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Voltammetric Determination of Dopamine Mediated By Nanoparticle WO_3 /MWCNT Modified Glassy Carbon Electrode

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Abstract

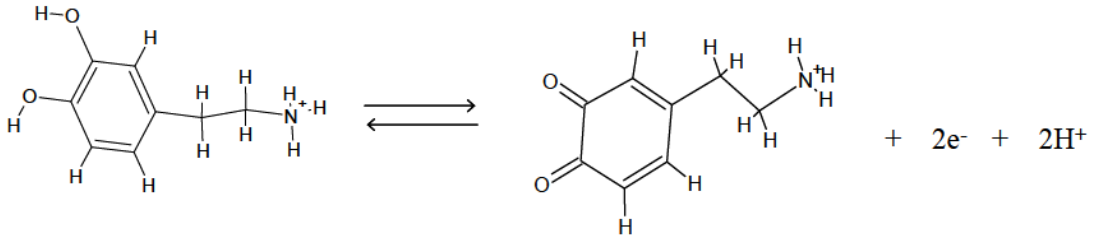
Chemically-modified electrode fabricated by mechanical attachment of multi-walled carbon nanotubes/tungsten oxide (MWCNTs/WO_3) in the electrocatalytic study of dopamine was investigated. The MWCNTs/WO_3 nanocomposite has been characterized using voltammetric techniques of cyclic voltammetry, chronoamperometry and chronocoulometry. The CNT/WO_3/GCE induces a 2.9 enhancement oxidative peak with peak separation of approximately 200 mV, shifting towards a lower potential in the electrochemical oxidation of 0.4 mM dopamine at pH 7.0, in comparison with the WO_3/GCE, MWCNTs/GCE and bare GCE. The lowering positive potential and enhancement current are evident of electrocatalysis process. From the calibration plot, the high sensitivity response of 57.00 μA/μM for the anodic peak with the detection limit of 0.018 μM (100 mV/s scan rate) of dopamine at the CNT/WO_3/GCE were obtained. Based on the chronocoulometric study on 0.4 mM dopamine in 0.1 M KCl, the diffusion coefficient was found to be 5.43 x 10^{-8} cm^2/s with the surface charge of 6.86 x 10^{-4} C/cm^2. The easily prepared nanocomposite-modified electrode showed to have high sensitivity, selectivity and good reproducibility.

Keywords: tungsten oxide (WO_3), dopamine, multi0walled carbon nanotubes (MWCNTs), cyclic voltammetry

INTRODUCTION

Dopamine or 3,4-dihydroxy-fenil-ethyl amine (DA) is a catecholamine

neurotransmitter, which is one of the basic neurotransmitter of the Central Nervous System, CNS. In recent years, electroanalysts focused on the development of new chemically modified electrodes in the detection of dopamine which has attracted tremendous attraction due to their importance in biomedical oriented research[1–3].



Scheme 1. The reaction mechanism of the electrooxidation of DA

Ascorbic acid (AA) and dopamine (DA) always occur together in biological environments. They both share similar oxidation potential in electrochemical detection, resulting in overlapped voltammetric responses. Existing methods to determine DA such as spectroscopic and chromatographic have proven to be time consuming and complicated [4,5]. Hence, development of analytical methods for low cost, rapid and large scale determination is required at hand.

Multi-walled carbon nanotubes (MWCNTs), constitute a new structure of graphitic carbon consisting of several concentric tubules each with a helically wound hexagonal honeycomb lattice. MWCNTs possess large specific surface areas due to their high aspect ratio, while their structural integrity and chemical inertness support relatively high oxidation stability in comparison with graphite [6]. Recent published works on the detection of dopamine using electrodes modified with a thin layer of CNTs film [7–9] claimed benefits include good detection limits, increased sensitivity, decreased potential and accepted storage stability.

Tungsten oxide (WO_3) is known as an important wide band gap n-type semiconductor that has garner much attention because of its potential applications in electrochromics, photochromics, optochromics, sensors and batteries. There were many publications reporting on the ability of WO_3 in gas sensing [10–12]. Recently, it was also found that WO_3 is can act as a pseudocapacitor for supercapacitor applications [13,14]

To date, there are no published reports on the usage of MWCNTs/WO_3 nanocomposite-modified GCE in the detection of dopamine. Hence the main goal of the present study is to develop a newly nanocomposite-modified electrode based on MWCNTs/WO_3/GCE. The outcome could hold good application in the fields of electroanalytical chemistry and biosensors.

MATERIALS AND METHODS

Instrumentation and electroanalytical methods

The electrochemical measurement was done using an electrochemical analyzer BAS (Bioanalytical Systems, West Lafayette, IN, USA): CV-50W Cyclic Voltammetry connected to an external computer. The electrochemical cell used consisted of a three electrode system setup in which the electrodes used are glassy carbon electrode (GCE) as the working electrode, silver/silver chloride (Ag/AgCl) electrode with an internal solution of 3 M NaCl acting as a reference electrode and platinum wire as the counter electrode.

Materials

MWCNTs, a black powder form with purity > 95 %, diameter ~ 20-40 nm, length ~ 5-15 μm were purchased from Aldrich. WO_3 nanoparticles dispersed in powder form (5 % w/w) with particle size of <100 nm were also purchased from Aldrich (USA). The commercial samples of dopamine hydrochloride at minimum purity of 99.87 % were obtained from Fluka Chemicals (Switzerland). Other inorganic salts obtained from Sigma such as potassium chloride (KCl), potassium sulphate (K_2SO_4), potassium acetate (CH_3CO_2K), and potassium dihydrogen orthophosphate (KH_2PO4). All chemicals were of analytical grade quality without needing to undergo further purification. Solutions were prepared using ultrapure 18MΩ-cm deionised water obtained from Barnstead Nanopure Ultrapure Water Systems (Thermo Scientific).

Preparation of MWCNTs/WO_3/GCE

Before any analysis was carried out, the surface of the bare GCE was polished on a microcloth polishing pad with 0.3 μm alumina slurry. The electrode was rinsed with deionised water and was allowed to undergo ultrasonification for 1 minute and subsequent drying in order to obtain a workable working electrode with a refurbished electrode surface. In this particular method, a mass ratio of 1:1 of MWCNTs and WO_3 nanoparticles were weighted, added together and mixed. The clean GCE surface was then pressed onto the composite mixture powder on a filter paper. The process is repeated at a constant force for 30 times to obtain an even composition of the composite casted on the electrode surface.

RESULTS AND DISCUSSION

Enhancement Study

Based on Figure 1, the appearance of a well-defined redox couple with a 200 mV

peak separation shows the reversibility of DA on the MWCNTs/WO_3/GCE is the best upon compared to using bare GCE, WO_3/GCE, and MWCNTs/GCE. At bare GCE (Figure 2(a)), the oxidation potential was obtained at about 664 mV. The electrochemical response obtained increases with the usage of WO_3/GCE, MWCNTs/GCE and MWCNTs/WO_3/GCE. The MWCNTs/WO_3 modified electrode gives the best current enhancement. It gives a redox current peak of DA increased by 2.9 times for both the oxidation peak and reduction peak compared to the bare GCE. The redox couple of DA appears quasi reversible at the MWCNTs/WO_3/GCE. The peak currents obtained are well-defined with the ratio of i_{pa}/i_{pc} = 1.20 and a peak separation of 200 mV as its E_{pa}= +475 mV and E_{pc}= 275 mV vs. Ag/AgCl (3M NaCl).

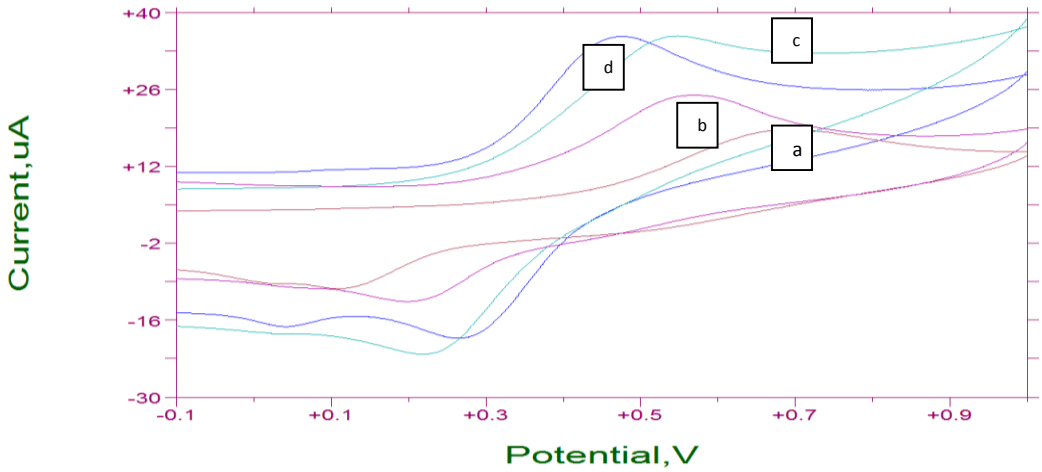


Figure 1. Cyclic voltammograms of 0.4 mM dopamine on (a) bare GCE, (b) WO_3/GCE, (c) MWCNTs/GCE and (d) MWCNTs/WO_3/GCE in 0.1 M KCl (pH 6.5) with a scan rate of 100 mV/s.

Effect of Varying Supporting Electrolytes

Based on the enhancement study, different types of 0.1 M aqueous supporting electrolytes consisting of potassium chloride (KCl), potassium nitrate (KNO_3), potassium dihydrogenophosphate (KH_2PO_4), potassium sulphate (K_2SO_4) and potassium acetate (CH_3CO_2K) with neutral condition were studied. In the presence of Cl^-, the DA peak current was in slightly negative potential as compared to the others. Meanwhile in the presence of NO_3^- the DA peak current was in the negative potential shift as depicted in Figure 2. Most of the other aqueous solutions observed showed no distinct changes. Almost similar potential ranges were obtained using electrolytes solutions of KH_2PO_4, K_2SO_4 and CH_3COOK. The aqueous solution of KCl was chosen as the preferred supporting electrolyte based on the highest oxidation peak shown. However, the CH_3OOK and KNO_3 also show a satisfactory result to be used

as supporting electrolyte for the electrooxidation of DA using the CNT/WO_3 composite modified GCE.

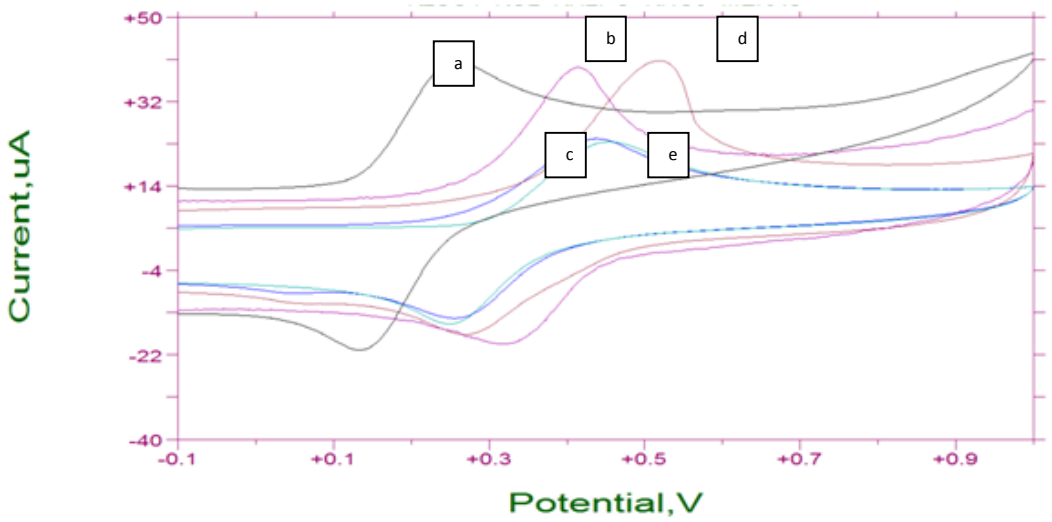


Figure 2: Overlapping graph of cyclic voltammogram 0.40 mM dopamine in different supporting electrolyte where a) KCl b) KH_2PO_4 c) CH_3COOK d) KNO_3 and e) K_2SO_4 at 25^{o}C with a scan rate of 100 mV/s

Effect of varying scan rate

The effect of scan rate on the anodic peak current of 0.40 mM DA in 0.1 M KCl at pH 2.0 mediated by MWCNTs/WO_3/GCE was studied using scan rates in the range of 2 mV/s to 1000 mV/s. It can be observed that as the scan rate increased, the oxidation peak current (i_{pa}) increased as shown in Figure 3. The i_{pa} was directly proportional to the scan rate (v) over the designated range which suggest a surface-controlled process at the modified electrode surface [12]. The anodic peak and cathodic peak potential were shifted slightly to the positive direction and negative direction, respectively. This can be explained by the oxidative current of the DA which increases that was affected by the heterogenous kinetics and the ohmic resistance (IR) drop effect.

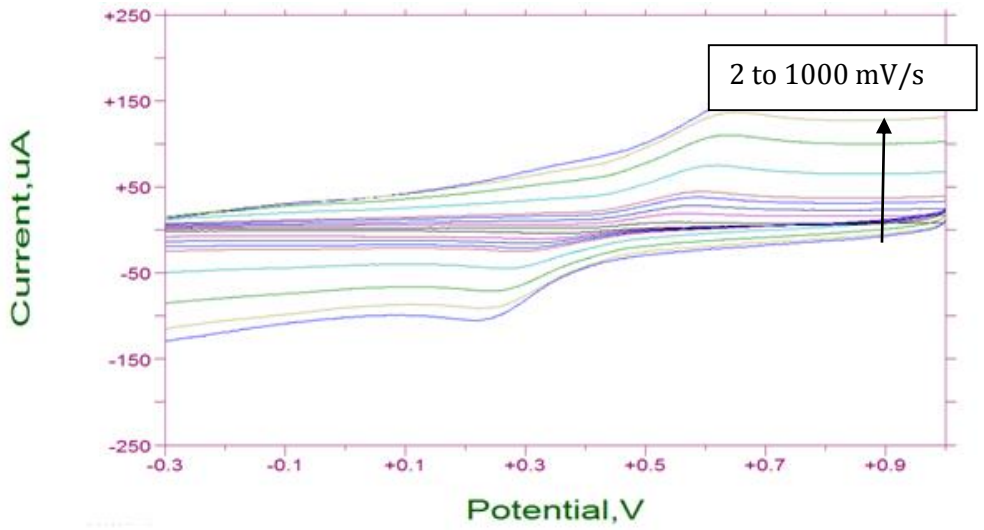


Figure 3: Cyclic voltammograms of 0.40 mM DA at different scan rates (2, 10, 50, 100, 500, 750, 1000 mV/s) in 0.1 M KCl (pH 2.0) mediated by MWCNTs/WO_3/GCE

Effects of varying pH

This experiment was carried out to determine the effect of pH on the voltammogram of DA mediated by MWCNTs/WO_3-modified GCE as depicted in Figure 4. According to the Nernst equation, the slope of -32 mV reveals that the proportion of the electron and the proton involved in the reaction is 1:1 [15] The plot of oxidative peak current vs. pH shows that the oxidation peak current of 0.40 mM dopamine increases with the decrease of pH. It was observed that the oxidative peak current of DA was high and more pronounced under acidic condition but slightly decrease in neutral condition. The current decreased gradually as the pH increased from 2.0 to 4.0 and stabilised at moderate pH of 4.0 to 9.0. However, in alkaline condition from pH 9.0 to 11.0, it can be seen that the oxidation current of dopamine are slightly decrease at its minimum current response of 7.79 μA at pH 11.0.

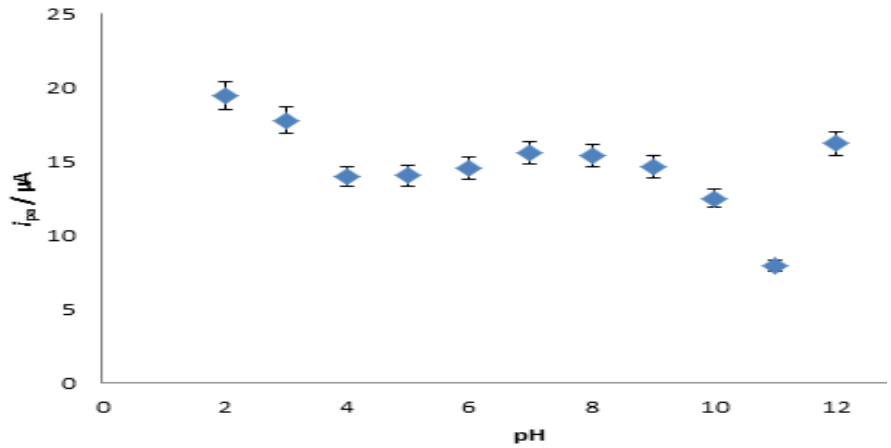


Figure 4. A plot of the dependence of pH value for the oxidative current of 0.40 mM dopamine in 0.1 M KCl mediated by MWCNTs/WO_3/GCE at different pHs ranging from 2.0 to 12.0 at a scan rate of 100 mV/s.

Effect of Varying Concentration of Dopamine

Figure 5 represents the effect of various concentration of DA redox current at the WO_3/CNT composite modified GCE in 0.1M KCl aqueous solution. The voltammogram clearly depicts that both the anodic and cathodic peak currents increased linearly with the increasing concentration of DA ranging from 0.05 mM to 0.40 mM.

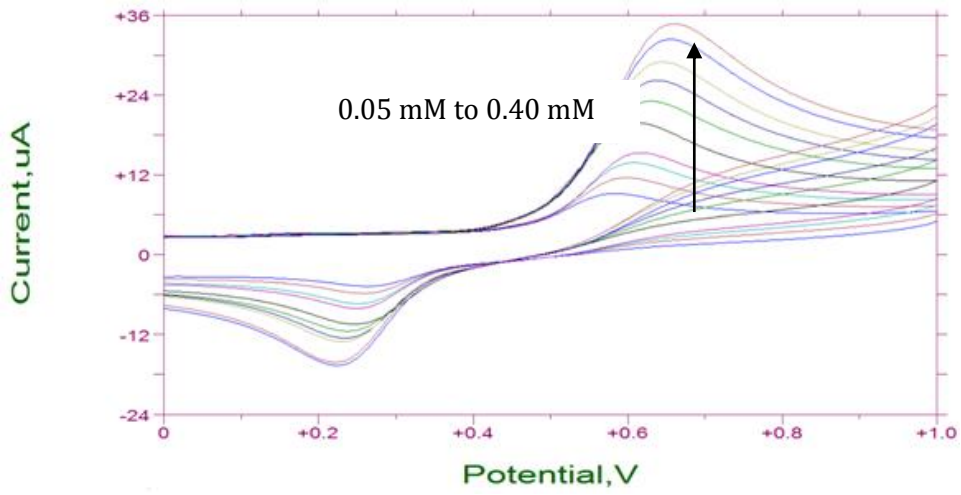


Figure 5. Overlapping graph of voltammograms of varying concentration of DA (0.05 mM to 0.40 mM) in 0.1 M KCl mediated by CNT/WO_3/GCE modified electrode at pH 2.0 with a scan rate of 100 mV/s

The high sensitivity response of 56.994 µA/µM for the anodic with detection limit of 0.018 µM were obtained based on the 3σ/*m,* where σ is the standard deviation of the blank signal and *m* is the slope.

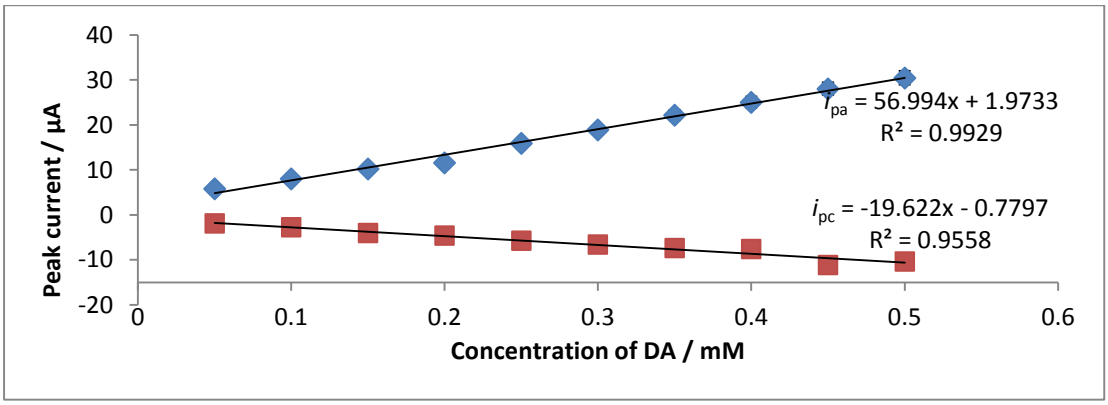


Figure 6: Calibration graph of DA ranges from 0.02 to 0.50 mM in 0.1 M KCl (pH 2.0) mediated by MWCNTs/WO_3/GCE at a scan rate of 100 mV/s

Calibration plots bearing linear relationship of anodic peak current = 56.99concentration of DA + 1.97 for the oxidation and cathodic peak current = -19.62concentration of DA - 0.78 for the reduction process showed a satisfactory correlation coefficient of 0.9929 and 0.9555 for oxidation peak and reduction peak, respectively as depicted in Figure 6.

The detection limit of DA obtained from the MWCNTs/WO_3/GCE is comparable to several other reported literatures, in some cases performed better as depicted in Table 1

Table 1. Comparison in the linear range and the detection limit of dopamine

Ref	GCE Modifier	Linear Range	Detection Limit
[16]	graphene-Au (Au/Gr-Au)	3×10^{-7} to 3×10^{-4} M	2.05×10^{-7} M
[17]	MWCNT/GO	0.2 to 400 µM	2.2×10^{-8} M
[18]	Au/RGO/GCE	6.8×10^{-6} to 4.1×10^{-5} M	1.4×10^{-6} M,
[19]	Fe_3O_4@CNT-N	2.5-65 10^{-6} M	0.050×10^{-6} M
[20]	PEDOT/CNT	0.1 to 20 µM	20×10^{-9} M
[21]	MWNTs-PEI-AuNPs	50 to 4000 nM	6.56×10^{-9} M
[22]	Pristine graphene(PG)/GCE	5 – 710 µM	2.00 µM
[23]	Polyvinylpyrrolidone (PVP)/graphene/GCE	50 – 4000nM	6.56 nM
	This work	0.02 to 0.50 mM	1.8×10^{-8} M

Reproducibility

The reproducibility or repeatability of the MWCNTs/WO_3/GCE in the determination of DA in KCl (pH 2.0) at 25^{o}C with a scan rate of 100 mV/s on 10 different days or times were carried out. This process ensures the electrode exhibits good durability and reproducibility. The mean peak current obtained for 10 replicates of MWCNTs/WO_3/GCE was 23.561 µA as shown in Table 1, which is an enhancement of about 1.5 fold upon comparing to the bare GCE. The relative standard deviation (RSD) calculated was 4.213 %, which indicates that the MWCNTs/WO_3/GCE has good reproducibility.

Table 2: Reproducibility data of 0.40 mM DA in 0.1 M KCl (pH 2.0) mediated by MWCNTs /WO_3 /GCE at a scan rate of 100 mV/s on different days or times.

Repeat	**Ipa, µA**	**Ipc, µA**
1	21.65	-7.036
2	24.61	-15.29
3	24.21	-8.973
4	21.71	-8.145
5	21.28	-8.354
6	22.61	-8.544
7	21.96	-8.623
8	26.00	-8.099
9	26.27	-8.136
10	25.31	-9.549
Mean	23.561	-9.0749
Standard Deviation	1.932663	2.278502

Chronoamperometry and Chronocoulometry

The double potential step technique of chronoamperometry was applied to the electrooxidation process of DA mediated by CNT/WO_3/GCE in 0.1 M KCl (pH 2.0) electrolyte solution at 25^{o}C for 250 ms. Figure 7 depicts a monotonous rising current transient for the redox process of DA indicating a largely diffusion-controlled process at the electrode-solid-electrolyte interface. The diffusion coefficient is the current decayed as the electrolysis proceeded to deplete the solution near the electrode of electroactive species.

On a similar note, the equation for the charge against time curve (Anson plot) can be obtained by integrating as below:

$$Q = {2nFACD^{1/2}t^{1/2}}/{\pi^{1/2}} \quad (1)$$

where Q is the charge, n is the number of moles of electron transferred in the reaction (equiv/mole), A is the electrode surface area (cm^2), F is the Faraday constant (96,485 C/mol), C is the electroactive species concentration (mol/cm^3), t is time (s) and D is the diffusion coefficient (cm^2/s).

The Anson plot shows linear dependency of Q upon $t^{1/2}$ which indicates that the electrooxidation process is diffusion-controlled. Upon analyzing the Anson's plot, a total charge of 6.86 x 10^{-4} C/cm^2 was obtained upon oxidation of 0.40 mM DA. Based on the chronocoulometry study on 0.4 mM dopamine in 0.1 M KCl at pH 2.0, the diffusion coefficient was found to be 5.43 x 10^{-8} cm^2/s.

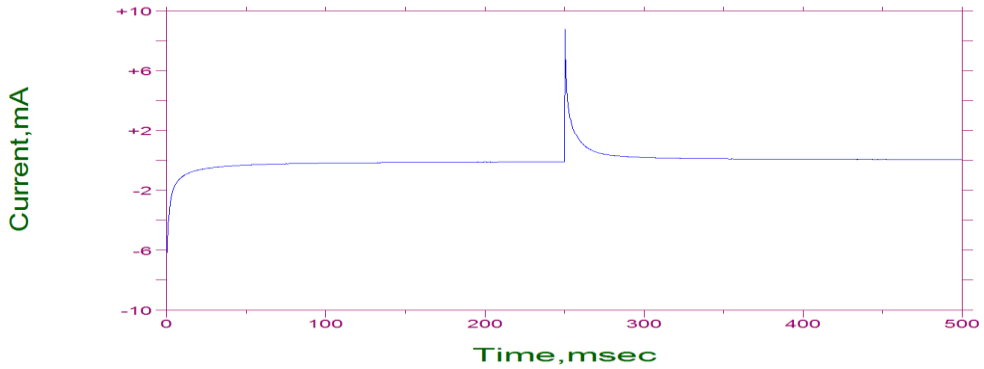


Figure 7: Chronoamperogram of DA at MWCNTs/WO_3/GCE in 0.1 M KCl (pH 2.0) at 25°C with 250 ms pulse width.

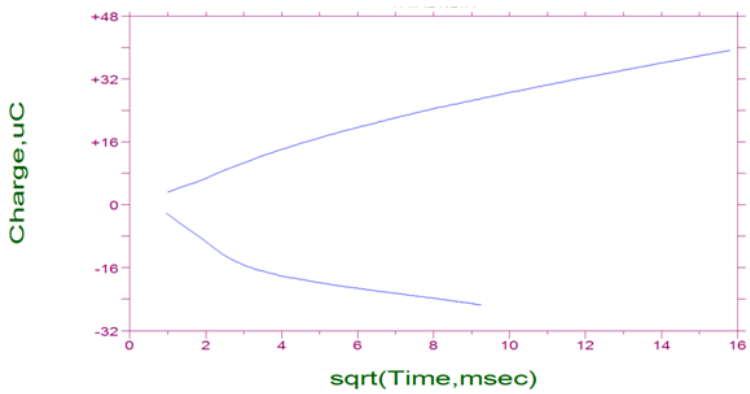


Figure 8: Chronocoulogram depicting the rising current time transient with the maximum of oxidation wave in 0.1 M KCl at the CNT/WO_3/GCE using solution at 25°C with 250 ms pulse width

Interference Study

Interference study was conducted to assess the reproducibility of the MWCNTs/WO_3 modified GCE. The determination of DA concentration in interference with AA in 0.1M KCl (pH 2.0) was studied. The AA was freshly prepared in the range of 0.04 M to 0.12 M. Figure 9(a) depicts the voltammogram for the interference of DA with AA using bare GCE. It can be seen that unresolved peaks of DA and AA were significant in the manner of 0.01 mL/M until 0.12 mL/M of AA in the solution of 0.4 M DA in 0.1 M KCl electrolyte. Upon utilization of the MWCNTs/WO_3 composite-modified electrode, the result showed that as the concentration of AA is increased, a more distinct separation can be seen in the voltammogram which can be depicted in Figure 9(b).

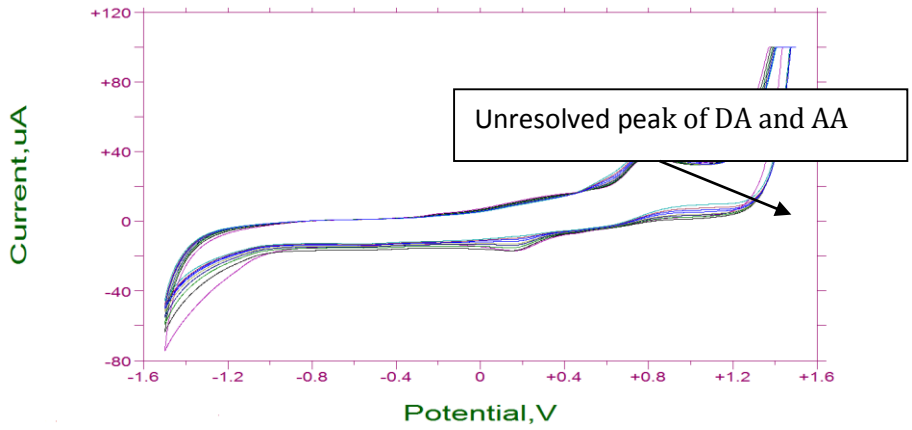


Figure 9(a). Cyclic voltammograms for interference of DA (0.40 mM) with AA (0.40mM to 1.20mM) using a solution of 0.1 M KCl (pH 2.0) mediated by bare GCE at scan rate of 100 mV/s.

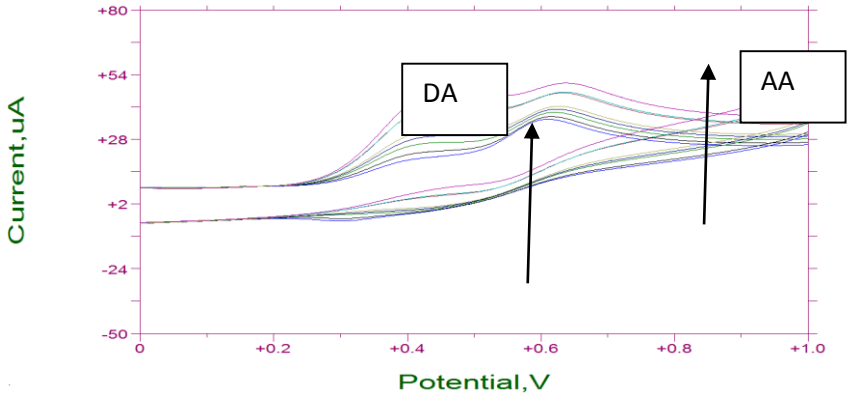


Figure 9(b). Cyclic voltammograms for interference of DA (0.40 mM) with AA (0.40mM to 1.20 mM) using a solution of 0.1 M KCl (pH 2.0) mediated by MWCNTs/WO_3/GCE at scan rate of 100 mV/s.

CONCLUSION

A MWCNTs/WO_3 nanocomposite-modified GCE was successfully fabricated in producing a stable composite which enhanced the DA electrooxidation current. The results demonstrate that the MWCNTs/WO_3/GCE has high sensitivity, selectivity and stability in the electrochemical measurements. Satisfactory detection limit was achieved with this nanocomposite-modified electrode. This modified electrode showed high catalytic activities towards the oxidation of DA in the presence of AA with satisfactory selectivity and sensitivity. The investigation of MWCNTs/WO_3/GCE as electrocatalyst can be further studied in the detection of other biological and chemical compounds.

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