ELECTROCHEMICAL ANALYSIS OF CARBON NANOTUBES/TITANIUM DIOXIDE COMPOSITE MODIFIED GLASSY CARBON ELECTRODE

GANCHIMEG PERENLEI

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By

GANCHIMEG PERENLEI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of this thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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October 2010

Chair : Associate Professor Tan Wee Tee, PhD

Faculty : Science

The new chemically modified electrode based on carbon nanotubes/titanium dioxide (CNT/TiO_2) composite modified glassy carbon electrode (GCE) was fabricated by two different (i) mechanical attachment and (ii) solvent casting methods. The CNT/TiO_2/GCE composite has been characterized using voltammetric techniques of linear sweep voltammetry, cyclic voltammetry, chronoamperometry and chronocoulometry in this work. The surface morphology of the CNT/TiO_2 composite film was studied by scanning electron microscopy and the percentage of the elements in components was examined by energy dispersive X-ray.

The CNT/TiO_2/CGE was applied in the electrochemical determination of 0.5 mM ascorbic acid in 0.1 M NaCl (pH 6.2), 0.1 mM potassium ferricyanide in 0.1 M Na_2HPO_4 (pH 8.5) and 0.2 mM paracetamol in 0.1 M PBS (pH 7.0). The current enhancements of 5.0 folds for the oxidation of ascorbic acid, 3.0-3.1 folds for the redox of potassium ferricyanide and 8.5-11.0 folds for the redox of paracetamol were obtained using the CNT/TiO_2/GCE when compared with unmodified GCE. The responses of each analyte at various electrodes are in the order:

CNT/TiO_2/GCE > CNT/GCE > GCE > TiO_2/GCE

Under the optimized parameters, the linear calibration graph showed correlation coefficient of 0.997 for the oxidation of 0.05-2 mM ascorbic acid, 0.999 for the redox of 0.01-0.2 mM potassium ferricyanide and the concentration isotherm of paracetamol in the range of 0.01 - 2 mM, with linearity of up to 1.2 mM. From this calibration plot, high sensitivity response of 45 μA/mM with detection limit of 7.8 μM (100 mV/s scan rate) for the oxidation of ascorbic acid; 68.9-77.6 μA/mM with 1.1 μM (5 mV/s) for the redox of potassium ferricyanide; and 89.94-111.3 μA/mM with 3.9 μM (5 mV/s) for the redox of paracetamol at the CNT/TiO_2/GCE were obtained. Effect of scan rate of ascorbic acid was studied in the ranges of 10-300 mV/s, and linear relation was observed up to 70 mV/s. Based on the log plot of oxidation current vs. scan rate, an experimental slope of 0.45 was obtained, which is very close to the theoretical value of 0.5, indicating that the current is under diffusion controlled. Based on redox currents of potassium ferricyanide vs. potential plot, the zero-current potentials were obtained at E^o_{pa}=209 mV and E^o_{pc}=189 mV in the scan rates ranges of 10-600 mV/s. Diffusion

coefficient was calculated as 1.52×10^{-5} cm^2/s from the chronocoulometry study and an activation energy obtained was 6 kJ/mol in the presence of potassium ferricyanide in aqueous media at the composite electrode. The redox peak currents of paracetamol were significantly dependent on dosages of CNT to TiO_2 in the composite at GCE. The recovery experiment of paracetamol in commercially available samples was carried out and the recovery rates of 95±2% and 96±2% were found using the CNT/TiO_2/GCE. The results revealed that the electrochemical ability of CNT is improved when combined with TiO_2 nanoparticles as a composite. The use of the CNT/TiO_2/GCE is highly sensitive, selective and stable in electrochemical measurement.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

ANALISIS ELEKTROKIMIA KOMPOSIT KARBON KACA TERUBAHSUAI KARBON NANOTIUB/TITANIUM DIOKSIDA

Oleh

GANCHIMEG PERENLEI

Oktober 2010

Pengerusi : Profesor Madya Tan Wee Tee, PhD

Fakulti : Sains

Electrod kimia terubahsuai berdasarkan nanotube karbon/titanium dioksida (CNT/TiO_2) komposit elektrod karbon yang diubahsuai kaca (GCE) telah dibuat dgn 2 kaedah berbeza (i) lekatan mekanikal (ii) kaedah tuangan pelarut. Komposit CNT/TiO_2/GCE telah dianalisis menggunakan teknik voltametri dari linear sweep voltametri kadar linear, voltametri siklik, chronoamperometri dan chronocoulometri. Morfologi permukaan filem komposit CNT/TiO_2 dianalisa dengan imbasan mikroskop elektron dan peratusan elemen dalam komponen dianalisa oleh tenaga sinar-X dispersif.

CNT/TiO_2/GCE digunakan dalam penentuan elektrokimia 0.5 mM asid askorbik dalam 0.1 M NaCl (pH 6.2), 0.1 mM kalium ferricyanide dalam 0.1 M Na_2HPO_4 (pH 8.5) dan parasetamol 0.2 mM dalam 0.1 M PBS (pH 7.0). Pertambahan arus sebanyak 5.0 kali

ganda untuk pengoksidaan asid askorbik, 3.0-3.1 kali ganda untuk redoks kalium ferrisianida dan 8.5-11.0 kali ganda untuk redoks parasetamol diperolehi dengan menggunakan CNT/TiO_2/GCE apabila dibandingkan dengan GCE tanpa ubah suai. Respon analit masing-masing pada pelbagai elektrod adalah dalam urutan:

CNT/TiO_2/GCE > CNT/GCE > GCE > TiO_2/GCE

Berdasarkan parameter yang dioptimumkan, graf kalibrasi linear menunjukkan pekali korelasi 0.997 untuk pengoksidaan 0.05-2 mM asid askorbik, 0.999 untuk redoks 0.01-0.2 mM kalium ferrisianida dan isoterm konsentrasi parasetamol dalam julat 0.01 - 2 mM, dengan julat linear hingga 1.2 mM. Dari plot kalibrasi, sensitiviti response adala tinggi sebanyak 45 μA/mM dengan limit pengesanan 7.8 μM (100 mV/s kador imbasan) untuk pengoksidaan asid askorbik; 68.9-77.6 μA/mM dengan 1.1 μM (5 mV/s) untuk redoks kalium ferrisianida; dan 89.94-111.3 μA/mM dengan 3.9 μM (5 mV/s) untuk redoks parasetamol di CNT/TiO_2/GCE diperolehi. Pengaruh kadar imbasan asid askorbik dipelajari dalam julat 10-300 mV/s, dan hubungan linear diperolehi sehingga 70 mV/s. Berdasarkan plot log arus pengoksidaan vs. kadar imbasan, kecerunan eksperimen 0.45 diperolehi, yang menghampin nilai teori iaitu 0.5, menunjukkan bahawa arus ini di bawah difusi terwakal. Berdasarkan arus redoks plot kalium ferrisianida melawan potensi, arus potensi sifar diperoleh pada E^o_{pa}=209 mV dan E^o_{pc}=189 mV dengan kadar imbasan 10-600 mV/s. Pekali difusi dikira sebagai 1.52×10^{-5} cm^2/s daripada kajian chronocoulometri dan tenaga pengaktifan yang diperolehi adalah 6 kJ/mol dengan kehadiran kalium ferrisianida dalam media akues pada electrod komposit. Arus puncak redoks parasetamol secara signifikannya bergantung pada dos

CNT pada TiO_2 dalam komposit pada CGE. Kajian aplikasi untuk parasetamol dalam sampel yang tersedia secara komersil dilakukan dan tahap pemulihan dari 95±2% dan 96±2% dijumpai menggunakan CNT/TiO_2/GCE tersebut. Keputusan kajian menunjukkan bahawa kemampuan elektrokimia CNT dipertingkatkan bila digabungkan dengan nanopartikel TiO_2 sebagai komposit. CNT/TiO_2/GCE ini sangat sensitif, selektif dan stabil dalam pengukuran electrokimia.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FUGURES

LIST OF SYMBOLS

A	Electrode surface area (cm^2)
C	Concentration of the analyte in the bulk solution ($mole/cm^3$)
D	Diffusion coefficient (cm^2/s)
D^o	Initial diffusivity of the material
e^-	Electron transferred or involved in the reaction
E	(a) Potential of an electrode (V)
	(b) Peak potential (V)
$E_{1/2}$	Measure half-wave potential in voltammetry (V)
E_a	Activation energy (kJ/mol)
E_i	Initial potential (V)
E_f	Final potential (V)
E_p	Peak potential (V)
E_{pa}	Anodic peak potential (V)
E_{pc}	Cathodic peak potential (V)
E^o	(a) Standard potential of an electrode
	(b) Standard emf for a half cell reaction
ΔE^0	Difference in standard potentials for two couples (E_1^0-E_2^0) (V)
ΔE_p	Separation between the peak potentials $\lvert E_{pa}\text{-}E_{pc}\rvert$ (V)
F	Faraday constant, charge on one mole of electrons
I_f	Faradaic current (A)
I_p	Peak current (A)

I_{pa}	Anodic peak current (A)
I_{pa}/I_{pc}	Anodic-to-cathodic peak current ratio
I_{pc}	Cathodic peak current (A)
K	(a) Constant;
	(b) Equilibrium constant
m	Slope
n	(a) Number of electron transfer (equiv/mole)
	(b) Number of electrons exchanged between one ion or molecule of a reactant and the electrode (equiv/mole)
n_a	Number of electrons involved in the rate determining step (equiv/mole)
Q	Charge (Coulomb)
Q_d	Capacitive charge (double layer), (Coulomb)
R	Gas constant
R^2	Correlation coefficient
t	Time (s)
T^0	Absolute temperature (^oC)
v	Scan rate (V/s)
τ	Forward step width (s)
Γ	Surface excess of reactant (mole/cm^2)
σ	Conductivity
σ^0	Standard conductivity of the material
δ	Standard diviation

LIST OF ABBREVIATIONS

Ag/AgCl	Silver-silver chloride reference electrode
BAS	Bioanalytical Systems
BPPGE	Basal plane pyrolytic graphite electrode
CA	Chronoamperometry
CC	Chronocoulometry
CE	Counter electrode
CME	Chemically modified electrode
CNT	Carbon nanotubes
CNT/TiO_2	Carbon nanotubes/titanium dioxide
$CNT/TiO_2/GCE$	Carbon nanotubes/titanium dioxide/glassy carbon electrode
CV	Cyclic voltammogram
CVD	Chemical vapor decomposition
DMF	Dimethylformamide
EDX	Energy dispersive of X-ray
GCE	Glassy carbon electrode
KCl	Potassium chloride
$KClO_4$	Potassium perchlorate
KH_2PO_4	Potassium dihydrogen orthophosphate
K_2SO_4	Potassium sulphate
LSV	Linear sweep voltammogram

MAM	Mechanical attachment method
MWCNT	Multi-walled carbon nanotubes
NaCl	Sodium chloride
Na_2HPO_4	Sodium dihydrogen orthophosphate
NaOH	Sodium hydrooxide
NH4Cl	Ammonium chloride
HNO3	Nitrogen acid
Ox	Oxidation
Pt	Platinum
PBS	Phosphate buffer solution
RE	Reference electrode
Red	Reduction
SEM	Scanning electron microscopy
SCM	Solvent casting method
SPV	Solid phase voltammetry
SWCNT	Single-walled carbon nanotubes
TiO_2	Titanium dioxide
UV	Ultraviolent
WE	Working electrode

1.2 Nanostructured Material Modified Electrode

In recent years, the attention has been focused on growth of modified electrodes based on various nanostructured materials such as nanotubes, nanofibers, nanowires, nanoballs and nanoparticles. Nanostructured material modified electrodes can offer great benefits in electroanalytical research and application because of their great advantages of high effective surface area, mass transportation, catalysis and control over microenvironment (Katz *et al.*, 2004).

Increasing the electroactive surface area can be achieved by the attachment of nanostructures materials onto electrode surface. The large effective surface area may also cause there to be a larger number of active sites and often a higher signal to noise ratio (Welch and Compton, 2006). This increased electroactive surface area allows lower detection limit and higher sensitivity to analytes. The main challenge in achieving a high surface area electrode is the control over the size and distribution of the structures produced on the electrode. Thus enhanced mass transport of nanostructured electrodes, due to dominance of radial diffusion, decreased charging currents and deleterious effects of solution resistance. They may be defined as electrodes with a critical dimension in the nanometer range (1 nm –100 nm), where by critical dimension is meant that dimension which controls the electrochemical response (Arrigan, 2004). Conversely, the catalytic properties of some nanoparticles can cause a decrease in the over potential needed for a reaction to become kinetically viable, producing voltammetry which appears more reversible.

1.3 Carbon Nanotubes

CNT are long cylindrical structure of 3-coordinated carbon, slightly pyramidalized by curvature from the pure sp^2 hybridization of graphene, toward the diamond-like sp^3 (Fischer, 2006). CNT present a seamless structure with hexagonal 'helicity' of the carbon honeycomb lattices (Lambin *et al.*, 2002), being several nanometers in diameter and many microns in length (Ajayan, 1999). CNT are closed structures that present two well defined regions with clearly different properties, the tube and the cap, which is hemi-fullerenes-like molecule with topological defects that in this case are mainly pentagons (Rivas *et al.*, 2007).

There are two basic types of CNT, namely single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) as shown in Figure 1.1. SWCNT consist of a single graphite sheet rolled seamlessly defining a cylinder of 1-2 nm diameter. The minimum diameter of stable free standing SWCNT is limited by curvature-induced strain to 0.4 nm. Meanwhile, MWCNT can be visualized as concentric and closed graphite tubules with multiple layers of graphite sheets that define a hole of 2 - 25 nm separated by a distance of 0.34 nm (Fischer, 2006).

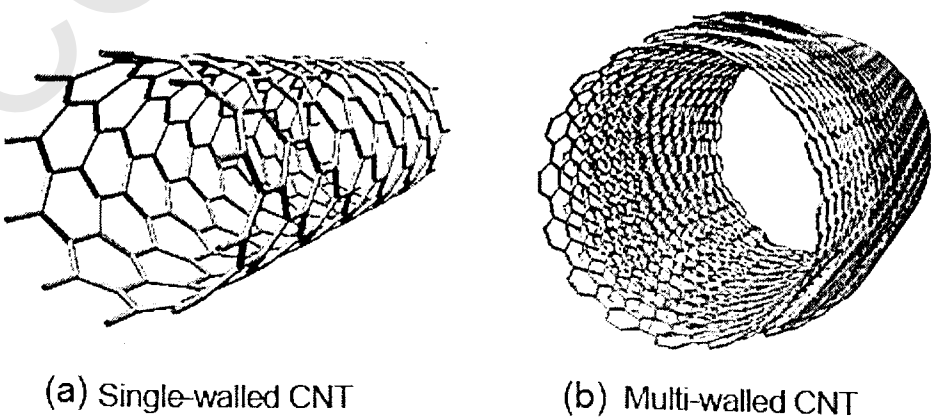

Figure 1.1. Scheme of single-walled (a) and multi-walled (b) carbon nanotubes

1.4 Titanium Dioxide

Titanium (iv) dioxide or titania, is well known as a white pigment, is the naturally occurring oxide of titanium with a chemical formula of TiO_2. Titania has a number of crystalline forms such as rutile, anatase and brookite. Those all crystalline structures contain six-coordinate titanium and shown in Figure 1.2.

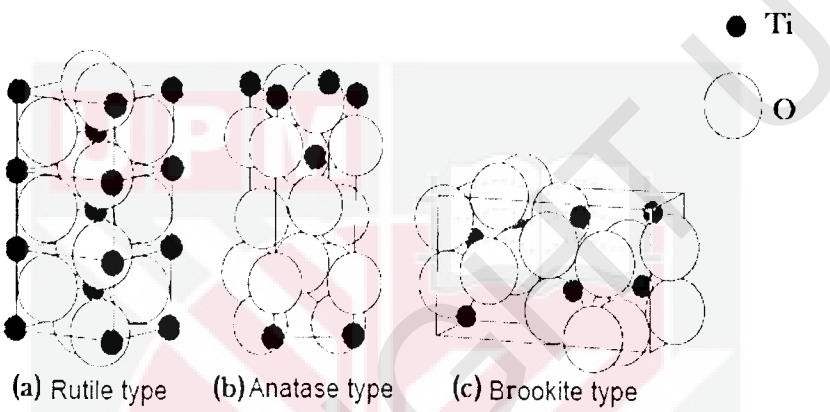

Figure 1.2. TiO_2 crystal structures: tetragonal (a), tetragonal (b) and orthorhombic (c)

Both anatase and brookite can be converted to rutile upon heating. The structure of anatase can be regarded to be built from octahedral connecting by vertices. In rutile, the edges are connected where as in brookite, both vertices and edges are connected. Anatase forms are shown to be more stable, photochemistry, active, and sensitive for catalyzed photodegradation. Meanwhile, rutile forms exhibit photochemical nature and relatively inactive. Brookite has less commercial importance.

1.5 Ascorbic Acid

L-ascorbic acid or L-3-ketothreohexuronic acid lactone, well known as vitamin C is usually prepared by synthesis from glucose, or extracted from plant sources like rose hips, blackcurrants or citrus fruits. It is used for the prevention and treatment of cold, fever, mental illness, infertility, the healing of wounds, elasticity of the skin, aids the absorption of iron and improves resistance to infection. Chemical formula of ascorbic acid is $C_6H_8O_6$ and molecular structure is shown in Figure 1.3.

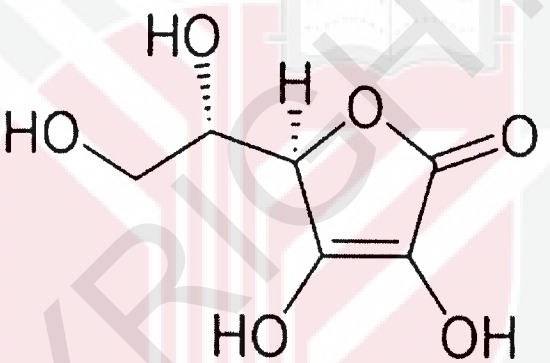

Figure 1.3. Molecular structure of ascorbic acid

Ascorbic acid is water soluble organic acid, that means human body does not store it automatically. Therefore, the supply must be taken daily either from food containing high vitamin C or supplements. There are many available sources in nature, from various kinds of food stuffs, which are rich in natural ascorbic acid, mostly rich in fresh fruits and leafy vegetables such as guava, papaya, cabbage and spinach (Goh *et al.*, 2008). Small amount can be also found from animal sources such as meat, fish, eggs and poultry. Among the all vitamins, ascorbic acid is the least stable vitamin, like easily oxidized in air and can be easily destroyed by heat and storage.

1.6 Paracetamol

Paracetamol (acetaminophen, 4-acetamidophenol, *N*-acetyl-*p*-aminophenol) is an antipyretic and analgesic drug, which was firstly introduced in medicine by Von Mering in 1893. It is commonly used to relieve pains such as aches, headaches, menstrual cramps and fever. Paracetamol is also used in combination with narcotic analgesics, which increases its efficacy and reduces the risk of narcotics abuse. It is sold under various brand names like Tylenol, Panadol and Aspirin-Free Anacin, usually formulated in tablets, containing 500 mg paracetamol per tablet. Molecular structure of paracetamol is similar to aspirin as shown in Figure 1.4.

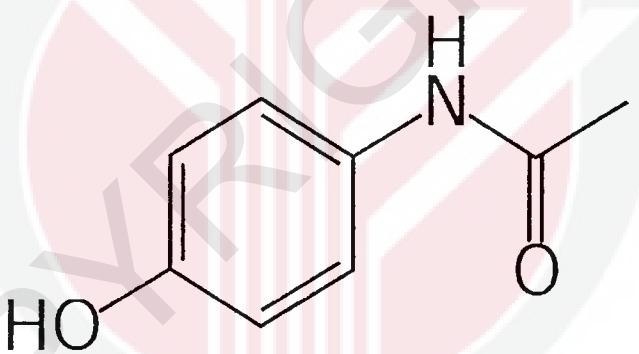

Figure 1.4. Molecular structure of paracetamol

Paracetamol is considered safe for human use when the recommended dose is not exceeded. But because of its wide availability, purposeful or accidental overdose is quite common. It is also used in suicide attempts, and in this respect it is potentially more dangerous than other over-the-counter drugs such as aspirin. This is because overdoses of paracetamol may cause nausea, vomiting, sweating, and exhaustion. Very large overdose can cause liver failure and death. Taken long-term, in proper therapeutic doses, the liver and also other organs can be harmed.

1.7 Fundamental of Voltammetric Techniques

Voltammetry is the branch of electrochemistry, which is one of the main analytical techniques. All areas of voltammetry (theory, methodology, and instrumentation) have been significantly advanced since when it developed from the discovery of polarography. Generally, voltammetry is based on the measure of the faradaic current passing through the electrolyte solution containing electro-active compounds while the time-dependent potential is applied to an electrode in electrochemical cell. A plot of current as a function of applied potential is called a voltammogram (Christian, 1994), which provides quantitative and qualitative information about the species involved in the reaction.

Solid phase voltammetry (SPV) or voltammetry of microparticles technique is used for solid state samples mechanically transfer onto the surface of the bare electrode and then forcing redox reaction to proceed. This method is designed to directly perform electrochemical studies of solid phases, such as metals and alloys, sparingly soluble complexes, organic compounds (Scholz and Lange, 1992). The simplicity and usefulness of the abrasion technique in SPV have been described (Scholz and Lange, 1992). Its usefulness includes the qualitative and quantitative identification of the constituents of alloys, minerals, pigments, corrosion processes and non-conducting organic and inorganic compounds. This technique is especially useful for the voltammetric studies of compounds that are insoluble.

1.7.1 Linear Sweep Voltammetry

Linear sweep voltammetry is the simplest voltammetric technique, which uses waveform. The current response is measured when the potential is applied to the working electrode as a function of time as shown in Figure 1.5.

The slope of this ramp has units of volts per unit time, and is generally called the scan rate of the experiment. With a linear potential ramp, the faradaic current is found to increase at higher scan rates. This is due to the increased flux of electroactive material to the electrode at the higher scan rates. The value of $E_{1/2}$ can be used to identify unknown species, and the height of the limiting current can be used to determine concentration.

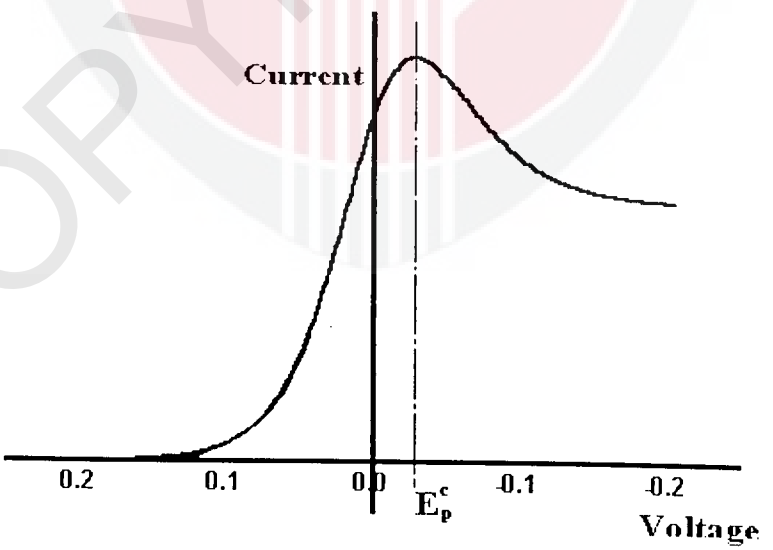

Figure 1.5. Linear sweep voltammetry

1.7.2 Cyclic Voltammetry

Cyclic voltammetry is widely used voltammetric technique, which is based on a linear potential waveform; the potential is changed as a linear function of time. It is usefl for rapidly providing considerable information on the thermodynamics of redox processes, the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes (Wang, 2000). The electrode potential is scanned linearly with a triangle wave form as shown in Figure 1.6.

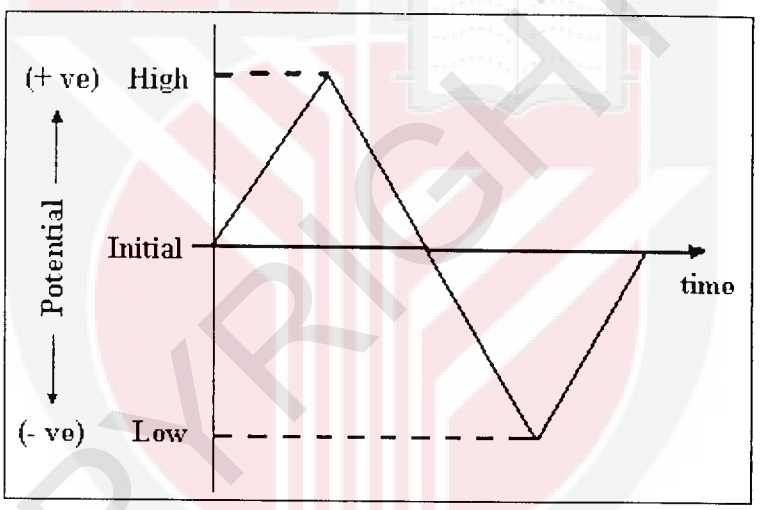

Figure 1.6. Triangular potential waveform for cyclic voltammetry

The important parameters of cyclic voltammogram are the peak currents and peak potentials of the anodic and cathodic peaks, respectively. If the heterogeneous electron transfer is rapid compared to the mass transfer, diffusion or migration flux of the reactants and products of the electrode reaction, the redox reaction is said to be electrochemically reversible (Girault, 2004). The peak current, in terms of the analyte concentration, for a reversible redox reaction at 25°C is given by Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5)\, n^{3/2} A C D^{1/2} \upsilon^{1/2} \qquad [1.1]$$

In this equation, n is the number of electron transferred per molecule (equiv/mole), υ is the scan rate (V/s), A is the electrode surface area (cm^2), D is the analyte's diffusion coefficient (cm^2/s) and C is the analyte's concentration ($mole/cm^3$).

Therefore, for a reversible reaction, the peak current is directly proportional to the concentration, and the square root of the scan rate. Meanwhile, the peak separation for a reversible redox reaction is given by:

$$\Delta E_p = E_{pa} - E_{pc} = 2.303\, RT / nF \qquad [1.2]$$

Thus, ΔE_p for a reversible redox reaction at 25°C should be $0.0592/n$V. For irreversible or quasi-reversible redox reaction, ΔE_p should be greater than $0.0592/n$V (Eklund *et al.*, 1999). The peak separation is useful in determining the number of electrons transferred, and as a criterion for Nernstian behavior (Wang, 2000). The formal reduction potential for a reversible redox couple is easily determined as the average of the two peak potentials as shown in Equation 1.3. Formal reduction potentials measured using cyclic voltammetry is usually accurate to within 50 mV of the true value.

$$E^\circ = (E_{pa} + E_{pc})/2 \qquad [1.3]$$

In addition, in a reversible redox couple: $I_{pa}/I_{pc}=1$ for all scan rates. But, in the irreversible reaction, the potential peaks are reduced in size and widely separated. The extent of irreversibility increases with rises in sweep rate. The behaviors of irreversible process are caused by slow electron transfer kinetics and the chemical reaction of oxidation (Ox) and reduction (Red). For the quasi-reversible redox system, the current is controlled by both the charge transfer and mass transport.

1.7.3 Chronoamperometry

Chronoamperometry (CA) is a technique where the current is measured as a function of time under potentiostatic control. In CA, the excitation signal is a square-wave signal. The potential is stepped from an initial potential value at which there is no electrolysis to a final potential value (Figures 1.7) at which a diffusion-controlled oxidation or reduction occurs. The potential can be stepped back to initial potential after pulse width time and this technique is known as double-potential step CA.

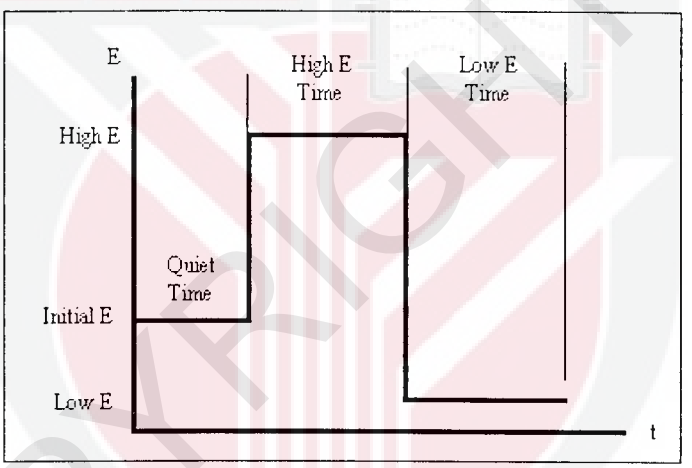

Figure 1.7. Potential waveform for chronoamperometry

In conjunction with Faraday's Law, the charge, Q, passed across the interface is related to the amount of material that has been converted, and the currentis related to the instantaneous rate at which the conversion occurs. The current decays smoothly as the electrolysis proceeds to deplete the solution near the electrode of electroactive species. Since electron transfer occurs in a faradaic electrode process, the current is the faradaic current. The current response decays as a function of time for a planar electrode is expressed by the Cottrell equation (Brett & Oliveira-Brett, 1993):

$$i_f\ (t)\ =\ nFAC(D/\pi t)^{1/2} \qquad [1.4]$$

Where, i_f is the Faradaic current (A), n is the number of electrons transfer per molecule (Equiv/mole), F is the Faraday's constant (96500 C/Equiv), A is the electrode area (cm^2), C is the analyte's concentration ($mole/cm^3$), D is the analyte's diffusion coefficient (cm^2/s) and t is the time (s).

CA can be applied to determine diffusion coefficient, electrode area and electron stoichiometry and the study of mechanism of electrode process. These parameters were determined from the gradient of i versus $t^{-1/2}$ graph. CA is also used to determine the effective electrochemical area of an electrode, when D and n are known. Once the electrode area is known, the electrode can be used to measure the value for diffusion coefficient (Brett & Oliveira-Brett, 1993).

1.7.4 Chronocoulometry

Chronocoulometry (CC) is frequently used one of the classical voltammetric techniques; hence, the charge is monitored as a function of time. Figures 1.8 shows the chronocoulogram. In CC, the electrode is being applied a linear potential ramp or potential step at an initial potential, where no current flows to a final potential, where the reaction of interest does occur. This results in a passage of charge across the electrode interface. General process of CC is similar to CA, but the difference is the measurement of charge instead of current directly as in CA.

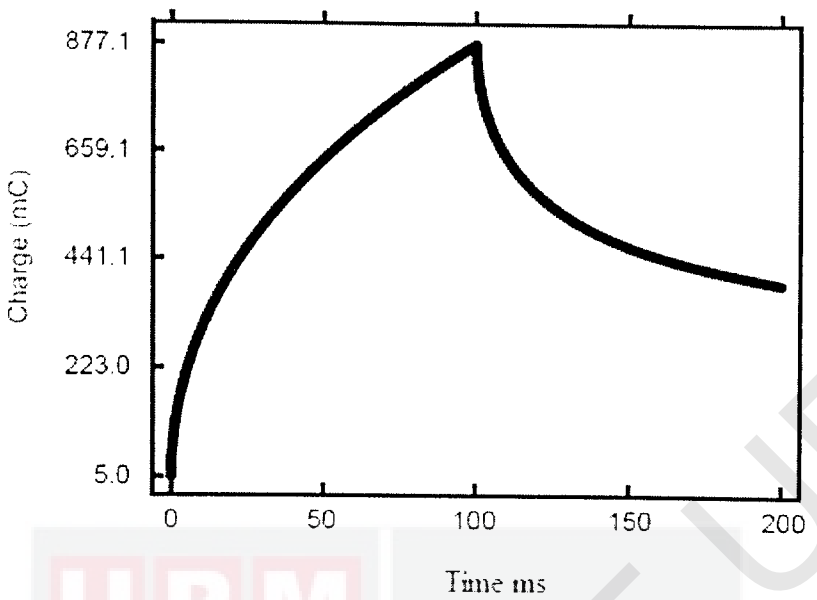

Figure 1.8. Chronocoulogram (charge-time) response for double potential step chronocoulometry

The expression for the forward chronocoulometric response of diffusing components is simply the Cottrell equation integrated with respect to time as shown below:

$$Q_d = 2nFAD^{1/2}C\pi^{-1/2}t^{1/2} \qquad [1.5]$$

Where, Q_d is the diffusing charge (C), n is the number of electrons per molecule (Equiv/mole), F is the Faraday's constant (96500 C/Equiv), A is the electrode area (cm^2), C is the concentration of electroactive species ($mole/cm^3$), D is the diffusion coefficient of electroactive species (cm^2/s), t is the time (s).

One of the applications of CC is its ability to detect species absorbed onto the surface of the working electrode. Such species are electrolyzed very rapidly once the potential is stepped. In a simplified mathematical treatment, three sinks of charges are considered separately as additive function. The three charges are charge from the diffusing species due to the charging of working electrode, capacitive charge of the

electrode double layer, and adsoptive charge due to electrolysis of the adsorbed species. Among the three components, only Q_d is time independent. The total forward chronocoulometric response can thus be described by:

$$Q_{total} = Q_d + Q_{dl} + Q_{ads} \quad [1.6]$$

$$Q_{total} = 2nFAD^{1/2}C\pi^{-1/2}t^{1/2} + Q_{dl} + nFA\Gamma \quad [1.7]$$

Where, Q_{total} is the total charge and Γ is the surface excess of reactant (mole/cm^2).

According to the equation above, the plot of Q versus $t^{1/2}$ should be linear and the linearization of the chronocoulometric response by CC is illustrated in Figure 1.14. This plot is often referred as Anson plot. The slope of this line is $2nFAD^{1/2}C\pi^{-1/2}\pi$ and the intercept is $Q_{dl} + nFA\Gamma$ (Wang, 2000). It is useful to step the potential back to the initial potential, and then record the charge due to the reaction of the species produced on the forward step. The expression of the reverse step is shown in Equation 1.8.

$$Q_r = 2nFAD^{1/2}C\pi^{-1/2}\theta + Q_{dl} + nFA\Gamma_r \quad [1.8]$$

Where, Q_r is equal to Q_{max} - Q_t, θ is equal to $(\tau^{1/2} + t - \tau^{1/2} - t^{1/2})$, τ means the forward step width and t is the total integration time.

The capacitive charge is eliminated to yield $nFA(\Gamma_o - \Gamma_r)$ when the intercept of the forward step subtracts the intercept of the reverse step. If only one species adsorbs, this then gives that species' surface excess directly.

1.8 Problem Statement

In recent years, electroanalysts are focused on development of new chemically modified electrodes, because currently available working electrodes such as glassy carbon, gold and platinum are lack of sensitivity and selectivity (Gooding, 2005). The new electrode should be able to possess following advantages: highly sensitive, good detection limit, stability, selectivity, reproducibility, low cost and simplicity. Recent published works used GCE modified with a thin layer or film of CNT (Dai, 2006). Typically using CNT modified GCEs for electroanalysis the claimed benefits include good detection limits, increased sensitivity, resistance to surface fouling and decreased overpotentials (Wang, 1995).

Combining the unique properties of CNT, such as high specific surface area, subtle electronic properties and strong adsorptive ability, with nanostructured TiO_2 as a composite material is expected to enhance the electrocatalytic activity of CNT/GCE. To date, there are no published reports on the usage of CNT/TiO_2 nanoparticle composite modified GCE. Therefore the main objectives of the present study were to develop new chemically modified electrode based on the CNT/TiO_2/GCE. The outcomes of this research will have substantial contribution to the field of electrochemical and nanosciences.

1.9 Objectives

The objectives of this study are:

i. To fabricate a chemically modified electrode based on the CNT/TiO_2/GCE composite using solution evaporation and mechanical attachment methods.

ii. To characterize the composite electrode using scanning electron microscopy, energy dispersive X-ray, and voltammetric techniques of cyclic voltammetry, linear sweep voltammetry, chronoamperometry and chronocoulometry.

iii. To compare the electrode responses of the CNT/TiO_2/GCE composite with that CNT/GCE; TiO_2/GCE and unmodified GCE in order to determine some biological and chemical analytes.

iv. To determine the optimum physical and chemical conditions under which maximum current enhancement can be obtained for the electrochemical response of above analytes.

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