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Voltammetry Detection of Ascorbic Acid at Glassy Carbon Electrode Modified by Single-Walled Carbon Nanotube/Zinc Oxide

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A simple procedure was developed to prepare a glassy carbon electrode (GCE) modified with single-walled carbon nanotube/zinc oxide (SWCNT/ZnO). The carbon nanotube/zinc oxide composites were immobilized on the GCE by mechanical attachment. The electrode surface was gently rubbed on a filter paper supporting the SWCNT/ZnO composites. Cyclic voltammetry study of the modified electrode indicated that the oxidation potential shifted towards a lower potential by approximately 240 mV and the peak current was enhanced by 2.0 fold in comparison to the bare GCE. The resulting modified electrode also indicated the absence of a well-defined redox couple implying that the reaction is irreversible. The electrochemical behaviour was further described by characterization studies of scan rate, concentration of ascorbic acid, pH and temperature. The stability of the modified electrode was evaluated by potential cycling study. Such attractive results from the SWCNT/ZnO-modified electrodes suggest a promising ascorbic acid sensor.

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

1. INTRODUCTION

Different modified electrodes have been fabricated using several techniques such as mechanical attachment [1, 2, 3], solvent casting [1, 2], etc. Mechanical attachment is a simple technique in which the electron transfer materials are attached to the electrode’s surface via abrasive immobilization [3]. Electroactive materials are chosen for their reliability, long term stability, simplicity and for being inexpensive. Metal oxides [4], biochemical compounds [5], and polymers [6, 7], have been used as mediators for the fabrication of modified electrodes.

The chemical fabrication of electrodes with nanoparticles has recently received much attention [8-10]. The carbon nanotube is a new kind of inorganic material, which is widely used in recent research due to its unique physicochemical properties [11-13]. Electrodes modified with carbon nanotubes have been successfully used for the determination of ascorbic acid [14, 15], metal ions [16, 17], DNA [18, 19], etc. Reports indicate that good electron transfer activities give carbon nanotubes the advantage in the design and preparation of electrochemical sensors. However, there is limited work on the hybrid of nanoparticles as a mediator for sensing applications.

In this study, a modified electrode is fabricated by using carbon nanotubes mixed with zinc oxide for the determination of ascorbic acid. The performance and characterization of the SWCNT/ZnO-modified electrode was successfully evaluated by voltammetry.

2. EXPERIMENTAL PART

2.1. Chemicals and reagents

Single-walled carbon nanotubes (SWCNTs) with a purity of 90% was purchased from SkySpring Nanomaterials, Inc. and used without any further purification. Zinc oxide (ZnO) nano powder (~30 nm, 99.7%) was obtained from Inframat Advanced Materials. Other chemicals were used as received from the manufacturers (potassium dihydrogen phosphate, ascorbic acid). Vitamin C effervescent tablets, Cebion Vitamin C by Merck and Redoxon Double Action by Bayer were obtained and used for the recovery study. Distilled water was used for the preparation of aqueous solutions.

2.2. Electrochemical apparatus

A conventional three-electrode configuration was employed with a glassy carbon electrode as the working electrode. Silver/silver chloride (Ag/AgCl, 3 M KCl) and platinum wire (1 mm diameter) were used as the reference electrode and auxiliary electrode respectively.

2.3. Instruments

Voltammetric experiments were performed with the electrochemical workstation CV-50W Voltammetric Analyzer (BASi or Bioanalytical Systems, Inc.), which was connected to an external desktop computer. Scanning electron microscopy (SEM) characterizations of the SWCNT/ZnO composites were performed by using a scanning electron microscope (JOEL JSM-6400) with acceleration voltage between 10-15 kV.

2.4. Preparation of modified electrode

The dissolved oxygen was removed from all solutions with pure nitrogen gas for 15 minutes prior to the voltammetric measurements. The working electrode used in this study was a 3 mm diameter GCE modified by SWCNT/ZnO composites. SWCNT/ZnO composites in the ratio of 1:2 were mechanically transferred to the electrode's surface by gently rubbing it with nanocomposites on a filter paper. After measurements were taken, the chemically modified electrode was cleaned by the physical removal of the nano-film, followed by polishing with 0.05 μm alumina slurry and 3 minutes of ultrasonic cleaning. Unless otherwise mentioned, all the voltammetric measurements were performed at a scan rate of 50 mV/s, at a temperature of 25 ± 2 °C, with 3.5 mM ascorbic acid at pH 5.2 in 0.1 M potassium dihydrogen phosphate (KH_2PO_4) as the supporting electrolyte.

3. RESULTS AND DISCUSSIONS

3.1. Enhancement study

The modified electrode was constructed by SWCNT/ZnO nanocomposites via mechanical attachment. Figure 1 shows the effects of using unmodified/modified GCE on the electrochemical oxidation of ascorbic acid based on data from cyclic voltammetry. It was observed that the electrochemical oxidation of ascorbic acid is an irreversible process due to the absence of a well-defined reduction peak. The SWCNT/ZnO-modified electrode shows a better sensitivity and selectivity in comparison to the ZnO-modified electrode and bare GCE. The oxidative peak potential of ascorbic acid shifted approximately 240 mV towards a less positive potential. The voltammograms indicate that the relative oxidative current produced an enhancement factor of 2.0 with the SWCNT/ZnO-modified electrode in comparison to the bare GCE. The degree of sensitivity response increases in the following order:

SWCNT/ZnO/GCE > ZnO/GCE > bare GCE

Several literatures have indicated that the GCEs modified by carbon nanotubes were found to perform better in comparison to bare GCE [14, 16]. This suggests that the presence of SWCNTs could improve the relative electron transfer.

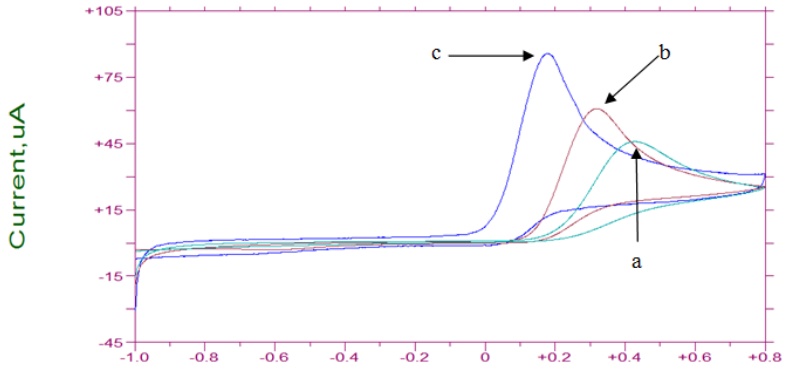

Figure 1. Cyclic voltammetry scanning of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 at a scan rate of 50 mV/s for (a) bare electrode, (b) ZnO-modified electrode and (c) SWCNT/ZnO-modified electrode.

3.2. Effect of scan rate

The effect of scan rates on the oxidative current of 3.5 mM ascorbic acid at a SWCNT/ZnO-modified electrode in 0.1 M KH_2PO_4 electrolyte solution was studied. Figure 2 shows the cyclic voltammograms obtained in the potential range of -1.0 to +0.8 V for the scan rate from 2 to 1000 mV/s to investigate the diffusion behaviour. Based on a plot of log peak current versus log scan rate as shown in Figure 3, a linear response of oxidative current on scan rate is described by y = 0.462x + 1.058 with R^2 = 0.996. The slope obtained is 0.46 which is in agreement with the theoretical slope 0.5 for diffusion controlled processes [20]. Figure 4 shows the linear relationship between oxidative current and the square root of scan rate. Good linearity between the anodic peak current and the square root of scan rate was obtained as y = 9.007x + 2.442 with R^2 = 0.997, which supports idea that the electrocatalysis of ascorbic acid is under diffusion control.

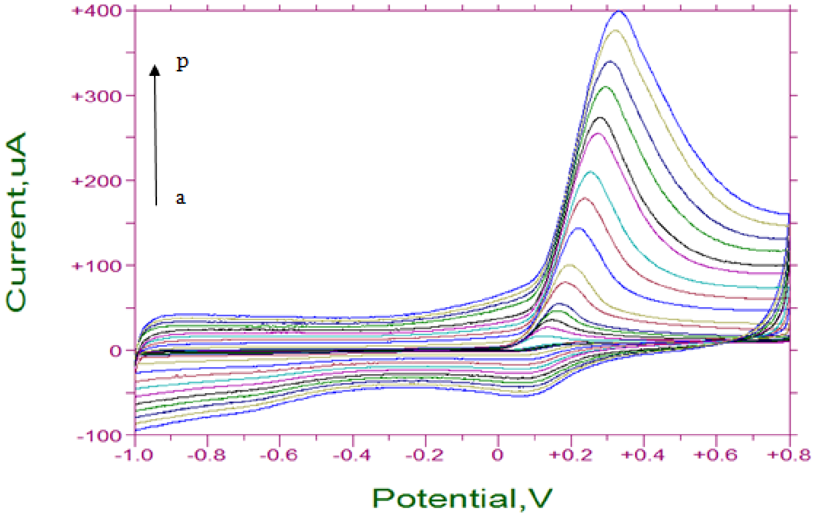

Figure 2. Effect of varying scan rate for 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 at SWCNT/ZnO-modified electrode versus Ag/AgCl. Scan rates: (a) 2, (b) 5, (c) 10, (d) 20, (e) 30, (f) 50, (g) 100, (h) 200, (i) 300, (j) 400, (k) 500, (l) 600, (m) 700, (n) 800, (o) 900, and (p) 1000 mV/s.

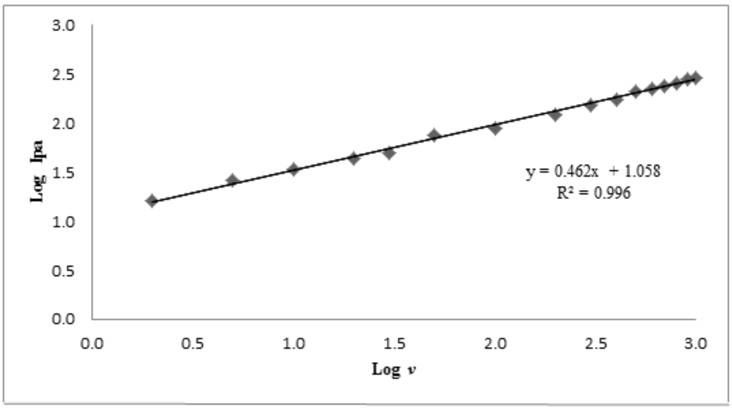

Figure 3. Plot of log I_{pa} versus log *v*. Other parameters, same as Fig. 2.

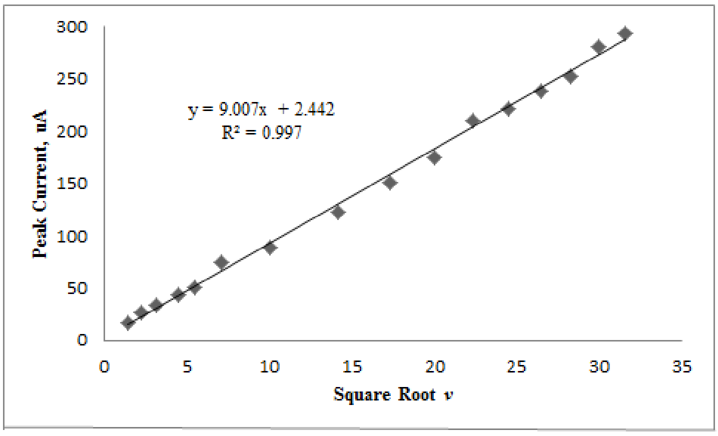

Figure 4. Plot of peak current versus square root of *v*. Other parameters, same as Fig. 2.

3.3. Effect of potential cycling

The stability of the SWCNT/ZnO-modified electrode was investigated in a potential cycling study. Under continuous potential cycling at 50 mV/s between -1.0 to +0.8 V in a 0.1 M KH_2PO_4 supporting electrolyte, a significant decay of oxidative current was observed in the initial cycle (10% in the first cycle) as shown in Figure 5. The oxidative current decreased by 7% from its original current response from the second to the fifth cycle. The result suggests that the stability of the nanocomposites' deposition on the GCE is achieved at the second cycle. The results were similar with that reported previously [14]. The significant decay in the initial cycle may be due to the weak bonds of the SWCNT/ZnO composites on the electrode surface.

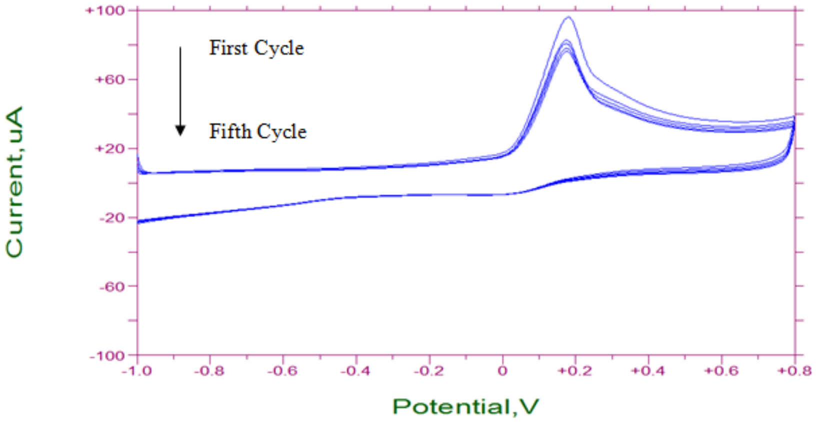

Figure 5. Multiple cycle voltammetry for 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 at a SWCNT/ZnO-modified electrode. Scan rate: 50 mV/s.

3.4. Effect of ascorbic acid concentration

Figure 6 shows the voltammograms of the oxidative peak current for ascorbic acid in different concentrations. It was observed that the well-defined peak current increased with the increases in the ascorbic acid concentration. The calibration plot of ascorbic acid is shown in Figure 7. A linear relationship was found and is described by y = 13.74x + 6.682, with an R^2 value of 0.995. The sensitivity of the SWCNT/ZnO-modified electrode is higher than bare GCE. A sensitivity response of 13.7 µA/mM was obtained, which is in the same order of magnitude with the previously reported value of 50 mA/M [20]. The SWCNT/ZnO nanocomposite film that attached on the electrode surface influenced the electron transfer. The detection limit of the method based on a SWCNT/ZnO-modified electrode was estimated to be 85 µm, which is similar to those reported by using different types of modified electrodes [14, 22]. This suggests that the hybrid of SWCNT/ZnO nanomaterials transfer electrons well to provide a lower detection limit.

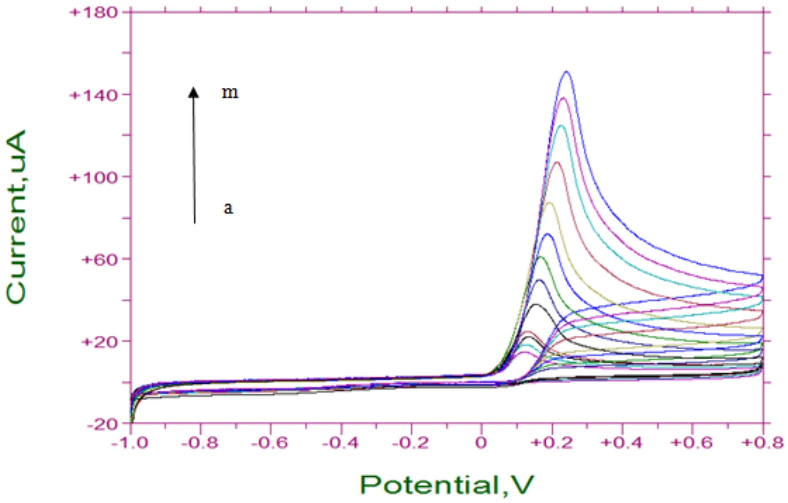

Figure 6. Plot of oxidation current versus ascorbic acid concentrations in 0.1 M KH_2PO_4 using a SWCNT/ZnO-modified electrode at a scan rate of 50 mV/s. Ascorbic acid concentrations: (a) 0.2, (b) 0.5, (c) 0.7, (d) 1.0, (e) 2.0, (f) 3.0, (g) 4.0, (h) 5.0, (i) 6.0, (j) 7.0, (k) 8.0, (l) 9.0 and (m) 10.0 mM.

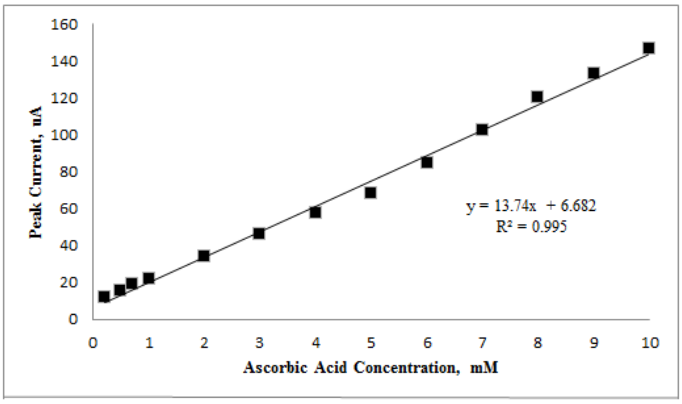

Figure 7. Calibration graph of ascorbic acid in 0.1 M KH_2PO_4 using a SWCNT/ZnO-modified electrode versus Ag/AgCl.

3.5. Effect of temperature

The study of temperature effect on the oxidative peak current of 3.5 mM ascorbic acid at SWCNT/ZnO-modified electrode in 0.1M KH_2PO_4 supporting electrolyte was conducted. Figure 8 shows a plot of log oxidative current of ascorbic acid versus reciprocal of temperature. The peak current increased gradually with the increases of temperature in the range of 20 °C – 85 °C.

The plot indicates a linear relationship of oxidative peak current with the elevation of temperature and the linear regression equation is y = -0.458x + 3.384 with R^2 = 0.984. The relationship fairly agrees with thermodynamic expectation of Arrhenius equations Eq. 1 and Eq. 2 [21].

$$\sigma = \sigma^o \exp(-E_a/RT) \quad (1)$$
$$D = D^o \exp(-E_a/RT) \quad (2)$$

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

The increase in the anodic peak current may be due to the changes in the conductivity of the modified electrode. This suggests that the SWCNT/ZnO nanocomposites on the electrode surface influenced the activation energy. From the slope of the relationship, the value of activation energy, E_a is 3.81 kJ/mol. The increase in temperature exerts some influence on the activation energy for the diffusion of ascorbic acid. The E_a value for the SWCNT/ZnO-modified GCE in the electrocatalysis of ascorbic acid is lower than the literature value of 5 kJ/mol, at a bismuth oxide modified GCE by Zidan and co-workers [20].

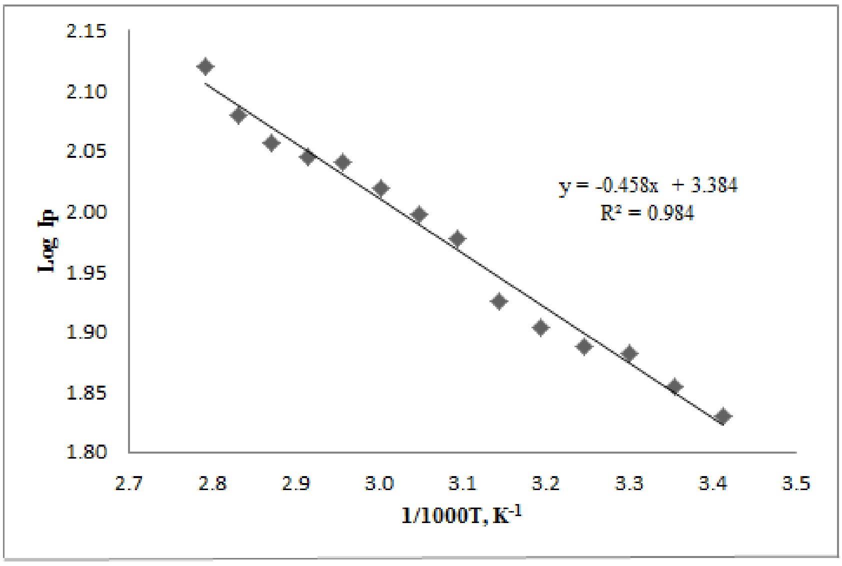

Figure 8. Plot of oxidative peak current versus reciprocal of temperature for the electrolysis of 3.5 mM ascorbic acid in 0.1 M KH_2PO_4 at SWCNT/ZnO-modified electrode. Scan rate: 50 mV/s.

3.6. Effect of pH

The effect of pH of the supporting electrolyte on the electrochemical response of ascorbic acid was investigated from pH 2 to 13. The pH of the KH_2PO_4 electrolyte solution was regulated by small amounts of NaOH and HCl solutions.

Figure 9 depicts the effect of pH on the oxidative peak current of ascorbic acid determination. The variation in pH values show remarkable effects on the oxidative peak current and peak potential. The peak current increased with the increase of pH from 2 to 5 and reached its maximum between pH 4 – 5. The peak current gradually decreased as the pH increased from 6 to 10 and had another rise in pH 11-12. This indicates that deprotonation involved in the oxidation process of ascorbic acid which facilitated at lower pH values. In the higher pH solution, the electrocatalytic reaction is more difficult due to the shortage of proton. The result also showed that the peak shift towards a lower potential as the pH increased from 2 to 13.

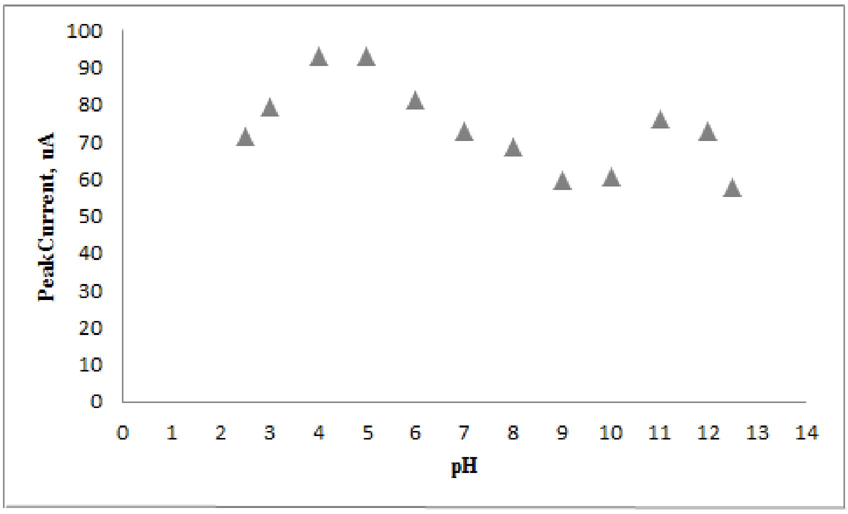

Figure 9. Plot of peak current versus pH (from 2 ~ 13) obtained at a SWCNT/ZnO-modified electrode for the oxidation of 3.5 mM ascorbic acid in a 0.1 M KH_2PO_4 supporting electrolyte.

3.7. Repeatability

Reproducibility or repeatability of the SWCNT/ZnO-modified electrode was examined by the determination of 3.5 mM ascorbic acid in a 0.1 M KH_2PO_4 supporting electrolyte. Five successive determinations were conducted on different days with a new modified electrode for each run. A relative standard deviation (*RSD*) value of 3.8% was obtained indicating that the SWCNT/ZnO-modified electrode has good reproducibility.

Table 1. Repeatability of ascorbic acid determination at SWCNT/ZnO-modified electrode.

Repeat No	Peak Current
	(µA)
1	82.79
2	75.43
3	77.87
4	80.28
5	82.16
Mean	79.71
SD	3.06
RSD (%)	3.8

3.8. Recovery of real samples

The recovery of SWCNT/ZnO-modified electrode was examined for the determination of 4.0 mM vitamin C effervescent tablets. A relative standard deviation (*RSD*) value was obtained for two real-life samples of Cebion Vitamin C (Merck) and Redoxon Double Action (Bayer). The *RSD* values of 101.1 ± 2.10% and 93.4 ± 2.96% were obtained from Cebion Vitamin C and Redoxon Double Action respectively, which demonstrated good recovery of the SWCNT/ZnO-modified electrode. The results obtained for recovery rate is similar with the bismuth oxide (Bi_2O_3) microparticles modified electrode in the concentration of 0.5 mM and 1.0 mM [20].

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/ZnO-modified electrode were used.

Real-Life Sample	Recovered Concentration (mM)		Recovery Rate (%)		Mean Recovery (%)		RSD (%)	
	Cebion	Redoxon	Cebion	Redoxon	Cebion	Redoxon	Cebion	Redoxon
1	4.15	3.92	103.7	98.1	101.1	93.4	2.10	2.96
2	4.09	3.74	102.3	93.5				
3	4.05	3.68	101.2	92.1				
4	4.02	3.68	100.4	92.0				
5	3.92	3.65	98.0	91.2				

3.9. Electrode morphology

The morphology of the nanocomposites on the electrode’s surface was characterized by using scanning electron microscope. The SEM images of the SWCNT/ZnO-modified electrode before and after electroanalysis are shown in Figure 10A and 10B. As shown in Figure 10A, the nanocomposites have a diameter in the range of 5 to 15 μm prior to electroanalysis. The irregular shape of nanocomposites formed a porous surface. Figure 10B shows the morphology of the electrode's surface after the cyclic voltammetric response of ascorbic acid in 0.1 M KH_2PO_4 electrolyte solution at a SWCNT/ZnO-modified electrode with a scan rate of 50 mV/s. It was observed that the nanocomposites increased in size from 5 – 15 to 10 – 25 μm.

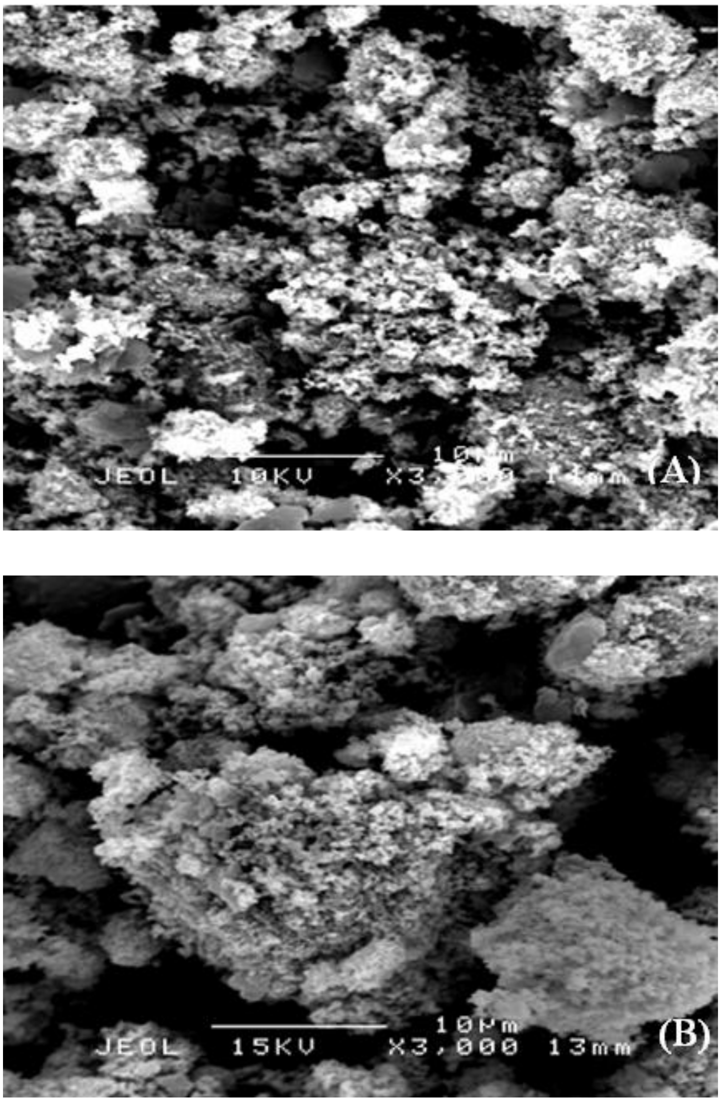

Figure 10. Scanning Electron Microscopy (SEM) of SWCNT/ZnO composites on a basal plane pyrolytic graphite electrode (BPPGE, 5 mm diameter) surface via mechanical attachment (A) before and (B) after the electroanalysis.

The elemental analysis via energy dispersive X-ray spectrometer (EDX) indicates the presence of carbon, oxygen and zinc on the electrode surface prior to electroanalysis. The spectra indicate the presence of trace amounts of phosphate and potassium in addition to carbon, oxygen and zinc subsequent to electroanalysis. This suggests that some elements from the electrolyte were introduced onto the nanocomposite's surface during electrocatalysis.

4. CONCLUSIONS

GCEs modified with the SWCNT/ZnO composites were used for the voltammetric determination of ascorbic acid. A few milligrams of carbon nanotube/nanoparticle composites were transferred to the solid electrode's surface via mechanical attachment. The characterization studies of the SWCNT/ZnO composites on the modified GCEs demonstrate high sensitivity in the detection of ascorbic acid. The fabricated electrode showed significant current enhancement and followed the diffusion controlled process. The oxidation process appears to be dependent on pH, temperature, ascorbic acid concentration and scan rate. Good repeatability and recovery rates were obtained from the oxidation of ascorbic acid in vitamin C effervescent tables. Evidently, the SWCNT/ZnO composites have potential as use as a mediator for electrochemical analysis due to its good electrode transfer properties.

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