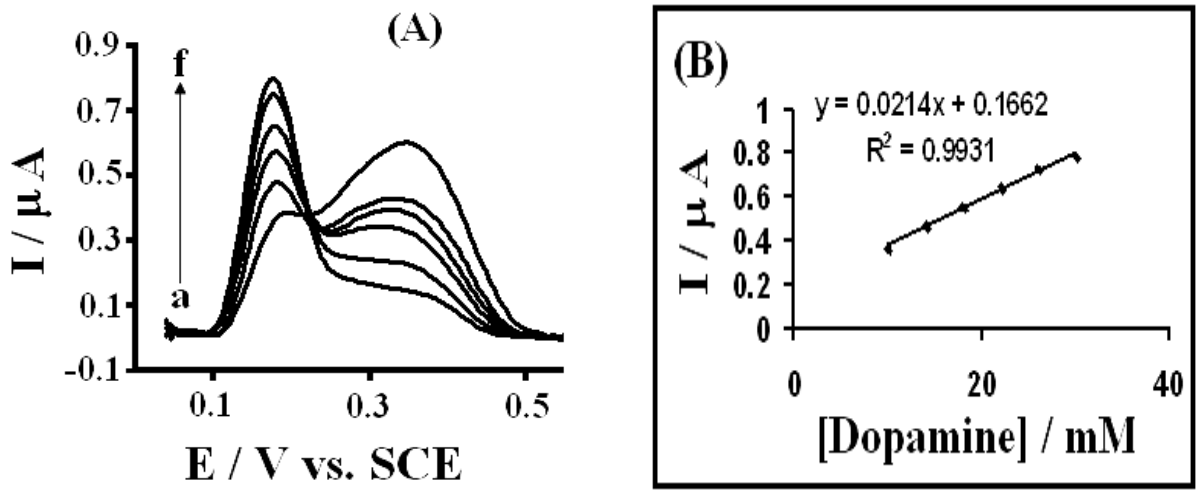

Fig. 2. (A) Differential pulse voltammograms of various concentrations of DA: a) 10, b) 14, c) 18, d) 22, e) 26 and f) 30 μM in 0.1 M, phosphate buffer + 0.1 M KCl (pH=7.00) at ban-MWCNTs-CPE at scan rate of potential 10 mV s^{-1}. (B) The plot of oxidation peak currents *vs.* DA concentrations derived from voltammograms of (A)

3.3. Investigation of ascorbic acid (AA) interference in the voltametrice determination of Da at ban-MWCNTs-CPE

The interference of AA on the voltammetrcic determination DA was studied. Fig. 3 shows differential pulse voltammograms of 2.5 μM of DA (curve a) and 2.5 μM of AA (curve b) at the surface of ban-MWCNTs-CPE. As can be seen, no redox peak for AA was obtained at ban-MWCNTs-CPE.

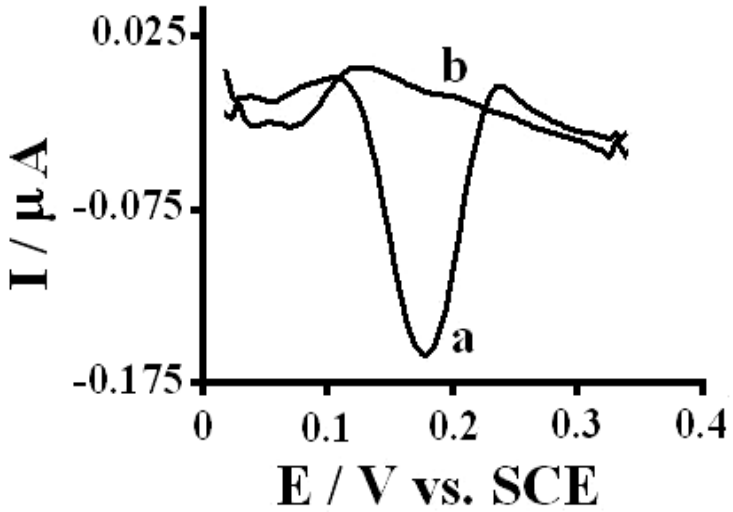

Fig. 3. differential pulse voltammograms of 2.5 μM of a) DA and b) AA in 0.1 M phosphate buffer +0.1 M KCl (pH=7.00) at ban-MWCNTs-CPE at the scan rate of potential of 10 mVs^{-1}

3.4. Ban-MWCNTs-CPE stability

Also, the stability of ban-MWCNTs-CPE was studied as follow. Differential pulse voltammograms (Fig. 4) of fresh dopamine solution (10 μM) was obtained at the surface of ban-MWCNTs-CPE just after fabrication of electrode (curve a) and after 20 days of fabrication (curve b). As the voltammograms show, after 20 days only 28% of electrode response was reduced.

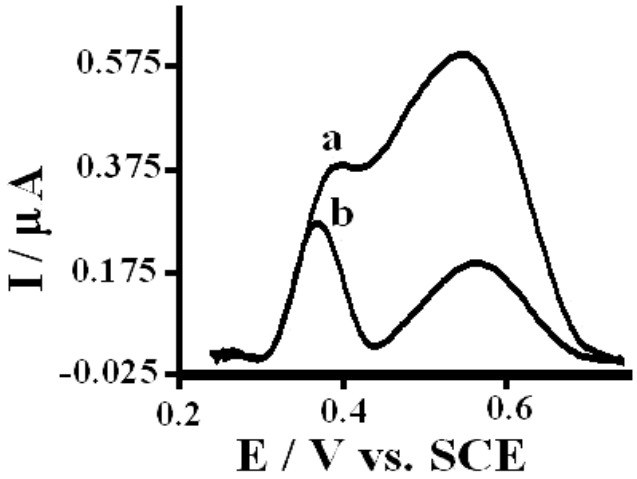

Fig. 4. Differential pulse voltammograms of dopamine (10 μM) in 0.1 M phosphate buffer +0.1 KCl (pH=7.00) at the surface of a) freshly prepared and b) 20 days after preparation ban-MCNTs-CPE. The scan rate of potential was 10 mV s^{-1}

4. CONCLUSION

A ban-MWCNTs modified carbon paste electrode was fabricated successfully. Electrochemical response of dopamine at low concentration was studied in each steps of modification and results show that the best response (the most oxidation current for DA) was obtained at ban-MWCNTs-CPE. So, we use this modified electrode for voltammetric determination of DA. Further, the obtained results were revealed that the modified electrode has no response to ascorbic acid, therefore, ascorbic acid has no interference on the voltammetric determination of DA at ban-MWCNTs-CPE. Also, this modified electrode was stable for about 20 days.

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