

UNIVERSITI PUTRA MALAYSIA

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

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By

DARLENE BANAN

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

April 2017

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

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

Magnesium boride–multiwalled carbon nanotube (MgB₂-MWCNT) modified electrode and poly-3,4-ethylenedioxythiophene/magnesium boride (PEDOT/MgB₂) 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 MgB₂-MWCNT mixture through mechanical attachment method while electrodeposition technique was used to prepare PEDOT/MgB₂ through electropolymerization process.

The modified MgB₂-MWCNT electrode showed good electrocatalytic properties towards AA oxidation. Compared to bare GCE, the MgB₂-MWCNT modified electrode enhanced the oxidation current for AA by about two folds. At the MgB₂-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 MgB₂-MWCNT modified GCE was used. The MgB₂-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 μ M and sensitivity is 89 mA/M AA. The MgB₂-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 MgB₂-MWCNT modified electrode was used to detect AA in real samples.

The PEDOT/MgB₂ 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/MgB₂ modified electrode compared to bare GCE. Oxidation of AA at the PEDOT/MgB₂ modified electrode surface was governed simultaneously by AA diffusion along with weak AA adsorption. The PEDOT/MgB₂ modified electrode has a detection limit of 1.3 μ M 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/MgB₂ 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 MgB₂-MWCNT DAN MgB₂/PEDOT

Oleh

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April 2017

Pengerusi : Prof. Madya Tan Wee Tee, PhD Fakulti : Sains

Elektrod terubahsuai magnesium borida – karbon nanotiub dinding ganda (MgB₂-MWCNT) dan poli-3,4-etilenadioksitiofena/ magnesium borida (PEDOT/MgB₂) digunakan untuk mengkaji pengoksidaan elektrokimia asid askorbik (AA). Teknik imobilisasi abrasif digunakan untuk mengubahsuai permukaan elektrod karbon kaca (GCE) dengan campuran MgB₂-MWCNT melalui kaedah lekatan mekanikal manakala teknik pengelektroenapan pula digunakan untuk menyediakan PEDOT/MgB₂ melalui proses pengelektropolimeran.

Elektrod terubahsuai MgB2-MWCNT menunjukkan sifat elektrokatalitik yang baik terhadap pengoksidaan AA. Berbanding GCE tanpa ubahsuai, elektrod terubahsuai MgB₂-MWCNT meningkatkan arus pengoksidaan AA kira-kira sebanyak dua kali ganda. Pada permukaan elektrod terubahsuai MgB₂-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 MgB₂-MWCNT digunakan. Elektrod terubahsuai MgB₂-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 $100.70 \pm 4.01\%$ diperolehi semasa elektrod terubahsuai MgB2-MWCNT digunakan untuk mengesan AA di dalam sampel nyata.

Elektrod terubahsuai PEDOT/MgB2 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/MgB2 berbanding GCE tanpa Pengoksidaan AA pada elektrod terubahsuai PEDOT/MgB₂ ubahsuai. dikawal serentak oleh pembauran AA dan penjerapan AA yang lemah. Elektrod terubahsuai PEDOT/MgB₂ 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 dopamin (DA) pada elektrod terubahsuai PEDOT/MgB₂ kehadiran 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 MgB₂-MWCNT and MgB₂/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.

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This is to confirm that:

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- 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
СР	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 (MgB₂) 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 MgB₂ applications in electroanalysis in 2009. To our knowledge, only one other paper (Zidan *et al.*, 2011) was published on the successful application of MgB₂ as electrode modifier after that.

This research is focused on the possible application of MgB₂ 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 MgB₂ as hybrid electrode modifiers, based on their distinct individual properties.

1.2 Problem Statement

Previous studies had shown that MgB₂ 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 MgB₂ hybrid modified electrode. Therefore, this research focuses on the prospect of fabricating a modified electrode by combining MgB₂ 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 MgB₂ 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 MgB₂ hybrid electrodes are also investigated.

1.3 Objectives of the Research

The objectives of the current research are as follows:

- i) To fabricate MgB₂ hybrid modified electrodes through mechanical attachment (MgB₂-MWCNT modified electrode) and electropolymerization (PEDOT/MgB₂ modified electrode)
- To compare the electrochemical reaction of ascorbic acid at bare, MgB₂-MWCNT and PEDOT/MgB₂ 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 MgB₂-MWCNT and PEDOT/MgB₂ 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 MgB₂, 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 MgB₂-MWCNT modified GCE, while the following two sections review experimental results from PEDOT/MgB₂ 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.

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