UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL DETECTION OF ASCORBIC ACID AT MgB2-MWCNT AND MgB2/PEDOT HYBRID MODIFIED GLASSY CARBON ELECTRODES

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By

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Chair : Associate Professor Tan Wee Tee, PhD
Faculty : Science

Magnesium boride–multiwalled carbon nanotube (MgB_2-MWCNT) modified electrode and poly-3,4-ethylenedioxythiophene/magnesium boride (PEDOT/MgB_2) modified electrode were used to study the electrochemical oxidation of ascorbic acid (AA). Abrasive immobilization technique was used to modify the surface of glassy carbon electrode (GCE) with MgB_2-MWCNT mixture through mechanical attachment method while electrodeposition technique was used to prepare PEDOT/MgB_2 through electropolymerization process.

The modified MgB_2-MWCNT electrode showed good electrocatalytic properties towards AA oxidation. Compared to bare GCE, the MgB_2-MWCNT modified electrode enhanced the oxidation current for AA by about two folds. At the MgB_2-MWCNT modified electrode surface, the oxidation of AA occurred through diffusion-adsorption process, where a reduction of 60% of the activation energy required to diffuse AA at bare GCE was recorded when MgB_2-MWCNT modified GCE was used. The MgB_2-MWCNT modified electrode exhibits a lower detection limit and better sensitivity towards AA oxidation compared to bare GCE; limit of detection for AA is 1.2 μM and sensitivity is 89 mA/M AA. The MgB_2-MWCNT modified electrode achieved good reproducibility for AA oxidation in which %RSD for both oxidation current and oxidation peak potential were in the range of 4-7% and 2-6% respectively. A recovery rate of 100.70 ± 4.01% was obtained when the MgB_2-MWCNT modified electrode was used to detect AA in real samples.

The PEDOT/MgB_2 modified electrode demonstrated excellent electrocatalytic ability towards the mediation of AA oxidation. Cyclic voltammograms

showed that the oxidation peak of AA was enhanced by about two folds and oxidation peak potential was shifted by about 100 mV towards the negative direction at the PEDOT/MgB_2 modified electrode compared to bare GCE. Oxidation of AA at the PEDOT/MgB_2 modified electrode surface was governed simultaneously by AA diffusion along with weak AA adsorption. The PEDOT/MgB_2 modified electrode has a detection limit of 1.3 μM and sensitivity of 82 mA/M AA where a reproducibility with %RSD of 5.65% for AA oxidation current and 4.20% for AA oxidation peak potential were obtained. Simultaneous detection of AA in the presence of dopamine (DA) at the PEDOT/MgB_2 modified electrode indicates better selectivity over bare GCE, where a peak separation of about 300 mV was obtained between the oxidation peaks of AA and DA.

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

PENGESANAN ELEKTROKIMIA ASID ASKORBIK PADA ELEKTROD KARBON KACA TERUBAHSUAI HIBRID MgB_2-MWCNT DAN MgB_2/PEDOT

Oleh

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April 2017

Pengerusi : Prof. Madya Tan Wee Tee, PhD
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Elektrod terubahsuai magnesium borida – karbon nanotiub dinding ganda (MgB_2-MWCNT) dan poli-3,4-etilenadioksitiofena/ magnesium borida (PEDOT/MgB_2) digunakan untuk mengkaji pengoksidaan elektrokimia asid askorbik (AA). Teknik imobilisasi abrasif digunakan untuk mengubahsuai permukaan elektrod karbon kaca (GCE) dengan campuran MgB_2-MWCNT melalui kaedah lekatan mekanikal manakala teknik pengelektroenapan pula digunakan untuk menyediakan PEDOT/MgB_2 melalui proses pengelektropolimeran.

Elektrod terubahsuai MgB_2-MWCNT menunjukkan sifat elektrokatalitik yang baik terhadap pengoksidaan AA. Berbanding GCE tanpa ubahsuai, elektrod terubahsuai MgB_2-MWCNT meningkatkan arus pengoksidaan AA kira-kira sebanyak dua kali ganda. Pada permukaan elektrod terubahsuai MgB_2-MWCNT, pengoksidaan AA berlaku melalui proses resapan-jerapan, di mana penurunan sebanyak 60% tenaga pengaktifan yang diperlukan untuk membaur AA pada GCE tanpa ubahsuai direkodkan semasa elektrod terubahsuai MgB_2-MWCNT digunakan. Elektrod terubahsuai MgB_2-MWCNT mempamerkan had pengesanan lebih rendah dan sensitiviti lebih baik terhadap pengoksidaan AA berbanding GCE tanpa ubahsuai; had pengesanan untuk AA ialah 1.2 µM dan sensitiviti ialah 89 mA/M AA. Elektrod terubahsuai MgB2-MWCNT mempunyai kebolehan reproduksi untuk pengoksidaan AA yang baik, di mana %RSD untuk kedua-dua arus pengoksidaan dan keupayaan puncak pengoksidaan berada dalam lingkungan 4-7% dan 2-6% masing-masing. Kadar dapat kembali sebanyak 100.70 ± 4.01% diperolehi semasa elektrod terubahsuai MgB_2-MWCNT digunakan untuk mengesan AA di dalam sampel nyata.

Elektrod terubahsuai PEDOT/MgB_2 menunjukkan keupayaan elektrokatalitik cemerlang terhadap pemangkinan pengoksidaan AA. Voltamogram kitaran menunjukkan bahawa puncak pengoksidaan AA ditingkatkan kira-kira dua kali ganda dan keupayaan puncak pengoksidaan beralih kira-kira 100 mV ke arah negatif pada elektrod terubahsuai PEDOT/MgB_2 berbanding GCE tanpa ubahsuai. Pengoksidaan AA pada elektrod terubahsuai PEDOT/MgB_2 dikawal serentak oleh pembauran AA dan penjerapan AA yang lemah. Elektrod terubahsuai PEDOT/MgB_2 mempunyai had pengesanan 1.3 μM dan sensitiviti 82 mA/M AA, di mana kebolehan reproduksi dengan %RSD sebanyak 5.65% untuk arus pengoksidaan AA dan 4.20% untuk keupayaan puncak pengoksidaan AA diperolehi. Pengesanan serentak AA dengan kehadiran dopamin (DA) pada elektrod terubahsuai PEDOT/MgB_2 menunjukkan selektiviti yang lebih baik berbanding GCE tanpa ubahsuai, di mana pemisahan puncak kira-kira sebanyak 300 mV diperolehi di antara puncak pengoksidaan AA dan DA.

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I certify that an Thesis Examination Committee has met on 2017 to conduct the final examination of Darlene Banan on her thesis entitled “Electrochemical Detection of Ascorbic Acid at MgB_2-MWCNT and MgB_2/PEDOT Hybrid Modified Glassy Carbon Electrodes” in accordance with 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

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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 Master of Science. 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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LIST OF ABBREVIATIONS

AA	Ascorbic Acid
BPPGE	Basal Plane Pyrolitic Graphite Electrode
CA	Chronoamperometry
CC	Chronocoulometry
CP	Conducting polymer
CNT	Carbon nanotube
CV	Cyclic Voltammetry
DA	Dopamine
EDOT	3,4-ethylenedioxythiophene
EDX	Energy Dispersion X-ray
GCE	Glassy Carbon Electrode
MWCNT	Multi-walled carbon nanotube
PEDOT	poly-3,4-ethylenedioxythiophene
SEM	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background

Electrochemical analysis has become one of the most important disciplines in analytical chemistry. Up to date, electrochemical techniques are being used widely in a variety of applications, which include utilization in the medicinal and pharmaceutical industry, monitoring of industrial materials and environmental analysis (Farghaly *et al*., 2014; Bozal *et al*., 2011). Electroanalysis is highly favored due to its advantages such as having a low operational cost, high sensitivity, low sample consumption (Farghaly *et al*., 2014), ease of operation (Ribeiro *et al*., 2016) as well as portability (Barton *et al*., 2016).

Since the emergence of various electroanalytical techniques, the most focused area for research and development revolves around electrode modification. The motivation of these researches lies greatly in finding electrode materials that have high sensitivity, better selectivity and good stability for operational and practical applications. It has been shown that hybrid electrode modifiers display great improvement in sensitivity and selectivity over single compound modifiers (Yang *et al*., 2016; Ngai *et al*., 2015). Hybrid modifiers are made by combining two or more compounds, either by physical (Ngai *et al*., 2015) or chemical means (Yang *et al*., 2016), and attaching it to the electrode surface. The property of the electrode would then be affected by the combined properties of the modifying materials being used.

Ascorbic acid (AA) is an organic molecule that acts as an important biological compound especially for the development of human metabolism. As an antioxidant, AA plays an important role in the biological system as well as in the pharmaceutical, cosmetic, chemical and food industry (Yilmaz *et al*., 2008). AA has also been applied in the prevention and treatment of different diseases and illnesses such as the common cold, infertility, cancer and mental illness (Vinoth *et al*., 2015). The electroanalysis of AA at bare electrode can be challenging as electrochemical oxidation of AA requires a high potential (Du *et al*., 2016) and furthermore, electrode fouling caused by adsorption of products on the electrode surface may occur during analysis (Shahrokhian and Zare-Mehrjardi, 2007). Electrochemical analysis of AA may also be difficult due to interference from coexisting compounds, such as dopamine (DA), which results in overlapping voltammetric response of both compounds and this consequently leads to low sensitivity and poor reproducibility of the electrode (Du *et al*., 2016).

For the electroanalysis of AA, numerous substances such as metals, surfactants, nanoparticles and nanocomposites, as well as polymers had been successfully used as electrode modifiers (Pisoschi *et al*., 2014). Among these substances are carbon nanotubes (CNT) and poly-3,4-ethylenedioxythiopene (PEDOT). CNT is known to be a good electron mediator due to its ability to promote electron transfer reaction as well as minimize surface fouling on electrochemical devices (Ahammad *et al*., 2009). PEDOT is a conductive polymer that offers promising features for practical applications due to its good stability and high conductivity (Pyshkina *et al*., 2010).

Magnesium boride (MgB_2) is a binary compound that has once sparked the interest of many researchers when its superconducting ability was made known by Akimitsu and his group in 2001 (Nagamatsu *et al*., 2001). Tan *et al*. first reported MgB_2 applications in electroanalysis in 2009. To our knowledge, only one other paper (Zidan *et al*., 2011) was published on the successful application of MgB_2 as electrode modifier after that.

This research is focused on the possible application of MgB_2 as an electrode modifier for the electrochemical detection of AA. For this research, multi-walled CNT (MWCNT) and PEDOT are chosen to be combined with MgB_2 as hybrid electrode modifiers, based on their distinct individual properties.

1.2 Problem Statement

Previous studies had shown that MgB_2 modified GCE were able to exhibit electrocatalytic activity towards the redox reaction of both ferricyanide (Tan *et al*., 2009) and paracetamol (Zidan *et al*., 2011). However, up to this date, no attempts have been made to fabricate and examine the performance of MgB_2 hybrid modified electrode. Therefore, this research focuses on the prospect of fabricating a modified electrode by combining MgB_2 with MWCNT and PEDOT, and investigating the possibility of electrocatalytic activity on AA oxidation.

At the surface of GCE, the cyclic voltammogram of AA often overlapped with interfering compounds such as DA. Therefore, this research also addresses the ability of MgB_2 hybrids in improving the selectivity of GCE during simultaneous detection of AA and DA. Another important aspect to look at is the feasibility of the modified electrodes in real life applications. In this research, detection of the presence of AA in real life samples at the MgB_2 hybrid electrodes are also investigated.

1.3 Objectives of the Research

The objectives of the current research are as follows:

i) To fabricate MgB_2 hybrid modified electrodes through mechanical attachment (MgB_2-MWCNT modified electrode) and electropolymerization (PEDOT/MgB_2 modified electrode)

ii) To compare the electrochemical reaction of ascorbic acid at bare, MgB_2-MWCNT and PEDOT/MgB_2 modified electrode using cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC) techniques.

iii) To detect AA in real life samples and samples containing DA using MgB_2-MWCNT and PEDOT/MgB_2 modified electrode

iv) To examine the morphology of the electrode surface before and after electrochemical reactions of AA using SEM-EDX

1.4 Thesis Outline

This thesis is divided into five main chapters. Chapter 1 gives a brief introduction, the problem statement that is to be addressed and the objectives of this research.

In Chapter 2, the basic principles underlying the three electrochemical methods that are used in this research (CV, CA and CC) are outlined. The properties of MgB_2, MWCNT and PEDOT and their applications as materials for electrode modification in electroanalysis are reviewed. Electrode preparation and modification approach used in previous studies are summarized in the last section of this chapter.

In Chapter 3, the types of electrodes, chemicals and instruments being used are listed. Methods of electrode preparation and modification are described and the experimental procedures and parameters of the CV, CA and CC analysis are explained. The mathematical equations used for result analysis are also included accordingly.

The experimental results are presented and discussed in Chapter 4. The first section in this chapter discusses the experimental results from MgB_2-MWCNT modified GCE, while the following two sections review experimental results from PEDOT/MgB_2 modified GCE. In the last section of this chapter, the SEM-EDX results of both modified electrodes are compared and discussed.

The last chapter of this thesis (Chapter 5) includes a summary and conclusion drawn based on the findings of this research. A few suggestions to improve the overall findings of the research are made and the possible applications of MgB_2 as a material for electrode modification for future study are recommended in the last section of this chapter.

BIBLIOGRAPHY

Agüí, L., Yáñez-Sedeño, P. and Pingarrón, J. M. Role of carbon nanotubes in electroanalytical chemistry: A review. *Analytica Chimica Acta* **2008**, *622*, 11-47.

Ahammad, A. J. S., Lee, J. J. and Rahman, M. A. Electrochemical Sensors Based on Carbon Nanotubes. *Sensors* **2009**, *9(4)*, 2289–2319.

Aldica, G., Burdusel, M., Popa, S., Hayasaka, Y. and Badica, P. Graphene addition to MgB_2 superconductor obtained by *ex-situ* spark plasma sintering technique. *Materials Research Bulletin* **2016**, *77*, 205–211.

Bard, A.J., Faulkner, L.R., Leddy, J. and Zoski, C.G. Electrochemical methods: fundamentals and applications. New York: Wiley; 1980.

Barton, J., García, M.B., Santos, D.H., Fanjul-Bolado, P., Ribotti, A., McCaul, M., Diamond, D. and Magni, P. Screen-printed electrodes for environmental monitoring of heavy metal ions: a review. *Microchimica Acta* **2016**, *183(2)*, 503-517.

Batalu, D., Stanciuc, A.M., Moldovan, L., Aldica, G. and Badica, P. Evaluation of pristine and Eu_2O_3-added MgB_2 ceramics for medical applications: hardness, corrosion resistance, cytotoxicity and antibacterial activity. *Mater Sci Eng C Mater Biol Appl.* **2014,** *42***, 350-361.**

Bello, A., Giannetto, M., Mori, G. Seeber, R., Terzi, F. and Zanardi, C. Optimization of the DPV potential waveform for determination of ascorbic acid on PEDOT-modified electrodes. *Sensors and Actuators B: Chemical* **2007**, *121*, 430-435.

Bertola, L., Cox, T., Wheeler, P., Garvey, S. and Morvan, H. Superconducting Electromagnetic Launch System for Civil Aircraft. *IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY* **2016**, 26(8).

Bianconi, A. and Poccia, N. Superstripes and complexity in high-temperature superconductors. *Journal of Superconductivity and Novel Magnetism* **2012**, *25(5)*, 1403-1412.

Bi, H., Li, Y., Liu, S., Guo, P., Wei, Z., Lv, C., Zhang, J. and Zhao, X. S. Carbon-nanotube-modified glassy carbon electrode for simultaneous determinations of dopamine, ascorbic acid and uric acid: The effect of functional groups. *Sensors and Actuators B: Chemical* **2012**, *171-172*, 1132-1140.

Bozal, B., Uslu, B. and Ozkan, S. A. A review of Electroanalytical Techniques for Determination of Anti-HIV Drugs. *International Journal of Electrochemistry* **2011**, *Article ID 343947.*

Brett, C.M. and Brett, A.M. Electrochemistry: principles, methods, and applications. Oxford university press; 1993.

Britto, P.J., Santhanam, K.S. and Ajayan, P.M. Carbon nanotube electrode for oxidation of dopamine. *Bioelectrochemistry and Bioenergetics*. **1996**, *41(1),* 121-125.

Brusnahan, J.S., Poret, J.C., Jared D. Moretti, Anthony P. Shaw, and Rajendra K. Sadangi Use of Magnesium Diboride as a "Green" Fuel for Green Illuminants. *ACS Sustainable Chem. Eng.*, **2016,** *4* (3), 1827–1833

Burdusel, M., Aldica, G., Popa, S., Enculescu, M., Mihalache, V., Kuncser, A., Pasuk, I. and Badica, P. B_4C in *ex-situ* spark plasma sintered MgB_2. *Current Applied Physics* **2015**, *15(10)*, 1262–1270.

Buzea, C. and Yamashita, T. Review of superconducting properties of MgB_2. *Superconductors, Science & Technology* **2001**, *14(11)*, R115-R146.

Canfield, P.C. and Crabtree, G.W. Magnesium diboride: Better late than never. *Physics Today* **2003**, *56(3)*, 34-40.

Castagnola, V., Bayon, C., Descamps, E. and Bergaud, C. Morphology and conductivity of PEDOT layers produced by different electrochemical routes. *Synthetic Metals* **2014**, *189*, 7–16.

Cazula, B. B. and Lazarin, A. M. Development of chemically modified carbon paste electrodes with transition metal complexes anchored on silica gel. *Materials Chemistry and Physics* **2017**, *186*, 470-477.

Chairam, S., Sriraksa, W., Amatatongchai, M. and Somsook, E. Electrocatalytic Oxidation of Ascorbic Acid Using a Poly(aniline-*co*-*m*-ferrocenylaniline) Modified Glassy Carbon Electrode. *Sensors* **2011**, *11*, 10166–10179.

Chen, S. M. and Peng, K. T.. The electrochemical properties of dopamine, epinephrine, norepinephrine, and their electrocatalytic reactions on cobalt(II) hexacyanoferrate films. *Journal of Electroanalytical Chemistry* **2003**, *547*, 179-189.

Choi, H.J., Roundy, D., Sun, H., Cohen, M.L. and Louie, S.G. Superconducting energy gaps, low temperature specific heat, and quasiparticle spectra of MgB_2. **2001**

Colleran, J.J. and Breslin, C.B. Simultaneous electrochemical detection of the catecholamines and ascorbic acid at PEDOT/S-β-CD modified gold electrodes. *Journal of Electroanalytical Chemistry* **2012**, *667*, 30-37.

Dietrich, M., Heinze, J., Heywang, G. and Jonas, F. Electrochemical and spectroscopic characterization of polyalkylenedioxythiophenes. *Journal of Electroanalytical Chemistry* **1994**, *369(1*), 87-92.

Du, X., Zhang, Z., Zhang, C., Zhang, Y. and Chen, Q. One-step electrodeposition of poly (3, 4-ethylenedioxythiophene) on carboxylated multi-wall carbon nanotubes and its application in ascorbic acid sensing. *Journal of Electroanalytical Chemistry* **2016**, *782*, 84-90.

El-Enany, G.M., Ghanem, M.A. and El-Ghaffar, M.A. Electrochemical deposition and characterization of poly (3,4-ethylene dioxythiophene), poly (aniline) and their copolymer onto glassy carbon electrodes for potential use in ascorbic acid oxidation. *Portugaliae Electrochimica Acta* **2010**, *28(5)*, 336-348.

Farghaly, O.A., Hameed, R.A. and Abu-Nawwas, A.A. Analytical application using modern electrochemical techniques. *Int. J. Electrochem. Sci.* **2014**, *9(1)*, 3287-3318.

Farzin, L. and Hosseini, M.R. Simultaneous determination of dopamine and L-ascorbic acid by modified carbon paste electrode with Ni (II) cyclam complex. *American Journal of Analytical Chemistry* **2011**, *2(02)*, 289.

Fernandes, D.M., Costa, M., Pereira, C., Bachiller-Baeza, B., Rodríguez-Ramos, I., Guerrero-Ruiz, A. and Freire, C. Novel electrochemical sensor based on N-doped carbon nanotubes and Fe_3O_4 nanoparticles: Simultaneous voltammetric determination of ascorbic acid, dopamine and uric acid. *Journal of colloid and interface science* **2014**, *432*, 207-213.

Filik, H., Avan, A.A. and Aydar, S. Simultaneous detection of ascorbic acid, dopamine, uric acid and tryptophan with Azure A-interlinked multi-walled carbon nanotube/gold nanoparticles composite modified electrode. *Arabian Journal of Chemistry* **2016**, *9(3)*,471-80.

Goh, J.K., Tan, W.T., Lim, F.T. and Maamor, N.A.M. Electrochemical Oxidation of Ascorbic Acid Mediated by Carbon Nanotubes/Li+/Carbon Paste Modified Solid Electrode. *The Malaysian Journal of Analytical Sciences* **2008**, *12(2)*, 480 – 485.

Greenwood, N.N., Parish, R.V. and Thornton, P. Metal borides. *Quarterly Reviews, Chemical Society* **1966**, *20(3)*, 441-464.

Grivel, J.C. Attempts at doping indium in MgB_2. *Physica C: Superconductivity and its Applications* **2016**, *531*, 67-71.

Grygar, T., Marken, F., Schröder, U. and Scholz, F. Electrochemical analysis of solids. A review. *Collection of Czechoslovak chemical communications* **2002**, *67(2)*, 163-208.

Gvozdenović, M.M., Jugović, B.Z., Stevanović, J.S. and Grgur, B.N. Electrochemical synthesis of electroconducting polymers. *Hemijska industrija* **2014**, *68(6)*, 673-684.

Habibi, B. and Pournaghi-Azar, M.H. Simultaneous determination of ascorbic acid, dopamine and uric acid by use of a MWCNT modified carbon-ceramic electrode and differential pulse voltammetry. *Electrochimica Acta* **2010**, *55(19)*, 5492-5498.

Häßler, W., Rodig, C., Damm, C., Scheiter, J., Schultz, L., Aubele, A., Sailer, B. and Schlenga, K. Increased critical current density of in-situ MgB_2 wires by Mg deficiency. *Physica C: Superconductivity and its Applications* **2015**, *510*, 8-12.

Hirsch, J.E. Hole superconductivity in MgB_2: a high T_c cuprate without Cu. *Physics letters A* **2001**, *282(6)*, 392-398.

Holló, P., Jókai, H., Hársing, J., Soós, G., Kárpáti, S. and Németh, K. Topically applied ascorbic acid solution for the treatment of basal cell carcinoma (BCC). *Journal of the American Academy of Dermatology* **2016**, *75(1)*, 212-213.

Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354(6348)*, 56.

Im, S.G., Olivetti, E.A. and Gleason, K.K. Systematic control of the electrical conductivity of poly (3,4-ethylenedioxythiophene) via oxidative chemical vapor deposition (oCVD). *Surface and Coatings Technology* **2007**, *201*, 9406-9412.

Inzelt, G. Conducting polymers: a new era in electrochemistry. *Springer Science & Business Media* **2012**

Kamyabi, M.A. and Shafiee, M. A. Electrocatalytic Oxidation of Dopamine, Ascorbic Acid and Uric Acid at Poly‑2,6‑Diaminopyridine on the Surface of Carbon Nanotubes/GC Electrodes. *J. Braz. Chem. Soc*. **2012**, *23(4)*, 593-601.

Kaushik, B.K. and Majumder, M.K. Carbon Nanotube Based VLSI Interconnects: Analysis and Design. *Springer* **2015**.

Kissinger, P.T. and Heineman, W.R. Cyclic voltammetry. *J. Chem. Educ.* **1983**, *60(9)*, 702.

Krzyczmonik, P. and Socha, E. Electrodes modified with composite layers of poly (3, 4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) for applications in bioelectroanalysis. *CHEMIK nauka-technika-rynek* **2013**, *1(67)*, 801-810.

Kumar, S. and Vicente-Beckett, V. Glassy carbon electrodes modified with multiwalled carbon nanotubes for the determination of ascorbic acid by square-wave voltammetry. *Beilstein journal of nanotechnology* **2012**, *3(1)*, 388-396.

Kumar, S.S., Mathiyarasu, J., Phani, K.L. and Yegnaraman, V. Simultaneous determination of dopamine and ascorbic acid on poly (3, 4-ethylenedioxythiophene) modified glassy carbon electrode. *Journal of Solid State Electrochemistry* **2006**, *10(11)*, 905-913.

Łapkowski, M. and Proń, A. Electrochemical oxidation of poly (3, 4-ethylenedioxythiophene)—"in situ" conductivity and spectroscopic investigations. *Synthetic Metals* **2000**, *110(1)*, 79-83.

Lawal, A.T. Synthesis and utilization of carbon nanotubes for fabrication of electrochemical biosensors. *Materials Research Bulletin* **2016**, *73*, 308-350.

Li, Y. Organic optoelectronic materials. *Berlin: Springer* **2015**, *Vol. 91.*

Liu, X., Shuai, H.L., Liu, Y.J. and Huang, K.J. An electrochemical biosensor for DNA detection based on tungsten disulfide/multi-walled carbon nanotube composites and hybridization chain reaction amplification. *Sensors and Actuators B: Chemical* **2016**, *235*, 603-613.

Martin, C.R., Rubinstein, I. and Bard, A.J. Polymer films on electrodes. 9. Electron and mass transfer in Nafion films containing tris (2, 2'-bipyridine) ruthenium (2+). *Journal of the American Chemical Society* **1982**, *104(18)*, 4817-4824.

Medeiros, R.A., Benchick, A., Rocha-Filho, R.C., Fatibello-Filho, O., Saidani, B., Debiemme-Chouvy, C. and Deslouis, C. Simultaneous detection of ascorbic acid and dopamine with electrochemically pretreated carbon nitride electrodes: Comparison with boron-doped diamond electrodes. *Electrochemistry Communications* **2012**, *24*, 61-64.

Merkoçi, A., Pumera, M., Llopis, X., Pérez, B., del Valle, M. and Alegret, S. New materials for electrochemical sensing VI: carbon nanotubes. *Trends in Analytical Chemistry* **2005**, *24(9)*, 826-838.

Moreno, M., Arribas, A.S., Bermejo, E., Chicharro, M., Zapardiel, A., Rodríguez, M.C., Jalit, Y. and Rivas, G.A. Selective detection of dopamine in the presence of ascorbic acid using carbon nanotube modified screen-printed electrodes. *Talanta* **2010**, *80(5)*, 2149-2156.

Mousavi, Z., Bobacka, J., Lewenstam, A. and Ivaska, A. Poly (3, 4-ethylenedioxythiophene) (PEDOT) doped with carbon nanotubes as ion-to-electron transducer in polymer membrane-based potassium ion-selective electrodes. *Journal of Electroanalytical Chemistry* **2009**, *633(1)*, 246-252.

Nagamatsu, J., Nakagawa, N., Muranaka, T., Zenitani, Y. and Akimitsu, J. Superconductivity at 39 K in magnesium diboride. *Nature* **2001**, *410(6824)*, 63-64.

Ngai, K.S., Tan, W.T., Zainal, Z., Zawawi, R.M. and Juan, J.C. Single-Walled Carbon Nanotube/Tungsten-Modified Glassy Carbon Electrode as a Novel Sensor for the Electrochemical Determination of Ascorbic Acid. *Sensor Letters* **2015**, *13(5)*, 411-418.

Ngai, K.S., Tan, W.T., Zainal, Z., Zawawi, R.M. and Zidan, M. Electrochemical Oxidation of Ascorbic Acid Mediated by SingleWalled Carbon Nanotube/Tungsten Oxide Nanoparticles Modified Glassy Carbon Electrode. *Int. J. Electrochem. Sci.* **2012**, 7, 4210 – 4222

Perenlei, G., Tan, W.T., Yusof, N.A. and Goh, J.K. Voltammetric oxidation of ascorbic acid mediated by multi-walled carbon nanotubes/titanium dioxide composite modified glassy carbon electrode. *Journal of Applied Sciences* **2011**, *11(5)*, 848-854.

Pisoschi, A.M., Pop, A., Serban, A.I. and Fafaneata, C. Electrochemical methods for ascorbic acid determination. *Electrochimica Acta* **2014**, *121*, 443-460.

Poole, C., Baig, T., Deissler, R.J., Doll, D., Tomsic, M. and Martens, M. Numerical study on the quench propagation in a 1.5 T MgB_2 MRI magnet design with varied wire compositions. *Superconductor Science and Technology* **2016**, *29(4)*,

Pournaghi-Azar, M.H. and Ojani, R. Catalytic oxidation of ascorbic acid by some ferrocene derivative mediators at the glassy carbon electrode. Application to the voltammetric resolution of ascorbic acid and dopamine in the same sample. *Talanta* **1995**, 42(12), 1839-1848.

Prathish, K.P., Carvalho, R.C. and Brett, C.M. Electrochemical characterisation of poly (3, 4-ethylenedioxythiophene) film modified glassy carbon electrodes prepared in deep eutectic solvents for simultaneous sensing of biomarkers. *Electrochimica Acta* **2016**, *187*, 704-713.

Prikhna, T., Shapovalov, A., Eisterer, M., Shaternik, V., Goldacker, W., Weber, H.W., Moshchil, V., Kozyrev, A., Sverdun, V., Boutko, V. and Grechnev, G. Pinning in high performance MgB_2 thin films and bulks: Role of Mg-BO nano-scale inhomogeneities. *Physica C: Superconductivity and its Applications* **2016**

Pyshkina, O., Aleksejs, K. and Vladimir, S. "Poly (3, 4-ethylenedioxythiophene): Synthesis and properties." **2010** : 51-54.

Reda, A.H. and Gebremeskel, F.G. Determination of Ascorbic Acid in Citrus Sinensis and Ananas Comosus Using Poly (3, 4-Ethylenedioxythiophene) Modified Glassy Carbon Electrode. *American Journal of Applied Chemistry* **2016**, *4(1)*, 1-7.

Ribeiro, J.A., Fernandes, P.M., Pereira, C.M. and Silva, F. Electrochemical sensors and biosensors for determination of catecholamine neurotransmitters: A review. *Talanta* **2016**, *160*, 653-679.

Rohani, T. and Taher, M.A. Novel functionalized multiwalled carbon nanotube-glassy carbon electrode for simultaneous determination of ascorbic acid and uric acid. *Arabian Journal of Chemistry* **2015**

Roncali, J. Conjugated poly (thiophenes): Synthesis, Functionalization, and Applications. *Chemical Reviews* **1992**, *92(4)*, 711-738.

Ruiz, J.J., Aldaz, A. and Dominguez, M. Mechanism of L-ascorbic acid oxidation and dehydro-L-ascorbic acid reduction on a mercury electrode. I. Acid medium. *Canadian Journal of Chemistry* **1977**, *55(15)*, 2799-2806.

Ruiz, J.J., Aldaz, A. and Dominguez, M. Mechanism of L-ascorbic acid oxidation on a mercury electrode. II. Basic medium. *Canadian Journal of Chemistry* **1978**, *56(11)*, 1533-1537.

Sajid, M., Nazal, M.K., Mansha, M., Alsharaa, A., Jillani, S.M. and Basheer, C. Chemically modified electrodes for electrochemical detection of dopamine in the presence of uric acid and ascorbic acid: A review. *Trends in Analytical Chemistry* **2016**, *76*, 15-29.

Salimi, A. and Hallaj, R. Catalytic oxidation of thiols at preheated glassy carbon electrode modified with abrasive immobilization of multiwall carbon nanotubes: applications to amperometric detection of thiocytosine, l-cysteine and glutathione. *Talanta* **2005**,*66(4)*, 967-975.

Salimi, A., Hallaj, R. and Khayatian, G.R., Amperometric Detection of Morphine at Preheated Glassy Carbon Electrode Modified with Multiwall Carbon Nanotubes. *Electroanalysis* **2005**, *17*, 873–879.

Sandu, V., Craciun, L., Ionescu, A.M., Aldica, G., Miu, L. and Kuncser, A. Superconductivity in MgB_2 irradiated with energetic protons. *Physica C: Superconductivity and its Applications* **2016**, *528*, 27-34.

Scholz, F. and Meyer, B. Voltammetry of solid microparticles immobilized on electrode surfaces. *Electroanalytical Chemistry* **1998**, *20*, 1-86.

Scott, C.L. and Pumera, M. Carbon nanotubes can exhibit negative effects in electroanalysis due to presence of nanographite impurities. *Electrochemistry Communications* **2011**, *13(5)*, 426-428.

Seetharamappa, J., Yellappa, S. and D'Souza, F. Carbon nanotubes: next generation of electronic materials. *The Electrochemical Society Interface* **2006**, *15(2)*, 23-26.

Sekli-Belaidi, F., Temple-Boyer, P. and Gros, P. Voltammetric microsensor using PEDOT-modified gold electrode for the simultaneous assay of ascorbic and uric acids. *Journal of Electroanalytical Chemistry* **2010**, *647(2)*, 159-168.

Shahrokhian, S., Zare-Mehrjardi, H.R. Application of thionine-nafion supported on multi-walled carbon nanotube for preparation of a modified electrode in simultaneous voltammetric detection of dopamine and ascorbic acid. *Electrochimica Acta* **2007**, *52(22)*, 6310-6317.

Simon, J.A., Grady, D., Snabes, M.C., Fong, J. and Hunninghake, D.B. Ascorbic acid supplement use and the prevalence of gallbladder disease. *Journal of clinical epidemiology* **1998**, *51(3)*, 257-265.

Skoog, D., Holler, F. and Crouch, S. Principles of Instrumental Analysis Sixth Edition Thompson Brooks/Cole **1998** pp: 529

Takeda, M., Inoue, Y., Maekawa, K., Matsuno, Y., Fujikawa, S. and Kumakura, H. Superconducting characteristics of short MgB_2 wires of long level sensor for liquid hydrogen, *Materials Science and Engineering*, **Vol.101**

Tamburri, E., Orlanducci, S., Toschi, F., Terranova, M.L. and Passeri, D. Growth mechanisms, morphology, and electroactivity of PEDOT layers produced by electrochemical routes in aqueous medium. *Synthetic metals* **2009**, *159(5)*, 406-414.

Tan, K.Y., Tan, K.B., Lim, K.P., Jumiah, H., Halim, S.A. and Chen, S.K. Frequency dependent dielectric properties of polycrystalline MgB_2. *Ceramics International* **2016**, *42(8),* 10266-10271.

Tan, W.T., Yusri, F. and Zainal, Z. Electrochemical reduction of potassium ferricyanide mediated by magnesium diboride modified carbon electrode. *Sensors & Transducers* **2009**, *104(5)*, 119.

Thomas, F.G. and Henze, G. Introduction to voltammetric analysis: theory and practice. Csiro Publishing; **2001**

Tsierkezos, N.G., Othman, S.H., Ritter, U., Hafermann, L., Knauer, A., Köhler, J.M., Downing, C. and McCarthy, E.K. Electrochemical analysis of ascorbic acid, dopamine, and uric acid on nobel metal modified nitrogen-doped carbon nanotubes. *Sensors and Actuators B: Chemical* **2016**, *231*, 218-229.

Türke, A., Fischer, W.J., Beaumont, N. and Kilmartin, P.A. Electrochemistry of sulfur dioxide, polyphenols and ascorbic acid at poly (3, 4-ethylenedioxythiophene) modified electrodes. *Electrochimica Acta* **2012**, *60*, 184-192.

Vasantha, V.S. and Chen, S.M. Electrocatalysis and simultaneous detection of dopamine and ascorbic acid using poly (3, 4-ethylenedioxy) thiophene film modified electrodes. *Journal of Electroanalytical Chemistry* **2006**, *592(1)*, 77-87.

Vinoth, V., Wu, J.J., Asiri, A.M. and Anandan, S. Simultaneous detection of dopamine and ascorbic acid using silicate network interlinked gold nanoparticles and multi-walled carbon nanotubes. *Sensors and Actuators B: Chemical* **2015**, *210*, 731-41.

Wang, J. *Analytical Electrochemistry*. 5th ed., John Wiley & Sons, **2006**

Wang, L., Gong, C., Shen, Y., Ye, W., Xu, M. and Song, Y. A novel ratiometric electrochemical biosensor for sensitive detection of ascorbic acid. *Sensors and Actuators B: Chemical* **2017**, *242*, 625-631.

Wang, Q., Geiger, A., Frias, R. and Golden, T. An Introduction to Electrochemistry for Undergraduates : Detection of Vitamin C (Ascorbic Acid) by Inexpensive Electrode Sensors. *Chem. Educator* **2000**, *5,* 58-60.

Yang, T., Xu, J., Lu, L., Zhu, X., Gao, Y., Xing, H., Yu, Y., Ding, W. and Liu, Z. Copper nanoparticle/graphene oxide/single wall carbon nanotube hybrid materials as electrochemical sensing platform for nonenzymatic glucose detection. *Journal of Electroanalytical Chemistry* **2016**, *761*, 118-124.

Yilmaz, S., Sadikoglu, M., Saglikoglu, G., Yagmur, S. and Askin, G. Determination of ascorbic acid in tablet dosage forms and some fruit juices by DPV. *Int. J. Electrochem. Sci.* **2008**, *3*, 1534-1542.

Zare, H.R. and Nasirizadeh, N. A comparison of the electrochemical and electroanalytical behavior of ascorbic acid, dopamine and uric acid at bare, activated and multi-wall carbon nanotubes modified glassy carbon electrodes. *Journal of the Iranian Chemical Society* **2011**, *8*, S55-66.

Zare, H.R., Moradiyan, B., Shekari, Z. and Benvidi, A. Application of L-DOPA modified carbon nanotubes as a bifunctional electrocatalyst for simultaneous determination of ascorbic acid, adrenaline, acetaminophen and tyrosine. *Measurement* **2016**, *90*, 510-518.

Zhang, L. and Lian, J. Electrochemical synthesis of copolymer of aniline and o-aminophenol and its use to the electrocatalytic oxidation of ascorbic acid. *Journal of Electroanalytical Chemistry* **2007**, *611(1)*, 51-59.

Zhao, Y., Zhang, C., Liu, T., Du, Q., Zhang, J., Liang, S. and Wang, X. Electrocatalytic activity of europium doped tantalum oxide for ascorbic acid oxidation in aqueous. *Int. J. Electrochem. Sci.* **2012**, 7, 6417-6425.

Zidan, M., Tan, W.T., Abdullah, A.H., Zainal, Z. and Goh, K.J. Electrochemical oxidation of ascorbic acid mediated by Bi_2O_3 microparticles modified glassy carbon electrode. *Int. J. Electrochem. Sci.* **2011**, *6*, 289-300.

Zidan, M., Tan, W.T., Abdullah, A.H., Zainal, Z., and Goh, J.K., Electrochemical Oxidation of Paracetamol Mediated by MgB_2 Microparticles Modified Glassy Carbon Electrode. *E-Journal of Chemistry* **2011** *8(2)*, 553-560.

Zidan, M., Tan, W.T., Zainal, Z., Abdullah, A.H. and Goh, J.K. Electrocatalytic oxidation of ascorbic acid mediated by lithium doped microparticles Bi_2O_3/MWCNT modified glassy carbon electrode. *Int. J. Electrochem. Sci.* **2010**, *5*, 501-508.