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Electrocatalytic Oxidation of Paracetamol Mediated by Lithium Doped Microparticles Bi_2O_3/MWCNT Modified Electrode

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Use of a lithium doped bismuth oxide and multi-walled carbon nanotubes modified glassy carbon electrode (Bi_2O_3/Li^+/CNT/GC) enhance the oxidation current of paracetamol during cyclic voltammetry compared to bare glassy carbon electrode 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 3.2 folds. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, temperature and scan rate. Calibration plot reveals linearity from the range 5.0×10^{-7}-2×10^{-3} M with a correlation coefficient of 0.998. The detection limit was estimated to be 7.4×10^{-7} M. Practically; Bi_2O_3/CNT modified electrode could be used for the determination of parecetamol in tablet samples.

Key Words: Electrocataysis, Bi_2O_3/MWCNT composite, Modified GCE, Paracetamol, Cyclic voltammetry.

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]. Acetaminophenol or paracetamol is one of the most commonly used analgesics in pharmaceutical formulations, for the reduction of fever and also as a painkiller for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain. Acetaminophen is electroactive and voltammetric mechanistic studies for the electrode processes of the acetaminophenol/N-acetyl-*p*-quinoneimine redox system has been presented[15-21]. To our best of knowledge, there is no report in the literature for the enhancement of electrocatalytic oxidation of paracetamol 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_2PO_4 electrolyte solution is investigated.

EXPERIMENTAL

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 (3 M 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 ºC using 0.1 M KH_2PO_4 as supporting electrolyte. Solutions were degassed with nitrogen for 10 min prior to recording the voltammogram. Scanning electrode microscopy (SEM) was used to characterize the surface of the MWCNT composites at 5 mm diameter basal plane paralytic graphite electrode (BPPGE) (Model Joel, JSM-64000 machine).

Multi-walled carbon nanotubes clearly shows nanofibers, where the graphitic planes are parallel to the axis[22] and some of them were joined together (Fig. 1). The stability of the film

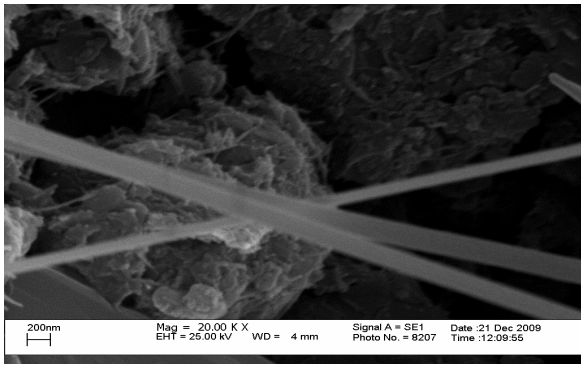


Fig. 1. Scanning electron micrographs of an array MWCNT microparticles mechanically attached to a basal plane pyrolitic graphite electrode, reduced at -1000 mV *versus* Ag/AgCl in aqueous electrolyte containing 0.1 KH_2PO_4

was evident as the scanning electron micrograph remains unscattered even after many cycling.

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. Paracetamol tablet brand named Tempol from, Pharmaceuticals Ltd. in (Malaysia) was used. 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_2PO_4 in aqueous media at room temperature. All solutions were deaerated with oxygen-free nitrogen gas for 15 min prior to making the measurement.

Procedures: Multi-walled carbon nanotubes (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 0.5 μm alumina slurry and ultrasonic cleaning for 1 min.

RESULTS AND DISCUSSION

Enhancement study: Fig. 2 cyclic voltammograms obtained for the oxidation of paracetamol in 0.1 M KH_2PO_4 supporting electrolyte at pH 4.6 at 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 paracetamol appears at 611 mV *versus* Ag/AgCl and there is an absence of electroactivity on the reverse scan or rereduction indicating the oxidation process is reversible. While at the modified GC electrode, peak shift of 180 and 210 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 3.2 times with a similar peak shift of 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.

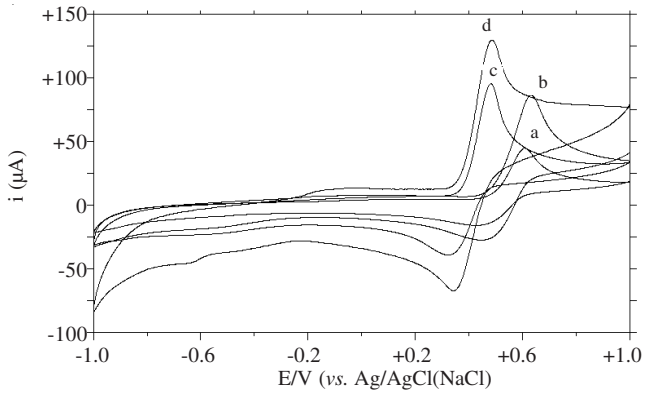


Fig. 2. Cyclic voltammetry of 0.1 mM paracetamol in 0.1 M KH_2PO_4, at pH 4.6 for the (a) GC working electrode, (b) Bi_2O_3/GC modified electrode (c) Bi_2O_3/Li^+/GC modified electrode (d) Bi_2O_3/Li^+/CNT/GC modified electrode

Effect of varying pH: The solution was varied from pH 2-11 in order to determine its effect on the catalytic oxidation of paracetamol at the lithium doped Bi_2O_3/Li^+/CNT/GC modified electrode. Fig. 3 shows that the oxidation current of 0.1 mM paracetamol increases with maximum current enhancement at pH 4.6. After that the current slowly decreased from pH 4.6-10.0. As can be seen, the peak potential for paracetamol oxidation varies linearly with pH and is shifted to more negative potentials with increase in pH.

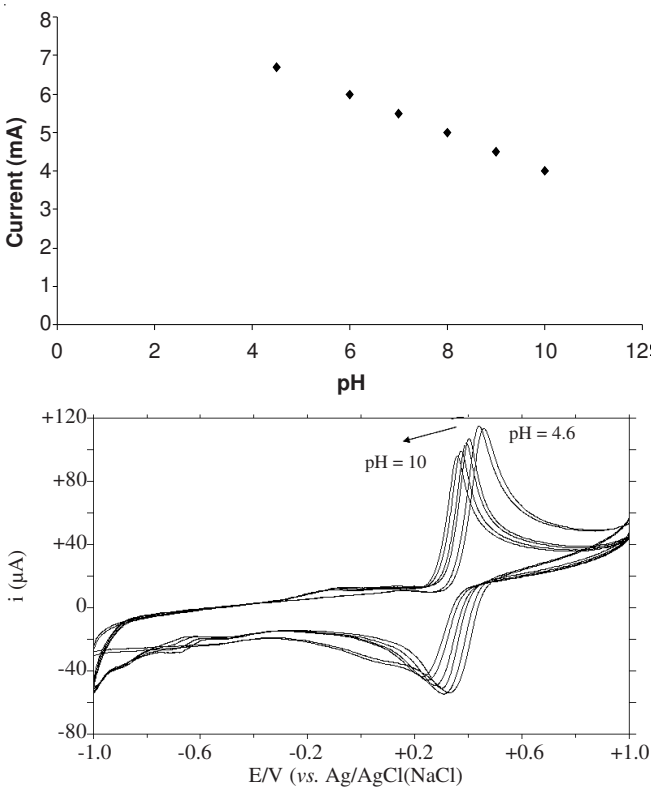


Fig. 3. Graph of current *versus* pH for 0.1 mM paracetamol in 0.1 M KH_2PO_4 in different pH, for the GC modified electrode with lithium doped Bi_2O_3/CNT/GC modified electrode

Effect of potential cycling: The stability of the lithium doped Bi_2O_3/CNT modified electrode was studied for the reversible process in 0.1 M KH_2PO_4 aqueous electrolyte using a 100 mV/s scan rate by CV. The result in Fig. 4 shows that the peak of redox current of paracetamol remained virtually constant throughout the 10 potential cycles, reflecting the stability of the Bi_2O_3/CNT composite modified GCE.

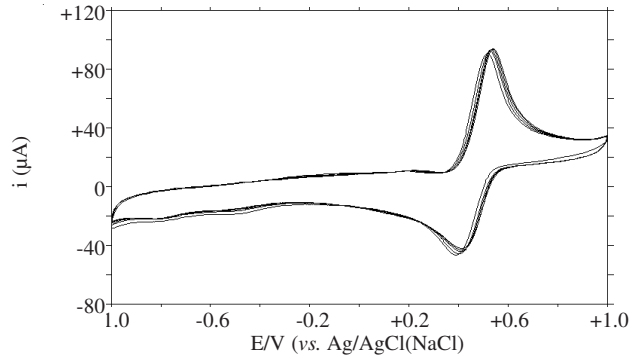
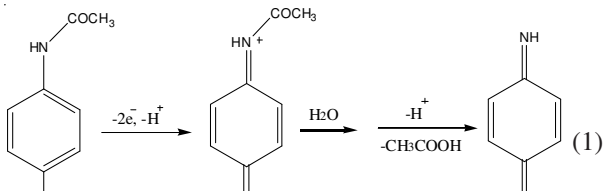


Fig. 4. Multiple cycle voltammetry of 0.1 mM paracetamol in 0.1 M KH_2PO_4 at pH 4.6, for the GC modified electrode with lithium doped Bi_2O_3/CNT/GC modified electrode

Effect of varying scan rate: The effect of varying scan rates on the cyclic voltammograms of 0.1 mM paracetamol using lithium doped Bi_2O_3/CNT modified working electrode in 0.1 M KH_2PO_4 supporting electrolyte was studied over 5-1000 mV/s. Oxidation currents of paracetamol was observed to increase with scan rate due to heterogeneous kinetics. Based on a plot of log peak current *versus* log scan rate (Fig. 5), ν for oxidation current of paracetamol, a straight line was obtained fulfilling the equation $y = 0.49x + 0.61$ with $R^2 = 0.998$. A slope of 0.49 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process. Paracetamol oxidation is a two-electron two-proton process in eqn. 3 given below. A conclusion that is consistent with that reported in the literature[23].



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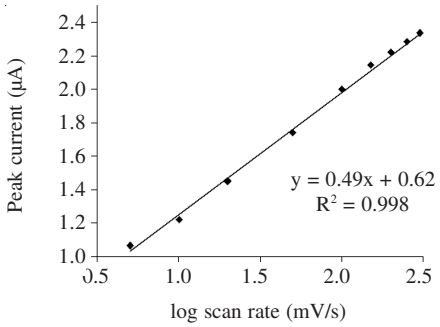

Fig. 5. Graph of log peak current *versus* log scan rate for 0.1 mM paracetamol in 0.1 M KH_2PO_4 in different scan rate, for the GC modified electrode with lithium doped Bi_2O_3/CNT/GC modified electrode

Effect of temperature: The values of the peak current and potential of varying temperature 25-80 ºC using Bi_2O_3/CNT/GC composite mechanically attached to a 3 mm GCE in presence of 0.1 mM paracetamol using CV shown in Fig. 6. The plot of log oxidation current of paracetamol *versus* reciprocal of temperature was found to be fairly linear in agreement with thermodynamic expectation of eqns. 2 and 3 given below. This indicates that the rate of the oxidation and reduction process of paracetamol species increases as the temperature increases as expected.

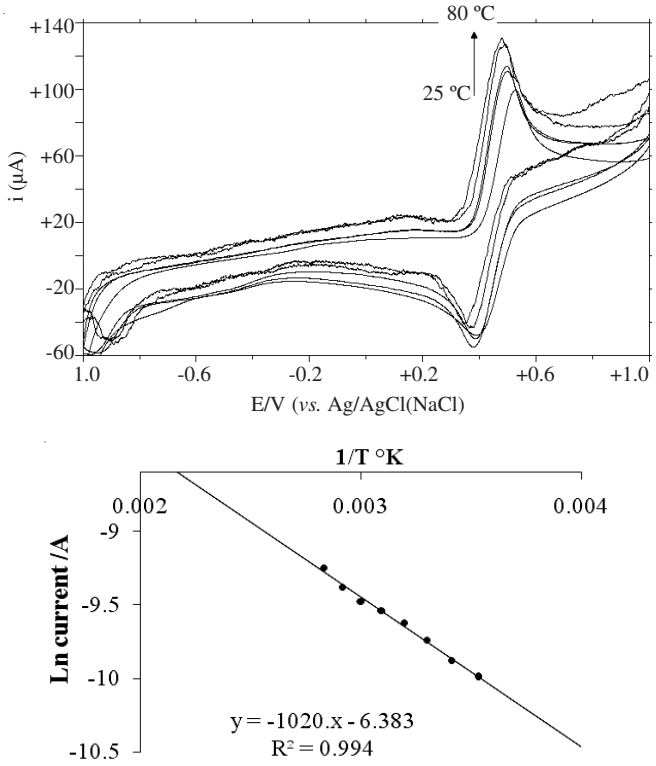

Fig. 6. Cyclic voltammograms obtained for the oxidation of 0.1 mM paracetamol using the Bi_2O_3/CNT/GCE immersed in 0.1 M KH_2PO_4 at various temperatures between 25 and 80 ºC and with a scan rate of 100 mV/s

$$\sigma = \sigma^o \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

$$D = D^o \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

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 ºC[24,25].

Effect of varying paracetamol concentrations: Fig. 7 shows the calibration graph of 0.1 mM paracetamol in 0.1 M KH_2PO_4. Linear response was achieved over the concentration range from 0-2 mM, which showed correlation of 0.998 R^2 value. The sensitivity of the modified electrode obtained from the linear equation slope was close to 14 mA L M^{-1}.

Recovery concentration of paracetamol in tablets: The recovery results are given in Table-1; the Bi_2O_3/CNT/GC

TABLE-1
RECOVERY RATES OF PARACETAMOL (0.1 mM) EXTRACTED FROM COMMERCIALLY PARACETAMOL TABLET SAMPLES IN 0.1 M KH_2PO_4 USING THE Bi_2O_3/CNT/GC MODIFIED ELECTRODE (FRESHLY PREPARED) *via* MECHANICAL ATTACHMENT METHOD

Sample	Mentioned concentration of paracetamol (mg/table)	Obtained concentration of paracetamol (mg/table)	Recovery rate (%)	Mean recovery (%)	RDS (%)
Paracetamol	125	115	94.5	95.05	2.07
		119	95.2		
		120	92.0		
		122	97.4		
		118	96.0		
Panadol	500	470	94.0	96.04	1.88
		477	95.4		
		485	97.0		
		475	95.0		
		494	98.8		

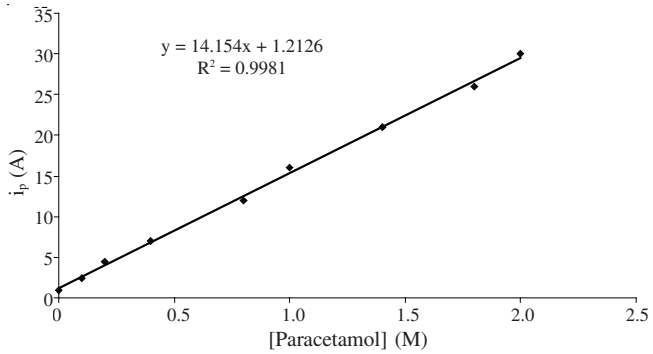

Fig. 7. Dependence of the oxidation current paracetamol on various concentrations in 0.1 M KH_2PO_4, pH 4.6 at Bi_2O_3/CNT modified GC electrode

modified electrode in detection of paracetamol was confirmed by its ability to detect in presence of paracetamol in commercially available paracetamol tablets. Cyclic voltammetry technique was used for the determination of the extracted paracetamol since it is a sensitive and rapid method with low detection limit to detect the trace amounts of paracetamol. 0.1 mM concentration of paracetamol extracted from commercial tablets such as paracetamol and panadol, which contain 125 and 500 mg paracetamol/tablet. The voltammetric detection for paracetamol extracted from commercial tablet sample using composite electrode was successfully applied and the recovery rates were 95.04 ± 2.07 % for the paracetamol tablet and 96.041 ± 1.88 % for the panadol tablet for five replicates.

Conclusion

The use of the MWCNT/Li^+/Bi_2O_3 composites modified glassy carbon electrode was extended and successfully applied in the determination of paracetamol in real pharmaceutical sample by CV technique. 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 3.2 folds indicating an electrocatalysis process due to the presence of Bi_2O_3/Li^+/CNT microparticles. The oxidation current of paracetamol remains stable after the 10th cycle. This technique is able to detect paracetamol sample in clinical application and recovery rates if 95.04 ± 2.07 and 96.041 ± 1.88 % were obtained.

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