

Electrochemical Oxidation of Ascorbic Acid Using MgB₂-MWCNT Modified Glassy Carbon Electrode

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The electrochemical properties of ascorbic acid (AA) have been studied using cyclic voltammetry technique at the surface of MgB₂-MWCNT mixture modified glassy carbon electrode (MgB₂-MWCNT/GCE) via mechanical attachment method. An enhancement factor of the ascorbic acid oxidation current by about 2 fold compared to the bare electrode was observed. The current was due to diffusion-adsorption process with diffusion activation energy of 2.7kJmol⁻¹. The MgB₂-MWCNT/GCE has a limit of detection of 1.3μM AA with a sensitivity of 76.6 mA M⁻¹AA. Good reproducibility and recovery rate was obtained when determining the presence of AA in real life samples.

Keywords: Ascorbic Acid; Cyclic Voltammetry; Glassy carbon electrode; Magnesium boride; Multiwalled carbon nanotube

1. INTRODUCTION

Ascorbic acid (AA) has been an analyte of interest for electroanalytical studies due to its biological importance as well as wide applications in major industries. However, its detection can be easily interfered by the presence of other compounds such as dopamine (DA) and uric acid (UA) [1]. The interference factor encountered by AA and other compounds lead many studies to be carried out on electrode modification which has been an important field of study in electrochemistry. Besides having a higher sensitivity, the ability to perform selective analysis, enhance flux design, charge storage devices, act as a catalysts, as well as become a support matrices for electrocatalysis activity while simultaneously coupled to an electrochemical reaction is the drive for the study of electrode modification [2].

Application of carbon nanotubes (CNT) in electrochemistry was first reported by Britto *et.al* [3] and since then, there have been a significant number of studies carried out on the usage of CNT for electrodes modification. Discussions on the role of CNT as electrochemical sensors have been reviewed and covered extensively [4-7]. It was revealed that CNT is able to promote electron transfer reaction as well as minimize surface fouling on electrochemical devices [7,8]. The electrocatalytic ability of CNT is suggested to be influenced by its dimensions, structures, presence of reactive groups and defects on its surface [4,6,7], as well as the presence of metallic impurities within CNT itself [9]. Its stability in both aqueous and non-aqueous solutions also makes it suitable for modification of various electrodes [10]. Studies conducted on the multiwalled CNT (MWCNT) modified GCE show that it is capable of mediating redox reaction of metals [11], organic compounds [12-14], drugs [15,16] and neurotransmitters [1,17]. Modification of GCE with hybrid combination of MWCNT and other particles such as metals [18,19], metal oxides [20,21], alloys [22,23], polymers [24,25], semiconductors [26,27] and superconductors [28] show great improvement in sensitivity and overvoltage minimization.

MgB₂ is one of the superconductors which has been the subject of great attention since its superconducting ability was made known by Akimitsu *et. al* in 2001 [29]. In the same year more than 260 studies have appeared with an average of 1.3papers/day [30]. With a critical temperature of 37K, it is believed that the superconductivity of MgB₂ is very much attributed by the metallic boron layers in its structure [31]. Although numerous publications had been reported on its superconducting properties and behavior [32-39], there are only minimum reports available on the electrochemical characterization as well as mediation ability of MgB₂ as an electrode modifier [40,41]. No reports, however, are available for the studies of MgB₂ hybrid modified electrode.

This work therefore reports on the study of the electrochemical properties of MgB₂-MWCNT modified GC electrode on the oxidation behavior of AA.

2. EXPERIMENTAL

2.1 Instrumentation and electroanalytical methods

Cyclic voltammetry analyses were carried out on electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring software connected to external computer. A three electrodes system was employed consisting of Ag/AgCl (3M NaCl) electrode as the reference electrode (RE), a platinum wire as the counter electrode and a GCE ($\phi = 3\text{mm}$) as the working electrode. Unless otherwise stated, the voltammetric experiments were carried out at $25 \pm 2^\circ\text{C}$ using 0.1M KNO₃ as supporting electrolyte. Solutions were degassed with nitrogen for ten minutes prior to recording the voltammograms.

2.2 Chemicals and Reagents

Multiwalled carbon nanotubes (MWCNT) were obtained from Shenzhen Nanotech Port Co., Ltd. with 95% purity. Magnesium diboride (MgB₂) (Alfa Aesar) and other chemicals were of

analytical reagent grade purity and were used without further purification. Vitamin C tablet brand named Chewies and Marigold Peel Fresh Orange Juice were purchased from a local pharmacy and used in real samples determination. Preparations of solutions were carried out using distilled water.

2.3 Preparation of MgB_2 -MWCNT/GCE

Prior to modification, the surface of the GCE to be used was first polished using $0.05\mu\text{m}$ alumina slurry, followed by ultrasonic cleaning for about 1-2 minutes before being dried with lint-free tissue paper. MgB_2 powder and MWCNT powder were mixed physically according to a weight ratio of 1:1 and a sample amount of 1-3mg of 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.

3. RESULTS AND DISCUSSION

3.1 Preliminary Study

The cyclic voltammograms (CV) of 0.5mM AA in 0.1M KNO_3 aqueous electrolyte solution were obtained with a potential scanning at a positive direction over the potential range of -200mV to +1400mV at a scan rate of 100mVs^{-1} for modified and bare GCE versus Ag/AgCl (Fig, 1). CV recorded for all the electrodes appear to be irreversible.

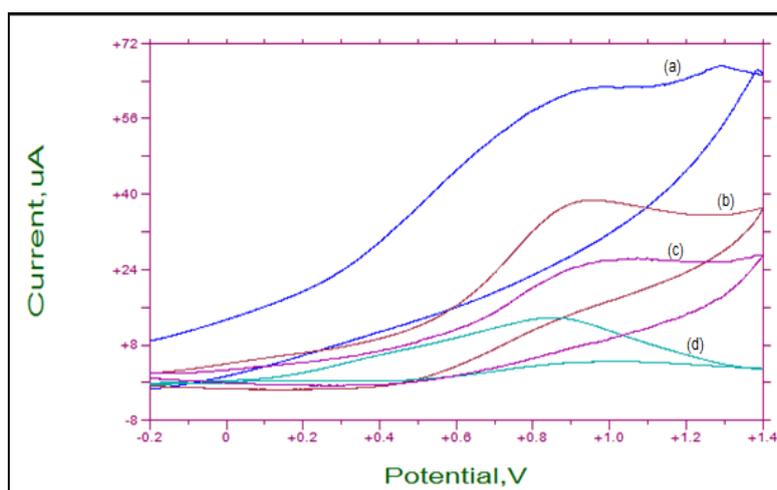


Figure 1. CV of 0.5mM AA in 0.1M KNO_3 at the (a) MgB_2 -MWCNT/GCE, (b) MWCNT/GCE, (c) MgB_2 /GCE and (d) bare GCE (against RE; scan rate 100mVs^{-1})

AA oxidation current enhancement was detected when using MWCNT/GCE and MgB_2 -MWCNT/GCE with enhancement factor of 1.5 and 1.7, respectively. However, it was noted that the peak potential shifted negatively towards the origin by about 86mV when using the MgB_2 -MWCNT/GCE indicating that lower activation energy is required for the oxidation process. The slight

At weakly acidic environment ($\text{pH } 5 \pm 0.4$), the current begins to decrease before leveling off as it approaches the neutral point. As the pH continues to increase, a decreasing trend of the peak current starts to be seen for both bare and modified electrode (Figure 2).

This may be contributed by the fact that AA is unstable in basic solution [45] and thus exists in anionic form [46]. There is a possibility that due to the shortage of proton, difficulty of electrochemical reaction arises [47,48] and a repulsive electrostatic interaction occurs between the anions and the modified electrode surface [46]. Since the maximum value of both oxidation current and enhancement factor (Figure 3) for the modified electrode was achieved at $\text{pH } 4 \pm 0.4$, therefore, the condition of supporting electrolyte at $\text{pH } 4 \pm 0.4$ was used for the following studies.

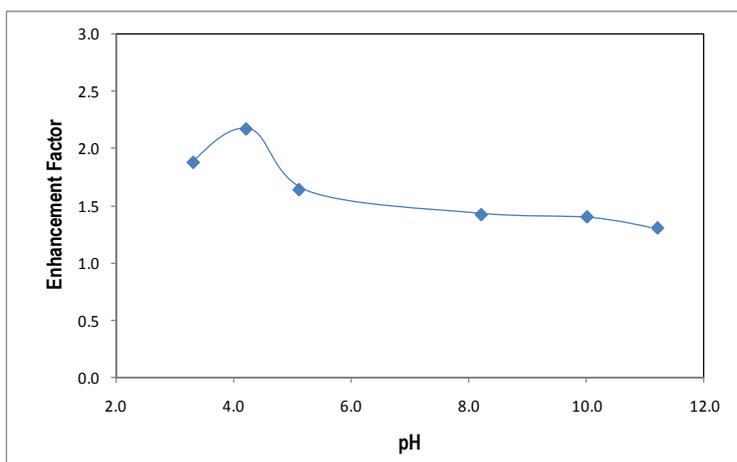


Figure 3. Plot of oxidation current enhancement factor of $\text{MgB}_2\text{-MWCNT/GC}$ electrode over bare electrode at different pH

3.3 Calibration graph

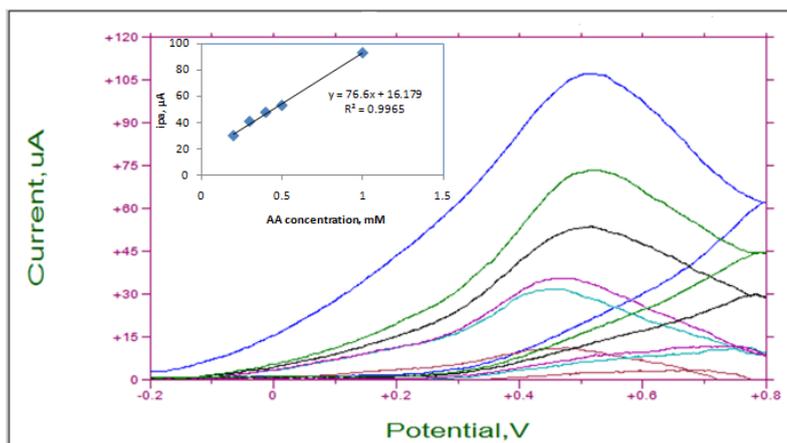


Figure 4. CV of different AA concentration in 0.1M KNO_3 , $\text{pH } 4 \pm 0.4$ at $\text{MgB}_2\text{-MWCNT/GCE}$ [Inset: Plot of oxidation current versus AA concentration in 0.1M KNO_3 , $\text{pH } 4 \pm 0.4$ at $\text{MgB}_2\text{-MWCNT/GCE}$]

In order to obtain the detection limit and sensitivity of the MgB₂-MWCNT/GC electrode, the calibration graph of AA was determined (Fig. 4).

A linear response with correlation value of 0.997 which obeys the Randles-Sevcik (Equation 3);

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (\text{Equation 3})$$

Where i_p , peak current; n , electron stoichiometry; A , electrode area; D , diffusion coefficient; C , concentration and v , scan rate are obtained over a concentration range of 0.2 to 1mM AA. Based on the linear equation slope, a sensitivity response of 76.6mA/M and detection limit of 1.3 μ M was acquired. This value is comparable to the results reported in literature, where the detection limit ranges from 0.3 to 80 μ M as tabulated in Table 1.

Table 1. Comparison of the analytical parameters of AA determination at various modified GCE via CV.

Ref	GCE Modifier	Detection Limit (μ M)	Sensitivity (mA M ⁻¹)
48	WO ₃ /SWCNT	80.0	14.6
49	Bi ₂ O ₃ /Li/MWCNT	50.0	24.0
50	Bi ₂ O ₃	8.1	50.4
51	(Co(II)TPP)	5.0	-
52	TiO ₂ /MWCNT	4.0	44.0
53	Aniline	1.0	-
54	PAA	0.8	-
55	Ni(Me ₂ (CH ₃ CO) ₂ [14]tetraenoN ₄)	0.3	-
this work	MgB ₂ -MWCNT	1.3	76.6

3.4 Effect of scan rate

Kinetics of the AA oxidation at the electrode surface was examined by conducting a scan rate study. The effect of scan rate on the CV of 0.1mM AA at the MgB₂-MWCNT/GCE in 0.1M KNO₃ at pH 4 \pm 0.4 was studied. Results show that both the oxidation current and oxidation peak were influenced by the scan rate. The oxidation current increased with scan rate due to heterogeneous kinetics, where as the oxidation peak shifted towards a more positive potential indicating the existence of kinetic limitation in the reaction between the redox sites of MgB₂-MWCNT film and AA [45,56,57]. The plot of oxidation peak current as a function of the square root of scan rate yields a straight line signifying a reaction that is diffusion limiting (Figure 5).

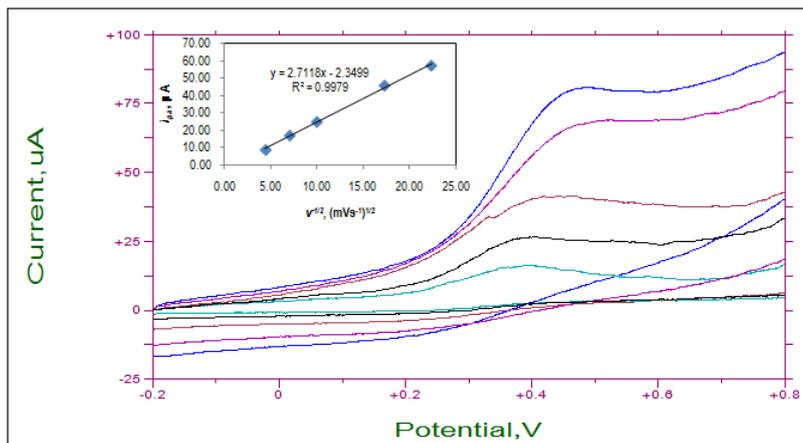


Figure 5. CV of AA in 0.1M KNO₃, pH 4 ± 0.4 at MgB₂-MWCNT/GCE with different scan rate [Inset: Plot of oxidation current versus the square root of scan rate for 0.1mM AA in 0.1M KNO₃, pH 4 ± 0.4 at MgB₂-MWCNT/GCE]

A straight line is obtained from the plot of log oxidation current versus log scan rate yielding an equation of $y = 0.572x + 0.236$ with an $R^2 = 0.994$ (Fig. 6). A slightly higher slope value than the theoretical value of 0.53 is due to pure diffusion control process [58]. This suggests the presence of weak AA adsorption occurring simultaneously along with AA diffusion in controlling the anodic process [59].

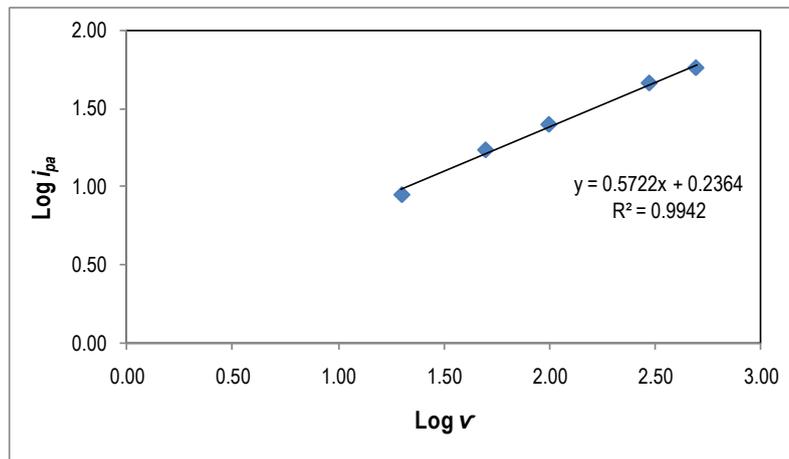


Figure 6. Plot of log oxidation current versus log of scan rate for 0.1mM AA in 0.1M KNO₃, pH 4 ± 0.4 at MgB₂-MWCNT/GCE

3.5 Effect of temperature

The effect of temperature on the conductivity of both bare and MgB₂-MWCNT/GCE was studied in order to determine the activation energy of AA diffusion at the respective electrodes. The temperature of the electrochemical cell was varied at a range of 26°C to 70°C by using a water bath. On both electrodes, it was observed that the current increased gradually as the temperature increased.

This is due to the elevation of diffusion rate at higher temperature level which caused current increment.

The relationship between the diffusion coefficient and temperature is indicated by the Arrhenius equation (Equation 4).

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \tag{Equation 4}$$

where D is diffusion, D_0 is initial diffusibility, E_a is the activation energy, R is the specific gas constant at $8.314 \text{ J K}^{-1}\text{mol}^{-1}$ and T is temperature in degrees Kelvin. The activation energy for the diffusion of AA can further be determined by taking the logarithm of Equation 4 and, hence, Equation 5;

$$\ln D = \ln D_0 - \frac{E_a}{RT} \tag{Equation 5}$$

A linear relationship of plot log oxidation current of AA versus the reciprocal of temperature for both bare and modified electrode was obtained (Fig. 7). From the slope the activation energy for the diffusion of AA on the modified electrode was found to be 2.7kJmol^{-1} which is about 60% of the activation energy (4.2kJmol^{-1}) required for diffusion of AA on the bare electrode. This further strengthens the evidence of electrocatalytic ability of the $\text{MgB}_2\text{-MWCNT/GCE}$. However, this value is quite low compared to the other modified GCE [50,52]. Presumably, this is due to nature of the materials used to modify the GCE and also the different matrix in the cell itself.

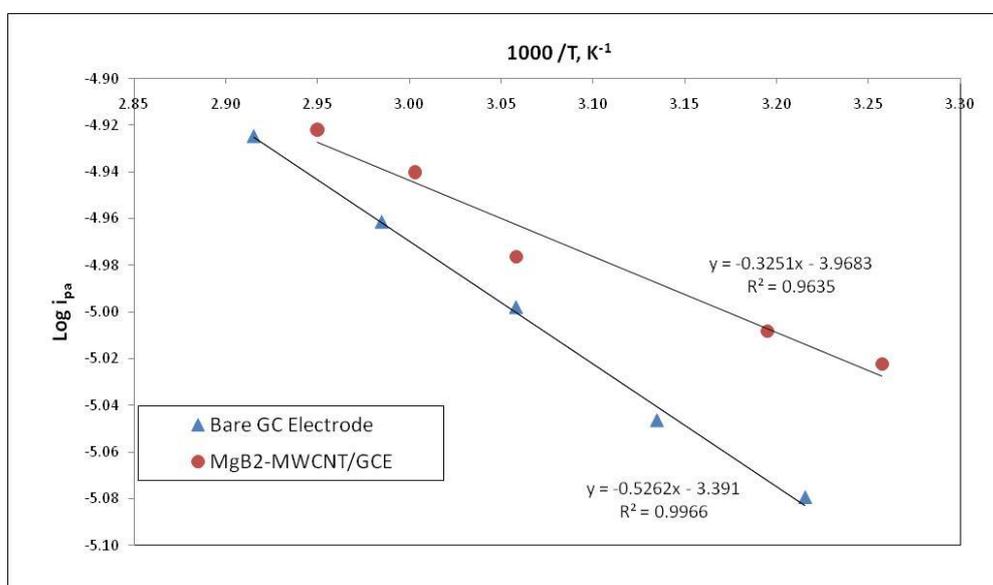


Figure 7. Plot of log oxidation current versus the reciprocal of temperature for 0.1mM AA in 0.1M KNO_3 , pH 4 ± 0.4 at bare and $\text{MgB}_2\text{-MWCNT/GCE}$.

3.6 Reproducibility

For this study, measurements were made at fresh surface of modified electrode. The process was repeated five times, where the electrolyte solution was unchanged and its condition was kept constant. The study was also carried out on real life sample using expired Vitamin C tablet obtained from a local clinic, originally containing 500mg of AA. The tablet was dissolved and later diluted to 0.3mM and 0.5mM. Table 2 and Table 3 show that a mean enhancement factor of 1.93 was obtained with a %RSD of 4.16%. Reproducibility was also good for both oxidation current and oxidation peak, where the %RSD obtained from all three data sets are in the range of 4–7% and 2–6% respectively. These results further confirm the 2 fold enhancement factor of the MgB₂-MWCNT/GCE over the bare electrode.

Table 2. Reproducibility data of 0.1mM AA determined using MgB₂-MWCNT/GC electrode under optimized conditions in 0.1M KNO₃ at pH 4 ± 0.4 (Bare electrode $i_{pa} = 6.3\mu\text{A}$)

Run	i_{pa} , μA	E_{pa} , mV	Enhancement Factor
1	12.90	468	2.0
2	11.60	487	1.8
3	11.80	482	1.9
4	12.30	496	2.0
5	12.30	475	2.0
Mean	12.18	482	1.93
Standard deviation	0.51	10.78	0.08
RSD (%)	4.16	2.24	4.16

Table 3. Detection of AA in expired Vitamin C tablets (originally containing 500mg AA) using MgB₂/MWCNT/GC electrode in 0.1M KNO₃ at pH 4±0.4

Run	0.3mM		0.5mM	
	i_{pa} , μA	E_{pa} , mV	i_{pa} , μA	E_{pa} , mV
1	10.37	540	17.08	541
2	10.75	543	15.69	574
3	9.17	561	16.49	521
4	9.84	494	17.08	505
5	9.17	496	15.88	486
Mean	9.86	527	16.44	525
Standard deviation	0.71	30.05	0.65	33.75
RSD (%)	7.20	5.71	3.96	6.42

3.7 Recovery Study of AA in Vitamin C Tablet and Fruit Juice

The detection ability of the MgB₂-MWCNT/GCE on AA was validated using real life samples of both known and unknown concentration. For the sample with known concentration, Chewies Vitamin C tablet containing 100mg of AA was dissolved in 100mL of DI water and mixed with a ratio of 1:9 to the supporting electrolyte solution; whereas for the sample with unknown concentration, Marigold Peel Fresh Orange Juice was mixed with a ratio of 1:1 to the supporting electrolyte solution. The standard addition method was applied using a stock solution of 0.1M AA. Five replicate were carried out for each sample and the results are shown in Table 4 and Table 5. A good recovery rate of $100.7 \pm 4.01\%$ (for 0.57mM AA) and mean concentration of $3.8\text{mM} \pm 4.35\%$ was obtained (for concentration of AA in orange juice) indicating a high reliability of the modified electrode detection ability.

Table 4. Recovery rate of AA in 0.57mM Chewies Vitamin C Tablet, determined using MgB₂-MWCNT/GCE in 0.1M KNO₃ at pH 4 ± 0.4

Real life sample	Recovered concentration (mM)	Recovery rate (%)	Mean recovery (%)	Standard Deviation	RSD (%)
1	0.60	105.3	100.7	4.0	4.01
2	0.54	94.7			
3	0.59	103.5			
4	0.57	100.0			
5	0.57	100.0			

Table 5. Recovery of AA in Marigold Peel Fresh Orange Juice, determined using MgB₂-MWCNT/GCE in 0.1M KNO₃ at pH 4 ± 0.4

Real life sample	Concentration (mM)	Mean concentration (mM)	Standard Deviation	RSD (%)
1	3.9	3.8	0.164	4.35
2	3.9			
3	3.8			
4	3.5			
5	3.8			

4. CONCLUSIONS

The fabrication of MgB₂-MWCNT/GCE was successfully done via mechanical attachment method. This study shows the electrode is able to catalyze the oxidation of AA. Low detection limit and good sensitivity coupled with excellent recovery and reproducibility in the determination of AA in real samples indicates MgB₂-MWCNT/GCE may be used to analyze AA. The application of MgB₂-

MWCNT/GCE to other analytes proves to be promising and can be further explored. This is the subject of the next report.

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