UNIVERSITI PUTRA MALAYSIA

GLASSY CARBON ELECTRODE MODIFIED WITH NANOPARTICLES OF SELECTED METAL/METAL OXIDES AND SINGLE-WALLED CARBON NANOTUBES FOR ELECTRO ANALYSIS OF ASCORBIC ACID AND PARACETAMOL

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

GLASSY CARBON ELECTRODE MODIFIED WITH NANOPARTICLES OF SELECTED METAL/METAL OXIDES AND SINGLE-WALLED CARBON NANOTUBES FOR ELECTRO ANALYSIS OF ASCORBIC ACID AND PARACETAMOL

By

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March 2015

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This thesis presents a research study on the novel electrochemical sensors based on single-walled carbon nanotube/nanoparticles for the voltammetric determination of ascorbic acid and paracetamol. The determination of ascorbic acid and paracetamol using bare electrodes have several limitations such as poor sensitivity and reproducibility. Electrode modified by using a hybrid of both nanoparticles and single-walled carbon nanotubes (SWCNTs) could provide better sensitive and reproducibility in the electrochemical determination of ascorbic acid and paracetamol.

The solid phase voltammetry of microparticles (SPVM) technique is applied for the fabrication and characterization of the electrochemical sensors. SWCNTs and metal/metal oxides-modified glass carbon electrodes (GCEs) were fabricated by a mechanical attachment technique. SWCNT/tungsten/GCE, SWCNT/tungsten oxide/GCE and SWCNT/zinc oxide/GCE were fabricated for the detection of ascorbic acid. Electrochemical determination of paracetamol in a potassium dihydrogen phosphate electrolyte solution was performed with SWCNT/zinc oxide/GCE and SWCNT/nickel/GCE. The electrochemical behavior and electrocatalytic properties of all the modified electrodes were characterized by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Nanocomposites of the selected metal/metal oxide and SWCNT were examined by the UV-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX).

When a SWCNT/nanoparticle was introduced as the mediator, current responses toward ascorbic acid in the potassium dihydrogen sulphate electrolyte solution dramatically increased in comparison to the bare GCE. In the cyclic voltammetric analysis, the enhancement factors were 2.5, 3.5, and 2.0 for the SWCNT/WO_3/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE, respectively. In the application of electrodes immobilized with a nanocomposite for ascorbic acid determination, the SWCNT/WO_3/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE displayed a sensitivity of 14.6, 23.8, 13.7 mA M^{-1} and a detection limit of 5.1, 1.9, 21.0 μM, respectively. Cyclic voltammetry studies indicated that the oxidation of ascorbic acid at all the

modified electrodes was a diffusion controlled process. The effect of pH was investigated and the optimal pH was obtained: pH 2 (SWCNT/WO_3/GCE), 2.5 (SWCNT/W/GCE), and 4-5 (SWCNT/ZnO/GCE) when 0.1 M potassium dihydrogen phosphate solution was used. The activation energy (E_a) of the electrocatalytic reaction was found to be 3.43, 1.02 and 3.81 kJ mol^{-1} corresponding to SWCNT/WO_3/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE, respectively using a temperature study. The electrochemical method was assessed with a repeatability study, and relative standard deviation (RSD) values of 5.3%, 3.5% and 3.8% were obtained for SWCNT/WO_3/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE, respectively. All the modified electrodes were used for ascorbic acid recovery determination in real samples, with excellent recovery rates of near 100% with RSD ranging from 2.0-6.5%.

The peak current response of paracetamol obtained at the SWCNT/ZnO/GCE and SWCNT/Ni/GCE were significantly better than that of a bare GCE, with the enhancement factors of 4 and 5, respectively. The improved current response of modified electrodes is attributed to the unique structure and physicochemical properties of SWCNT and nanoparticles. In the determination of paracetamol using cyclic voltammetry, a linear current response was observed for the concentration range of 0.05 to 0.50 mM. The SWCNT/ZnO/GCE and SWCNT/Ni/GCE displayed a sensitivity of 42.5, 63.8 mA M^{-1} and a detection limit of 0.32, 0.12 μM, respectively Redox reactions of paracetamol at the SWCNT/ZnO/GCE and SWCNT/Ni/GCE were controlled by both diffusion and adsorption. Both modified electrodes had higher oxidation peak currents at lower pH.

The reproducibility of the developed method in paracetamol detection was assessed. Relative standard deviations of 5.5% and 5.6% were obtained for SWCNT/ZnO/GCE and SWCNT/Ni/GCE, respectively in the repeatability study. Both modified electrodes show excellent results for detecting paracetamol in real life samples with a RSD of 1.9%. Scanning electron micrographs indicate the porous and uneven distribution of nanocomposites on the modified electrode surfaces. The particle size of nanocomposite was found to be bigger after electroanalysis. From the UV-Vis analysis, a decrease in band gap energy was discovered when a SWCNT was introduced to the nanoparticles. This could have improved the electrical conductivity of the nanocomposite and therefore enhance the electrocatalytic activity. It was indicated in the EIS analysis that the charge transfer resistance of the SWCNT/ZnO/GCE is higher compared to other modified electrodes.

In conclusion, several electrochemical sensors were fabricated and characterized on the voltammetric determination of ascorbic acid and paracetamol. The results demonstrated that SWCNT and selected metal/metal oxide are superior electrode materials. The electroanalytical method is a simple, fast, low cost and sensitive approach for the detection of ascorbic acid and paracetamol. The results indicate that the modified electrodes based on SWCNT and selected metal/metal oxides can be applied for the routine qualitative and quantitative determination of ascorbic acid or paracetamol.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

ELEKTROD KARBON BERKACA DIUBAHSUAI DENGAN NANOPARTIKEL LOGAM OKSIDA/LOGAM TERPILIH DAN NANOTIUB KARBON BERDINDING TUNGGAL UNTUK ANALISIS ELEKTROKIMIA ASID ASKORBIK DAN PARASETAMOL

Oleh

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Tesis ini membentangkan kajian mengenai penderia elektrokimia yang baru berdasarkan nanotiub karbon berdinding tunggal/nanopartikel untuk penentuan kandungan asid askorbik dan parasetamol secara voltammetri. Penentuan asid askorbik dan parasetamol dengan menggunakan elektrod yang tidak diubahsuai mempunyai beberapa kelemahan seperti sensitiviti dan kebolehulangan yang kurang memuaskan. Gabungan kedua-dua nanopartikel dan nanotiub karbon berdinding tunggal (SWCNT) mungkin boleh menyediakan elektrod ubahsuai yang lebih sensitif dan menpunyai kebolehulangan yang tinggi untuk menganalisis kandungan asid askorbik dan parasetamol secara elektrokimia.

Teknik voltametri fasa pepejal mikropartikel (SPVM) digunakan untuk fabrikasi dan pencirian penderia elektrokimia. Teknik penempalan mekanikal telah digunakan untuk fabrikasi elektrod karbon berkaca (GCE) baru ini dengan campuran SWCNT dan logam/oksida logam. SWCNT/tungsten/GCE, SWCNT/tungsten oksida/GCE dan SWCNT/zink oksida/GCE telah difabrikasi untuk mengesan kandungan asid askorbik. Kaedah elektrokimia telah digunakan untuk mengesan kandungan parasetamol di dalam larutan elektrolit kalium dihidrogen fosfat dengan menggunakan SWCNT/zink oksida/GCE dan SWCNT/nikel/GCE. Sifat elektrokimia dan ciri-ciri pemangkinan elektron di dalam semua elektrod yang ubahsuai telah dikaji dengan alat voltammetri berkitar (CV) and spektroskopi impedans elektrokimia (EIS). Nanokomposit logam/oksida logam terpilih dan SWCNT telah disemak menggunakan spektroskopi ultra lembayung nampak (UV-Vis), mikroskopi pengimbasan elektron (SEM) dan spektrometer penyerakan tenaga sinar-X (EDX).

Apabila SWCNT/nanopartikel digunakan sebagai bahan perantaraan, tindak balas arus elektrik terhadap asid askorbik di dalam elektrolit kalium dihidrogen sulfat meningkat secara mendadak, berbanding dengan GCE yang tidak diubahsuai. Dalam analisis voltammetri berkitar, faktor penambahbaikan adalah 2.5, 3.5, dan 2.0 untuk SWCNT/WO_3/GCE, SWCNT/W/GCE dan SWCNT/ZnO/GCE. Dalam penggunaan elektrod yang disekat gerak dengan nanokomposit untuk penentuan asid askorbik, SWCNT/WO_3/GCE, SWCNT/W/GCE dan SWCNT/ZnO/GCE memaparkan

sensitiviti sebanyak 14.6, 23.8, 13.7 mA M^{-1} dan had pengesanan 5.1, 1.9, 21.0 μM. Kajian voltammetri berkitar menunjukkan bahawa pengoksidaan asid askorbik pada semua elektrod yang diubahsuai adalah dikawal oleh proses resapan. Kajian pH telah dijalankan dan pH optimum untuk semua elektrod adalah pH 2 (SWCNT/WO_3/GCE), 2.5 (SWCNT/W/GCE), dan 4-5 (SWCNT/ZnO/GCE) apabila larutan elektrolit kalium dihidrogen fosfat 0.1 M digunakan. Tenaga pengaktifan (E_a) bagi tindak balas pemangkinan elektron adalah 3.43, 1.02 dan 3.81 kJ mol^{-1} untuk SWCNT/WO_3/GCE, SWCNT/W/GCE dan SWCNT/ZnO/GCE. Kebolehulangan kaedah elektrokimia ini telah dikaji dan nilai sisihan piawai relatif (RSD) SWCNT/WO_3/GCE, SWCNT/W/GCE dan SWCNT/ZnO/GCE ialah 5.3%, 3.5% dan 3.8%. Kadar perolehan semula pada semua elektrod yang diubahsuai untuk mengesan asid askorbik dalam sampel sebenar adalah sangat memuaskan iaitu menghampiri 100% dengan RSD berada di antara 2.0-6.5%.

Puncak tindak balas arus elektrik parasetamol yang diperolehi pada SWNCT/ZnO/GCE dan SWCNT/Ni/GCE adalah lebih baik berbanding pada GCE yang tidak diubahsuai, dengan faktor-faktor peningkatan sebanyak 4 dan 5. Tindak balas arus elektrik yang lebih baik untuk elektrod diubahsuai adalah disebabkan oleh strukturnya yang unik dan ciri-ciri fizikal dan kimia SWCNT dan nanopartikel. Dalam penentuan parasetamol menggunakan voltammetri berkitar, tindak balas arus elektrik yang linear untuk pelbagai kepekatan diperhatikan iaitu di antara 0.05-0.50 mM. SWCNT/ZnO/GCE dan SWCNT/Ni/GCE memaparkan sensitiviti bernilai 42.5, 63.8 mA M^{-1} dan had pengesanan sebanyak 0.32, 0.12 μM. Tindak balas redoks parasetamol di SWCNT/ZnO/GCE dan SWCNT/Ni/GCE dikawal oleh kedua-dua proses, iaitu resapan dan jerapan. Kedua-dua elektrod diubahsuai mempunyai puncak pengoksidaan yang lebih tinggi pada pH yang lebih rendah.

Kebolehulangan untuk pengesanan parasetamol menggunakan elektrod-elektrod tersebut telah dinilai. Dalam kajian ini, sisihan piawai relatif sebanyak 5.5% dan 5.6% telah diperolehi bagi SWCNT/ZnO/GCE dan SWCNT/Ni/GCE. Kedua-dua elektrod yang diubahsuai menunjukkan hasil yang sangat baik untuk mengesan parasetamol dalam sampel sebenar dengan RSD sebanyak 1.9%. Mikrograf pengimbasan elektron menunjukkan taburan nanokomposit yang poros dan bentuk tidak sekata pada permukaan elektrod yang diubahsuai. Saiz partikel nanokomposit didapati lebih besar selepas proses analisis elektrokimia. Daripada analisis UV-Vis, terdapat pengurangan dalam jurang jalur tenaga ditemui apabila SWCNT dicampurkan dengan nanopartikel. Ini boleh meningkatkan kekonduksian elektrik nanokomposit dan sekaligus meningkatkan aktiviti pemangkinan elektronnya. Ini telah ditunjukkan dalam analisis EIS bahawa rintangan pemindahan cas bagi SWCNT/ZnO/GCE adalah lebih tinggi daripada elektrod ubahsuai yang lain.

Sebagai rumusan dalam kajian ini, beberapa penderia elektrokimia telah difabrikasi dan ciri-cirinya dikaji atas penentuan kandungan asid askorbik dan parasetamol secara voltammetri. Keputusan penyelidikan menunjukkan bahawa SWCNT dan logam/ oksida logam terpilih adalah bahan elektrod yang unggul. Analisis secara elektrokimia adalah kaedah yang mudah, cepat, murah dan sensitif untuk analisis kandungan asid askorbik dan parasetamol. Hasil penyelidikan juga menunjukkan bahawa penderia elektrokimia dengan SWCNT dan logam oksida /logam terpilih amat sesuai digunakan untuk analisis kualitatif dan kuantitatif asid askorbik atau parasetamol.

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I certify that a Thesis Examination Committee has met on 4 March 2015 to conduct the final examination of Ngai Koh Sing on her thesis entitled "Glassy Carbon Electrode Modified with Nanoparticles of Selected Metal/Metal Oxides and Single-Walled Carbon Nanotubes for Electro Analysis of Ascorbic Acid and Paracetamol" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;

- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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Committee: RUZNIZA MOHD ZAWAWI	Committee: _____

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A	Electrode area
AA	Ascorbic acid
BASi	Bioanalytical Systems, Incorporation
BDDE	Boron-doped diamond electrode
BPPGE	Basal plane pyrolytic graphite electrode
C	Bulk concentration
C_{60}	Fullerene
CCE	Carbon-ceramic electrode
C_{dl}	Double layer capacitance
Ceb	Cebion
CME	Chemically modified electrode
CNT	Carbon nanotube
CPE	Carbon paste electrode
CV	Cyclic voltammetry
D	Diffusion coefficient/diffussibility
D^o	Standard diffusibility
DA	Dopamine
DNA	Deoxyribonucleic acid
E_a	Activation energy
E_c	Conduction band
EDX	Energy dispersive X-ray spectroscopy
E_g	Band gap energy

EIS	Electrochemical impedance spectroscopy
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
EPPGE	Edge plane pyrolytic graphite electrode
E_v	Valence band
F	Faraday's constant
FDA	Food and Drug Administration
FESEM	Field emission scanning electron microscopy
G	Conductance
GC	Glassy carbon
GCE	Glassy carbon electrode
GE	Graphite electrode
GSK	GlaxoSmithKline
h	Planck's constant
HMDE	Hanging mercury drop electrode
HPLC	High performance liquid chromatography
I	Current
i_o	Exchange current density
i_{pa}	Anodic peak current
L	Inductance
m	Number of protons/slope
MA	Mechanical attachment
MWCNT	Multi-walled carbon nanotube
n	Number of electrons
N/A	Not available

Ni/GCE	Nickel-modified glassy carbon electrode
NP	Nanoparticle
Q	Charge
R	Resistance/Specific gas constant
R^2	R-squared
R_∞	Diffuse reflectance
R_{ct}	Charge transfer resistance
Rex	Redoxon
R_s	Solution resistance
RSD	Relative standard deviation
SEM	Scanning electron microscopy
SPVM	Solid phase voltammetry of microparticles
SWCNH	Single-walled carbon nanohorn
SWCNT	Single-walled carbon nanotube
SWCNT/Ni	Single-walled carbon nanotube/nickel
SWCNT/W	Single-walled carbon nanotube/tungsten
SWCNT/WO_3	Single-walled carbon nanotube/tungsten oxide
SWCNT/ZnO	Single-walled carbon nanotube/zinc oxide
SWCNT/Ni/GCE	Single-walled carbon nanotube/nickel-modified glassy carbon electrode
SWCNT/W/GCE	Single-walled carbon nanotube/tungsten-modified glassy carbon electrode
SWCNT/WO_3/GCE	Single-walled carbon nanotube/tungsten oxide-modified glassy carbon electrode

SWCNT/ZnO/GCE	Single-walled carbon nanotube/zinc oxide-modified glassy carbon electrode
T	Temperature
t	Time
UA	Uric acid
UV-Vis	Ultraviolet-visible
V	Voltage
VPSEM	Variable pressure scanning electron microscopy
W/GCE	Tungsten-modified glassy carbon electrode
WO_3/GCE	Tungsten oxide-modified glassy carbon electrode
X	Reactance
X_L	Inductive reactance
X_C	Capacitive reactance
Z	Impedance
ZnO/GCE	Zinc oxide-modified glassy carbon electrode
α	Absorption coefficient
σ	Conductivity
σ^o	Standard conductivity
θ	Phase shift
v	Frequency of vibration

CHAPTER 1

INTRODUCTION

1.1 Modification of Electrode

The bare electrode is an unmodified electrode of inert substrate. Direct electrochemical oxidation of an electroactive species at a bare electrode is difficult. It is irreversible, slows electrode kinetics and requires high overpotentials for the reactions, which results in the fouling of the electrode by its oxidation products. This leads to poor sensitivity, low stability and poor reproducibility.

The electrochemical performance of electrodes can be improved via surface treatment or surface modification. Electrodes surface treatment or surface modification can enhance the performance of the electrodes in terms of sensitivity and selectivity. The modification of electrodes is aimed to improve the electrical conductivity, promote the electrode surface activity, reduce the overpotential and therefore enhance the electron transfer activity.

1.1.1 Electrode Surface Treatment

Electrode surface treatment is employed to clean and activate the electrode surface. The two common approaches of electrode surface treatment are surface cleaning and surface activation. Cleaning of electrode surface prior to fabrication or modification is significant to ensure the surface is free from impurities and contaminants. Surface cleaning can be done by physically wiping off the chemical or nanofilm from the electrode surface; and the polishing of the electrode using the polishing pad with alumina slurry, followed by an ultrasonic bath for the removal of alumina residues.

Surface activation can be achieved by potential cycling the electrode at a wide potential range; or preparing a highly oxidized/reduced electrode via potentiostatic polarization. The two common approaches for potentiostatic polarization are anodization and cathodization. Under anodization, an electrode is subjected to the potentials where oxidation will take place. Conversely in cathodization, the potentials applied is programmed to cause reduction. Therefore, positive or negative charges can be created on the electrode surface by anodization or cathodization.

1.1.2 Electrode Surface Modification

Electrode surface modification can overcome some limitations of bare electrode and enhance the electron transfer activity, reduce the high overpotential, improve the mass transfer velocity, improve the sensitivity of the desired substrate and restrain the interferences in real sample analysis. A chemically modified electrode (CME) is one where some type of electrode material is attached by one or more combinations of electron transfer mediator via a selected fabrication method. Electrode surface can be modified by fabrication with various electron transfer mediators via selected techniques (Topoglidis *et al*., 2005). In any type of fabrication technique, a thin film

which consists of the desired mediator is attached onto the electrode surface. The surface modification of a bare electrode offers several advantages if the electrode is to be used as an electrochemical sensor for some particular substance. Different techniques have been used for electrode fabrication such as mechanical attachment (Banan *et al*., 2013; Ganchimeg *et al*., 2011), surface casting (Motahary *et al*., 2010; Habibi *et al*., 2011a), electropolymerization (Wan *et al*., 2006), electrochemical deposition (Selvaraju and Ramaraj, 2007), covalent attachment, adsorption, sol-gel matrices, layer-by-layer assembly (Fernandes *et al*., 2011; Qian *et al*., 2005), cross-linking method etc.

1.2 Electron Transfer Mediators

Electron transfer mediators are electroactive materials which are usually used in the modification of electrode surfaces in order to improve the electrode performance in terms of sensitivity and selectivity. Those electron transfer mediators act as electron transfer agents, which can be deposited onto different electrodes surface via various fabrication techniques. There are a variety of electron transfer mediators used in the research, such as metals, polymers, biochemical compounds, deoxyribonucleic acid (DNA), organic compounds, inorganic compounds, chemicals, etc. Several nanomaterials such nanoparticles and carbon nanotubes are also commonly used as electron transfer mediators when fabricated on the electrode surface.

1.3 Ascorbic Acid

Ascorbic acid (vitamin C) is a water soluble compound which is naturally present in many types of fruits and vegetables (Figure 1.1). It possesses antioxidant property, and plays an important role in biochemical metabolism and physiological processes. Ascorbic acid is one of the essential nutrients that is required by humans, which can be obtained through diet or supplement. Various pharmaceutical, nutraceutical and food products are fortified with ascorbic acid. Food and Drug Administration (FDA) recommended a daily dosage of ascorbic acid at 60 mg for human consumption. Deficiency in ascorbic acid will cause scurvy disease. Therefore, the determination of ascorbic acid content is important in the quality control process of pharmaceutical, nutraceutical and food industries. Hence, a simple, rapid, sensitive and accurate method for the routine determination of ascorbic acid is needed.

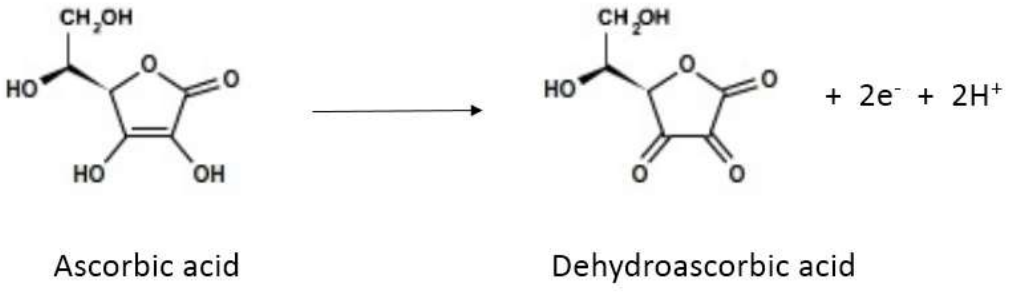

Figure 1.1. The structure and reaction of ascorbic acid.

1.4 Paracetamol

Paracetamol (acetaminophen, 4-acetamidophenol, N-acetyl-p-aminophenol or 4'-hydroxyacetanilide) is a drug with antipyretic and analgesic properties (Figure 1.2). It is an effective medicament used to relieve various pains associated with headache, toothache, neck ache, muscular pain, chronic pain, rheumatic pain, postoperative pain and pains from minor injuries. Paracetamol is also widely used to reduce body temperature; thus it is applied in fevers, colds, flu and it even relieves coughing. Suppliers recommend a daily limit of 4000 mg or 8 tablets in paracetamol intake. It is safe and without any harmful side effects under controlled or therapeutic dosage. Chronic use or overdose of paracetamol leads to the accumulation of toxic metabolites in the liver. The toxic metabolite is produced by cytochrome P-450, which may cause severe or fatal hepatoxicity and nephrotoxicity, skin rashes and pancreas inflammation. Quantitative determination of paracetamol is a significant process in the quality assurance of pharmaceutical industry. In the healthcare industry, the analytical detection of paracetamol content in the human specimen is also vital for diagnostic purpose. Therefore, the development of a simple, fast, sensitive and accurate analytical method for the determination of paracetamol is needed.

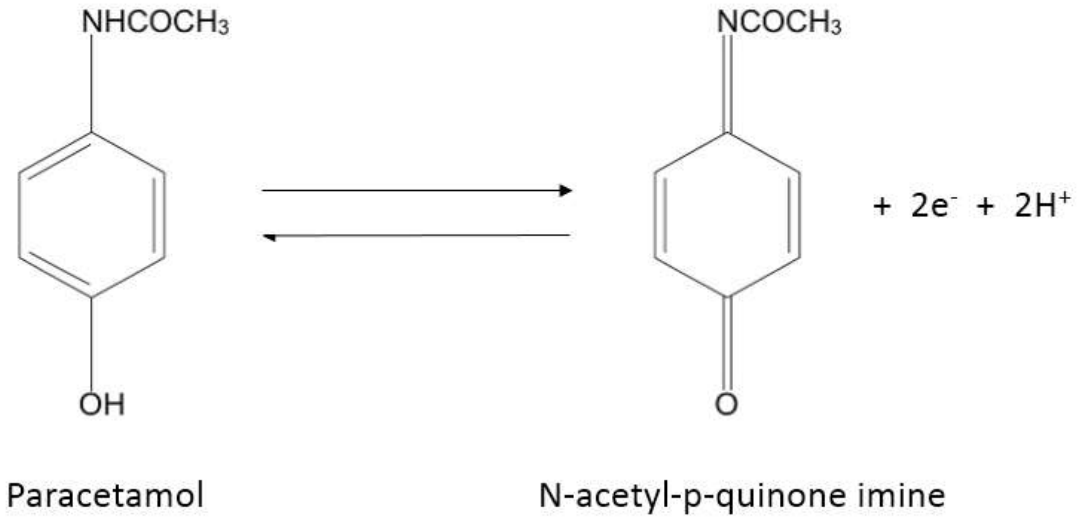

Figure 1.2. The structure and reaction of paracetamol.

1.5 Methods Used in the Determination of Ascorbic Acid and Paracetamol

Many methods have been developed to evaluate the concentration of ascorbic acid and paracetamol; alone, in a mixture solution, pharmaceutical formulations or biological fluids. A range of analytical methods which are most commonly used have been reported in the literature, such as chromatography (including gas chromatography, thin-layer chromatography and liquid chromatography) , spectrophotometry, fluorometry, colorimetry, titrimetry, electrophoresis and chemiluminescence.

Nevertheless, there are some shortcomings in using some of these methods. Those disadvantages such as poor sensitivity, high cost, time-consuming and complicated pretreatment or preparation procedure, making those methods unsuitable for routine analysis. Gas and liquid chromatography methods are sensitive but require expensive instrumentation and operating cost. Spectrophotometry and titrimetry analysis require a tedious extraction procedure and therefore the methods are time-consuming. Colorimetry method involves a formation of colour compound from the derivatization of the analyte, which is less sensitive and also time-consuming.

Over last few decades, development of alternative methods for detecting ascorbic acid and paracetamol has received great interest. Compared to other methods, electroanalytical method is more promising due to its simplicity, fast results and low cost. The use of electrochemical analysis in the detection of ascorbic acid and paracetamol is recommended because of its good sensitivity, reproducibility and stability. Both ascorbic acid and paracetamol are electroactive compounds, which can be oxidized electrochemically. At present, there are many literatures on the electrochemical study in determining ascorbic acid and paracetamol. The importance of both ascorbic acid and paracetamol led to the efforts to develop and improve the electroanalytical method for the determination of both compounds.

1.6 Problem Statement

Electrochemical determination of ascorbic acid or paracetamol is a promising methodology. Electrochemical sensors are of great interest due to the wide applications in the pharmaceutical, food and healthcare industries. Due to the importance of this simple, reliable and rapid method of determining ascorbic acid and paracetamol, the development of electrochemical sensors with excellent reproducibility, sensitivity, low detection limit and fast response has been a subject of concern.

The direct oxidation of ascorbic acid and paracetamol using a bare electrode has some limitations such as poor sensitivity and poor reproducibility. This is due to the high overpotential at the electron transfer process and the fouling problem which is caused by the adsorption of the products formed. Thus, the bare electrode is not appropriate in analytical application and is not widely employed in the routine analysis for quality control purposes. Recently, much attention has been focused on the use of modified electrodes to improve the electrocatalysis of ascorbic acid and paracetamol.

However, some of the modified electrodes may possess several disadvantages such as complicated, time-consuming or costly preparation procedure, poor stability and reproducibility. Therefore, it is important to explore a potential electron transfer mediator that provides a good sensitivity and to fabricate a modified electrode with a simple preparation technique. In this sense, mechanical attachment has been proposed for the immobilization of the electron transfer mediators onto the electrode surface.

The main advantages of the mechanical attachment technique are simplicity, low cost and faster speed of preparation. New reproducible surface can be easily obtained by a simple polishing or cleaning procedure. The porous and the roughness of electrode surface allowed the accessibility of reactants to the active sites on the electrode surface. Different modifiers such as organic compounds, biochemical compounds, synthetic polymers and nanoparticles can be used as electron transfer mediators.

The electrochemical determination by using modified electrodes based on different electron transfer mediators is an attractive technique. However, a major drawback of the modified electrode prepared by mechanical attachment is the leaching of electron transfer mediators into the electrolyte solution, which diminishes the mediator film that is deposited onto the electrode surface. This is because the mediators are in loose contact with the electrode surface. Another problem in preparing the electrochemical sensor based on the mechanical attachment is lack of long term stability. Repetitive use of the modified electrode leads to surface contamination and passivation. This is due to the adsorption and accumulation of intermediates which cause low electron transfer rate, poor sensitivity and poor detection limit. Therefore, the modified electrode could be degraded and passivation after some time.

To solve the problem, the electrode surface has to be renewed or refreshed to overcome mediators leaching as well as contamination by the intermediates or oxidation products. A fresh electrode surface deposited with the electron transfer mediators possesses good sensitivity and reproducibility which can be used as an effective sensor in the oxidation of the substrate of interest.

Many electrochemical sensors have been explored towards the improving of the sensitivity and reproducibility by using various electron transfer mediators. From this point of view, the selection of the type of electron transfer mediator used in the fabrication of electrochemical sensors still remains a challenge.

1.7 Hypotheses

The electrocatalytic property of the mediators is the main factor to determine the performance of the modified electrode. Most of the previous studies on the electrochemical oxidation of electroactive species involve the use of nanomaterials. Recent studies demonstrated the advantages of using nanocomposite as a mediator to accelerate the electron transfer activity. Carbon nanotube (CNT) exhibits excellent electrocatalytic activities due to its high electrical conductivity and electrochemical activity. Additionally, CNT could reduce the overpotential and lead to a remarkably increase of peak current response compared to bare electrode.

Recently, increasing attention has been focused on the composite of CNT and coating with various nanomaterials. Particular attention is paid on the interaction between single-walled carbon nanotube (SWCNT) and nanoparticle of metal/metal oxide. The electrocatalytic activity of the SWCNT/nanoparticle modified electrode for biochemical compounds is remarkably different from using just the individual nanoparticle.

This work describes the solid phase voltammetry of microparticles (SPVM) study on the electrocatalytic determination of ascorbic acid and paracetamol. Mechanical attachment (MA) technique is applied for the fabrication of novel electrochemical sensors. Cyclic voltammetry (CV) is used for the characterization of the modified electrodes in determining the concentration of ascorbic acid and paracetamol. Different modified electrodes were prepared and constructed based on the nanocomposites of SWCNT and selected metal/metal oxides using glassy carbon electrode (GCE). Nanocomposites of the electron transfer mediators were prepared and immobilized onto the freshly polished and cleaned GCE surfaces by using mechanical attachment technique. These mediators are commercially available, and the preparation of modified electrodes is simple and fast. Ascorbic acid and paracetamol were used as model compounds to study the electrochemical properties of the modified electrodes. Ascorbic acid is chosen as the model nutraceutical supplements; and paracetamol is used as the model pharmaceutical drug.

In the present work, three electrochemical sensors (SWCNT/WO_3, SWCNT/W and SWCNT/ZnO modified electrodes) were used for the determination of ascorbic acid. The use of SWCNT/ZnO and SWCNT/Ni modified GCEs for the determination of paracetamol is described. These nanocomposites will be immobilized onto the GCE surface and used for electrochemical sensing. It is expected that the SWCNT could enhance the property of the individual nanoparticle. The aims of this work are to establish the electrochemical sensors, and to compare the electrochemical performance of different modified electrodes in the determination of ascorbic acid and paracetamol.

Tungsten and nickel are transition metals which possess good electrical conductivity. Tungsten oxide and zinc oxide are transition metal oxides that possess high potential to be applied as electron transfer mediators due to their semiconducting nature. The transition metals and their oxides in nanostructures could possess better electron transfer activity and electrochemical properties. We propose the synergistic effect between the SWCNT and metal/metal oxides will produce an effective electrochemical sensor.

To the best of our knowledge, so far there is no report in the detection of ascorbic acid based on a SWCNT/WO_3 and SWCNT/W modified GCEs. For instance, the nanocomposites of SWCNT/W and SWCNT/WO_3 were not used as mediators to enhance the sensing activity of any electroactive species, including ascorbic acid and paracetamol. The novel CNT/ZnO has excited significant attention due to the electrochemical and photocatalytic properties of zinc oxide. CNT/ZnO has been reported in many literatures for various studies including synthesis, characterization, optical properties and applications (Gultekin *et al*., 2013; Kim *et al*., 2008; Wang and Adhikari, 2011; Zhang *et al*., 2009). Multi-walled carbon nanotube/zinc oxide (MWCNT/ZnO) was applied in the determination of glucose by Palanisamy and co-workers (2012). However, the fabrication of SWCNT/ZnO/GCE in determining ascorbic acid as well as paracetamol has not been reported so far. We assume the combination of SWCNT and ZnO will show a better sensitivity than the MWCNT/ZnO modified GCE. Another experiment on carbon-coated nickel magnetic nanoparticles fabricated electrode was used in detecting paracetamol (Wang *et al*., 2007b). We suggest the presence of SWCNT in nickel could also produce satisfactory electrode performance.

1.8 Objectives

The general objective is to carry out solid phase voltammetry study on all the modified electrodes prepared.

The specific objectives of this study are as follows:

1. To fabricate modified glassy carbon (GC) solid electrodes using nanocomposites of single-walled carbon nanotubes (SWCNT) and nanoparticles of selected metal and metal oxides (W, Ni, ZnO and WO_3) via mechanical attachment technique.

2. To determine (a) the band gap energy of the selected nanocomposites using UV-Vis spectrophotometers; (b) the surface morphology and elemental composition of the above mentioned modified solid electrodes using SEM and EDX, respectively; (c) the impedance of the electrochemical reaction of ascorbic acid at SWCNT/WO_3/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE; and the detection of paracetamol at SWCNT/ZnO/GCE and SWCNT/Ni/GCE, using EIS.

3. To carry out the electrocatalytic studies on the electrochemical reaction of (a) ascorbic acid mediated by SWCNT/WO_3/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE; (b) paracetamol mediated by SWCNT/ZnO/GCE and SWCNT/Ni/GCE using cyclic voltammetry under various physical and chemical conditions.

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