

Voltammetric Detection of Potassium Ferricyanide Mediated by Multi-walled Carbon Nanotube/Titanium Dioxide Composite Modified Glassy Carbon Electrode

Ganchimeg Perenlei^{1, *}, Tan Wee Tee¹, Nor Azah Yusof^d, Goh Joo Kheng²

¹ Department of Chemistry, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor D.E., Malaysia

² School of Science, Monash University Sunway Campus, 46150 Bandar Sunway, Selangor D.E., Malaysia

*E-mail: ganaa_p2002@yahoo.com

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The MWCNT/TiO₂ composite was homogeneously coated on the surface of GCE and applied in the electrochemical determination of 0.1 mM potassium ferricyanide in 0.1 M Na₂HPO₄ (pH 8.5). The redox couple of potassium ferricyanide with current enhancements of 3.0-3.1 folds was obtained using the MWCNT/TiO₂/GCE when compared with unmodified GCE. A linear calibration plot showed a correlation coefficient of 0.999, with detection limits of 48.6 μM (100 mV/s scan rate) and 1.1 μM (5 mV/s scan rate) in the concentration ranges of 0.01-0.2 mM of potassium ferricyanide. High sensitivity responses of 77.6 μA/mM for the anodic and of 68.9 μA/mM for the cathodic peak currents were also obtained with an excellent correlation coefficient of 0.999. Based on plot of peak current against peak potential, the zero-current potentials were obtained as $E_{pa}^0=209$ mV and $E_{pc}^0=189$ mV. Diffusion coefficient was found as 1.52×10^{-5} cm²/s from chronocoulometry study. The effect of temperature study was carried at 10 °C – 80 °C and activation energy obtained was 5.8-6 kJ/mol. The morphology of composite surface was examined by scanning electron microscopy.

Keywords: Multi-walled carbon nanotubes, Titanium dioxide, Modified electrode, Potassium ferricyanide, Cyclic voltammetry

1. INTRODUCTION

Recently many researchers in academics and industry have developed a widespread interest in using nano-material especially carbon nanotubes (CNT) as a biosensor. This is mainly due to their high electrical conductivity, chemical stability and mechanical strength [1]. In addition, CNT-based electrodes 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 electrode modifying materials [3]. Different type of electrodes based on CNT have been reported, such as CNT paste electrode [4,5],

CNT film coated electrode [6], CNT powder microelectrode [7], aligned CNT electrode [8,9] and CNT composite electrode [10,11]. More attention has been focused on CNT study in the presence of nano-sized material [12-14]. Lately, the role of CNT in electroanalytical chemistry especially in the development of new electrochemical sensor and analytical application based on CNT-driven electrocatalytic effect has been comprehensively reviewed [15]. Nano-sized materials support constructively the catalytic sensitivity of CNT due to the combination of their electronic, absorptive, mechanical and thermal properties [16].

Similarly, it have been demonstrated that titanium dioxide (TiO_2) nanoparticles is one of the most capable materials, which is of potential interest as a sensor electrode in electrochemistry [17].

The combination of CNT and TiO_2 can provide significant effect for enhancing catalytic process. For example, some researchers have reported that the MWCNT/ TiO_2 composite can be synthesized using different methods, including a sol-gel method [18-20], a chemical vapor deposition method [21,22] and a direct mixing method [23]. Nowadays, most of the researches on the MWCNT/ TiO_2 composite concentrate on how to improve TiO_2 photocatalytic activity [24-26] because TiO_2 is a very active photocatalytic material. Available records revealed that, no work has been reported on the use of the MWCNT/ TiO_2 composite modified glassy carbon electrode (GCE) in detection of ferricyanide by voltammetric method. As such, this research will be an attempt to bridge this gap. This will demonstrate the electroactivity of the MWCNT/ TiO_2 composite and its subsequent use as an electrochemical sensor electrode. This paper will attempt to describe how the presence of TiO_2 nanoparticles in the MWCNT/ TiO_2 composite will enhance the electrochemical activity (or edge effect) of the MWCNT homogeneously coated onto GCE surface for $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox system.

2. EXPERIMENTAL

2.1. Reagents

MWCNTs (purity of 95%, diameter~20–40 nm and length~5-15 μm) were purchased from Shenzhen Nanotech and used without any further purification. TiO_2 nanoparticles (particle size of <100 nm, TiO_2 dispersed in water solution by 5% weight) was purchased from Aldrich (USA). Potassium ferricyanide, disodium hydrogen phosphate, dimethylformamide (DMF) and all other chemicals used in this experiment were of analytical grade.

All reagents were prepared before running each measurement. All solutions were prepared with deionized distilled water and deaerated with oxygen-free nitrogen gas for 15 minutes before they were used in the experiment. Unless otherwise stated, all the experiments were carried out at room temperature of $25\pm 2^\circ\text{C}$.

2.2. Apparatus

A voltammetric analyzer CV-50W electrochemical workstation BAS (Bioanalytical Systems, West Lafayette, USA) was used to perform electrochemical measurement for cyclic voltammetry. A

conventional three-electrode system, a platinum wire as a counter electrode, an Ag/AgCl (in 3 M NaCl) as a reference electrode and 3 mm diameter glassy carbon electrode (GCE) as a working electrode were employed. Prior to the surface modification, bare GCE was polished with alumina slurry and ultrasonic grinded for 1 minute in distilled water before being rinsed with distilled water and subsequent drying before use. The morphology of the MWCNT/TiO₂ composite film was characterized on the surface of basal plane pyrolytic graphite electrode (BPPGE) by scanning electron microscopy (SEM - Model JOEL, JSM-6400 machine).

2.3. Preparation of the MWCNT/TiO₂ composite modified GCE

A suspension of MWCNT in DMF by ultrasonication was prepared in accordance to that reported in [27]. 5 μL black suspension of MWCNT/DMF and 5 μL of TiO₂ solution were deposited onto the surface of GCE, the two solutions diffused into each other to form a homogeneous mix. The composite was then dried in an oven for 2 minutes (at 40°C) to remove the solvent. Finally, the modified electrode was cooled at room temperature before it was used as a working electrode in this experiment.

3. RESULTS AND DISCUSSION

3.1. Voltammetric behavior of ferricyanide at MWCNT/TiO₂/GCE

Fig. 1 shows the cyclic voltammograms of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ couple obtained at GCE modified with the MWCNT/TiO₂, MWCNT, TiO₂ and unmodified GCE immersed in 0.1 M Na₂HPO₄ electrolyte solution (pH 8.5) containing 0.1 mM potassium ferricyanide. The redox couple of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ appeared to vary with the use of different electrodes. When TiO₂ modified electrode was used (Fig. 1c), there was suppression in the redox peaks as compared to unmodified GCE (Fig. 1d). When MWCNT modified GCE was used (Fig. 1b), redox current peaks of potassium ferricyanide increased by 1.3 folds for the oxidation and 1.4 folds for the reduction peak current. The observed cyclic voltammograms were similar to those reported earlier [27] for MWCNT modified GCE. Remarkably, the current enhancement was observed when TiO₂ nanoparticles coupled with MWCNT as a MWCNT/TiO₂ composite modified GCE (Fig. 1a) as compared with that of MWCNT modified GCE (Fig. 1b). The redox couple of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ appears quite reversible at the MWCNT/TiO₂/GCE. It is because the peak currents obtained are well-defined with I_{pa}/I_{pc}=1.01, and a peak separation of 70 mV as its E_{pa}=+235 mV and E_{pc}=+165 mV vs. Ag/AgCl. Nonetheless, 3.1 folds increase in the oxidation current and 3.0 folds increase in the reduction currents were detected at the MWCNT/TiO₂/GCE (Fig. 1a) as compared to those obtained at unmodified GCE (Fig. 1d). Peak current enhancement accompanied with peak potential shift suggests that electrocatalytic activity of the MWCNT/TiO₂ composite modified GCE is available when compared with the other electrodes.

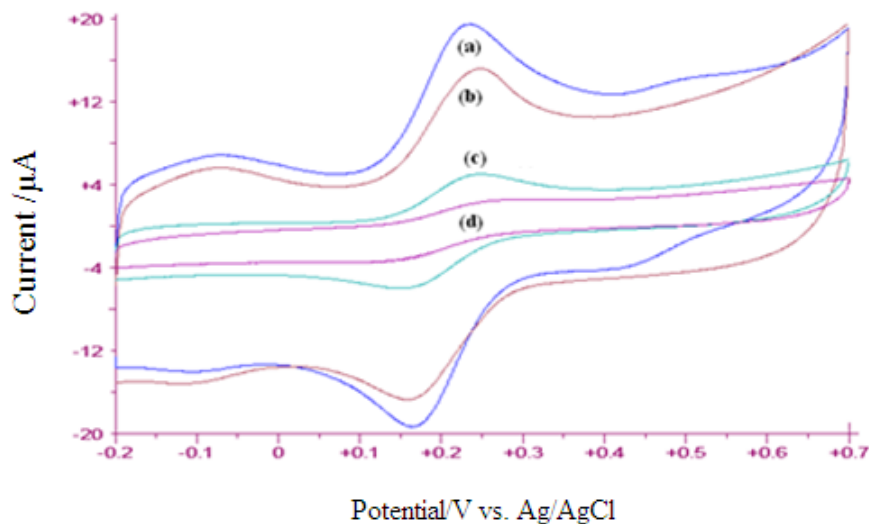


Figure 1. Cyclic voltammetric responses obtained for 0.1 mM potassium ferricyanide in 0.1 M Na_2HPO_4 at the MWCNT/ TiO_2 /GCE (a); MWCNT/GCE (b); TiO_2 /GCE (d) and GCE (c) with a scan rate of 100 mV/s.

3.2. Potential cycling of voltammogram at MWCNT/ TiO_2 /CGE

The stability of the MWCNT/ TiO_2 composite modified GCE was studied for the reversible redox couple of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M Na_2HPO_4 aqueous electrolyte using a 100 mV/s scan rate by cyclic voltammetry. The result in Fig. 2 shows that the oxidative peak current of potassium ferricyanide remained virtually constant throughout the 10 potential cycles and reflecting the stability of the MWCNT/ TiO_2 composite modified GCE.

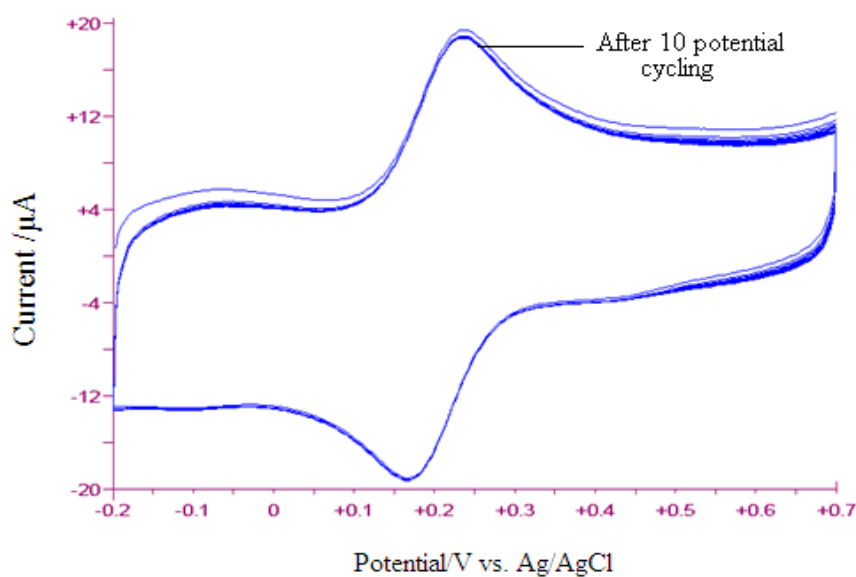


Figure 2. Cyclic voltammetric response of 10 potential cycling for the redox process of 0.1 mM potassium ferricyanide in 0.1 M Na_2HPO_4 at the MWCNT/ TiO_2 /GCE; scan rate of 100 mV/s.

3.3. Effect of varying pH

The effect of pH on the voltammetric response of potassium ferricyanide was studied to determine the catalytic condition of the redox process at the MWCNT/TiO₂ composite modified GCE in the range of pH 2.0 to 12.0, using pH buffer solutions adjusted to desired condition. Background current or capacitive current is generally pH dependent. It usually increases with increase in acidity at the MWCNT/TiO₂/GCE. As a result, the redox peaks of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ become smaller at pH 2.0 to pH 4.0. With the increase of pH, from 5.0 to 8.0, the redox peak current increased significantly, and then decreased as the pH increases (9.0 to 12.0) as shown in Fig. 3.

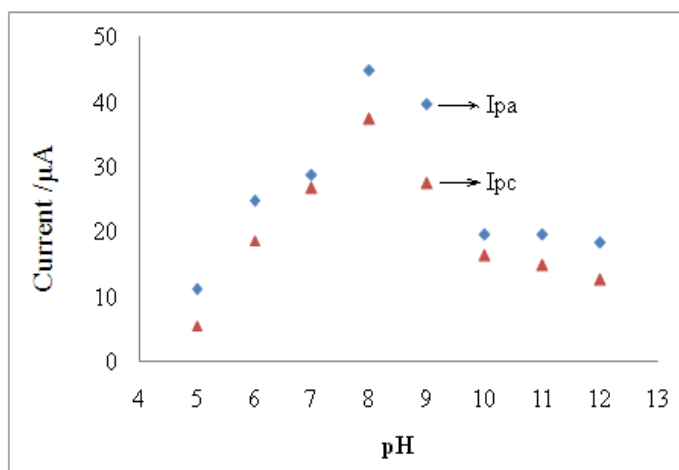


Figure 3. A plot of the pH against the redox peak current of 0.1 mM potassium ferricyanide at the MWCNT/TiO₂/GCE with various pH solutions ranging from 5.0 to 12.0.

The optimum pH range for good sensitivity response appears between pH 6.0 and pH 9.0 with the maximum sensitivity response at pH 8.0. Since hydrolysis may set in at higher pH of >7.0 and on bodily fluid is usually weakly acidic, consequently pH 6.0 is chosen for subsequent studies. It is interesting to note that when pH value increased, the peak potential shifted linearly to negative potentials.

3.4. Effect of varying scan rate

The effect of varying scan rates ranges between 10 mV/s and 600 mV/s was studied at the MWCNT/TiO₂ composite modified GCE in 0.1 M Na₂HPO₄ electrolyte solution containing 0.1 mM potassium ferricyanide. With an increasing scan rate, the peak current separation increased, and also the peak potential shifted slightly with the anodic peak to positive and the cathodic peak to negative potential directions. From the plot of logarithm peak current against logarithm of scan rate as shown in Fig. 4a, the current increases approximately in linear approach as described by $y = 0.63x + 0.13$; $R^2=0.998$ for the anodic and $y = 0.55x + 0.03$; $R^2=0.997$ for the cathodic peak currents.

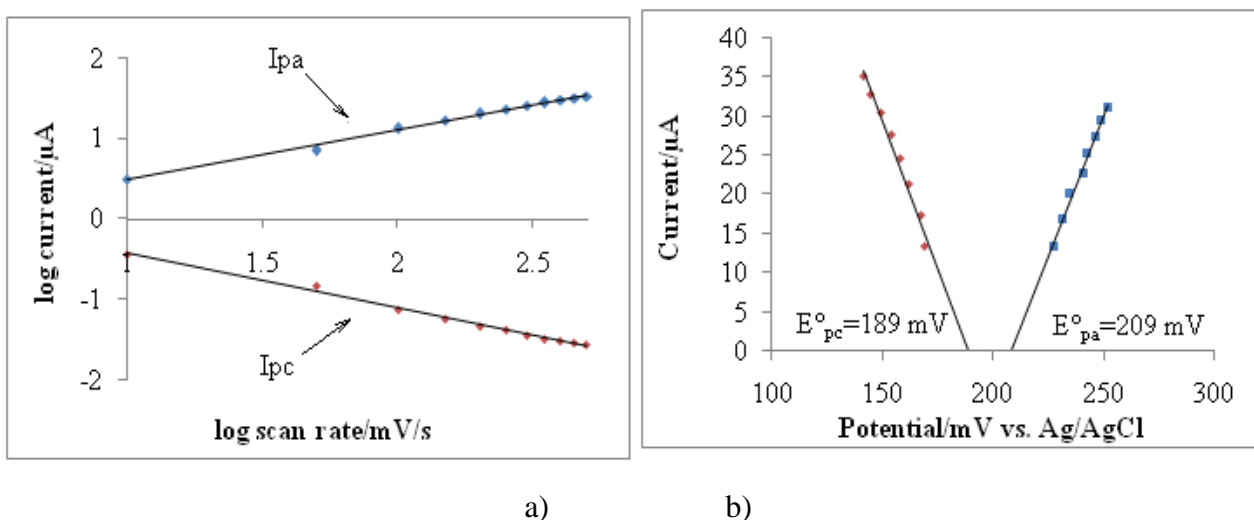


Figure 4. A plot of the $\log I_p$ against \log scan rate (a); A plot of the peak current against peak potential (b) obtained for the 0.1 mM potassium ferricyanide in 0.1 M Na_2HPO_4 at the MWCNT/ TiO_2 /GCE with different scan rates of 10 mV/s - 600 mV/s.

An experimental slope of 0.55-0.63 obtained is slightly larger than the theoretical value of 0.5, which suggests that process is not purely diffusion controlled. From a plot of peak current against peak potential (Fig. 4b), the 'zero-current' oxidation potential was found at 209 mV and reduction potential was at 189 mV vs. Ag/AgCl at the MWCNT/ TiO_2 composite modified GCE.

3.5. Effect of varying concentration of potassium ferricyanide

Fig. 5 illustrates the effect of the varying concentration of potassium ferricyanide on $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox current at the MWCNT/ TiO_2 composite modified GCE in 0.1 M Na_2HPO_4 aqueous solution. It can be observed from the voltammogram (Fig. 5a), that both the anodic and cathodic peak currents increased linearly with increasing concentration of potassium ferricyanide ranging from 0.01 mM to 0.2 mM. High sensitivity responses of 77.6 $\mu\text{A}/\text{mM}$ for anodic and 68.9 $\mu\text{A}/\text{mM}$ for cathodic peak current were also obtained. Calibration plots bearing linear relationships of $y = 77.6x + 0.38$ for oxidation and $y = 68.9x + 0.89$ for reduction peak current showed an excellent correlation coefficient of 0.999 (Fig. 5b). Based on the expression of $3\sigma/\text{slope}$ (oxidation process) detection limit is found to be 48.6 μM when using a scan rate of 100 mV/s. At a low scan rate of 5 mV/s, detection limit is considerably improved to 1.1 μM .

3.6. Effect of varying temperature

The effect of temperature on the potassium ferricyanide in 0.1 M Na_2HPO_4 was examined at the MWCNT/ TiO_2 composite modified GCE as shown in Fig. 6a. The redox peak currents increased remarkably and peak potential shifted more negatively with increase in temperatures over 10°C – 80°C.

Based on Arrhenius plot of \ln peak current against $1/T \text{ K}^{-1}$ (Fig. 6b), the estimated activation energy is 6 kJ/mol for the oxidation peak current and 5.8 kJ/mol for the reduction peak current.

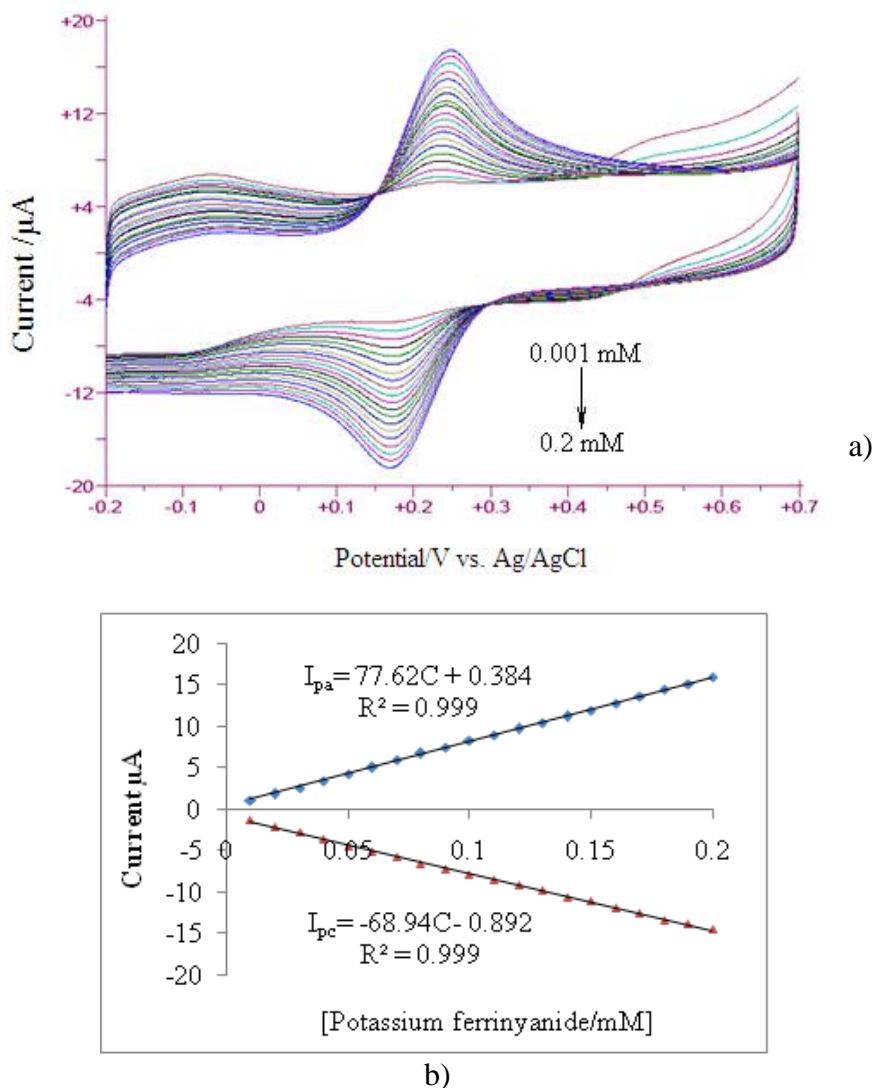


Figure 5. Cyclic voltammetric response of potassium ferricyanide with different concentration of 0.01 mM - 0.2 mM at the MWCNT/TiO₂/GCE in 0.1 M Na₂HPO₄ with a scan rate of 100 mV/s (a); The dependence of peak current against concentration of potassium ferricyanide ranges of 0.01 mM – 0.2 mM (b).

Also it gave linear relationship of $y = 2.07x + 1.081$ with $R^2 = 0.971$ for the oxidation peak current due to the thermodynamic expectation, following the equations below:

$$\sigma = \sigma^{\circ} \exp (-E_a/RT) \quad [1]$$

$$D = D^{\circ} \exp (-E_a/RT) \quad [2]$$

Where, σ/D - conductivity/diffusivity and σ°/D° - standard conductivity/initial diffusivity

As expected, when temperature was increased, there was a significant rise in the rate of diffusion of the potassium ferricyanide, hence the corresponding increase in peak current.

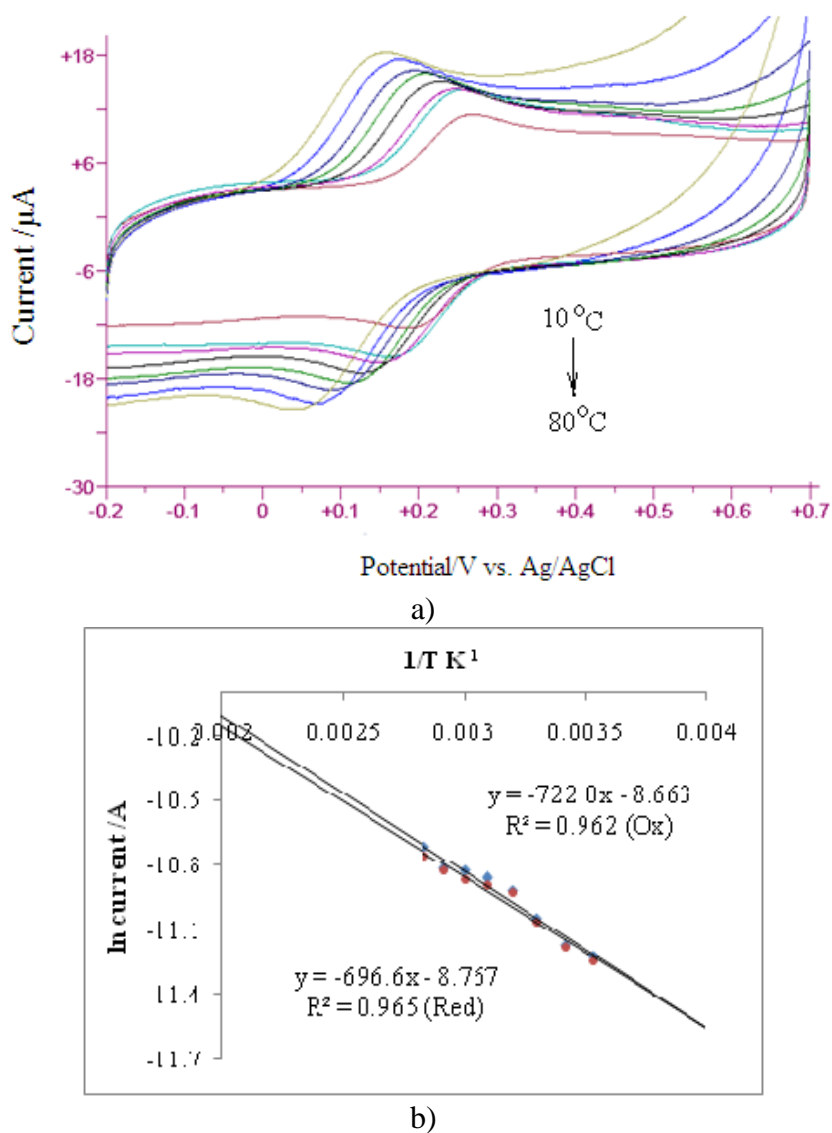


Figure 6. Cyclic voltammetric response obtained for the redox of potassium ferricyanide using the MWCNT/TiO₂/GCE in 0.1 M Na₂HPO₄ at various temperatures of 10°C - 80°C (a); A plot of $\ln I_p$ against $1/T \text{ K}^{-1}$ for the MWCNT/TiO₂/GCE in the presence of 0.1 mM potassium ferricyanide in aqueous media (b).

3.7. Chronoamperometry study

The technique of double potential step chronoamperometry was applied on potassium ferricyanide using the MWCNT/TiO₂ composite modified GCE immersed in 0.1 M Na₂HPO₄ solution at $25 \pm 2^\circ\text{C}$ for 250 ms. Fig. 7 shows a monotonous rising current transient for the redox process of potassium ferricyanide indicating presence of diffusion controlled process.

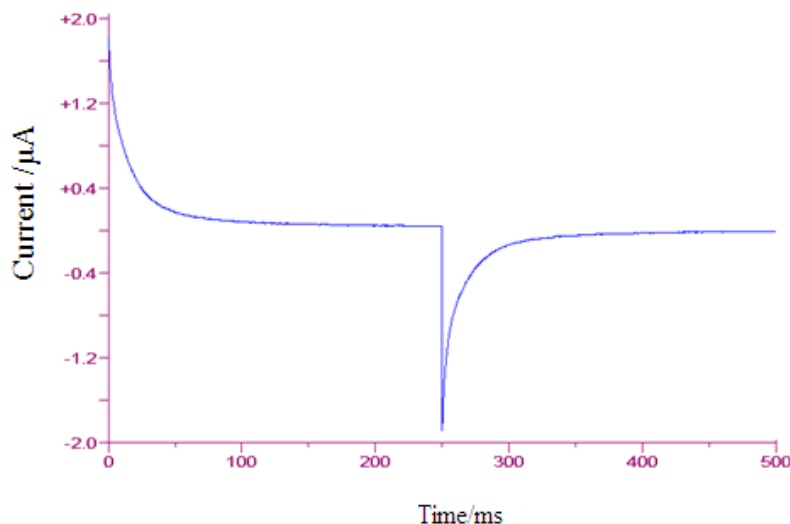


Figure 7. Chronoamperogram of 0.1 mM potassium ferricyanide in 0.1 M Na₂HPO₄ using the MWCNT/TiO₂/GCE at 25±2°C with 250 ms pulse width

The current decayed as the electrolysis proceeded to deplete the solution near the electrode of electroactive species of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple. The current response is described by the Cottrell equation for a planar electrode [28]:

$$i = nFAC(D/\pi t)^{1/2} \quad [3]$$

Where, *i* - current, n - number of electrons per molecule, F - faraday’s constant, *A* - electrode area, *C* - bulk concentration, *D* - diffusion coefficient, *t* - time

3.8. Chronocoulometry study

Since charge is the integral of current with respect to time, response for the chronocoulometry can be obtained simply by integrating the current response for chronoamperometry as shown in Fig. 8.

Likewise, the equation for the charge against time curve (the Anson plot) can be obtained by integrating as below:

$$Q = 2nFAD^{1/2} C_o t^{1/2} / \pi^{1/2} \quad [4]$$

Where, *Q* = Charge, and the other parameters are same as before.

Based on the Cottrell equation, the analysis of chronocoulometry data shows the charge-time dependence for linear diffusion control. The Anson plot shows linear dependency of *Q* upon *t*^{1/2} indicating that the process involved is diffusion controlled. Diffusion coefficient can be calculated and

obtained as a $1.52 \times 10^{-5} \text{ cm}^2/\text{s}$ in the presence of 0.1 mM potassium ferricyanide in 0.1 M Na_2HPO_4 at the MWCNT/ TiO_2 /GCE

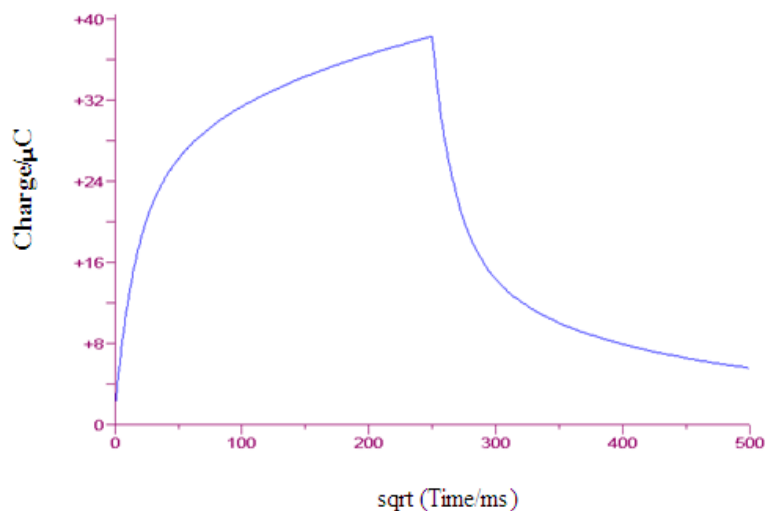


Figure 8. Chronocoulougram of 0.1 mM potassium ferricyanide in 0.1 M Na_2HPO_4 at the MWCNT/ TiO_2 /GCE at $25 \pm 2^\circ\text{C}$ with 250 ms pulse width

3.9. Scanning electron microscopy study

Fig. 9 presents scanning electron microscopy image of surface of the MWCNT/ TiO_2 composite film at a 5 mm diameter BPPGE in the presence of potassium ferricyanide in aqueous media (after electrolysis). The structure of the composite showed a homogeneous film on the surface of BPPGE. It can be seen clearly at magnification of 20,000 times that MWCNT was shown as thin fibers which merged to form bundles, entwined together. The stability of the film was evident as the scanning electron micrograph remains un-scattered even after 10 potential cycling.

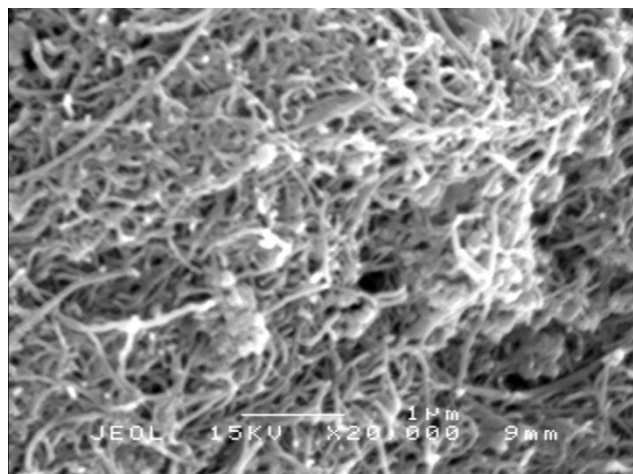


Figure 9. A morphology of the MWCNT/ TiO_2 /GCE composite film at BPPGE with a magnification of 20,000 times after electrolysis.

4. CONCLUSIONS

The result presented here demonstrates the use of the MWCNT/TiO₂ composite modified GCE is highly sensitive and stable in electrochemical measurement. Electrocatalytic response and stability were improved when the MWCNT/TiO₂/GCE was used as compared to when MWCNT/GCE and unmodified GCE were used. Electrochemical response was dependent significantly on the scan rate, pH, temperature and concentration of potassium ferricyanide. From the foregoing report, we predict the MWCNT/TiO₂ composite will have significant electro-analytical efficiency for practical purpose. For the future work, the capability of the MWCNT/TiO₂ composite modified electrode to detect some biological and environmental compounds will be investigated using voltammetric techniques.

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References

1. S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56.
2. Y.H. Yun, Z. Dong, V. Shanov, W.R. Heineman, H.B. Halsall, A. Bhattacharya, L. Conforti, R.K.Narayan, W.S. Ball, M.J. Schulz, Nanotube electrodes and biosensors, *Nano Today* 2 (2007) 30.
3. P.M. Ajayan, Nanotubes from carbon, *Chem. Rev.* 99 (1999) 1787.
4. M.D. Rubianes, G.A. Rivas, Carbon nanotubes paste electrode, *Electrochem. Commun.* 5 (2003) 689.
5. F. Valentini, A. Amine, S. Orlanducci, M.L. Terranova, G. Palleschi, Carbon nanotube purification: Preparation and characterization of carbon nanotube paste electrodes, *Anal. Chem.* 75 (2003) 5413.
6. M.M. Rahman, I.C. Jeon, Studies of electrochemical behavior of SWNT-film electrodes, *J. Braz. Chem. Soc.* 18 (2007) 1150.
7. Y.D. Zhao, W.D. Zhang, H. Chen, Q.M. Luo, Electrocatalytic oxidation of cysteine at carbon nanotube powder microelectrode and its detection, *Sensors and Actuators B* 92 (2003) 279.
8. L.C. Jiang, W.D. Zhang, Electrodeposition of TiO₂ nanoparticles on multiwalled carbon nanotube arrays for hydrogen peroxide sensing, *Electroanalysis* 21 (2009) 988
9. H. Tang, J. Chen, L. Nie, S. Yao, Y. Kuang, Electrochemical oxidation of glutathione at well-aligned carbon nanotube array electrode, *Electrochim. Acta* 51 (2006) 3046.
10. F. Faridbod, M. R. Ganjali, M. Pirali-Hamedani, P. Norouzi, MWCNTs-ionic liquids-ionophore-graphite nanocomposite based sensor for selective determination of Ytterbium(III) Ion. *Int. J. Electrochem. Sci.*, 5 (2010) 1103 - 1112.
11. K. Gong, Y. Dong, S. Xiong, Y. Chen, L. Mao, Novel electrochemical method for sensitive determination of homocysteine with carbon nanotube-based electrodes, *Biosensors and Bioelectronics* 20 (2004) 253.
12. D. Zhang, S. Tadashi, O. Take, Dual catalysts system based on nano-manganese oxide and multiwall carbon nanotube for four-electron oxygen reduction, *Chemistry Letters* 35 (2006) 520.
13. N. Alexeyeva, T. Laaksonen, K.s. Kontturi, F. Mirkhalaf, D.J. Schiffrin, K. Tammeveski, Oxygen reduction on gold nanoparticle/multi-walled carbon nanotubes modified glassy carbon electrodes in acid solution, *Electrochem. Commun.* 8 (2006) 1475.

14. S.F. Wang, F. Xie, R.F. Hu, Carbon-coated nickel magnetic nanoparticles modified electrodes as a sensor for determination of acetaminophen, *Sensors and Actuators B* 123 (2007) 495.
15. L.A. í, P.Y.n.e.-S. o, J.M. Pingarro, Role of carbon nanotubes in electroanalytical chemistry, *Anal. Chim. Acta* 622 (2008) 11.
16. P. Serp, M. Corrias, P. Kalck, Carbon nanotubes and nanofibers in catalysis, *Appl. Catal. A* 253 (2003) 337.
17. M. Mazloum-Ardakani, H. Rajabi, H. Beitollahi, B.B.F. Mirjalili, A. Akbari, N. Taghavinia. Voltammetric determination of dopamine at the surface of TiO₂ nanoparticles modified carbon paste electrode. *Int. J. Electrochem. Sci.*, 5 (2010) 147 - 57.
18. C.Y. Yen, Y.F. Lin, C. H. Hung, Y.H. Tseng, C.C. Ma, M.C. Chang, H. Shao, The effects of synthesis procedures on the morphology and photocatalytic activity of multi-walled carbon nanotubes/TiO₂ nanocomposites, *Nanotechnology* 19 (2008) 11.
19. B. Gao, G.Z. Chen, G.L. Puma, Carbon nanotubes/titanium dioxide (CNTs/TiO₂) nanocomposites prepared by conventional and novel surfactant wrapping sol-gel methods exhibiting enhanced photocatalytic activity, *Appl. Catal. B* 89 (2009) 503.
20. Y. Yu, J.C. Yu, J.G. Yu, Y.C. Kwok, Y.-K. Che, J.C. Zhao, L. Ding, W.K. Ge, P.K. Wong, Enhancement of photocatalytic activity of mesoporous TiO₂ by using carbon nanotubes, *Appl Catal A* 289 (2005) 186.
21. L. Chen, B.L. Zhang, M.Z. Qu, Z.L. Yu, Preparation and characterization of CNTs-TiO₂ composites, *Powder Technology* 154 (2005) 70
22. C.S. Kuo, Y.H. Tseng, H.Y. Lin, C.H. Huang, C.Y. Shen, Y.Y. Li, S.I. Shah, C.P. Huang, Synthesis of a CNT-grafted TiO₂ nanocatalyst and its activity triggered by a DC voltage, *Nanotech.* 18 (2007) 465607.
23. T. Sawatsuk, A. Chindaduang, C. Sae-kung, S. Pratontep, G. Tumcharern, Dye-sensitized solar cells based on TiO₂-MWCNTs composite electrodes: Performance improvement and their mechanisms, *Diamond & Related Materials* 18 (2009) 524.
24. B. Ahmmad, Y. Kusumoto, S. Somekawa, M. Ikeda, Carbon nanotubes synergistically enhance photocatalytic activity of TiO₂, *Catal. Commun.* 9 (2008) 1410.
25. W. Wang, P. Serp, P. Kalck, J.L.s. Faria, Photocatalytic degradation of phenol on MWNT and titania composite catalysts prepared by a modified sol-gel method, *Appl. Catal. B* 56 (2005) 305.
26. C.Y. Kuo, Preventive dye-degradation mechanisms using UV/TiO₂/carbon nanotubes process, *J. Hazardous Materials* 163 (2009) 239.
27. M. Musameh, N.S. Lawrence, J. Wang, Electrochemical activation of carbon nanotubes, *Electrochem. Commun.* 7 (2005) 14.
28. S. Z. Kang, Z. Cui, J. Mu, Electrochemical behavior of K₃[Fe(CN)₆] on the electrode coated with modified multi-walled carbon nanotubes, *J. Dispersion Science and Technology* 28 (2007) 573.