



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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FS 2015 81

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

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ELECTRO ANALYSIS OF ASCORBIC ACID AND PARACETAMOL**

By

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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/WO₃/GCE, SWCNT/W/GCE and SWCNT/ZnO/GCE, respectively. In the application of electrodes immobilized with a nanocomposite for ascorbic acid determination, the SWCNT/WO₃/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/WO₃/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/WO₃/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/WO₃/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 ASKORBİK DAN PARASETAMOL**

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Tesis ini membentangkan kajian mengenai penderia elektrokimia yang baru berdasarkan nanotub 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 keboleholangan yang kurang memuaskan. Gabungan kedua-dua nanopartikel dan nanotub karbon berdinding tunggal (SWCNT) mungkin boleh menyediakan elektrod ubahsuai yang lebih sensitif dan mempunyai keboleholangan 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/WO₃/GCE, SWCNT/W/GCE dan SWCNT/ZnO/GCE. Dalam penggunaan elektrod yang disekat gerak dengan nanokomposit untuk penentuan asid askorbik, SWCNT/WO₃/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 berkisar 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/WO₃/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/WO₃/GCE, SWCNT/W/GCE dan SWCNT/ZnO/GCE. Kebolehulangan kaedah elektrokimia ini telah dikaji dan nilai sisihan piawai relatif (RSD) SWCNT/WO₃/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 SWCNT/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 berkisar, 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 porus 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.

ACKNOWLEDGEMENTS

I was born to the Earth in the year of 1978, without anything but a body and soul. The achievement of a degree of Doctor of Philosophy after 36 years, is not an assignment from any person or party, but solely my personal goal. I would like to dedicate my sincere gratitude to those persons who, directly and indirectly, provided influence, care, companionship and support in technical, knowledge, advice and financial terms, towards the completion of this degree.

First of all, a very special thanks to Assoc. Prof. Dr. Tan Wee Tee, my supervisor who always provided advice and guidance in my research and in other aspects. Prof. Dr. Zulkarnain Zainal and Dr. Ruzniza Mohd Zawawi, my co-supervisors, whose guided and participated in the technical review of my manuscripts.

My father and mother who provided me with primary and secondary education during my childhood; and supported my tertiary education even under financial constrain. Asst. Prof. Dr. Loh Yen Lee, my idol, who inspired me to be a person in science for my lifetime. Assoc. Prof. Dr. Ng Chew Hee, my supervisor during undergraduate years who offered research opportunities and guidance to complete my first publication. Dr. Goh Joo Kheng, my research senior who provided training and foundation knowledge in electrochemistry during my undergraduate collaboration. Datuk Dr. Soon Ting Kueh, my former lecturer and referee in all kinds of applications for my career or education, who always supported me. Dr. Muhammed Zidan, my research senior who provided hands-on training and guidance in the early stages of my postgraduate research. Assoc. Prof. Dr. Lo Foong Loong and Assoc. Prof. Dr. Sim Kooi Mow, my former colleagues, whose always cared about my research and concerned about my progress from time to time. Asst. Prof. Dr. Ngai Siew Ching, my sister who accompanied me during most of my postgraduate time.

Special thanks are credited to the Universiti Putra Malaysia (UPM) for providing research facilities and administrative assistances; Kementerian Pengajian Tinggi Malaysia for providing financial aids in MyBrain15 (MyPhD).

Lastly, I would like to acknowledge Assoc. Prof. Dr. Juan Joon Ching, who accompanied me throughout the entire process in pursuing my degree of Doctor of Philosophy; giving me advice and support in chemistry, and life.

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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LIST OF ABBREVIATIONS

| | |
|-------------|------------------------------------------|
| <i>A</i> | Electrode area |
| AA | Ascorbic acid |
| BASi | Bioanalytical Systems, Incorporation |
| BDDE | Boron-doped diamond electrode |
| BPPGE | Basal plane pyrolytic graphite electrode |
| <i>C</i> | 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 |
| <i>D</i> | Diffusion coefficient/diffusibility |
| D° | 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 |
| R_{ex} | 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^0 | Standard conductivity |
| θ | Phase shift |
| ν | 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.

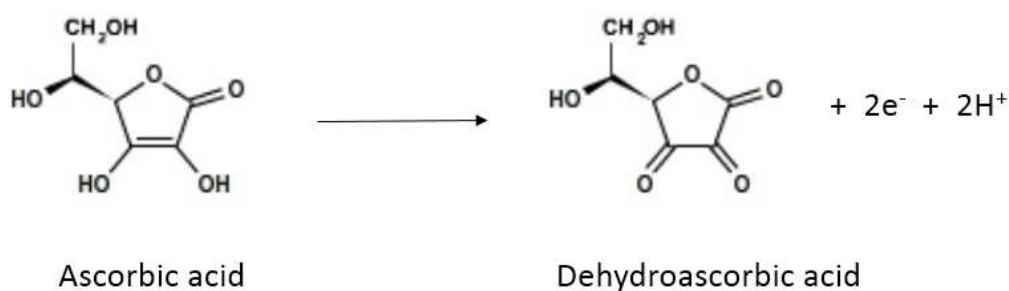


Figure 1.1. The structure and reaction of ascorbic acid.

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 hepatotoxicity 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.

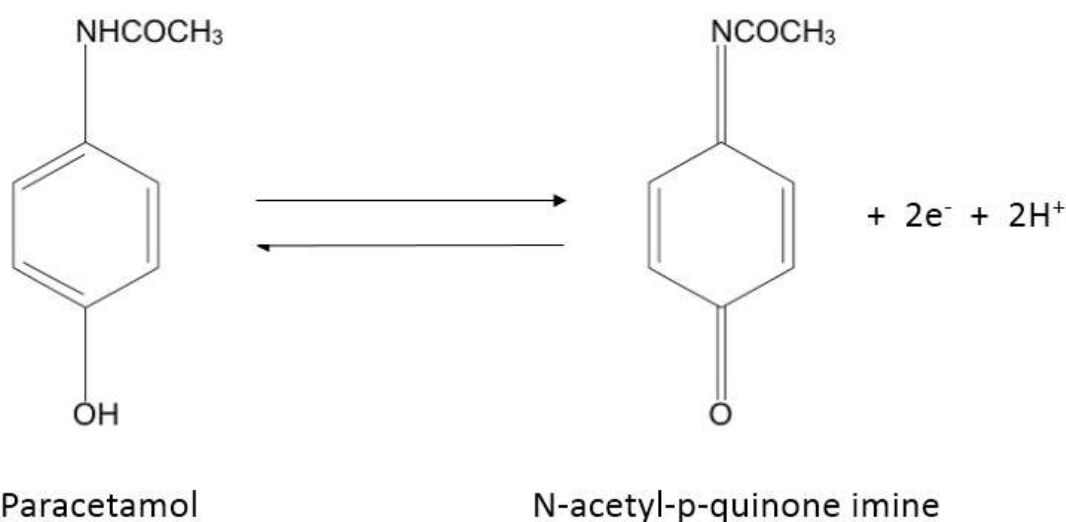


Figure 1.2. The structure and reaction of paracetamol.

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/WO₃, 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/WO₃ and SWCNT/W modified GCEs. For instance, the nanocomposites of SWCNT/W and SWCNT/WO₃ 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.

REFERENCES

- Abdullah, E.T., Hasan, S.M. and Naje, A.N. (2013). Optical properties of PVC-MWCNT nano composites. *Indian Journal of Pure & Applied Physics* 51: 77-80.
- Alothman, Z.A., Bukhair, N., Wabaidur, S.M. and Haider, S. (2010). Simultaneous electrochemical determination of dopamine and acetaminophen using multiwall carbon nanotubes modified glassy carbon electrode. *Sensors and Actuators B: Chemical* 146: 314–320.
- Arani, A.G., Shams, S., Amir, S. and Maraghi, Z.K. (2012). Effects of electro-thermal fields on buckling of a piezoelectric polymeric shell reinforced with DWBNNTs. *Journal of Nanostructures* 2: 345-355.
- Atta, N.F., El-Kady, M.F. and Galal, A. (2009b). Palladium nanoclusters-coated polyfuran as a novel sensor for catecholamine neurotransmitters and paracetamol. *Sensors and Actuators B: Chemical* 141: 566–574.
- Babaei, A., Babazadeh, M. and Afrasiabi, M. (2011a). A sensitive simultaneous determination of adrenalin and paracetamol on a glassy carbon electrode coated with a film of chitosan/room temperature ionic liquid/single-walled carbon nanotubes nanocomposite. *Chinese Journal of Chemistry* 29: 2157–2164.
- Babaei, A., Garrett, D.J. and Downard, A.J. (2011b). Selective simultaneous determination of paracetamol and uric acid using a glassy carbon electrode modified with multiwalled carbon nanotube/chitosan composite. *Electroanalysis* 23: 417–423.
- Banan, D., Tan, W.T., Sulaiman, Y., Yusri, M.F., Zidan, M. and Ghani, S.A. (2013). Electrochemical oxidation of ascorbic acid using MgB₂-MWCNT modified glassy carbon electrode. *International Journal Electrochemical Science* 8: 12519–12530.
- Baranowska, I. and Koper, M. (2009). The preliminary studies of electrochemical behavior of paracetamol and its metabolites on glassy carbon electrode by voltammetric methods. *Electroanalysis* 21: 1194–1199.
- Beitollahi, H., Raoof, J.-B. and Hosseinzadeh, R. (2011). Fabrication of a nanostructure-based electrochemical sensor for simultaneous determination of *N*-acetylcysteine and acetaminophen. *Talanta* 85: 2128–2134.
- Bond, A.M. (1997). Voltammetric techniques for studying the redox chemistry of solids. *Journal of Solid State Electrochemistry* 1: 185-186.
- Chandra, S., Lokesh, K.S., Nicolai, A. and Lang, H. (2009). Dendrimer-rhodium nanoparticle modified glassy carbon electrode for amperometric detection of hydrogen peroxide. *Analytica Chimica Acta* 632: 63–68.

- Chen, J., Lin, Z. and Chen, G. (2007). Enhancement of electrochemiluminescence of lucigenin by ascorbic acid at single-wall carbon nanotube film-modified glassy carbon electrode. *Electrochimica Acta* 52: 4457–4462.
- Chen, J., Zhang, W.-D. and Ye, J.-S. (2008). Nonenzymatic electrochemical glucose sensor based on MnO₂/MWNTs nanocomposite. *Electrochemistry Communications* 10: 1268–1271.
- Chen, X., Zhu, J., Xi, Q. and Yang, W. (2012). A high performance electrochemical sensor for acetaminophen based on single-walled carbon nanotube–graphene nanosheet hybrid films. *Sensors and Actuators B: Chemical* 161: 648–654.
- Cismaru, A., Voicu, M., Radoi, A., Dinescu, A., Neculoiu, D. and Dragoman, M. (2011). EMBG resonators based on carbon nanotubes for DNA detection. *Romanian Journal of Information Science and Technology* 14: 212–221.
- Dai, Y.-Q. and Shiu, K.-K. (2004). Glucose biosensor based on multi-walled carbon nanotube modified glassy carbon electrode. *Electroanalysis* 16: 1697–1703.
- Danaee, I., Jafarian, M., Forouzandeh, F., Gobal, F. and Mahjani, M.G. (2008). Impedance spectroscopy analysis of glucose electro-oxidation on Ni-modified glassy carbon electrode. *Electrochimica Acta* 53: 6602–6609.
- Danaee, I., Jafarian, M., Forouzandeh, F., Gobal, F. and Mahjani, M.G. (2009). Electrochemical impedance studies of methanol oxidation on GC/Ni and GC/NiCu electrode. *International Journal of Hydrogen Energy* 34: 859–869.
- Dehbashi, M. and Aliahmad, M. (2012). Experimental study of structural and optical band gap of nickel doped tin oxide nanoparticles. *International Journal of Physical Sciences* 7: 5415–5420.
- Ensafi, A.A., Karimi-Maleh, H., Mallakpour, S. and Hatami, M. (2011). Simultaneous determination of *N*-acetylcysteine and acetaminophen by voltammetric method using *N*-(3,4-dihydroxyphenethyl)-3,5-dinitrobenzamide modified multiwall carbon nanotubes paste electrode. *Sensors and Actuators B: Chemical* 155: 464–472.
- Fan, Y., Liu, J.-H., Lu, H.-T. and Zhang, Q. (2011a). Electrochemical behavior and voltammetric determination of paracetamol on Nafion/TiO₂–graphene modified glassy carbon electrode. *Colloids and Surfaces B: Biointerfaces* 85: 289–292.
- Fan, Y., Liu, J.-H., Yang, C.-P., Yu, M. and Liu, P. (2011b). Graphene–polyaniline composite film modified electrode for voltammetric determination of 4-aminophenol. *Sensors and Actuators B: Chemical* 157: 669–674.
- Fernandes, D.M., Ghica, M.E., Cavaleiro, A.M.V. and Brett, C.M.A. (2011). Electrochemical impedance study of self-assembled layer-by-layer iron–silicotungstate/poly(ethylenimine) modified electrodes. *Electrochimica Acta* 56: 7940–7945.

- Foster, K. and McCormac, T. (2006). Electrochemical properties of an osmium(II) copolymer film and its electrocatalytic ability towards the oxidation of ascorbic acid in acidic and neutral pH. *Electroanalysis* 18: 1097–1104.
- Gamry Instruments. Basic of electrochemical impedance spectroscopy. Retrieved 17 November 2014 from <http://www.gamry.com/application-notes/basics-of-electrochemical-impedance-spectroscopy/>
- Ganchimeg, P., Tan, W.T., Yusof, N.A. and Goh, J.K. (2011). Voltammetric oxidation of ascorbic acid mediated by multi-walled carbon nanotubes/titanium dioxide composite modified glassy carbon electrode. *Journal of Applied Sciences* 11: 848-854.
- Ghorbani-Bidkorbeh, F., Shahrokhian, S., Mohammadi, A. and Dinarvand, R. (2010). Simultaneous voltammetric determination of tramadol and acetaminophen using carbon nanoparticles modified glassy carbon electrode. *Electrochimica Acta* 55: 2752–2759.
- Goyal, R.N. and Singh, S.P. (2006). Voltammetric determination of paracetamol at C₆₀-modified glassy carbon electrode. *Electrochimica Acta* 51: 3008–3012.
- Goyal, R.N., Gupta, V.K. and Chatterjee, S. (2010). Voltammetric biosensors for the determination of paracetamol at carbon nanotube modified pyrolytic graphite electrode. *Sensors and Actuators B: Chemical* 149: 252–258.
- Goyal, R.N., Rana, A.R.S., Aziz, M.A. and Oyama, M. (2011). Effect of gold nanoparticle attached multi-walled carbon nanotube-layered indium tin oxide in monitoring the effect of paracetamol on the release of epinephrine. *Analytica Chimica Acta* 693: 35–40.
- Gültekin, D., Alaf, M. and Akbulut, H. (2013). Synthesis and characterization of ZnO nanopowders and ZnO-CNT nanocomposites prepared by chemical precipitation route. *Acta Physica Polonica A* 123: 274-276.
- Habibi, B., Jahanbakhshi, M. and Pournaghi-Azar, M.H. (2011a). Differential pulse voltammetric simultaneous determination of acetaminophen and ascorbic acid using single-walled carbon nanotube-modified carbon–ceramic electrode. *Analytical Biochemistry* 411: 167–175.
- Habibi, B., Jahanbakhshi, M. and Pournaghi-Azar, M.H. (2011b). Simultaneous determination of acetaminophen and dopamine using SWCNT modified carbon–ceramic electrode by differential pulse voltammetry. *Electrochimica Acta* 56: 2888–2894.
- Huang, H., Ran, P. and Liu, Z. (2007). Impedance sensing of allergen–antibody interaction on glassy carbon electrode modified by gold electrodeposition. *Bioelectrochemistry* 70: 257–262.

- Hu, C., Dang, X. and Hu, S. (2004). Studies on adsorption of cetyltrimethylammonium bromide at carbon paste electrode and the enhancement effect in thyroxine reduction by voltammetry and electrochemical impedance spectroscopy. *Journal of Electroanalytical Chemistry* 572: 161–171.
- Hu, C., Yuan, S. and Hu, S. (2006). Studies on electrochemical properties of MWNTs-Nafion composite films based on the redox behavior of incorporated Eu^{3+} by voltammetry and electrochemical impedance spectroscopy. *Electrochimica Acta* 51: 3013–3021.
- Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature* 354: 56–58.
- Jain, R. and Rather, J.A. (2011). Stripping voltammetry of tinidazole in solubilized system and biological fluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 378: 27–33.
- Jia, Z., Liu, J. and Shen, Y. (2007). Fabrication of a template-synthesized gold nanorod-modified electrode for the detection of dopamine in the presence of ascorbic acid. *Electrochemistry Communications* 9: 2739–2743.
- Jo, S., Jeong, H., Bae, S.R. and Jeon, S. (2008). Modified platinum electrode with phytic acid and single-walled carbon nanotube: Application to the selective determination of dopamine in the presence of ascorbic and uric acids. *Microchemical Journal* 88: 1–6.
- Kachosangi, R.T., Wildgoose, G.G. and Compton, R.G. (2008). Sensitive adsorptive stripping voltammetric determination of paracetamol at multiwalled carbon nanotube modified basal plane pyrolytic graphite electrode. *Analytica Chimica Acta* 618: 54–60.
- Kalimuthu, P. and John, S.A. (2009). Electropolymerized film of functionalized thiadiazole on glassy carbon electrode for the simultaneous determination of ascorbic acid, dopamine and uric acid. *Bioelectrochemistry* 77: 13–18.
- Kang, I., Heung, Y.Y., Kim, J.H., Lee, J.W., Gollapudi, R., Subramaniam, S., Narasimhadevara, S., Hurd, D., Kirikera, G.R., Shanov, V., Schulz, M.J., Shi, D., Boerio, J., Mall, S. and Ruggles-Wren, M. (2006). Introduction to carbon nanotube and nanofiber smart materials. *Composites: Part B* 37: 382–394.
- Kang, X., Mai, Z., Zou, X., Cai, P. and Mo, J. (2007). A sensitive nonenzymatic glucose sensor in alkaline media with a copper nanocluster/multiwall carbon nanotube-modified glassy carbon electrode. *Analytical Biochemistry* 363: 143–150.
- Kang, X., Wang, J., Wu, H., Liu, J., Aksay, I.A. and Lin, Y. (2010). A graphene-based electrochemical sensor for sensitive detection of paracetamol. *Talanta* 81: 754–759.
- Kartal, M. (2001). LC method for the analysis of paracetamol, caffeine and codeine phosphate in pharmaceutical preparations. *Journal of Pharmaceutical and Biomedical Analysis* 26: 857–864.

- Ke, N.J., Lu, S.-S. and Cheng, S.-H. (2006). A strategy for the determination of dopamine at a bare glassy carbon electrode: *p*-Phenylenediamine as a nucleophile. *Electrochemistry Communications* 8: 1514–1520.
- Kim, D.S., Lee, S.-M., Scholz, R., Knez, M., Gösele, U., Fallert, J., Kalt, H. and Zacharias, M. (2008). Synthesis and optical properties of ZnO and carbon nanotube based coaxial heterostructures. *Applied Physics Letters* 93: 103108.
- Kim, K.S., Park, K.A., Kim, H.J., Bae, D.J., Lim, S.C., Lee, Y.H., Kim, J.R., Lim, J.-J. and Choi, W.B. (2003). Band gap modulation of a carbon nanotube by hydrogen functionalization. *Journal of the Korean Physical Society* 42: 137-142.
- Ko, H., Pikus, Y., Jiang, C., Jauss, A., Hollricher, O. and Tsukruk, V.V. (2004). High-resolution Raman microscopy of curled carbon nanotubes. *Applied Physics Letters* 85: 2598-2600.
- Korany, M.A., Fahmy, O.T., Mahgoub, H. and Maher, H.M. (2011). High performance liquid chromatographic determination of some guaiphenesin-containing cough-cold preparations. *Journal of Advanced Research* 2: 121–130.
- Kul, D., Ghica, M.E., Pauliukaite, R. and Brett, C.M.A. (2013). A novel amperometric sensor for ascorbic acid based on poly(Nile blue A) and functionalised multi-walled carbon nanotube modified electrodes. *Talanta* 111: 76–84.
- Lavorante, A.F., Pires, C.K. and Reis, B.F. (2006). Multicommutated flow system employing pinch solenoid valves and micro-pumps spectrophotometric determination of paracetamol in pharmaceutical formulations. *Journal of Pharmaceutical and Biomedical Analysis* 42: 423–429.
- Li, F., Song, J., Gao, D., Zhang, Q., Han, D. and Niu, L. (2009). Simple and rapid voltammetric determination of morphine at electrochemically pretreated glassy carbon electrodes. *Talanta* 79: 845–850.
- Li, M. and Jing, L. (2007). Electrochemical behavior of acetaminophen and its detection on the PANI–MWCNTs composite modified electrode. *Electrochimica Acta* 52: 3250–3257.
- Lin, X. and Li, Y. (2006). A sensitive determination of estrogens with a Pt nano-clusters/multi-walled carbon nanotubes modified glassy carbon electrode. *Biosensors and Bioelectronics* 22: 253–259.
- Li, X., Chen, Y. and Huang, X. (2007). Electrochemical behavior of neomycin at DNA-modified gold electrodes. *Journal of Inorganic Biochemistry* 101: 918–924.
- Li, Y. and Chen, S.-M. (2012). The electrochemical properties of acetaminophen on bare glassy carbon electrode. *International Journal of Electrochemical Science* 7: 2175-2187.

- Li, Y. and Lin, X. (2006). Simultaneous electroanalysis of dopamine, ascorbic acid and uric acid by poly (vinyl alcohol) covalently modified glassy carbon electrode. *Sensors and Actuators B: Chemical* 115: 134–139.
- Li, Z., Wang, Z., Sun, X., Fang, Y. and Chen, P. (2010). A sensitive and highly stable electrochemical impedance immunosensor based on the formation of silica gel–ionic liquid biocompatible film on the glassy carbon electrode for the determination of aflatoxin B₁ in bee pollen. *Talanta* 80: 1632–1637.
- Liu, A.-L., Wang, K., Chen, W., Gao, F., Cai, Y.-S., Lin, X.-H., Chen, Y.-Z. and Xia, X.-H. (2012a). Simultaneous and sensitive voltammetric determination of acetaminophen and its degradation product for pharmaceutical quality control and pharmacokinetic research by using ultrathin poly (calconcarboxylic acid) film modified glassy carbon electrode. *Electrochimica Acta* 63:161–168.
- Liu, A.-L., Zhang, S.-B., Chen, W., Lin, X.-H. and Xia, X.-H. (2008a). Simultaneous voltammetric determination of norepinephrine, ascorbic acid and uric acid on polycalconcarboxylic acid modified glassy carbon electrode. *Biosensors and Bioelectronics* 23: 1488–1495.
- Liu, B., Hu, X., Deng, Y., Yang, S. and Sun, C. (2010). Selective determination of trichloroacetic acid using silver nanoparticle coated multi-walled carbon nanotubes. *Electrochemistry Communications* 12: 1395–1397.
- Liu, H., Wang, G., Chen, D., Zhang, W., Li, C. and Fang, B. (2008b). Fabrication of polythionine/NPAu/MWNTs modified electrode for simultaneous determination of adenine and guanine in DNA. *Sensors and Actuators B: Chemical* 128: 414–421.
- Liu, X., Luo, L., Ding, Y., Kang, Z. and Ye, D. (2012b). Simultaneous determination of L-cysteine and L-tyrosine using Au-nanoparticles/poly-eriochrome black T film modified glassy carbon electrode. *Bioelectrochemistry* 86: 38–45.
- Lourencao, B.C., Medeiros, R.A., Rocha-Filho, R.C., Mazo, L.H. and Fatibello-Filho, O. (2009). Simultaneous voltammetric determination of paracetamol and caffeine in pharmaceutical formulations using a boron-doped diamond electrode. *Talanta* 78: 748–752.
- Lovic, M. and Scholz, F. (1997). A model for the propagation of a redox reaction through microcrystals. *Journal of Solid State Electrochemistry* 1: 108–113.
- Łuczak, T. (2008). Preparation and characterization of the dopamine film electrochemically deposited on a gold template and its applications for dopamine sensing in aqueous solution. *Electrochimica Acta* 53: 5725–5731.
- Lu, T.-L. and Tsai, Y.-C. (2011). Sensitive electrochemical determination of acetaminophen in pharmaceutical formulations at multiwalled carbon nanotube-alumina-coated silica nanocomposite modified electrode. *Sensors and Actuators B: Chemical* 153: 439–444.

- Malik, S.R., Maqbool, M.A., Hussain, S. and Irfan, H. (2008). Carbon nano-tubes: Description, properties and applications. *Journal of the Pakistan Materials Society* 2: 21:26.
- Mazloun-Ardakani, M., Beitollahi H., Amini, M.K., Mirkhalaf, F. and Abdollahi-Alibeik, M. (2010a). New strategy for simultaneous and selective voltammetric determination of norepinephrine, acetaminophen and folic acid using ZrO₂ nanoparticles-modified carbon paste electrode. *Sensors and Actuators B: Chemical* 151: 243–249.
- Mazloun-Ardakani, M., Beitollahi, H., Sheikh-Mohsenia, M.A., Naeimi, H. and Taghavinia, N. (2010b). Novel nanostructure electrochemical sensor for electrocatalytic determination of norepinephrine in the presence of high concentrations of acetaminophene and folic acid. *Applied Catalysis A: General* 378: 195–201.
- Medeiros, R.A., Rocha-Filho, R.C. and Fatibello-Filho, O. (2010). Simultaneous voltammetric determination of phenolic antioxidants in food using a boron-doped diamond electrode. *Food Chemistry* 123: 886–891.
- Mehretie, S., Admassie, S., Tessema, M. and Solomon, T. (2012). Electrochemical study of niclosamide at poly(3,4-ethylenedioxythiophene) modified glassy carbon electrode. *Sensors and Actuators B: Chemical* 168: 97– 102.
- Messina, G.A., Vito, I.E.D. and Raba, J. (2006). On-line microfluidic sensor integrated with an enzyme-modified pre-cell for the monitoring of paracetamol in pharmaceutical samples. *Analytica Chimica Acta* 559: 152–158.
- Motahary, M., Ghoreishi, S. M., Behpour, M. and Golestaneh, M. (2010). Electrochemical determination of ascorbic acid at the surface of a graphite electrode modified with multi-walled carbon nanotubes/ tetradecyltrimethyl ammonium bromide. *Journal of Applied Electrochemistry* 40: 841-847.
- Muralidharan, B., Gopu, G., Vedhi, C. and Manisankar, P. (2008). Voltammetric determination of analgesics using a montmorillonite modified electrode. *Applied Clay Science* 42: 206–213.
- Murugaraj P., Mainwaring, D., Khelil, N.A., Peng, J.L, Siegele, R. and Sawant, P. (2010). The improved electromechanical sensitivity of polymer thin films containing carbon clusters produced in situ by irradiation with metal ions. *Carbon* 48: 4230-4237.
- Nair, S.S., John, S.A. and Sagara, T. (2009). Simultaneous determination of paracetamol and ascorbic acid using tetraoctylammonium bromide capped gold nanoparticles immobilized on 1,6-hexanedithiol modified Au electrode. *Electrochimica Acta* 54: 6837–6843.
- Nasri, Z. and Shams, E. (2009). Application of silica gel as an effective modifier for the voltammetric determination of dopamine in the presence of ascorbic acid and uric acid. *Electrochimica Acta* 54: 7416–7421.

- Nuryetti, Hermansyah. H. and Nasikin, M. (2012). Structure, energy band gap and electrical conductivity of tapioca/metal oxide composite. *Journal of Chemistry and Chemical Engineering* 6: 911-919.
- Odom, T.W., Huang, J.-L., Kim, P. and Lieber, C.M. (1998). Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature* 391: 62-64.
- Qian, L., Gao, Q., Song, Y., Li, Z. and Yang, X. (2005). Layer-by-layer assembled multilayer films of redox polymers for electrocatalytic oxidation of ascorbic acid. *Sensors and Actuators B: Chemical* 107: 303–310.
- Qiao, J.X., Luo, H.Q. and Li, N.B. (2008). Electrochemical behavior of uric acid and epinephrine at an electrochemically activated glassy carbon electrode. *Colloids and Surfaces B: Biointerfaces* 62: 31–35.
- Ozcan, L. and Sahin, Y. (2007). Determination of paracetamol based on electropolymerized-molecularly imprinted polypyrrole modified pencil graphite electrode. *Sensors and Actuators B: Chemical* 127: 362–369.
- Palanisamy, S., Cheemalapati, S. and Chen, S.-M. (2012). Enzymatic glucose biosensor based on multiwalled carbon nanotubes-zinc oxide composite. *International Journal of Electrochemical Science*. 7: 8394 – 8407.
- Perenlei, G., Tee, T.W., Yusof, N.A. and Kheng, G.J. (2011). Voltammetric detection of potassium ferricyanide mediated by multi-walled carbon nanotube/titanium dioxide composite modified glassy carbon electrode. *International Journal Electrochemical Science* 6: 520 – 531.
- Premkumar, J. and Khoo, S.B. (2005). Electrocatalytic oxidations of biological molecules (ascorbic acid and uric acids) at highly oxidized electrodes. *Journal of Electroanalytical Chemistry* 576: 105–112.
- Radhi, M.M., Tan, W.T., Rahman, M.Z.B.A. and Kassim, A.B. (2010a). Electrochemical Redox of Hg^{2+} Mediated by activated carbon modified glassy carbon electrode. *International Journal Electrochemical Science* 5: 615 – 629.
- Radhi, M.M., Tan, W.T., Rahman, M.Z.B.A. and Kassim, A.B. (2010b). Electrochemical characterization of the redox couple of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ mediated by a grafted polymer modified glassy carbon electrode. *Journal of Chemical Engineering of Japan* 43: 927–931.
- Radhi, M.M. Tan, W.T., Zaki, M., Rahman, B.A. and Kassim, A.B. (2010c). Voltammetric detection of Hg (ii) at C_{60} activated carbon and MWCNT modified glassy carbon electrode. *Research Journal of Applied Sciences* 5: 59-64.
- Radhi, M.M., Tan, W.T., Rahman, M.Z.B.A. and Kassim, A.B. (2010d). Voltammetric detection of Mn(II) in blood sample at C_{60} and MWCNT modified glassy carbon electrodes. *American Journal of Applied Sciences* 7: 439-445.

- Radovan, C., Cofan, C. and Cinghita, D. (2008). Simultaneous determination of acetaminophen and ascorbic acid at an unmodified boron-doped diamond electrode by differential pulse voltammetry in buffered media. *Electroanalysis* 20: 1346–1353.
- Raof, J.B., Baghayeri, M. and Ojani, R. (2012a). A high sensitive voltammetric sensor for qualitative and quantitative determination of phenobarbital as an antiepileptic drug in presence of acetaminophen. *Colloids and Surfaces B: Biointerfaces* 95: 121– 128.
- Raof, J.B., Ojani, R., Amiri-Aref, M. and Baghayeri, M. (2012b). Electrodeposition of quercetin at a multi-walled carbon nanotubes modified glassy carbon electrode as a novel and efficient voltammetric sensor for simultaneous determination of levodopa, uric acid and tyramine. *Sensors and Actuators B: Chemical* 166–167: 508– 518.
- Razmi, H and Habibi, E. (2010). Amperometric detection of acetaminophen by an electrochemical sensor based on cobalt oxide nanoparticles in a flow injection system. *Electrochimica Acta* 55: 8731–8737.
- Rifaya, M.N., Theivasanthi, T. and Alagar, M. (2012). Chemical capping synthesis of nickel oxide nanoparticles and their characterizations studies. *Nanoscience and Nanotechnology* 2: 134-138.
- Salimi, A., Hallaj, R. and Khayatian, G-R. (2005). Amperometric detection of morphine at preheated glassy carbon electrode modified with multiwall carbon nanotubes. *Electroanalysis* 17: 873-879.
- Salimi, A., Mamkhezri, H., Hallaj, R. and Soltanian, S. (2008). Electrochemical detection of trace amount of arsenic(III) at glassy carbon electrode modified with cobalt oxide nanoparticles. *Sensors and Actuators B: Chemical* 129: 246–254.
- Salimi, A., Noorbakhsh, A. and Soltanian, S. (2006). Electroless deposition of thionin onto glassy carbon electrode modified with single wall and multiwall carbon nanotubes: improvement of the electrochemical reversibility and stability. *Electroanalysis* 18: 703-711.
- Sandulescu, R., Mirel, S. and Oprean, R. (2000). The development of spectrophotometric and electroanalytical methods for ascorbic acid and acetaminophen and their applications in the analysis of effervescent dosage forms. *Journal of Pharmaceutical and Biomedical Analysis* 23: 77–87.
- Santos, D.P., Zandoni, M.V.B., Bergamini, M.F., Chiorcea-Paquim, A.-M., Diculescu, V.C. and Brett, A.-M.O. (2008). Poly(glutamic acid) nanofibre modified glassy carbon electrode: Characterization by atomic force microscopy, voltammetry and electrochemical impedance. *Electrochimica Acta* 53: 3991–4000.
- Scholz, F. and Lange, B. (1990). High-performance abrasive stripping voltammetry. *Fresenius' Journal of Analytical Chemistry* 338: 293-294.

- Scholz, F., Lange, B., Jaworski, A. and Pelzer, J. (1991). Analysis of powder mixtures with the help of abrasive stripping voltammetry and coulometry. *Fresenius' Journal of Analytical Chemistry* 340: 140-144.
- Scholz, F., Nitschke, L. and Henrion, G. (1989a). Identification of solid materials with a new electrochemical technique – the abrasive stripping analysis. *Fresenius' Journal of Analytical Chemistry* 334: 56-58.
- Scholz, F., Nitschke, L., Henrion, G. and Damaschun, F. (1989b). Abrasive stripping voltammetry - the electrochemical spectroscopy for solid state: Application for mineral analysis. *Fresenius' Journal of Analytical Chemistry* 335: 189-194.
- Selvaraju, T. and Ramaraj, R. (2007). Simultaneous detection of ascorbic acid, uric acid and homovanillic acid at copper modified electrode. *Electrochimica Acta* 52: 2998–3005.
- Shahrokhian, S. and Asadian, E. (2010). Simultaneous voltammetric determination of ascorbic acid, acetaminophen and isoniazid using thionine immobilized multi-walled carbon nanotube modified carbon paste electrode. *Electrochimica Acta* 55: 666–672.
- Shahrokhian, S. and Nassab, N.H. (2013). Nanodiamond decorated with silver nanoparticles as a sensitive film modifier in a jeweled electrochemical sensor: Application to voltammetric determination of thioridazine. *Electroanalysis* 25: 417-425.
- Shahrokhian, S., Ghalkhani, M., Adeli, M. and Amini, M.K. (2009). Multi-walled carbon nanotubes with immobilised cobalt nanoparticle for modification of glassy carbon electrode: Application to sensitive voltammetric determination of thioridazine. *Biosensors and Bioelectronics* 24: 3235–3241.
- Shakkthivel, P. and Chen, S.-M. (2007). Simultaneous determination of ascorbic acid and dopamine in the presence of uric acid on ruthenium oxide modified electrode. *Biosensors and Bioelectronics* 22: 1680–1687.
- Shao, C., Lu, N. and Deng, Z. (2009). DNA-assisted electroless deposition of highly dispersed palladium nanoparticles on glassy carbon surface: Preparation and electrocatalytic properties. *Journal of Electroanalytical Chemistry* 629: 15-22.
- Sims, M.J., Li, Q., Kachoosangi, R.T., Wildgoose, G.G. and Compton, R.G. (2009). Using multiwalled carbon nanotube modified electrodes for the adsorptive stripping voltammetric determination of hesperidin. *Electrochimica Acta* 54: 5030–5034.
- Sirajuddin, Khaskheli, A.R., Shah, A., Bhangar, M.I., Niaz, A. and Mahesar, S. (2007). Simpler spectrophotometric assay of paracetamol in tablets and urine samples. *Spectrochimica Acta Part A* 68: 747–751.
- Situmorang, M., Hibbert, D.B. and Gooding, J.J. (2000). An experimental design study of interferences of clinical relevance of a polytyramine immobilized-enzyme biosensor. *Electroanalysis* 12: 111-119.

- Staden, J.F. and Tsanwani, M. (2002). Determination of paracetamol in pharmaceutical formulations using a sequential injection system. *Talanta* 58: 1095-1101.
- Suryakanth, J., Arivazhagan, V., Parvathi, M.M. and Rajesh, S. (2011). Enhanced surface modification of MWCNT: Indium and vanadium doped SnO₂ composite by sol-gel route and sonication. *Journal of Ovonic Research* 7: 93-98.
- Svorc, L., Sochr, J., Tomcik, P., Rievaj, M. and Bustin, D. (2012). Simultaneous determination of paracetamol and penicillin V by square-wave voltammetry at a bare boron-doped diamond electrode. *Electrochimica Acta* 68: 227–234.
- Tan, W.T. and Goh, J.K. (2008). Electrochemical oxidation of methionine mediated by a fullerene-C₆₀ modified gold electrode. *Electroanalysis* 20: 2447–2453.
- Tan, W.T., Lim, E.B. and Bond, A.M. (2003). Voltammetric studies on microcrystalline C₆₀ adhered to an electrode surface by solvent casting and mechanical transfer methods. *Journal of Solid State Electrochemistry* 7: 134–140.
- Terzyk, A.P., Rychlicki, G., Biniak, S. and Łukaszewicz, J.P. (2003). New correlations between the composition of the surface layer of carbon and its physicochemical properties exposed while paracetamol is adsorbed at different temperatures and pH. *Journal of Colloid and Interface Science* 257: 13–30.
- Tharayil, N.J., Raveendran, R., Vaidyan, A.V. and Chithra, P.G. (2008) Optical, electrical and structural studies of nickel-cobalt oxide nanoparticles. *Indian Journal of Engineering & Materials Sciences* 15: 489-496.
- Tian, L., Chen, L., Liu, L., Lu, N., Song, W. and Xu, H. (2006) Electrochemical determination of ascorbic acid in fruits on a vanadium oxide polypropylene carbonate modified electrode. *Sensors and Actuators B: Chemical* 113: 150–155.
- Topoglidis, E., Palomares, E., Astuti, Y., Green, A., Campbell, C.J. and Durrant, J.R. (2005). Immobilization and electrochemistry of negatively charged proteins on modified nanocrystalline metal oxide electrodes. *Electroanalysis* 17: 1035-1041.
- Waller, M.R., Townsend, T.K., Zhao, J., Sabio, E.M., Chamousis, R.L., Browning, N.D. and Osterloh, F.E. (2012) Single-crystal tungsten oxide nanosheets: Photochemical water oxidation in the quantum confinement regime. *Chemistry of Materials* 24: 698-704.
- Wang, C.Y. and Adhikari, S. (2011). ZnO-CNT composite nanotubes as nanoresonators. *Physics Letters A* 375: 2171–2175.
- Wang, C.Y., Hu, X.Y., Jin, G.D. and Leng, Z.Z. (2002). Differential pulse adsorption voltammetry for determination of procaine hydrochloride at a pumice modified carbon paste electrode in pharmaceutical preparations and urine. *Journal of Pharmaceutical and Biomedical Analysis* 30: 131–139.

- Wangfuengkanagul, N. and Chailapakul, O. (2002). Electrochemical analysis of acetaminophen using a boron-doped diamond thin film electrode applied to flow injection system. *Journal of Pharmaceutical and Biomedical Analysis* 28: 841–847.
- Wang, M., Xu, X. and Gao, J. (2007a). Voltammetric studies of a novel bicopper complex modified glassy carbon electrode for the simultaneous determination of dopamine and ascorbic acid. *Journal of Applied Electrochemistry* 37: 705–710.
- Wang, S.-F., Xie, F. and Hu, R.-F. (2007b). Carbon-coated nickel magnetic nanoparticles modified electrodes as a sensor for determination of acetaminophen. *Sensors and Actuators B: Chemical* 123: 495–500.
- Wang, X., Yang, N. and Wan, Q. (2006). Cyclic voltammetric response of nicotinic acid and nicotinamide on a polycrystalline gold electrode. *Electrochimica Acta* 52: 361–368.
- Wan, Q., Wang, X., Wang, X. and Yang, N. (2006). Poly(malachite green) film: Electrosynthesis, characterization, and sensor application. *Polymer* 47: 7684–7692.
- Wan, Q., Wang, X., Yu, F., Wang, X. and Yang, N. (2009). Poly(taurine)/MWNT-modified glassy carbon electrodes for the detection of acetaminophen. *Journal of Applied Electrochemistry* 39: 785–790
- Weber, J.E., Pillai, S., Ram, M.K., Kumar, A. and Singh, S.R. (2011). Electrochemical impedance-based DNA sensor using a modified single walled carbon nanotube electrode. *Materials Science and Engineering C* 31: 821–825.
- Xiao, F., Zhao, F., Li, J., Yan, R., Yu, J. and Zeng, B. (2007). Sensitive voltammetric determination of chloramphenicol by using single-wall carbon nanotube–gold nanoparticle–ionic liquid composite film modified glassy carbon electrodes. *Analytica Chimica Acta* 596: 79–85.
- Xu, C.-X., Huang, K.-J., Fan, Y., Wu, Z.-W. and Li, J. (2012). Electrochemical determination of acetaminophen based on TiO₂–graphene/poly(methyl red) composite film modified electrode. *Journal of Molecular Liquids* 165: 32–37.
- Xu, Y., Jiang, Y., Cai, H., He, P.-G. and Fang, Y.-Z. (2004). Electrochemical impedance detection of DNA hybridization based on the formation of M-DNA on polypyrrole/carbon nanotube modified electrode. *Analytica Chimica Acta* 516: 19–27.
- Yamanaka, S., Gonda, R., Kawasaki, A., Sakamoto, H., Mekuchi, Y., Kuno, M. and Tsukada, T. (2007). Fabrication and thermal properties of carbon nanotube/nickel composite by spark plasma sintering method. *Materials Transactions* 48: 2506–2512.

- Yang, G., Wang, L., Yang, Y., Chen, X., Zhou, D., Jia, J. and Li, D. (2012). 4-Phosphatephenyl covalently modified glassy carbon electrode for real-time electrochemical monitoring of paracetamol release from electrospun nanofibers. *Electroanalysis* 24: 1937–1944.
- Yang, P., Wei, W. and Tao, C. (2007). Determination of trace thiocyanate with nano-silver coated multi-walled carbon nanotubes modified glassy carbon electrode. *Analytica Chimica Acta* 585: 331–336.
- Yang, S., Qu, L., Li, G., Yang, R. and Liu, C. (2010). Gold nanoparticles/ethylenediamine/carbon nanotube modified glassy carbon electrode as the voltammetric sensor for selective determination of rutin in the presence of ascorbic acid. *Journal of Electroanalytical Chemistry* 645: 115–122.
- Zayed, S.I.M. and Issa, Y.M. (2009). Cathodic adsorptive stripping voltammetry of drotaverine hydrochloride and its determination in tablets and human urine by differential pulse voltammetry. *Bioelectrochemistry* 75: 9–12.
- Zhang F.-J. and Oh, W.-C. (2011) Visible light photocatalytic properties of novel molybdenum treated carbon nanotube/titania composites. *Bulletin of Materials Science* 34: 543-549.
- Zhang, R., Wang, X. and Chen, C. (2007). Electrochemical biosensing platform using carbon nanotube activated glassy carbon electrode. *Electroanalysis* 19: 1623-1627.
- Zhang, Y., Sun, X., Pan, L., Li, H., Sun, Z., Sun, C. and Tay, B.K. (2009). Carbon nanotube–ZnO nanocomposite electrodes for supercapacitors. *Solid State Ionics* 180: 1525-1528.
- Zhi, C.Y., Bando, Y., Wang, W.L., Tang, C.C., Kuwahara, H. and Golberg, D. (2008). Mechanical and thermal properties of polymethyl methacrylate-BN nanotube composites. *Journal of Nanomaterials* 2008: 642036.
- Zhu, S., Li, H., Niu, W. and Xu, G. (2009). Simultaneous electrochemical determination of uric acid, dopamine, and ascorbic acid at single-walled carbon nanohorn modified glassy carbon electrode. *Biosensors and Bioelectronics* 25: 940-943.
- Zidan, M., Tan, W.T., Abdullah, A.B., Zainal, Z. and Kheng, G.J. (2011a). Electrochemical oxidation of ascorbic acid mediated by Bi₂O₃ microparticles modified glassy carbon electrode. *International Journal Electrochemical Science* 6: 289 – 300.
- Zidan, M., Tan, W., Zainal, Z., Abdullah, A.H. and Goh, J.K. (2010). Electrocatalytic oxidation of ascorbic acid mediated by lithium doped microparticles Bi₂O₃/MWCNT modified glassy carbon electrode. *International Journal Electrochemical Science* 5: 501 – 508.

Zidan, M., Tee, T.W., Abdullah, A.B., Zainal, Z. and Kheng, G.J. (2011b). Electrochemical oxidation of paracetamol mediated by nanoparticles bismuth oxide modified glassy carbon electrode. *International Journal Electrochemical Science* 6: 279 – 288.

Zidan, M., Tee, T.W., Abdullah, A.H., Zainal, Z. and Kheng, G.J. (2011c). Electrochemical oxidation of paracetamol mediated by MgB_2 microparticles modified glassy carbon electrode. *E-Journal of Chemistry* 8: 553-560.

