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Electrocatalytic Behavior of Levodopa at MultiWall Carbon Nanotubes and 4-((E)-(2-Methyl-4-Nitrophenylimino) Methyl) Benzene-1,2-Diol Modified Glassy Carbon Electrode

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This work describes a glassy carbon electrode (GCE) modified by 4-((E)-(2-methyl-4-nitrophenylimino) methyl) benzene-1,2-diol (abbreviated as MBD) and multiwall carbon nanotubes (MWNT) as an electrochemical sensor for monitoring of levodopa (LD) concentration. Different electrochemical parameters of MBD were obtained at MWCNT-GCE by cyclic voltammetry. Also the electrocatalytic behavior of LD was investigated at the MBD-MWNT-GCE by cyclic voltammetry, chronoamperometry and differential pulse voltammetry. Using the electrocatalysis of LD V in phosphate buffer solution pH 7.0 on this modified electrode it is possible to obtain a linear calibration curve from 5.0×10^{-7} to 9.0×10^{-4} M and a detection limit of 0.37 μM for LD by differential pulse voltammetry. The electrode was successfully applied for determination of LD in real sample.

Keywords: Carbon nanotubes, Levodopa, Glassy carbon electrode, Electrocatalysis.

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1. INTRODUCTION

Levodopa (3,4-dihydroxyphenyl - l -alanine) is an important chemical substance and used in the treatment of Parkinson's disease. This substance is known to be converted into dopamine by an enzymatic reaction for the deficiency of dopamine in brain [1].

Several methods have been reported for the determination of levodopa including high performance liquid chromatography, gas chromatography, NMR spectroscopy and electrochemical methods. The electrochemical methods caused a lot of attention because of their celerity and sensitivity [1].

Carbon nanotubes (CNT), a novel carbon material discovered by Iijima in 1991, can be divided into multiwall carbon nanotubes (MWNT) and single-wall carbon nanotubes (SWNT). They have been the subject of numerous investigations in many areas due to their novel structural, mechanical, electronic, and chemical properties. Because of their excellent electrocatalytic performance, more and more electrochemistry researchers have begun to pay close attention to them [2]. We have studied the electrochemical behavior of MBD at MWNT-GCE. Also some electrocatalytic parameters of levodopa were measured at MBD-MWNT-GCE.

2. EXPERIMENTAL

2.1 Chemicals

All solutions were freshly prepared with doubly distilled water. All the reagents were of analytical grade. Buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0 – 12.0. MBD was synthesized in our laboratory.

2.2 Apparatuses

The electrochemical experiments were performed using a potentiostat/galvanostat (SAMA 500, electroanalyzer system, I.R. Iran). The cell configuration contained a glassy carbon as a working electrode, a Pt wire as an auxiliary electrode and a saturated calomel electrode as the reference electrode. All the potentials were recorded with respect to the reference electrode. A Metrohm 691 pH/ion meter was also used for pH measurements.

2.3 Preparation of MBD-MWNT-GCE

For preparation of MBD-MWNT-GCE the flowing procedure was applied. The GCE surface was polished mechanically with alumina powders, using a polishing cloth until the electrode surfaces had a mirror-finish and then rinsed thoroughly with double distilled water. Electrochemical activation of the electrode was performed by continuous potential cycling in sodium bicarbonate solution until a stable voltammogram was obtained. The activated GCE was coated by casting mixture of 3 μL MWNT. After being dried in the air overnight to remove the solvent, the MWNT-GCE was prepared. For modification by MBD, it was placed in a 0.1 M phosphate buffer solution containing MBD and was modified by cycling the potential between 0.0 and 0.5 V for 10 cycles. Finally, the electrode was rinsed thoroughly with water and dipped into the buffer solution (pH 7.0) to test its electrochemical behavior.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of MBD-MWNT-GCE

Experimental results show reproducible anodic and cathodic peaks (with Epa = 0.148 V, Epc = 0.135 V versus SCE and ΔEp = 0.013 V) for MBD-MWNT-GCE at scan rate 100 mV/s in pH 7.0. The effects of the potential scan rate on the electrochemical properties of the MBD-MWNT-GCE were studied with cyclic voltammetry. Plots of the anodic and cathodic peak currents were linearly dependent on scan rates (Fig. 1 A). Fig. 1B shows the variations of peak potentials as a function of the logarithm of the potential scan rate. Based on this

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equation the cathodic transfer coefficient (α) and electron transfer rate constant for MBD-MWNT-GCE calculated as 0.43 and 18.54 s^{-1}, respectively.

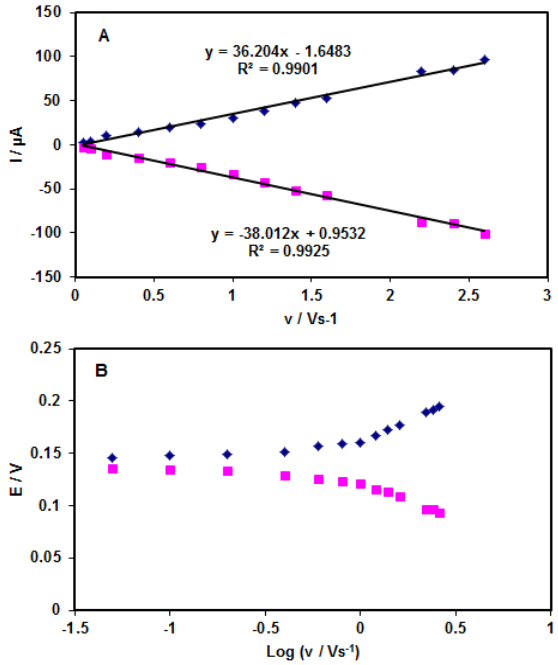

Fig. 1 – (A) Variation of Ip versus scan rates (B) Variation of Ep versus the logarithm of the high scan rate

3.2 Electrocatalysis of levodopa at MBD-MWNT-GCE

The effect of scan rate on the electrocatalytic oxidation of LD at the MBD-MWNT-GCE was investigated by cyclic voltammetry (Fig. 2). The plot of peak height versus the square root of the scan rate was constructed (Fig. 2 inset). This plot was found to be linear, suggesting that the process of oxidation of LD was diffusion-controlled [3].

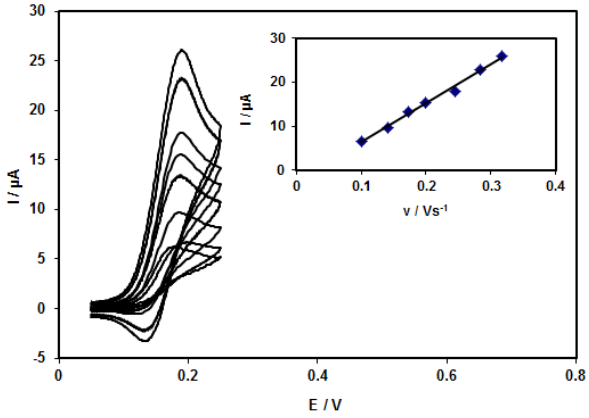

Fig. 2 – Cyclic voltammograms of MBD-MWNT-GCE in phosphate buffer (pH 7.0) containing 1.0 mM levodopa at different scan rates (from inner to outer 10, 20, 30, 40, 60, 80 and 100 mV/s), Insets: Variation of the electrocatalytic currents versus the square root of the scan rate

3.3 Determination of levodopa by differential pulse voltammetry

Differential pulse voltammetry (DPV) was used for determination of levodopa at MBD-MWNT-GCE. Fig. 3 shows the DPVs of different concentrations of levodopa at MBD-MWNT-GCE. Linear calibration curve was obtained in the rang of 5.0×10^{-7} to 9.0×10^{-4} M. Also the detection limit was calculated as 0.37 µM for levodopa.

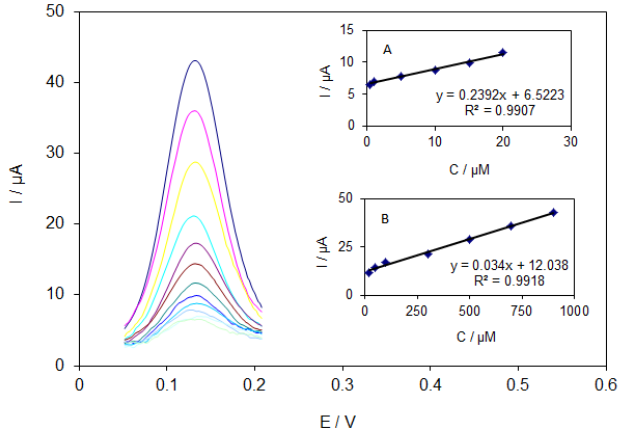

Fig. 3 – DPVs of MBD-MWNT-GCE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of levodopa (from inner to outer): 0.5, 1.0, 5.0 10.0, 15.0, 20.0, 50.0, 100.0, 300.0, 500.0, 700.0 and 900.0. Insets show the plots of the electrocatalytic peak current as a function of levodopa concentration in the range of: (A) 0.5 to 20.0 µM and (B) 20.0 to 900.0 µM

CONCLUSIONS

A glassy carbon electrode has been modified with MBD and MWNT. The electrochemical behaviors of MBD were investigated. Also this modified electrode was used for electrocatalytic determination of LD. The results demonstrated that the electrooxidation of LD at the surface of MBD-MWNT-GCE occurs at a potential about 328 mV less positive than bare glassy carbon electrode. The modified electrode has been shown to be promising for LD detection with many desirable properties including good reproducibility, high sensitivity, excellent catalytic activity, low detection limit and especially its antifouling properties towards LD and its oxidation products.

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