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Voltammetric Oxidation of Ascorbic Acid Mediated by Multi-Walled Carbon Nanotubes/Titanium Dioxide Composite Modified Glassy Carbon Electrode

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Abstract: A MWCNT/TiO₂ composite was modified onto glassy carbon electrode and fabricated by mechanical attachment, then applied to detection of ascorbic acid using cyclic voltammetry. Electrode responses were obtained for the oxidation of 0.5 mM ascorbic acid at the glassy carbon electrode modified with MWCNT, TiO₂, MWCNT/TiO₂ composite and an unmodified glassy carbon electrode. A well-defined and highly resolved oxidation peak of ascorbic acid at the MWCNT/TiO₂/GCE with current enhancement and peak potential shift toward the origin being observed, this indicates evidence of electrocatalytic process. In comparison with other electrodes, the observed current enhancements at the MWCNT/TiO₂/GCE were 1.3 folds higher than those obtained by MWCNT/GCE and 1.5 folds by a bare glassy carbon electrode. The response peak current revealed a good linear relationship of up to 2.5 mM ascorbic acid with correlation coefficient of 0.998. A good detection limit of 4.0 μM was found using MWCNT/TiO₂/GCE. Other usual parameters such as effect of pH, scan rate, temperature, supporting electrolyte and concentration of ascorbic acid were studied.

Key words: Nanoparticles, composite, mechanical attachment, ascorbic acid, cyclic voltammetry

INTRODUCTION

Nanostructured materials such as carbon nanotubes (CNT), nanoparticles of metal and metal oxide have recently received much attention from researchers. CNT is known to exhibit excellent electrocatalytic activity, which gives rise to its good electrochemical behavior. Thus, it has been used as an electrode modified composite when combined with metal and metal oxide nanoparticles, such as Au (Alexeyeva *et al.*, 2006), Pt (Wang *et al.*, 2007a), Pd (Chen *et al.*, 2009), Ag (Xiao *et al.*, 2007), Cu (Chai *et al.*, 2008), Ni (Wang *et al.*, 2007b) and ZnO₂ (Deng *et al.*, 2008), RuO₂ (Deng *et al.*, 2005), MnO₂ (Sivakkumar *et al.*, 2007), SnO₂ (Pang *et al.*, 2009), Fe₂O₃ (Hang *et al.*, 2008), TiO₂ (Jiang and Zhang, 2009) or polymeric binder composite (Tsai *et al.*, 2004; Wang and Musameh, 2003).

Similarly, multi-walled carbon nanotubes (MWCNT) has attracted considerable attention in the voltammetric study since its discovery by Iijima (1991), because of its unique structural, electronic, mechanical and electrochemical properties (Nguyen *et al.*, 2001; Gooding, 2005). These properties suggest that CNT causes fast electron transfer reaction when used as an electrode

modifying material (Nugent *et al.*, 2001). On the other hand, titanium dioxide (TiO₂) is a good semiconductor, which shows an excellent chemical reaction in the photocatalysis (Khuanmar *et al.*, 2007), especially oxidation and reduction of organic or inorganic substances (Fox and Dulay, 1993). Although TiO₂ alone has poor electrochemical activity, when combined with MWCNT, the electrocatalytic property of MWCNT is much improved.

Also, the surface chemistry has been studied at poly- and mono-crystalline phase of TiO₂ nanoparticles (Diebold, 2003), hence when coupled with MWCNT; it provides a synergistic effect that improves the electrochemical performance of MWCNT. A number of reports have shown that MWCNT/TiO₂ composition material has been receiving due attention in many investigations. Various researchers have studied the preparation of MWCNT/TiO₂ either through the use of composition or mixture, using several methods, for example, sol-gel (Gao *et al.*, 2009), CVD (Kuo, 2009; Wang *et al.*, 2008), VPT (Zhang *et al.*, 2008), UV (Ueda *et al.*, 2009), EPD (Jarembon *et al.*, 2008) and also simple direct mixing method (Sawatsuk *et al.*, 2009; Ahmmad *et al.*, 2008). However, to the best of our

knowledge, only scant attention has been paid to MWCNT and TiO₂ composite modified electrode in the voltammetric determination of some vitamins and amino acids.

In this study, we prepared a known amount of MWCNT with TiO₂ as a composite using simple mixing method. The MWCNT/TiO₂ composite was modified on the surface of glassy carbon electrode (GCE) via mechanical attachment and studied in the oxidation process of ascorbic acid in aqueous electrolyte. Result has shown that the modified electrode has a good electrochemical behavior in terms of stability, reproducibility and an achievable detection limit. We also found that it exhibits a good potential as a chemically modified electrode for electrochemical and biochemical research.

MATERIALS AND METHODS

Black powder of MWCNTs (purity >95%, diameter~20-40 nm, length~5-15 μm) were obtained commercially (from Shenzhen Nanotech) and used without further purification. TiO₂ nanoparticles solution (TiO₂ dispersed in water by 5% weight, <100nm particle size) and L-ascorbic acid (minimum purity of 99.7%) were purchased from Aldrich (USA). Solution containing ascorbic acid was freshly prepared before running each experiment. Other chemicals used during the experiment were of analytical grade reagents. All solutions were prepared with deionized distilled water and deaerated with oxygen-free nitrogen gas for 15 min before each measurement.

Instrumentation and apparatus: The most of the voltammetric experiments were performed by BAS (Bioanalytical Systems, West Lafayette, Indiana, USA): CV-50W electrochemical workstation, which connected to an external computer was used. A conventional three-electrode cell system was employed; a platinum wire served as a counter electrode; an Ag/AgCl (in 3 M NaCl) as a reference electrode; a bare GCE and a CGE modified with TiO₂, MWCNT, MWCNT/TiO₂ composite as working electrodes. A bare working electrode (3 mm diameter) was polished with alumina slurry, ultrasonic grinded for 1 min and rinsed with distilled water before use. The morphology of the MWCNT/TiO₂ composite was characterized on the surface of 5 mm diameter basal plane pyrolytic graphite electrode (BPPGE) before and after electrolysis by scanning electron microscopy (SEM - Model JOEL, JSM-6400 machine).

Preparation of the MWCNT/TiO₂ composite: MWCNT powder and stock solution of TiO₂ (dispersed in water by

5% weight) were prepared and ready for usage. Five milligram of MWCNT was placed in a glass plate and then mixed with 0.1 mL TiO₂. The composite were dried at room temperature for 30 min; it was later mechanically transferred to the surface of bare GCE.

RESULTS AND DISCUSSION

Scanning electron microscopy study: Figure 1 shows SEM image of the MWCNT/TiO₂ composite surface before (Fig. 1a, c) and after (Fig. 1b, d) electrolysis in the presence of ascorbic acid at 5 mm diameter BPPGE. The morphology of the MWCNT/GCE via mechanical attachment was reported (Radhi *et al.*, 2010). The structure of composite shaped a homogeneous film/coating on the BPPGE surface (Fig. 1a, b). As can be seen at magnification of 10,000 (Fig. 1c, d) times, MWCNT was clearly shown and thin fibers which formed into bundles with some of them joined together. The stability of the film was evident as the SEM image remains un-scattered even after 10 potential cycling.

Enhancement study: Cyclic voltammograms were obtained for the oxidation of 0.5 mM ascorbic acid in 0.1 M KCl aqueous solution over the potential range of -400 mV to +1000 mV versus Ag/AgCl (in 3 M NaCl) at GCE modified with TiO₂, MWCNT, MWCNT/TiO₂ composite and an unmodified (bare) GCE. The oxidation process of ascorbic acid appears irreversible. Voltammograms were successfully recorded on the surface of various modified and unmodified electrodes with different responses. Result of Fig. 2 shows that the MWCNT modified GCE (Fig. 2 (curve b)) produces a greater oxidative current response of ascorbic acid while the TiO₂ modified GCE (Fig. 2 (curve d)) appears to cause a decrease in the oxidation current of ascorbic acid.

However, when a TiO₂ was coupled to MWCNT, it further enhances the electrocatalytic activity of MWCNT as evident in the enhanced oxidation peak observed at +220 mV at the MWCNT/TiO₂ composite modified GCE (Fig. 2 (curve a)). The oxidation peak currents of ascorbic acid at the MWCNT/GC modified and the MWCNT/TiO₂/GCE modified surfaces were obtained with enhancements of about 1.3 folds and 1.5 folds as compared with an unmodified GCE (Fig. 2 (curve c)). It was interesting to note that the peak current of ascorbic acid at the MWCNT/TiO₂/GCE was more resolved than those obtained for the MWCNT/GCE modified and an unmodified electrode. The oxidation peak potential of ascorbic acid was found to shift by -60 mV, -26 mV toward the origin (negative) and +27 mV to positive value when the MWCNT/TiO₂/GC, MWCNT/GC and TiO₂/GC

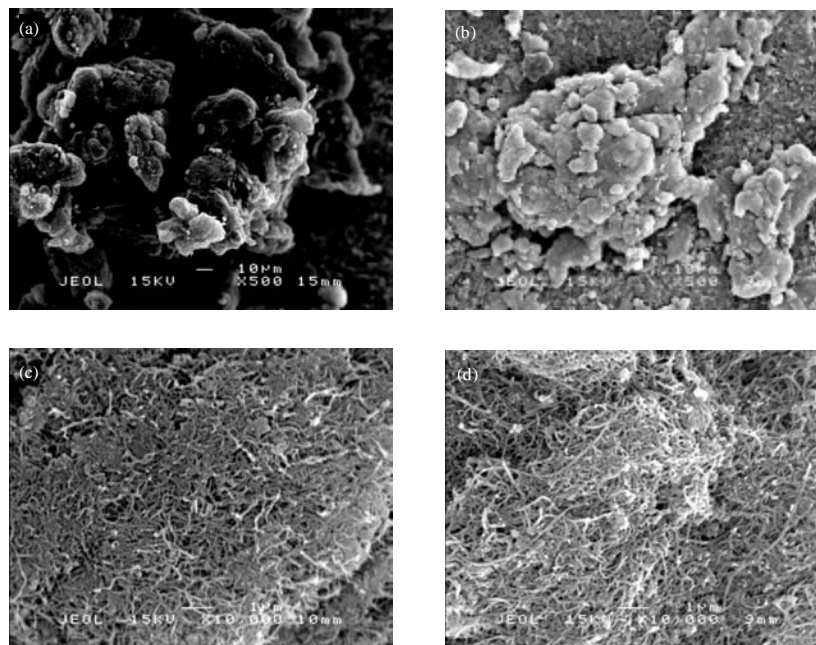


Fig. 1: SEM image of the MWCNT/TiO₂ composite shows on BPPGE surface before electrolysis (a, c) and after electrolysis (b, d) at magnifications of 500 and 10,000 times

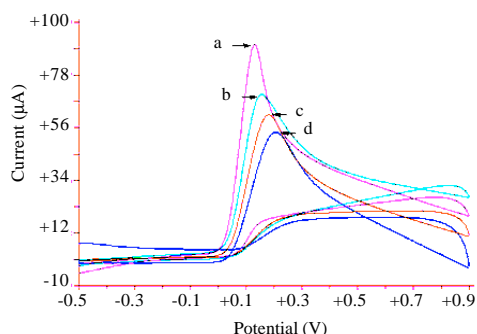


Fig. 2: Cyclic voltammogram obtained for the oxidation of 0.5 mM ascorbic acid in 0.1 M KCl solution with a scan rate of 100 mV sec⁻¹ at the (a) MWCNT/TiO₂/GCE; (b) MWCNT/GCE; (c) bare GCE and (d) TiO₂/GCE without MWCNT (after background subtracted)

modified electrodes when compared to that of an unmodified GCE. Therefore, the MWCNT/TiO₂/GCE modified electrode which appears to be more sensitive of all the electrodes was used in the subsequent studies.

Effect of potential cycling: The potential cycling for the oxidation of ascorbic acid in 0.1 M KCl was carried out at the MWCNT/TiO₂ composite modified GCE by Cyclic

voltammetry (Fig. 3). From the first cycle of the voltammogram, the peak current of ascorbic acid decreased slightly. Then it was established and even after 10th potential cycle, the oxidation peak remained high. Only about 20% decrease in current was observed; reflecting its stability. Furthermore, Faradaic activity was reproducible at the MWCNT/TiO₂ composite modified solid state electrode.

Effect of pH: The next experiments were carried out to determine the effect of pH on the voltammogram of ascorbic acid mediated by the MWCNT/TiO₂ composite modified electrode (Fig. 4). It was observed that the oxidative peak current of ascorbic acid was high, more pronounced and almost constant under acidic condition, but slightly decreased in neutral condition. Additionally, potential responses were similar, which means working range of pH is wider in this condition, but fell with the increase of pH value. The peak current decreased significantly and shifted to negative potential direction from pH value of 6.0 onward. The capacitance current of all solutions varied little under different pH conditions. So, it is reasonable to apply pH range of between 2.0 and 6.0 for further experimentation.

Effect of varying scan rate: The effect of scan rate on the anodic peak current of 0.5 mM ascorbic acid in 0.1 M KCl at the MWCNT/TiO₂/GCE was studied using different

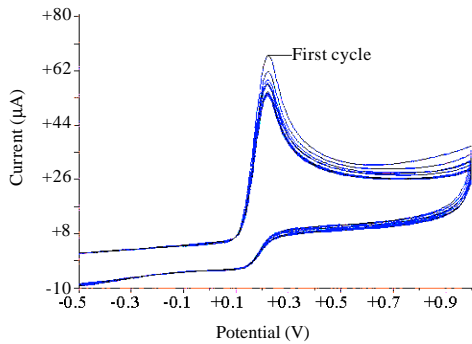


Fig. 3: Cyclic voltammogram of potential cycling for the oxidation of ascorbic acid at the MWCNT/TiO₂/GCE in 0.1 M KCl solution with a scan rate of 100 mV sec⁻¹ for 10 cycles

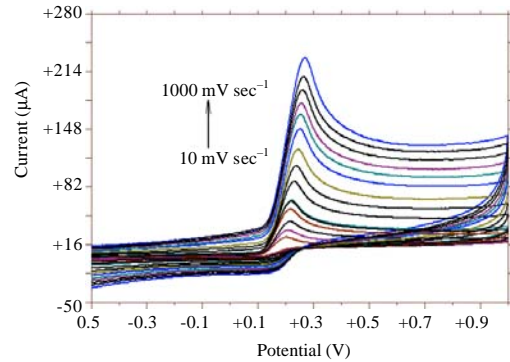


Fig. 5: Cyclic voltammogram obtained for the oxidation of ascorbic acid in 0.1 M KCl at the MWCNT/TiO₂/GCE with different scan rates of 10-1000 mV sec⁻¹

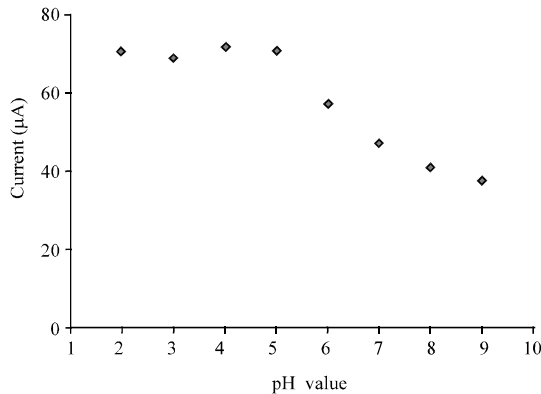


Fig. 4: A plot showing the dependence of pH value for the oxidation of ascorbic acid in 0.1 M KCl mediated by the MWCNT/TiO₂/GCE at different pH solutions

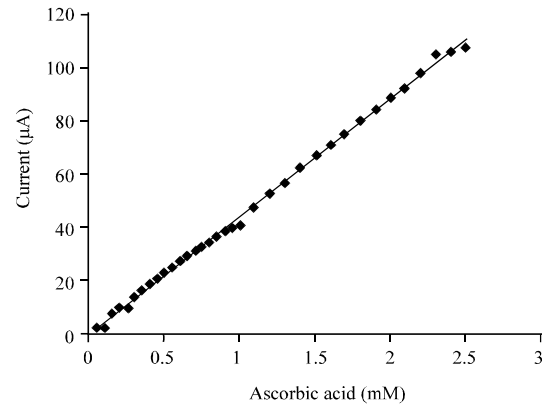


Fig. 6: A plot showing the dependence of the oxidation current on different concentration of ascorbic acid in 0.1 M KCl solution at the MWCNT/TiO₂/GCE with a scan rate of 100 mV sec⁻¹

scan rates in the range of 10-1000 mV sec⁻¹. It was observed that when the scan rate increased, the anodic peak potential was shifted slightly to the positive direction and the oxidative current of ascorbic acid increases, which was also affected by heterogeneous kinetics and IR drop effect as shown in Fig. 5. Oxidation peak current of ascorbic acid versus scan rate was plotted linearly and equation is shown as $y = 0.45x + 0.88$ with $R^2 = 0.992$. An experimental slope of 0.45 was obtained, which is close to the theoretical value of 0.5, indicating that the current is largely diffusion controlled.

Calibration graphs: Figure 6 presents the dependence of the voltammetric response to the MWCNT/TiO₂ composite modified GCE in the addition of different ascorbic acid concentrations ranging between 0.05-2.5 mM in 0.1 M KCl electrolyte solution. From the

oxidative current against concentration of ascorbic acid up to 2.5 mM, it showed a linear relationship of $R^2 = 0.998$, based on the equation $y = 44.03x + 0.314$ with a high sensitivity of response at 44 $\mu\text{A mM}^{-1}$ and a good detection limit of 4 μM for ascorbic acid detection.

Effect of varying supporting electrolytes: Based on the pH study, different types of 0.1 M aqueous supporting electrolytes with neutral conditions were studied. In the presence of SO_4^{2-} and H_2PO_4^- in electrolyte, ascorbic acid peak currents were in slightly negative potential shift as compared to others in electrolyte solution (Fig. 7). Most of the aqueous solutions observed showed no distinct changes. Similar potential ranges were obtained using electrolytes solutions of KCl, NH_4Cl and KClO_4 . Consequently, an aqueous solution of KCl was chosen as a main supporting electrolyte based on the highest peak

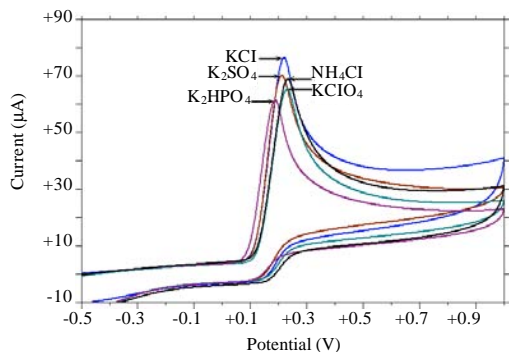


Fig. 7: Overall graph of the oxidation current of ascorbic acid at the MWCNT/TiO₂/GCE in different supporting electrolytes at 25°C with a scan rate of 100 mV sec⁻¹

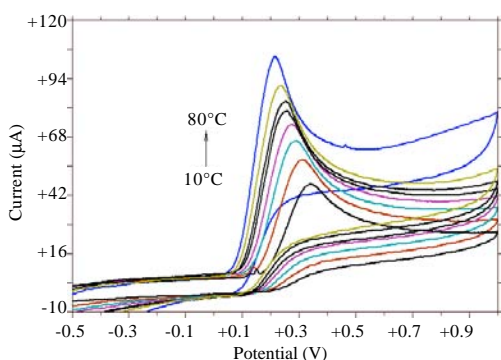


Fig. 8: Cyclic voltammograms obtained for the oxidation of ascorbic acid using the MWCNT/TiO₂/GCE immersed in 0.1 M KCl at various temperatures between 10°C and 80°C with a scan rate of 100 mV sec⁻¹

shown. Electrolyte solutions of NH₄Cl and K₂SO₄ also show good potential for usage as supporting electrolyte for oxidation of ascorbic acid using the MWCNT/TiO₂ composite modified GCE.

Effect of varying temperature study: The effect of temperature on the oxidation process of ascorbic acid was studied. Figure 8 shows a series of cyclic voltammograms obtained over temperature ranging from 10 to 80°C for the oxidation of ascorbic acid using the MWCNT/TiO₂ composite modified GCE with a scan rate of 100 mV sec⁻¹. The peak currents increased significantly and the oxidation peak potential shifted to origin when the temperature of electrolyte solution increased from

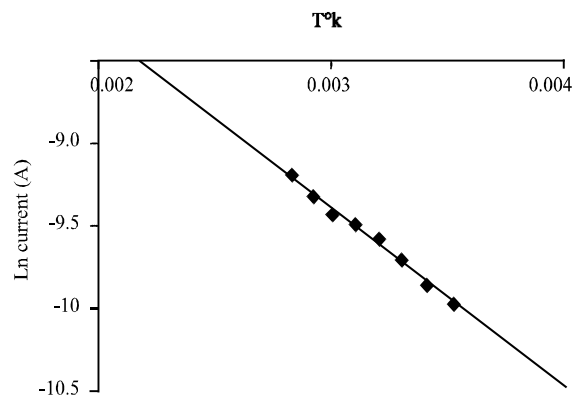


Fig. 9: A plot of Ln current against 1/Tk⁻¹ for the MWCNT/TiO₂/GCE in 0.1 M KCl electrolyte in the presence of 0.5 mM ascorbic acid in 0.1 M KCl

10-80°C. It indicates a strong dependence of solid state oxidation process on temperature.

The values of the peak current and potential of varying temperature using the MWCNT/TiO₂ composite mechanically attached to a 3 mm GCE in the presence of 0.5 mM ascorbic acid. Based on Fig. 8, a plot of the natural logarithm of oxidation current of ascorbic acid against temperature (Fig. 9) was found fairly linear with thermodynamic expectation. This plot illustrates that the oxidation current of ascorbic acid is significantly temperature dependent. Conductivity and diffusivity of solid with the increase in temperature dependence, the reason is temperature has a significant influence on the activation energy of compounds following Arrhenius equations. Based on this Arrhenius plot, the activation energy E_a = 8.5 kJ mol⁻¹ was obtained. The conductivity of the MWCNT/TiO₂ composite with the increase in temperature also plays a significant influence on the activation energy for diffusion of the substrate of interest.

CONCLUSIONS

We have demonstrated the MWCNT/TiO₂ composite using direct mixing method and fabricated by mechanical attachment method on the surface of GCE. This study shows that in the presence of TiO₂, by appear to exert negative electrocatalytic effect and require the presence of MWCNT to produce positive catalytic effect for the oxidation of ascorbic acid. The MWCNT/TiO₂ composite modified GCE response showed enhanced electrocatalytic activity as indicated by the current enhancement and peak shift to origin when it was compared to an unmodified GCE. The linear relationship was obtained from a plot of calibration graph with a high sensitivity and a good

detection limit. Though, the detected percentage of elements in composite is not very homogeneous, the preparation of composites is very simple, straight forward and easy to apply. The stability and selectivity of the composite modified electrode are adequate from the obtained results, thus, the electrode appears to be potentially of great benefit in electrochemical research.

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