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Effect of MgB_2-MWCNT Modified Glassy Carbon Electrode on Voltammetric Measurements of Dopamine

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The effect of glassy carbon electrode modified with magnesium boride-multiwalled carbon nanotube (MgB_2-MWCNT) prepared *via* mechanical attachment method was studied on the redox reaction of dopamine using cyclic voltammetry and chronocoulometry technique. Cyclic voltammogram showed a 1.9 fold enhancement of the dopamine oxidation peak current at the surface of the modified electrode and the current was due to diffusion process. It was also observed that the sensitivity of the modified electrode is significantly dependent on electrolyte, pH and scan rate.

Keywords: Dopamine, Cyclic voltammetry, Glassy carbon electrode, Magnesium boride, Multi-walled carbon nanotube.

INTRODUCTION

The use of carbon nanotubes (CNT) for electrode modification has gained a lot of interest since its application in electrochemistry was reported by Britto *et al.*[1]. Due to its unique structural, mechanical, chemical and electronic properties, it has fast become one of the major attractions in the field of electrochemical sensing[2]. The activity of edge-plane-like graphite sites at the CNT ends contributes well towards the electrocatalytic ability of CNT[3]. Numerous works has been reported on the development of CNT based electrochemical biosensors[4-6]. Studies have also been done on the modification of electrodes using a hybrid combination of CNT with other materials such as polymers[7,8], nanomaterials[9,10] and superconductor[11] which proves to help improve sensitivity and minimizing overvoltage. While studies on MgB_2 superconductor has been the subject of great attention due to its high critical temperature, the use of MgB_2 as a material for electrode modification, however, has not been fully explored. The potential of MgB_2 to mediate electrochemical reaction has been shown in the determination of ferricyanide[12] and paracetamol[13].

Various methods have been applied for electrode modification with CNT, which includes solvent dispersion and casting immobilization[14], additive assisted dispersion and immobilization[15], self-assembling immobilization[16], carbon nanotube paste electrodes[17], electropolymerization immobilization[18] as well as abrasive immobilization[19]. Abrasive immobilization or also known as the mechanical attachment method is one of the techniques in solid phase voltammetry of microparticles (SPVM). In this technique, the working electrode surface is rubbed or pressed onto a filter paper which supports the modifying material. Apart from the simplicity of this technique, the means for recovery of the electrode surface after usage can also be done with much ease[12].

We have previously reported the successful fabrication of MgB_2-MWCNT hybrid modified GCE *via* mechanical attachment method[20]. The MgB_2-MWCNT/GCE showed an electrocatalytic ability towards the oxidation of dopamine and recorded a better sensitivity and lower detection limit of dopamine.

In this work, we focus on the study done on the modification of the surface of glassy carbon electrode with a mixture of MgB_2 and MWCNT using mechanical attachment method and its effect on the oxidation behaviour of dopamine.

EXPERIMENTAL

Electrochemical measurements were carried out on electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50 W using a conventional three-electrode electrochemical cell. The three-electrode system consists of Ag/AgCl (3 M NaCl) electrode as the reference electrode (RE), a platinum wire as the counter electrode and a GCE (ϕ = 3 mm) as the working electrode. Solutions were degassed with nitrogen for 10 min prior to recording the voltammograms.

Multiwalled carbon nanotubes (MWCNT) was obtained from Shenzhen Nanotech Port Co., Ltd. with 95% purity whereas magnesium boride was obtained from Alfa Aesar and dopamine was supplied by Merck. All chemicals were of analytical reagent grade purity and were used without further purification. Preparations of solutions were carried out using distilled water.

Preparation of MgB_2-MWCNT/GCE: MgB_2-MWCNT/GCE was prepared *via* mechanical attachment method. The surface of GCE was first cleaned by polishing it with 0.05 μm alumina slurry. The GCE was then placed in a sonicator for ultrasonic cleaning in about 1-2 min before being dried with lint-free tissue paper. The powder of MgB_2 and MWCNT were physically mixed according to a weight ratio of 1:1 and the mixture was then placed on a coarse grade filter paper. The GCE was then pressed and rubbed onto the mixture to get the mixture adhered to the electrode surface.

RESULTS AND DISCUSSION

The cyclic voltammograms (CV) of 1.0 mM dopamine in 0.1 M potassium acetate aqueous electrolyte solution were obtained with a potential scanning at a positive direction over the potential range of -200 mV to +800 mV at a scan rate of 100 mV s^{-1} for modified and bare GCE *versus* Ag/AgCl (Fig. 1). The oxidation current of dopamine was enhanced by a factor of 1.2 at the MWCNT/GCE. At MgB_2/GCE, the dopamine oxidation peak is ill-defined and no current enhancement was detected. A hybrid combination of MgB_2 and MWCNT successfully enhanced the current by a factor of 1.9 compared to the bare electrode. These results indicate that modifying GCE with MgB_2-MWCNT can enhance the electron transfer at the electrode surface. As suggested by Banks *et al.*[21], the fast reaction mechanism occurring at the electrode surface is well attributed to the properties of the CNT ends, which bears similarity to that of an edge plane graphite electrode.

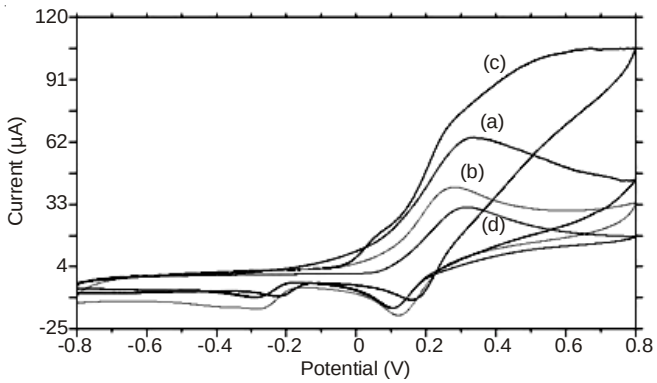
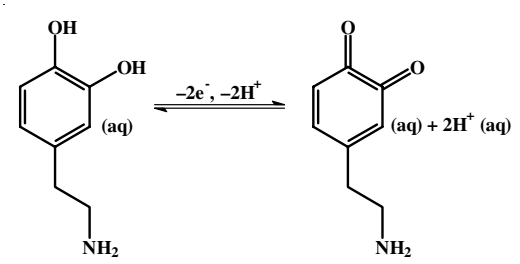


Fig. 1. Cyclic voltammograms of 1.0 mM dopamine in 0.1 M potassium acetate at the (a) MgB_2-MWCNT/GCE, (b) MWCNT/GCE, (c) MgB_2/GCE and (d) bare GCE (against reference electrode; scan rate 100 mV s^{-1})

Cyclic voltammograms of dopamine appears to be reversible and shows the presence of both oxidation and reduction peak for all the electrodes. The oxidation of dopamine involves the loss of two electrons to form dopaminoquinone (eqn. 1)[22]. Dopaminoquinone is later reduced back to its original form which gives rise to the reduction peak at a potential of ~100 mV as appeared in the cyclic voltammograms.



(1)

Effect of potential cycling: Potential cycling of dopamine oxidation was carried out on the MgB_2-MWCNT/GCE surface during cyclic voltammery. It was observed that the redox current of dopamine at the modified electrode was affected by continuous potential cycling in which the oxidation current dropped significantly after the first cycle (Fig. 2). This indicates the instability of the modified electrode and could be due to the fact that the MgB_2-MWCNT particles had dropped off from the electrode surface and dispersed into the supporting electrolyte solution. Therefore, subsequent studies will only be conducted on freshly modified glassy carbon electrode surface.

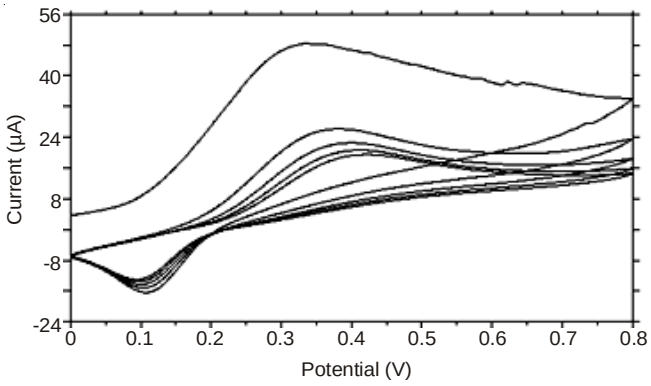


Fig. 2. Cyclic voltammograms of potential cycling for 1.0 mM dopamine in 0.1 M potassium acetate at the MgB_2-MWCNT/GCE for 10 cycles (against reference electrode; scan rate 100 mV s^{-1})

Effect of varying supporting electrolyte: The effect of various supporting electrolytes on the redox behaviour of dopamine at MgB_2-MWCNT/GCE electrode was studied. Supporting electrolytes with a common cation, K^+, were used. Results show that the oxidation of dopamine occurred at a lower potential in potassium acetate compared to the other supporting electrolytes (Fig. 3). Potassium acetate also gives the highest enhancement of dopamine oxidation peak current as shown in Table-1. Therefore, potassium acetate was chosen as the supporting electrolyte for the next studies. In general, the degree of the current enhancement in the various supporting electrolytes can be summarized in the following order:

$$CH_3COOK > KNO_3 > K_2SO_4 > KCl \approx KH_2PO_4$$

Effect of pH: The pH of the supporting electrolyte solution varied from pH 2.0 to 12.0 by drop wise addition of 0.1 M HCl and 0.1 M KOH in order to determine its effect on the catalytic oxidation of dopamine at the MgB_2-MWCNT modified electrode. The anodic peak potential of dopamine varies linearly with pH and shift to a more negative potential with increasing pH (not shown). This indicates the occurrence

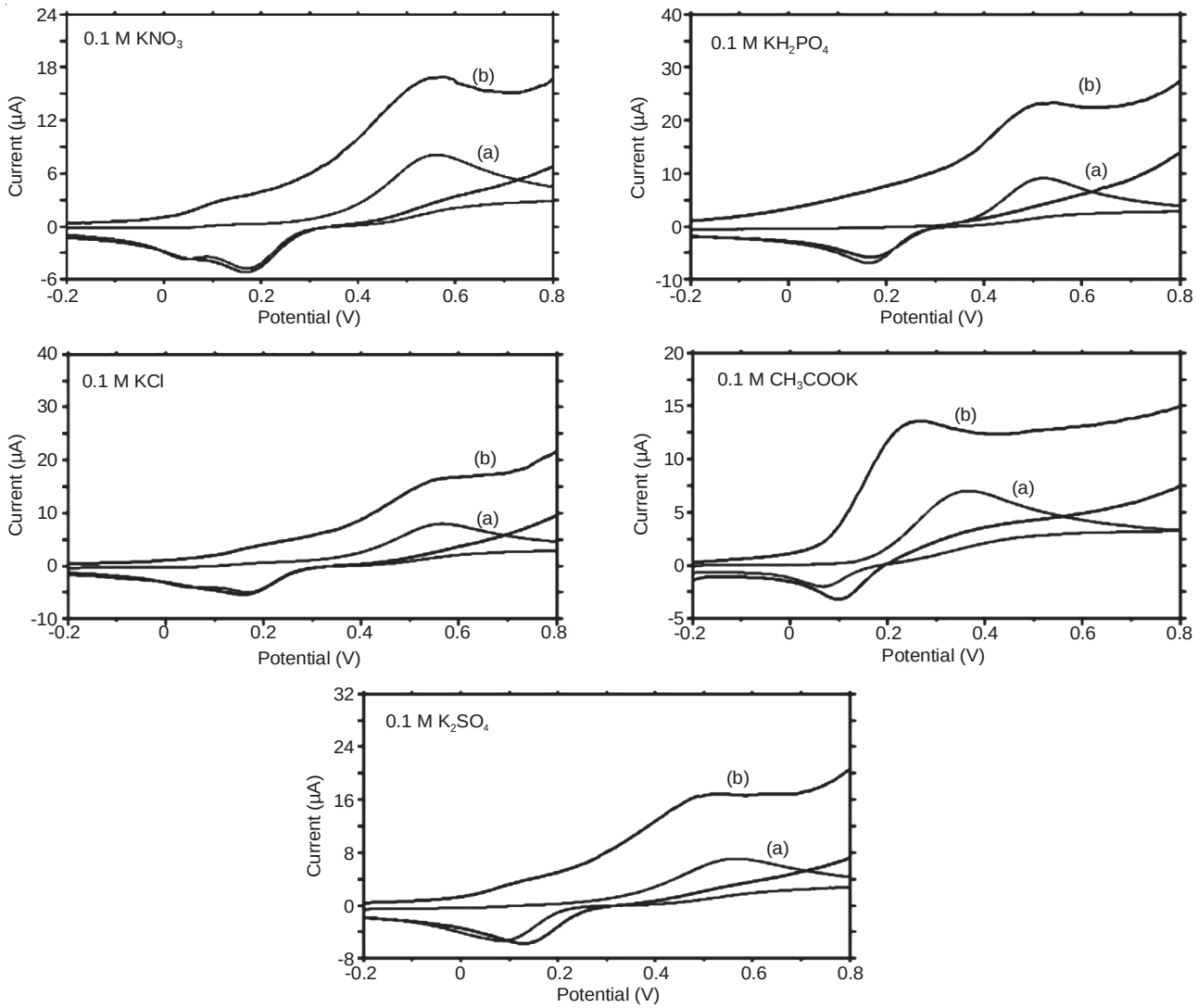


Fig. 3. Cyclic voltammograms of 0.1 mM dopamine in 0.1 M KNO_3, 0.1 M KH_2PO_4, 0.1 M KCl, 0.1 M CH_3COOK and 0.1 M K_2SO_4 at the (a) bare GCE and (b) MgB_2-MWCNT/GCE (against reference electrode; scan rate 100 mV s^{-1})

TABLE-1
OXIDATION PEAK CURRENT OF 0.1 mM DOPAMINE IN 0.1 M OF SUPPORTING ELECTROLYTE

Supporting electrolyte	i_{pa} (μA)		Enhancement
	GCE	MgB_2-MWCNT/GCE	
Potassium sulphate	5.60	7.10	1.3
Potassium chloride	6.00	7.30	1.2
Potassium acetate	6.40	11.40	1.8
Potassium nitrate	7.00	9.70	1.4
Potassium phosphate	8.70	10.70	1.2

of deprotonation during the oxidation process which is facilitated at higher pH values[14]. The peak current decreases from pH 3 to pH 5 before increasing and reaching a maximum at pH 8. At a more basic solution, the current starts to show a decreasing trend. This could be due to the instability of dopamine at higher pH values[23]. It was also observed that the highest peak enhancement was obtained at pH 8 (Fig. 4). The condition of supporting electrolyte at pH 8 was therefore used for the following studies.

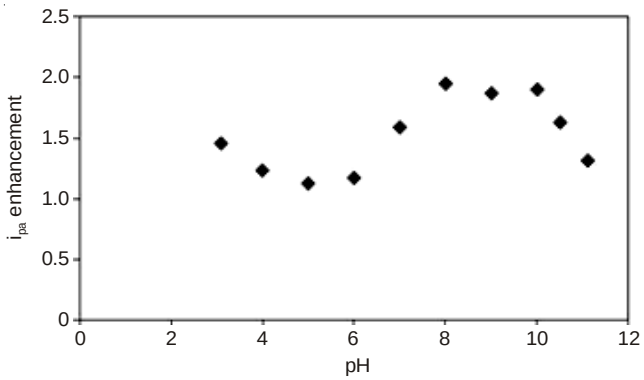


Fig. 4. Oxidation current enhancement factor of MgB_2-MWCNT/GC electrode over bare electrode at different pHs

Calibration graph: Fig. 5 shows the cyclic voltammograms of dopamine at different concentrations. A linear response of dopamine oxidation current is obtained over a concentration range of 0.1 to 2 mM dopamine which is described by the equation of $y = 87.58x + 8.34$ with $R^2 = 0.986$. Based on the slope of the graph, m, a sensitivity response

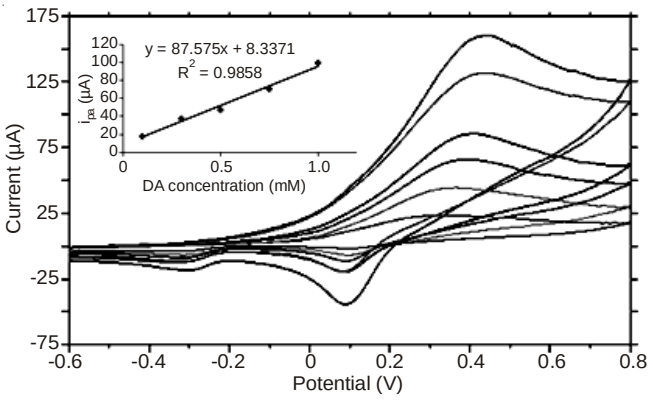


Fig. 5. Cyclic voltammograms of different dopamine concentration in 0.1 M potassium acetate, pH 8 ± 0.4 at MgB_2-MWCNT/GCE [Inset: Plot of oxidation peak current *versus* dopamine concentration in 0.1 M potassium acetate, pH 8 ± 0.4 at MgB_2-MWCNT/GCE]

of 87.58 mA/M dopamine was acquired using the modified electrode. The detection limit, taken as 3 σ/m, is calculated as 0.88 μM.

Effect of scan rate: Scan rate study was performed in order to examine the kinetics of dopamine oxidation at the electrode surface. The effect of varying scan rate on the cyclic voltammograms of 0.1 mM dopamine at the MgB_2-MWCNT/GCE in 0.1 M potassium acetate was studied over a scan rate range of 5-500 mV/s. Oxidation currents of dopamine increased with scan rate as shown in Fig. 6(a), implying the reaction is diffusion-controlled. A straight line which fulfills the equation of y = 0.4994x + 0.2414 with an R^2 = 0.965 was obtained from the plot of log oxidation current as a function of log scan rate [Fig. 6(b)]. The slope obtained is comparable to the theoretical value of 0.53 for a diffusion controlled process[24]. The diffusion coefficient value, D, was calculated to be 8.64 × 10^{-5} cm^2/s which is comparable to previous report[25].

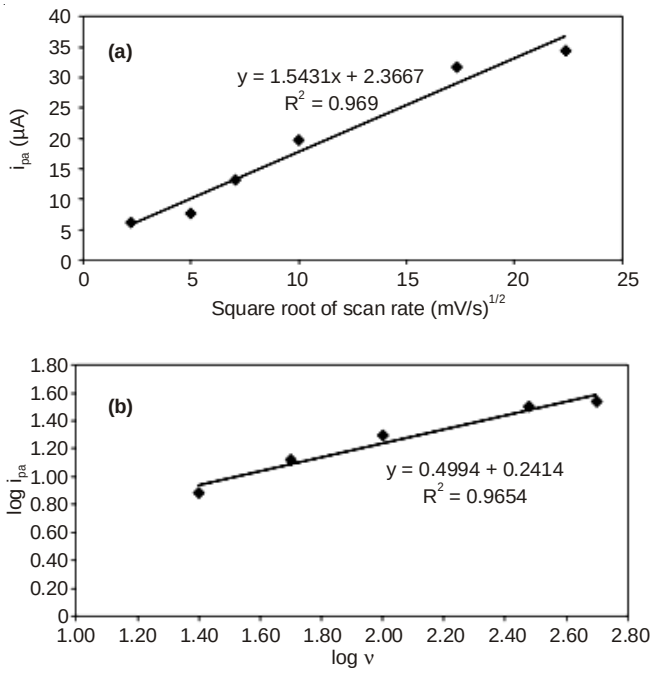


Fig. 6. Plot of (a) oxidation current *versus* the square root of scan rate and (b) oxidation current *versus* log of scan rate for 0.1 mM dopamine in 0.1 M potassium acetate at MgB_2-MWCNT/GCE

Effect of temperature: The effect of temperature on the oxidation process of dopamine at both bare GCE and MgB_2-MWCNT/GCE was studied over a temperature range of 28 to 68 °C. The oxidation peak current increased gradually and the peak potential shifted to origin with an increase in temperature. This can be suggested by the fact that as the temperature of the electrolyte solution increases, the electron-transfer rate of dopamine oxidation is enhanced and that the oxidation potential barrier of dopamine is decreased[26].

A plot of log dopamine oxidation current as a function of the reciprocal of temperature for both bare and modified electrode (Fig. 7) yields a straight line which indicates good agreement with thermodynamic expectations of the Arrhenius equations [eqns. 2 and 3].

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (2)$$

$$D = \Delta_0 \exp(-E_a/RT) \quad (3)$$

where σ/D are conductivity/diffusibility and σ_0/D_0 are standard conductivity/initial diffusibility. The activation energy for the diffusion of dopamine on both bare and modified electrode was found to be 7.7 and 3.9 kJ mol^{-1} respectively. A 50 % reduction in the activation energy required for the diffusion of dopamine at the surface of the modified electrode as compared to bare electrode further signifies the electrocatalytic ability of the MgB_2-MWCNT/GCE.

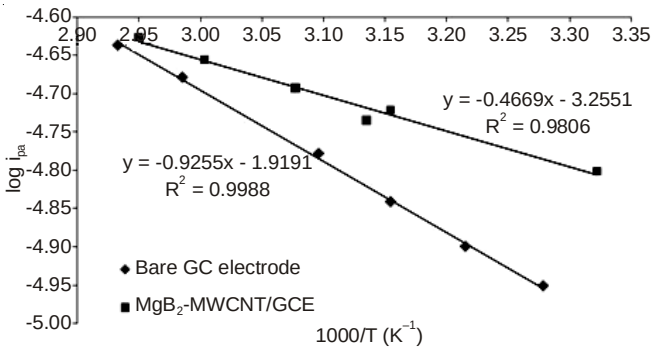


Fig. 7. Plot of log oxidation current *versus* the reciprocal of temperature for 0.1 mM dopamine in 0.1 M potassium acetate, pH 8 ± 0.4 at bare and MgB_2-MWCNT/GCE

Chronocoulometry: Chronocoulometry analysis was carried out on the oxidation process of dopamine at the MgB_2-MWCNT/GCE and the chronocoulogram obtained is depicted in Fig. 8.

The data analysis was performed based on the Anson equation (eqn. 4) which relates the dependency of charge over time for a linear diffusion control process.

$$Q = 2nFAC(D/\pi)^{1/2}t^{1/2} \quad (4)$$

where Q = charge and the other parameters have its usual meanings.

Based on the Anson plot, a linear dependency of Q upon $t^{1/2}$ is obtained and this indicates the involvement of a process controlled by diffusion. The value of surface charge, $Q_{surface}$, can be determined by taking the difference between the intercepts of forward and reverse steps at t = 0 of the Anson plot while charge density is calculated as $Q_{surface}/A$. From the Anson plot, it was found that a total charge of 9.92 μC was

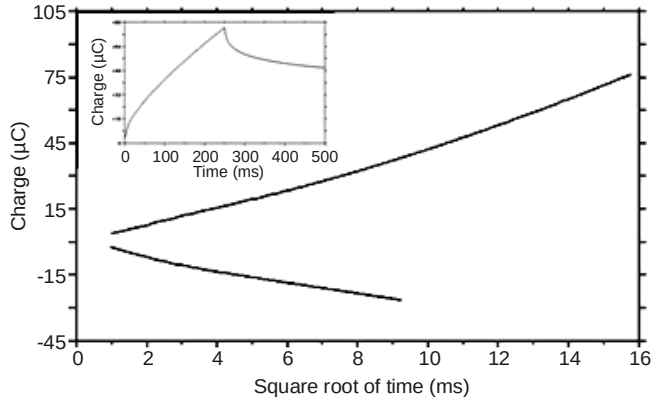


Fig. 8. Anson plot of charge *versus* square root of time for 1 mM dopamine in 0.1 M potassium acetate at MgB_2-MWCNT/GCE [Inset: Chronocoulogram of 1mM dopamine in 0.1 M potassium acetate, pH 8 ± 0.4 at MgB_2-MWCNT/GCE]

transferred during the oxidation of 1 mM dopamine at the MgB_2-MWCNT/GCE and that the charge density is 140 μC/cm^2.

Conclusion

In this paper, we focus on the study of MgB_2-MWCNT modified GCE *via* mechanical attachment method. The MgB_2-MWCNT is able to enhance the anodic peak current of dopamine. The modified electrode exhibits electro-catalyzation properties in the determination of dopamine as well as give low detection limit and good sensitivity. Although the mechanical attachment method is a simple fabrication procedure, the modified electrode however shows poor stability. Therefore, our next report will focus on other methods to improve the stability of this modified electrode for a more practical application and its expansion towards determination of other analytes.

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