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Electrochemical Oxidation of Ascorbic Acid Mediated by Single-Walled Carbon Nanotube/Tungsten Oxide Nanoparticles Modified Glassy Carbon Electrode

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The electrocatalytic study of ascorbic acid using single-walled carbon nanotube/tungsten oxide ($SWCNT/WO_3$) modified glassy carbon electrode prepared by mechanical attachment was conducted. The oxidation peaks obtained indicate that the $SWCNT/WO_3$-modified glassy carbon electrode has good electrochemical behaviour in terms of sensitivity. The mechanical attachment of a $SWCNT/WO_3$ composite on the glassy carbon electrode (GCE) surface enhanced the oxidative current when compared to the WO_3-modified electrode and bare GCE. The oxidation peak of $SWCNT/WO_3$-modified electrode was considerably enhanced by 2.5 times with about a 230 mV peak shift towards a lower potential when the $SWCNT/WO_3$-modified electrode was used in comparison with a bare GCE.

Keywords: Ascorbic acid, Cyclic voltammetry, Glassy carbon, Single-walled carbon nanotubes, Tungsten oxide

1. INTRODUCTION

In recent years, modified electrodes have been widely used in the voltammetric determination of biochemical compounds [1-4], metal ions [5, 6], DNA or DNA bases [7, 8], etc. Chemical fabrication [9, 10] and electrochemical pretreatment [11, 12] are widely applied in the modification of electrodes. The use of mechanical attachment/abrasive immobilization [13-15] and solvent casting [14, 15] have gained interest because of their simplicity and wide choice of micromaterials. Mechanical attachment is one of the modification techniques in solid phase voltammetry of microparticles which involves the pressing of a clean electrode surface onto a few miligrams of micromaterials.

The electrodes, which are modified by metal oxides [16], polymers [17-19] and biological compounds [20] are commonly found. Recently electrodes which are chemically modified by nanomaterials [21-23] or carbon nanotubes have received much attention.

Due to the unique physicochemical properties of carbon nanotubes, several voltammetric studies report better performance in sensitivity [24, 25] and detection limits [25]. There are several publications on electrochemical catalytic studies of the multi-walled carbon nanotubes (MWCNTs) [24-27] and single-walled carbon nanotubes (SWCNTs) [28, 29]. However, there is limited work on hybrid SWCNT/nanoparticle modified electrodes, which could provide potential novel strategies for better sensitivity and reproducibility of the electrochemical determinations of chemicals or biochemical compounds, including ascorbic acid.

In this report, the electrocatalytic study of ascorbic acid using single-walled carbon nanotube/tungsten oxide (SWCNT/WO_3) modified glassy carbon electrode by mechanical attachment was investigated. The oxidation peaks obtained indicate that the SWCNT/WO_3-modified glassy carbon electrode has good electrochemical behaviour in terms of sensitivity and reproducibility.

2. EXPERIMENTAL PART

2.1. Chemicals and reagents

Single-walled carbon nanotubes (SWCNTs) were obtained from SkySpring Nanomaterials, Inc., with 90% purity. Tungsten oxide (WO_3) (SkySpring Nanomaterials, Inc., 99.5% with diameter < 100 nm) and other chemicals were used as received. Vitamin C tablets named Cebion Vitamin C (Merck) and Redoxon Double Action (Bayer) were purchased and used as samples for the determination of ascorbic acid concentration. Distilled water was used for the preparation of aqueous solutions.

2.2. Electrochemical apparatus

A conventional three-electrode configuration was employed with a silver/silver chloride (Ag/AgCl, 3 M KCl) as the reference electrode. Platinum wire and a glassy carbon electrode (GCE) were used as an auxiliary electrode and working electrode respectively.

2.3. Instruments

Cyclic voltammetry (CV) analysis was performed with the electrochemical workstation BASi (Bioanalytical Systems, Inc.) CV-50W Voltammetric Analyzer with a potentiostat driven by CV-50W Version 2.0 software was connected to a desktop computer. Scanning electron microscopy (SEM) characterizations of the SWCNT/WO_3 composites were studied by using a scanning electron microscope (JOEL JSM-6400) attached to an energy dispersive X-ray spectrometer (EDX) JSM-6000 series with an acceleration voltage of 15 kV.

2.4. Preparation of modified electrode

All solutions were degassed with oxygen-free nitrogen gas for 15 minutes prior to measurement. The surface of a GCE (Area: 0.07 cm^2) was cleaned by using 0.05 μm polishing alumina powder, followed by 3 minutes of ultrasonic cleaning. Mechanical attachment was used in which a clean GCE surface was pressed onto a few milligrams of SWCNT/WO_3 composite powder.

2.5. Preparation of SEM

A scanning electron microscopy (SEM) was used to examine the morphology of the SWCNT/WO_3 composites on a graphite electrode surface. A basal plane pyrolytic graphite electrode (BPPGE, 5 mm in diameter) was cut into several pieces of approximately 3 mm in thickness. The SWCNT/WO_3 composite was attached to the graphite electrode‘s surface whereby two sets of the sample were prepared (A) before and (B) after the controlled potential electroanalysis in the presence of ascorbic acid. Both samples were dehydrated for 45 minutes prior to being coated with gold particles via a sputter coater BAL-TEC SCD 005. The scanning electron microscope was operated at 15 kV and scanning electron images were recorded at a magnification of 5000x.

2.6. Electrochemcial measurement

Unless otherwise mentioned, all electrochemical measurements were performed with 3.5 mM ascorbic acid in 0.1 M potassium dihydrogen phosphate (pH 5.2) as a supporting electrolyte at SWCNT/WO_3-modified electrode. Cyclic voltammetry was used to detect the electrochemical response of ascorbic acid. A potential cycling between -1.0 to +0.8 V was applied to the working electrode at room temperature 25 ± 1 ^oC. Two real samples were prepared to demonstrate the application of the SWCNT/WO_3-modified electrode. Both samples with a known amount of ascorbic acid were prepared from 1000 mg of Vitamin C orange effervescent tablets.

3. RESULTS AND DISCUSSION

3.1. Enhancement study

The mechanical attachment of a single-walled carbon nanotube/tungsten oxide (SWCNT/WO_3) composite on a glassy carbon electrode (GCE) enhanced the oxidative current in comparison with the bare GCE. Figure 1 shows the cyclic voltammograms obtained for the oxidation of 3.5 mM ascorbic acid in 0.1 M potassium dihydrogen phosphate (KH_2PO_4) supporting electrolyte at pH 5.2 with a scan rate of 50 mV/s at 25 ^oC. (a) bare GCE, (b) WO_3-modified electrode and (c) SWCNT/WO_3-modified electrode.

The voltammograms indicate an absence of a well-defined reduction peak, implying that the oxidation process is irreversible. Figure 1 shows the oxidation peak of SWCNT/WO_3-modified

electrode considerably enhanced by 2.5 times with about a 230 mV peak shift towards a lower potential when a SWCNT/WO_3-modified electrode was used in comparison with a bare GCE. The degree of sensitivity of the bare/modified electrode was determined and stated as follows: SWCNT/WO_3/GCE > WO_3/GCE > bare GCE.

Previous reports have indicated that the modified GCEs were found to perform better in comparison to bare GCE in the presence of carbon nanotubes [8, 24, 25]. As is documented, carbon nanotubes exhibit the unique physicochemical property due to its large fraction of surface atoms per unit volume.

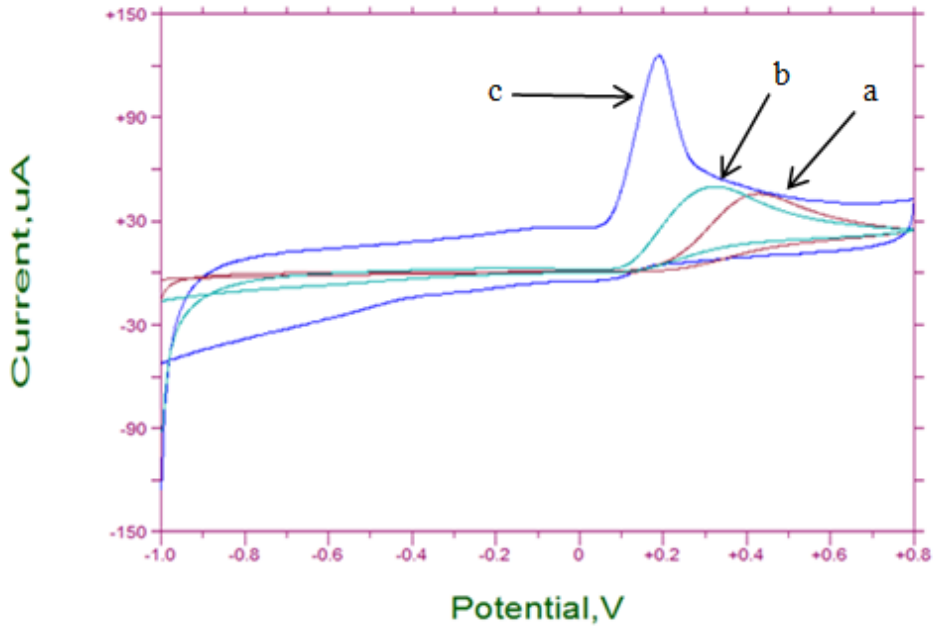

Figure 1. Cyclic voltammograms for the oxidation of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 versus Ag/AgCl, scan rate 50 mV/s using (a) bare glassy carbon electrode, (b) WO_3-modified electrode and (c) SWCNT/WO_3-modified electrode.

The influence of the SWCNT's percentage in the composite on the electrochemical response of the modified electrode was studied. The results indicate that the oxidative currents increased with the increase in SWCNT's percentage in the SWCNT/WO_3 composite, which suggests that the presence of SWCNTs could enhance the relative electron transfer.

3.2. Effect of scan rate

The effect of a varying scan rate on the oxidation process of ascorbic acid was studied. Cyclic voltammograms of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 supporting electrode using a SWCNT/WO_3-modified electrode was obtained for the scan rate from 2 – 1000 mV/s (Figure 2).

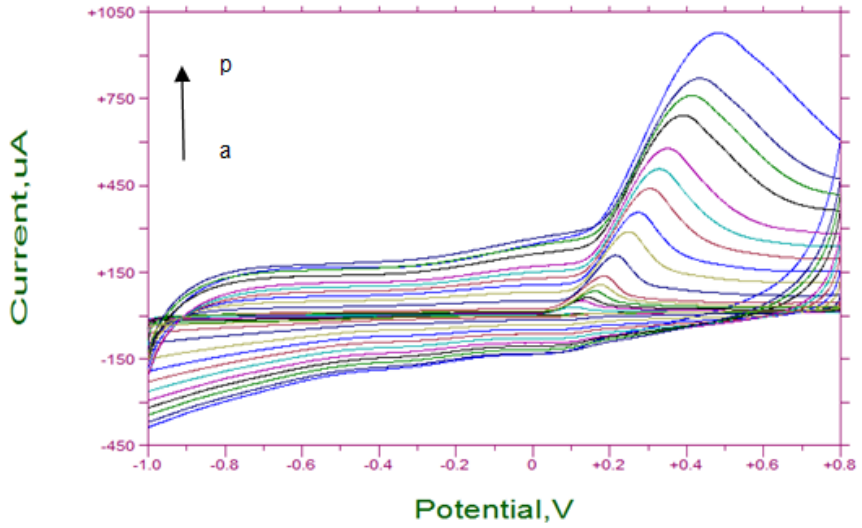

Figure 2. Cyclic voltammograms of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 at SWCNT/WO_3-modified electrode. Scan rates: (a) 2, (b) 5, (c) 10, (d) 20, (e) 30, (f) 50, (g) 100, (h) 200, (i) 300, (j) 400, (k) 500, (l) 600, (m) 700, (n) 800, (o) 900, and (p) 1000 mV/s.

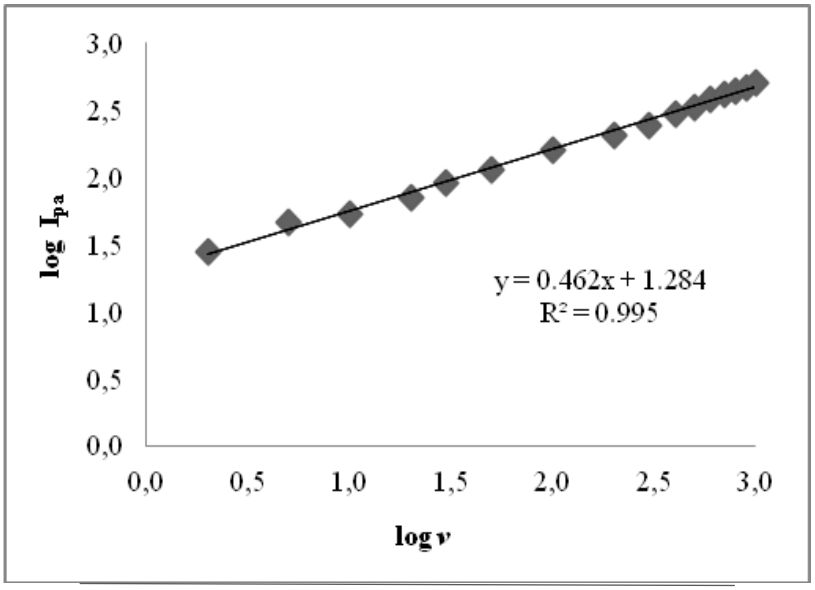

Figure 3. Plot of log I_{pa} versus log *v*. Other parameters, same as Figure 2.

Figure 3 shows the plot of log I_{pa} (peak current) of versus log *v* (scan rate). A linear relationship between the peak current and the scan rate is described by y = 0.462x + 1.284, where R^2 = 0.995. The oxidative current of ascorbic acid increasing with the scan rate is due to heterogeneous kinetics. The slope of 0.46 is comparable with the theoretical slope of 0.5 for a diffusion controlled process [30]. Good linearity between the anodic peak current and square root of scan rate was obtained by y = 15.33x + 1.984 with R^2 = 0.996 (Figure 4), which supports the idea that the electrode reactions of ascorbic acid were under diffusion control.

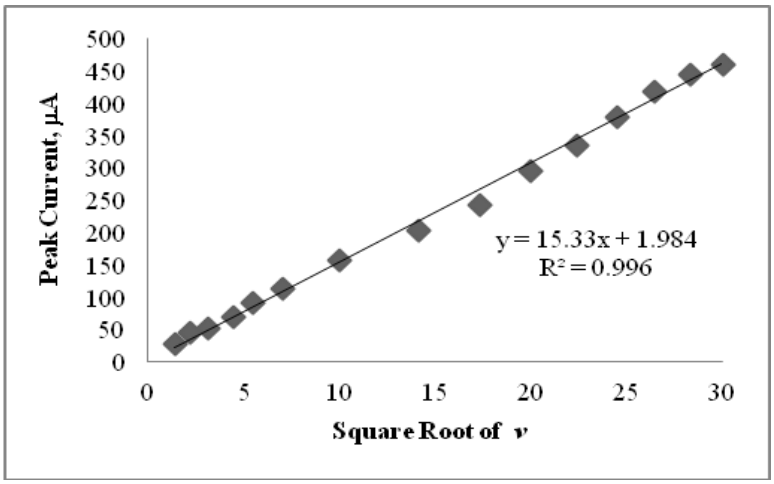

Figure 4. Plot of peak current versus square root of *v*. Other parameters, same as Figure 2.

3.3. Effect of potential cycling

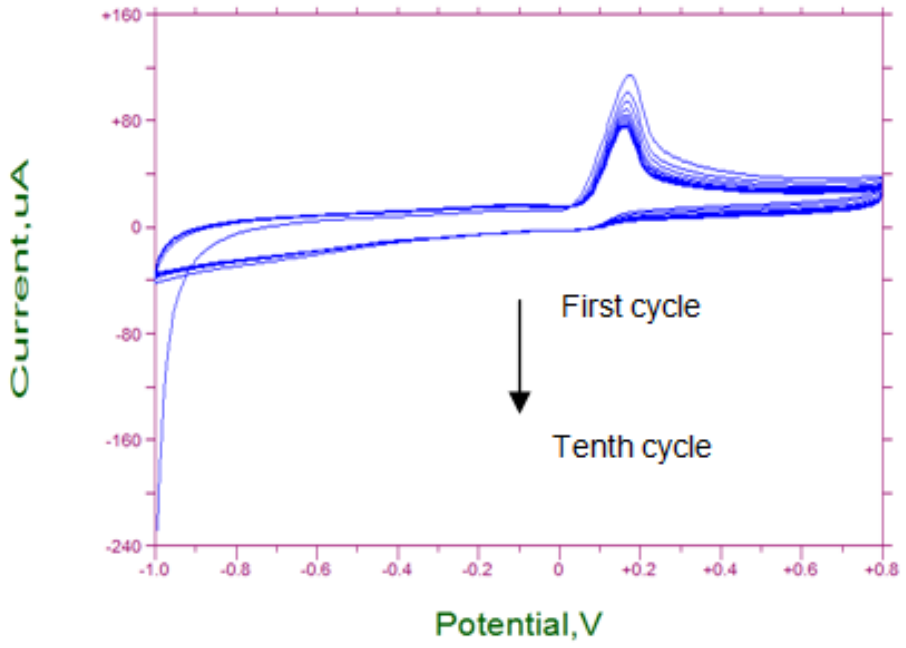

Figure 5. Cyclic voltammograms of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 for 10 continuous potential cycles at a SWCNT/WO_3-modified GC electrode. Scan rate: 50 mV/s.

The effect of potential cycling was studied to determine the stability of the SWCNT/WO_3-modified electrode. Figure 5 shows the multiple cyclic voltammograms in the determination of ascorbic acid in 0.1 M KH_2PO_4 supporting electrolyte at a scan rate of 50 mV/s. The voltammograms indicate that the oxidative peak current decreased slightly after the first cycle. There is no significant reduction in the peak current from the second to the tenth cycles. The results were similar with that reported previously [24]. This reflects the stability of SWCNT/WO_3 deposition on GCE.

3.4. Effect of ascorbic acid concentration

Figure 6 shows the effect of varying ascorbic acid concentration on the oxidation peak current. The oxidative current increased with the increase in concentration of ascorbic acid.

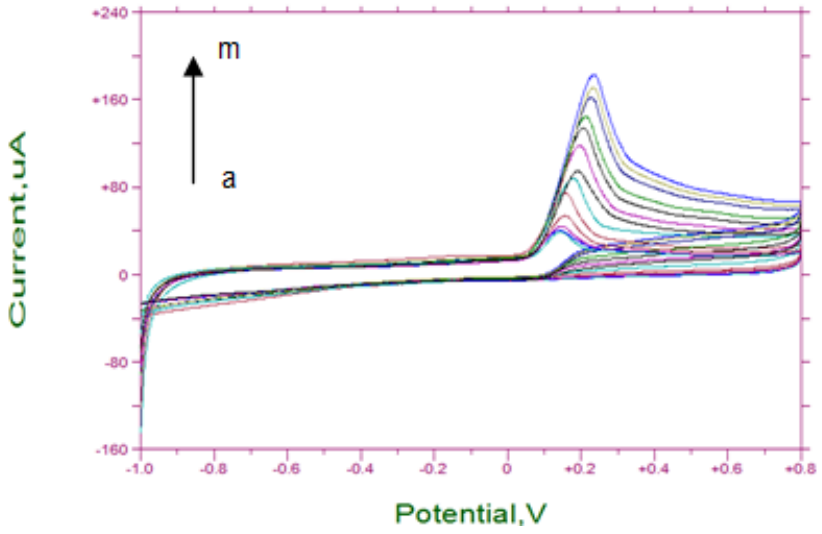

Figure 6. Cyclic voltammograms of SWCNT/WO_3-modified electrode in 0.1 M KH_2PO_4 at scan rate 50 mV/s with increasing ascorbic acid concentration (a) 0.2, (b) 0.5, (c) 0.7, (d) 1.0, (e) 2.0, (f) 3.0, (g) 4.0, (h) 5.0, (i) 6.0, (j) 7.0, (k) 8.0, (l) 9.0 and (m) 10.0 mM.

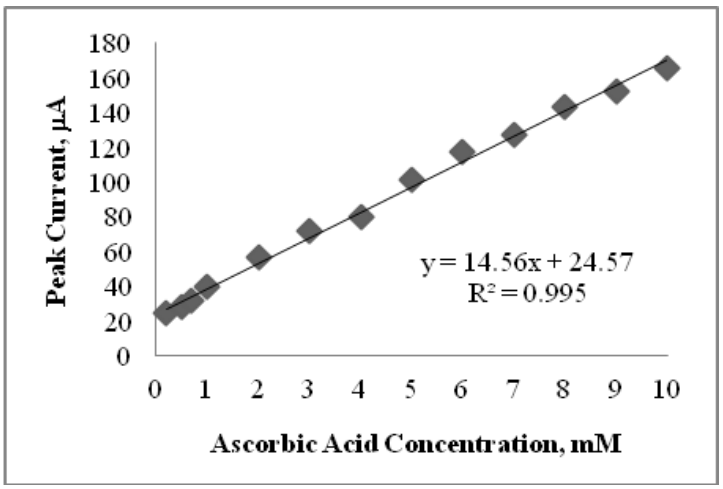

Figure. 7. Calibration graph of ascorbic acid in 0.1 M KH_2PO_4 using a SWCNT/WO_3/GC modified electrode at a scan rate of 50 mV/s.

The calibration graph of ascorbic acid in different concentrations was obtained by using a SWCNT/WO_3-modified electrode as shown in Figure 7. A linear response was achieved in the concentration range of 0.20 to 10.0 mM, with an R^2 value of 0.995 and sensitivity response of 14.6

mA/M. The detection limit of the determination of ascorbic acid by using a SWCNT/WO_3-modified electrode was found to be 80 μM compared to another work of 50 μM [24].

3.5. Repeatability

Reproducibility or repeatability of the SWCNT/WO_3-modified electrode in the determination of ascorbic acid was studied. The mechanical attachment was used to prepare the SWCNT/WO_3-modified electrode for 10 replicates on different days or times. The mean peak current obtained for 10 replicates of SWCNT/WO_3-modified electrodes was 107.8 μA (Table 1), which is an enhancement of approximately 2.5 fold if compared to the bare GCE. The relative standard deviation (*RSD*) calculated was 5.28%, which shows that the SWCNT/WO_3-modified electrode is reproducible.

Table 1. Repeatability data of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 supporting electrolyte determined with a SWCNT/WO_3-modified electrode at a scan rate of 50 mV/s on different days or times

Repeat No	Peak Current	Peak Potential
	μA	mV
1	105.0	201
2	114.5	209
3	103.9	196
4	104.1	206
5	105.9	200
6	114.1	185
7	101.5	195
8	118.1	196
9	107.9	195
10	103.2	192
Mean	107.8	197.5
SD	5.69	6.88
RSD (%)	5.28	3.49

3.6. Effect of temperature

The cyclic voltammograms were performed with the SWCNT/WO_3-modified electrode in 0.1 M KH_2PO_4 supporting electrolyte for a temperature range of 20 – 80 ^oC. The oxidative current increased gradually with an increase in temperature. This indicates that an increase in conductivity of the SWCNT/WO_3-modified electrode occurs with a temperature increase. The temperature exerts some influence on the activation energy (E_a) for the diffusion of the substrate of interest.

Figure 8 is a plot of log oxidative current of ascorbic acid versus the reciprocal of temperature. The relationship was found to be in fair agreement with the thermodynamic expectation of Arrhenius equations 1 and 2 [31].

$$\sigma = \sigma^o \exp(-E_a/RT) \quad (1)$$

$$D = D^o \exp(-E_a/RT) \quad (2)$$

where σ/D are conductivity/diffusibility and σ^o/D^o are standard conductivity/the initial diffusibility.

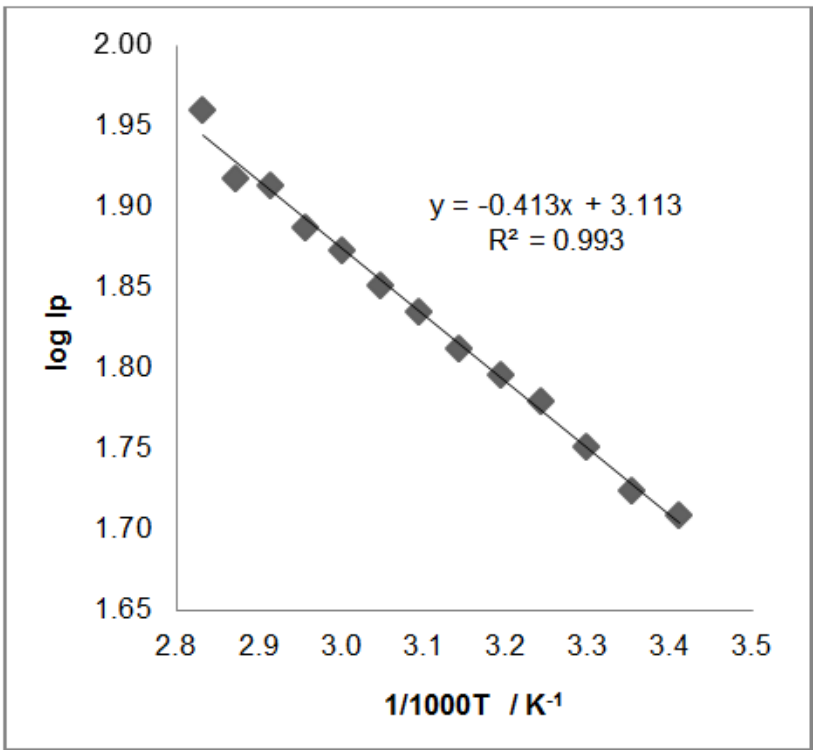

Figure 8. Plot of log oxidative current versus the reciprocal of temperature for 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 using a SWCNT/WO_3-modified electrode. Scan rate: 50 mV/s.

3.7. Effect of pH

The effect of pH on the oxidation process of ascorbic acid was studied. The 0.1 M KH_2PO_4 supporting electrolyte solutions with pH values varying from 2 to 14 were used to determine its effect on the oxidation of ascorbic acid at SWCNT/WO_3-modified electrode. Figure 9 is the plot of oxidative peak current versus pH and shows that the oxidation peak current of 3.5 mM ascorbic acid increases with a decrease in pH with a maximum current response at pH 2. The current decreased gradually as the pH increased from 2 to 7. However, in an alkaline condition from pH 8 to 14, it was observed that the oxidation current of ascorbic acid slightly decreases and plateaus at a higher pH level. It has been

suggested that the electrochemical reaction becomes more difficult in basic solution due to the shortage of proton [32].

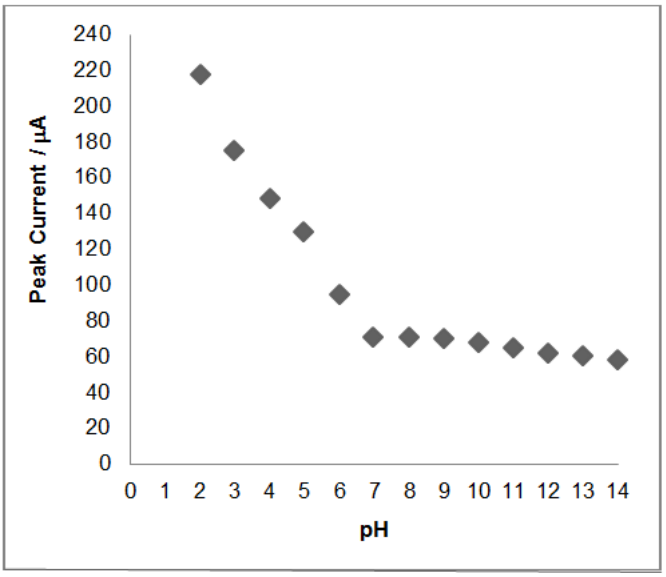

Figure 9. Plot of oxidative peak current versus pH for 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 in different pH condition at SWCNT/WO_3-modified electrode. Scan rate: 50 mV/s.

3.8. Recovery of real samples

The validity of the SWCNT/WO_3-modified electrode was verified in the determination of ascorbic acid of the real sample. The calibration of ascorbic acid was performed by using 0.1 M KH_2PO_4 as a supporting electrolyte (Figure 7). Cebion Vitamin C (Merck) and Redoxon Double Action (Bayer) orange effervescent tablets of 1000 mg ascorbic acid were used to prepare sample solutions.

Table 2. Recovery concentration for the oxidation process of real samples. Five replicates of ascorbic acid in Cebion Vitamin C and Redoxon Double Action tablet solutions for 4.0 mM concentration at SWCNT/WO_3-modified electrode were used.

No. of Replicates	Recovered Concentration (mM)		Recovery Rate (%)		Mean Recovery (%)		Standard Deviation		Relative Standard Deviation (%)	
	Cebion	Redoxon	Cebion	Redoxon	Cebion	Redoxon	Cebion	Redoxon	Cebion	Redoxon
1	4.47	4.11	111.7	102.8	103.7	96.5	6.74	5.89	6.50	6.10
2	4.39	4.02	109.8	100.6						
3	4.07	3.94	101.7	98.5						
4	3.97	3.61	99.2	90.2						
5	3.85	3.61	96.2	90.3						

A known amount of ascorbic acid sample solution was spiked into the supporting electrolyte. Five replications were performed as shown in Table 2. Table 2 also shows the recovery concentration and percentage of the ascorbic acid in real samples. Good recovery rates of 103.7 ± 6.50% (Cebion) and 96.5 ± 6.10% (Redoxon) were obtained for the 4.0 mM concentration of ascorbic acid. This value for recovery rate is similar than that obtained for lower concentration of ascorbic acid (0.5 and 1.0 mM) with the surface of glassy carbon electrode immobilized by bismuth oxide (Bi2O3) microparticles [30].

3.9. Scanning Electron Microscopy

The SWCNT/WO_3-modified electrodes were characterized by using scanning electron microscopy (SEM) which provides evidence for the morphology of SWCNT/WO_3 nanocomposites and surface structure for the modified electrode.

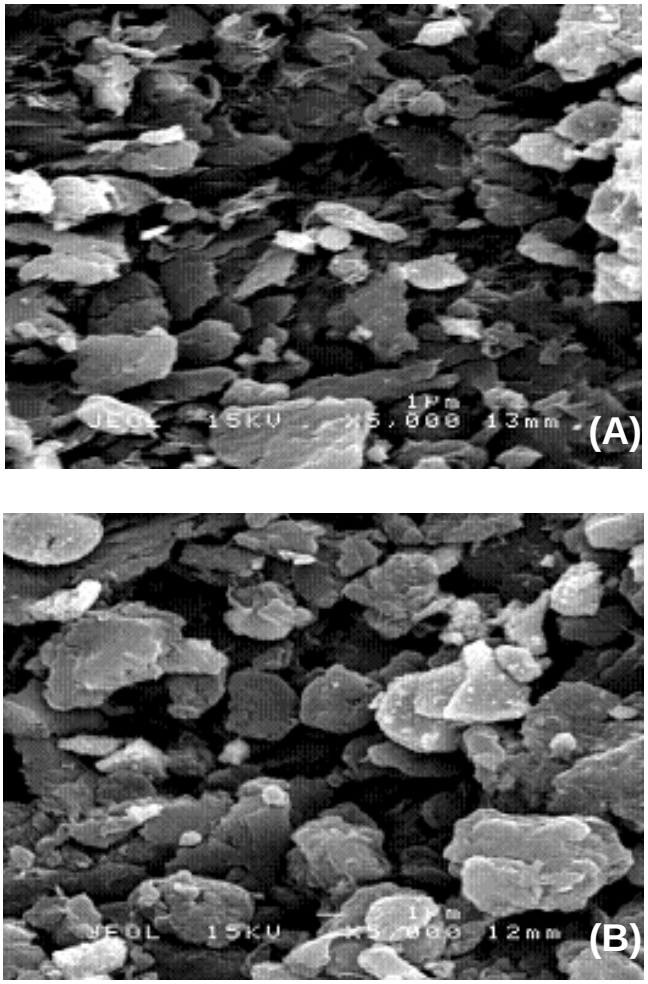

Figure 10. Scanning electron microscopy (SEM) of SWCNT/WO_3 nanocomposites on the graphite electrode‘s surface prepared by mechanical attachment (A) before and (B) after the electroanalysis.

Figure 10 shows the scanning electron images of SWCNT/WO3 nanocomposites on the graphite electrode surface (A) before and (B) after electroanalysis at a magnification of 5000. As shown in Figure 10A, the SWCNT/WO3 nanocomposites had a range in size of 0.5 – 5 □m in diameter with irregular shapes and were randomly distributed on the electrode's surface prior to electroanalysis. After the application of the controlled cycling potential in the presence of ascorbic acid, the SEM image illustrates that the porosity and roughness remain unchanged. However, the SWCNT/WO3 nanocomposite shows a slight increase in size from 0.5 – 5 □m to 1 – 6 □m as shown in Figure 10B. Previous report have indicated that the size of the particles were found to be increased after the controlled-potential electrolysis [24]. Elemental analysis via energy dispersive X-ray spectrometer (EDX) indicates the presence of carbon, oxygen and tungsten on the electrode's surface.

4. CONCLUSIONS

A SWCNT/WO_3 modified glassy carbon electrode was successfully fabricated by using a GCE which enhanced the ascorbic acid's oxidative current. GCEs were mechanically attached with SWCNTs mixed with WO_3 nanoparticles. Both oxidative current and sensitivity improved when SWCNT/WO_3-modified electrode were used instead of WO_3-modified electrode and bare GCE. The electrocatalytic response of ascorbic acid was irreversible and the oxidative current obtained was under diffusion control. The current peaks were dependent on the concentration of ascorbic acid, scan rate, pH and temperature. Determination of ascorbic acid in a real sample had good recovery results in the concentration of 4.0 mM.

Evidently, the SWCNT/WO_3-modified glassy carbon electrodes possess better sensitivity when compared to WO_3-modified electrode and bare GCE. The stability of the SWCNT/WO_3-modified electrode is reached after the second cycle.

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