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Electrocatalytic Oxidation of Ascorbic Acid Mediated by Lithium doped Microparticles Bi_2O_3/MWCNT Modified Glassy Carbon Electrode

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Use of a lithium doped Bismuth oxide and MWCNT modified glassy carbon electrode (Bi_2O_3/Li^+/CNT/GC) enhance the oxidation current of ascorbic acid during cyclic voltammetry compared to bare GC and (Bi_2O_3 /Li^+/ CNT) modified electrode. Peak potential was observed to shift slightly to less positive value by about 220 mV and current was significantly enhanced by about two folds. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, temperature, electrolyte and scan rate. The result of scanning electron micrograph shows that the size increased slightly by ≤ 1 µm after electrolysis using Bi_2O_3 /Li^+/ CNT modified electrode. The detection limit of this modified electrode was found to be 50µM. The oxidation current of ascorbic acid decreased slightly after the first cycle and became stable with minor decreases after second cycle. It is therefore evident that the Bi_2O_3/CNT modified GC electrode possesses some degree of stability. Potential use of Bi_2O_3/CNT as a useful electrode material is therefore clearly evident.

Keywords: Electrocataysis, Bi_2O_3 /MWCNT composite; Modified GCE; Ascorbic Acid; Cyclic Voltammetry

1. INTRODUCTION

Recently, interest in using nano-materials especially carbon nanotubes (CNT) in biosensor is becoming widespread. This is mainly the result of its high electrical conductivity, chemical stability and mechanical strength [1], in addition, CNT based electrodes also show high sensitivity with good detection limit [2]. These properties indicate that CNT has a great ability to change electron transfer reaction when used as an electrode modifying material [3]. Different types of electrodes based on CNT have been reported, such as CNT paste electrode [4-5]. These properties suggest that carbon nanotubes have fast electron transfer reaction when use as an electrode modifying material [6]. In recent years, the fabrication of chemically modified electrode (CME) is widely reported to improve sensitivity and selectivity of DNA, amino acid, vitamin, etc. [7-11]. On the other hand, Bismuth oxide is known to be an important transition metal oxide due to its characteristic parameters such as energy band gap, and photoconductivity that are suitable for large range applications [12-14]. Ascorbic acid also known as vitamin C is an organic acid soluble in water. It is responsible for building and maintaining our tissues and strengthening our immune system. It also takes part in metabolisms including the synthesis of adrenalin, inflammatory steroids, collagen, and neurotransmitters [15-19]. To our knowledge, there is no report in the literature on the enhancement of electrocatalytic oxidation of Ascorbic acid using bismuth oxide with CNT modified GC electrode. The characterization of known amount of Bi_2O_3/CNT that could catalyze the oxidation process of ascorbic acid in 0.1 M KH_2P0_4 electrolyte solution is investigated.

2. EXPERIMENTAL PART

2.1. Instrumentation and electroanalytical analysis methods

Electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring softwares were connected to computer to perform cyclic voltammetry (CV), chronoamperometry (CC) and chronoamperometry (CA). An Ag/AgCl (3M NaCl) and platinum wire were used as a reference and counter electrodes respectively. The working electrode used in this study was 3 mm diameter glassy carbon (GC). Unless otherwise stated, the voltammetric experiments were carried out at 25 ± 2^{o}C using 0.1 M KH_2P0_4 as supporting electrolyte. Solutions were degassed with nitrogen for ten minutes prior to recording the voltammogram. Scanning electrode microscopy (SEM) was used to characterize the surface of the Bi_2O_3/MWCNT composites at 5 mm diameter basal plane paralytic graphite electrode (BPPGE) (Model JOEL,JSM-64000 machine).

2.2. Reagents

A multi-walled carbon nanotubes (MWCNT) with purity of ≥95%, diameter 20–40 nm, and length of 5-15 µm was purchased from Shenzhen Nanotech and used without any further purification. Bismuth oxide (Bi_2O_3) was obtained from A Johnson Mattney Company, with 99.9% purity . Deionized water by reverse osmosis (RO) via Elken's water filteration system (BIO PURE) was used in the preparation of solutions. Unless otherwise specified, the supporting electrolyte was 0.1 M KH_2P0_4 in aqueous media at room temperature. All solutions were deaerated with oxygen-free nitrogen gas for 15 minutes prior to making the measurement.

2.3. Procedures

MWCNTs powder and Bismuth oxide (Bi_2O_3) were transferred to the surface of glassy carbon (GC) as follows: ratio amounts of 1:3 mg of Bi_2O_3 and MWCNTs respectively. Mixture (composites) of Bi_2O_3/MWCNTs was mechanically transferred to the surface of a 3 mm diameter GCE. Bi_2O_3/MWCNTs modified glassy carbon surface was cleaned after the measurement by physical removal of the coat/film, followed by polishing with 0.5µm alumina slurry, and ultrasonic cleaning for 1 minute.

3. RESULTS AND DISCUSSION

3.1. Enhancement Study

Figure 1 shows the cyclic voltammograms obtained for the oxidation of ascorbic acid in 0.1 M KH_2P0_4 supporting electrolyte at pH 6.0 at bare (unmodified) GC electrode (a), Bi_2O_3 /GC modified electrode (b), Bi_2O_3/Li^+/GC modified electrode (c)and Bi_2O_3/Li^+/CNT/GC modified electrode (d). The voltammogram showed that the oxidation potential of ascorbic acid appears at 420 mV vs Ag/AgCl and there is an absence of electroactivity on the reverse scan or rereduction indicating the oxidation process is irreversible. While at the modified GC electrode, peak shift of 180 mV and 220 mV towards less positive region was observed for Bi_2O_3/Li^+/CNT/GC and Bi_2O_3/Li^+/GC respectively with a slight current increase as compared to those of an unmodified electrode. However, at Bi_2O_3/Li^+/CNT/GCE current increases by 2.1 times with a similar peak shift as those of Bi_2O_3/Li^+/GCE, indicating presence of a electrocatalysis process effected by the Bi_2O_3/Li^+, and Bi_2O_3/Li^+/CNT coating. In subsequent studies, various chemical and physical effects were assessed in order to determine the optimum conditions under which maximum current response at the Bi_2O_3/Li^+/CNT/GC electrode can be obtained.

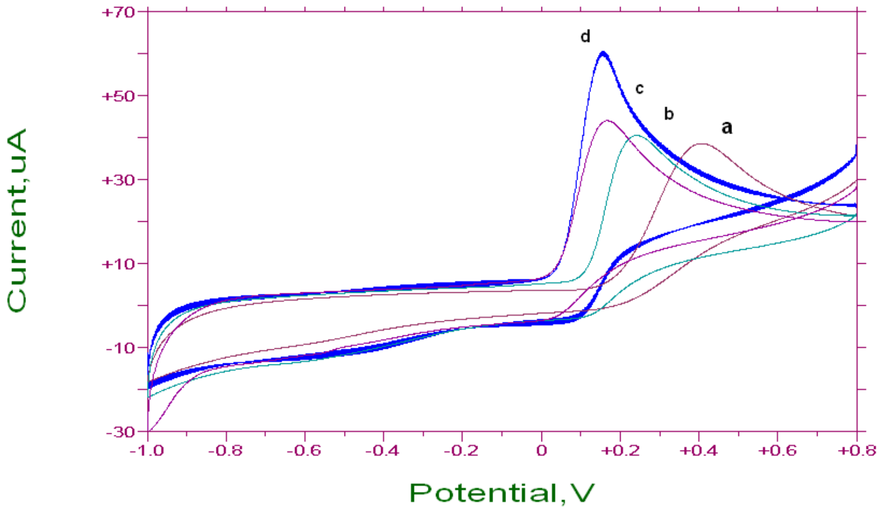

Figure 1. Cyclic voltammetry of 0.5mM ascorbic acid in 0.1 M KH_2P0_4 , at pH4.6 for the (a) GC working electrode, (b) Bi_2O_3/GC modified electrode (c) Bi_2O_3/Li^+/GC modified electrode (d) Bi_2O_3/Li^+/CNT/GC modified electrode.

3.2. Effect of varying pH

The solution was varied from pH 2.0 to 11 in order to determine its effect on the catalytic oxidation of ascorbic acid at the lithium doped $Bi_2O_3/Li^+/CNT/GC$ modified electrode. Figure 2 shows that the oxidation current of 0.5 mM ascorbic acid increases with an increase in pH between 2.7 to 4.5 with a maximum current response at pH6. However, the pH range for current decreased gradually from pH 6 onward until pH 11.

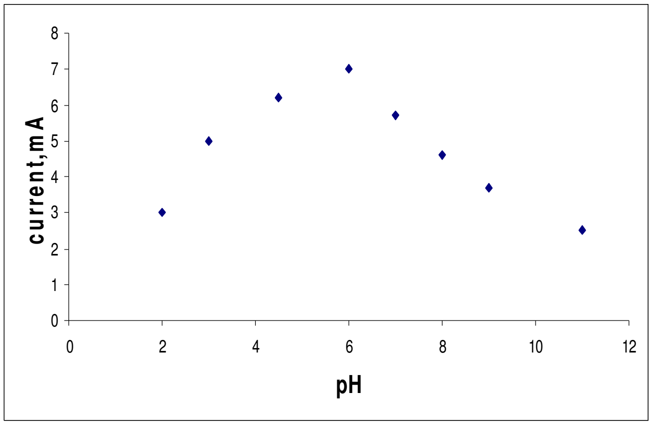

Figure 2. Graph of current versus pH for 0.5 mM ascorbic acid in 0.1 M KH_2P0_4 in different pH, for The $Bi_2O_3/Li^+/CNT/GC$ modified electrode.

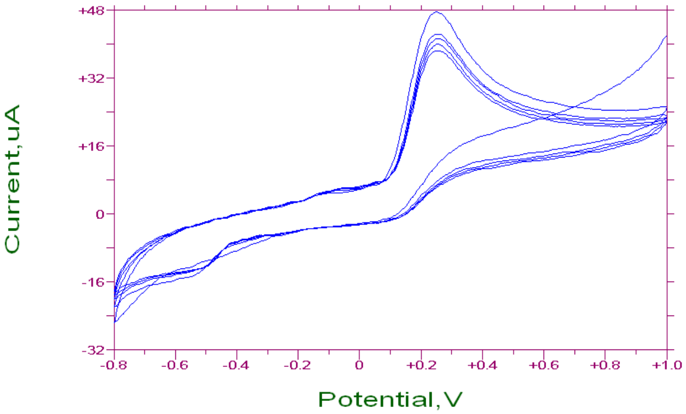

Figure 3. Multiple Cycle voltammetry of 0.5 mM ascorbic acid in 0.1 M KH_2P0_4 at pH 6, for the $Bi_2O_3/Li^+/CNT/GC$ modified electrode.

3.3. Effect of potential cycling

The stability of the lithium doped Bi_2O_3/CNT modified electrode and its effect on the ascorbic acid oxidation current were assessed by continuous potential cycling over the potential range where ascorbic acid is electroactive. Fig. 3 shows that the current associated with oxidation of ascorbic acid decreased slightly after the first cycle of and remains unchanged from the fourth cycle onward. Even after 20th potential cycle, the oxidation peak of ascorbic acid remains high; reflecting the stability of $Bi_2O_3/Li^+/CNT$ coating.

3.4. Effect of varying scan rate

The effect of varying scan rates on the cyclic voltammograms of 0.5 mM ascorbic acid using lithium doped Bi_2O_3/CNT modified working electrode in 0.1 M KH_2P0_4 supporting electrolyte was studied over 5 – 1000 mV/s. Oxidation currents of ascorbic acid was observed to increase with scan rate due to heterogeneous kinetics. Based on a plot of log peak current versus log scan rate (Figure 4), v for oxidation current of ascorbic acid, a straight line was obtained fulfilling the equation $y = 0.47x + 0.67$ with $R^2=0.9953$. A slope of 0.47 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process.

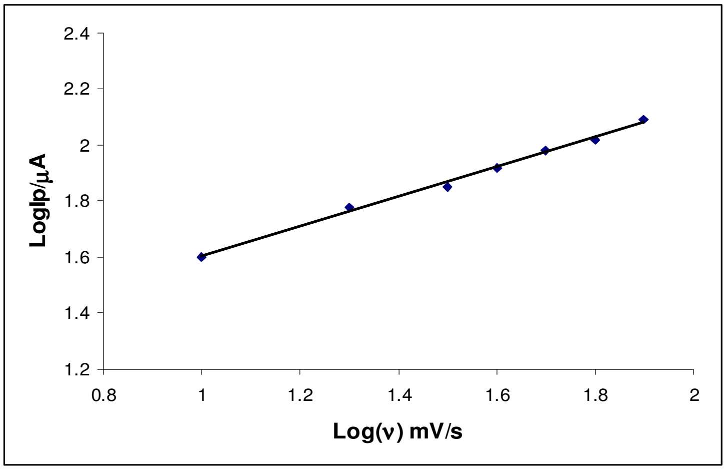

Figure 4. Graph of log peak current versus log scan rate for 0.5mM ascorbic acid in 0.1 M KH_2P0_4 in different scan rate, for the Bi_2O_3/Li^+/CNT/GC modified electrode.

3.5. Effect of Temperature

Effect of temperature on the oxidation process of ascorbic acid was studied. The current increases gradually at the temperature of 20°C to 80°C . (Voltammogram is not shown) The plot of log oxidation current of ascorbic acid versus reciprocal of temperature was found to be fairly linear in agreement with thermodynamic expectation of Equations 1 and 2. The increase in oxidation current of ascorbic acid may be due to the conductivity of the Bi_2O_3/CNT particles with the increase in temperature, as can be described by the Arrhenius equations (Eq.1 and 2) given below.

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

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

Where σ/D are conductivity/diffusibility and σ^o/D^o are standard conductivity/the initial diffusibility. However while use at elevated temperature can give an increase in current, in a practical sense application need to be continued close to ambient temperature, 25°C [20-22].

3.6. Effect of varying ascorbic acid concentrations

Figure 5 shows the calibration graph of ascorbic acid in 0.1M KH_2P0_4. Linear response was achieved over the concentration range from 0.02 to 5 mM, which showed correlation of 0.995 R^2 value. The sensitivity of the modified electrode obtained from the linear equation slope was close to 24 mA L M^{-1}.

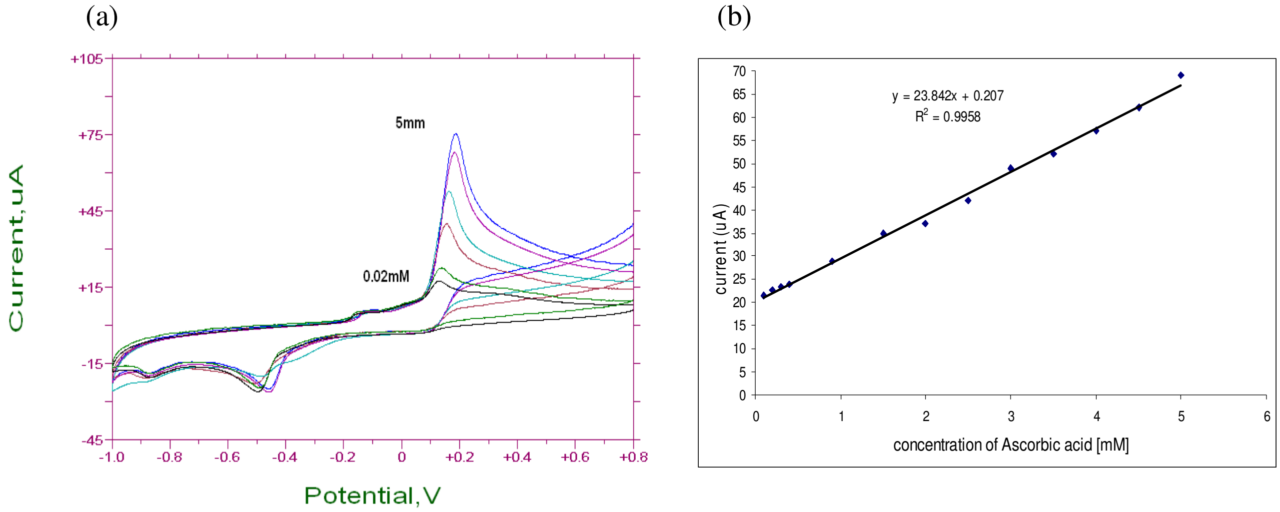

Figure 5. (a) Typical cyclic voltammograms of various ascorbic acid concentrations at $Bi_2O_3/Li^+/CNT/GC$ electrode immersed in 0.1 M KH_2P0_4, pH 6.0, at scan rate of 100 mV/s (b) Calibration graph of ascorbic acid (Similar conditions as above).

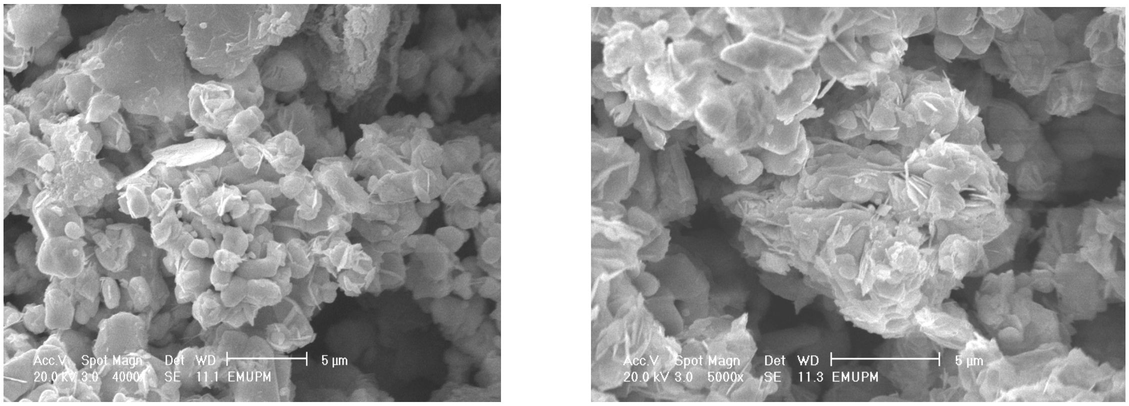

Figure 6. Scanning electron micrographs of $Bi_2O_3/Li^+/CNT$ modified GC electrode to a basal plane pyrrolitic graphite electrode (a) before and (b) after electroanalysis.

3.7. Scanning Electron Microscopy

As is shown in figure 2, prior to the application of a reducing potential, Bismuth oxide had a size range of the order of 0.4 - 3 µm in diammeter. After the controlled-potential electrolysis in the presence of ascorbic acid using Bi_2O_3/ CNT modified electrode, the size increased slightly to 1 – 4 µm with improved crystaline structure under the magnification of 4000-5000 times.

4. CONCLUSIONS

The result presented here demonstrates the use of MWCNT/ Li^+/ Bi_2O_3 composites modified glassy carbon electrode is highly sensitive and stable in electrochemical measurement. Electrocatalytic response and stability were improved when MWCNT/ Li^+/ Bi_2O_3 were used as compared to when only Bi_2O_3/GCE modified and unmodified GCE were used. Peak potential was observed to shift slightly to less positive value by about 220 mV and current was significantly enhanced by about two folds indicating an electrocatalysis process due to the presence of Bi_2O_3/Li^+/CNT microparticles. The oxidation current of ascorbic acid decreases slightly after the first cycle and remains stable after the fourth cycle. It is therefore evident that the Bi_2O_3 modified GC electrode possess some degree of stability. Potential use of Bi_2O_3/CNT as a useful electrode material is therefore clearly evident.

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