UNIVERSITI PUTRA MALAYSIA

FABRICATION OF ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE COMPOSITE BASED ELECTROCHEMICAL SENSOR FOR THE DETECTION OF 3-NITROPHENOL

NAFIU MUHAMMAD

FS 2015 18

FABRICATION OF ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE COMPOSITE BASED ELECTROCHEMICAL SENSOR FOR THE DETECTION OF 3-NITROPHENOL

By

NAFIU MUHAMMAD

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

October 2015

DEDICATION

This research work is dedicated to my beloved parents, lovely wife and elegant son Musab Ibn Nafiu Gidangona

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

FABRICATION OF ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE COMPOSITE BASED ELECTROCHEMICAL SENSOR FOR THE DETECTION OF 3-NITROPHENOL

By

NAFIU MUHAMMAD

October, 2015

Chair: Jaafar Abdullah PhD

Faculty: Science

In this research electrochemical sensor for the detection of 3-nitrophenol has been successfully developed based on electro-reduced graphene oxide (ERGO) functionalized with cyltrimethylammonium bromide (CTAB) and electro-reduced graphene oxide functionalized with poly(3,4-ethylenedioxythiophene) (PEDOT) on screen printed carbon electrode (SPCE). Two methods of preparations were used. Firstly, graphene oxide-CTAB was dropped cast onto the SPCE and later reduced using cyclic voltammetry technique to produce ERGO/CTAB. Secondly, ERGO/PEDOT was prepared by direct electrodeposition of mixture containing EDOT/GO in $LiClO_4$ to produce PEDOT/ERGO on SPCE. The modified SPCE were characterized using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), Raman spectroscopy, scanning electron microscope (SEM) and energy dispersive X-ray (EDX), respectively. Their electrochemical activities and sensing capability towards 3-nitrophenol was investigated using linear sweep voltammetry (LSV). The modified SPCEs showed a remarkable activity which attributed to the excellent conductivity, large surface area, electrocatalytic activity and good synergistic effect of the nanocomposite films toward 3-nitrophenol. To increase the sensitivity of the developed sensors experimental parameters such as pH buffer, scan rate, accumulation time and potential were optimized. Under the optimum experimental conditions, the ERGO/CTAB developed sensor displays two linear calibration curve in the concentration range of 0.5 and 100 µM with linear regression coefficients R^2 = 0.9915 and 0.9972 and detection limit of 0.04 µM. While PEDOT/ERGO modified SPCE gave linear calibration curve in the concentration range from 0.3 to 70 µM with linear regression equation $y = 5.0042C\ (\mu M) + 45.674,\ R^2 = 0.9934$ and detection limit of 0.08 µM. The proposed methods showed good selectivity of target analyte even in the presence of some foreign ions. A good reproducibility was recorded with RSD of 4.71% for ERGO/CTAB and 3.85 % for PEDOT/ERGO, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperiuan untuk Ijazah Sarjana Sains

FABRIKASI SENSOR ELEKTROKIMIA BERASASKAN KOMPOSIT GRAFEN OKSIDA TERTURUN SECARA ELECTROKIMIA UNTUK PENGESANAN 3-NITROFENOL

Oleh

NAFIU MUHAMMAD

Oktober, 2015

Pengerusi: Jaafar Abdullah Phd

Fakulti: Sains

Dalam kajian ini sensor elektrokimia untuk pengesanan 3-nitrofenol telah berjaya dibangunkan berasaskan elektro-terturun graphene oksida (ERGO) difungsikan dengan siltrimetilammonium bromida (CTAB) dan elektro-terturun graphene oksida difungsikan dengan poli(3,4-etilenadioksitiofena) (PEDOT) pada elektrod skrin bercetak karbon (SPCE). Dua kaedah penyediaan telah digunakan. Pertama, graphene oksida-CTAB disalut-titis ke atas SPCE dan kemudian diturunkan menggunakan teknik voltammetri kitaran untuk menghasilkan ERGO/ CTAB. Kedua, ERGO/PEDOT telah disediakan melalui pemendapan langsung campuran yang mengandungi EDOT/GO dalam $LiClO_4$ untuk menghasilkan PEDOT/ERGO di atas SPCE. SPCE terubahsuai telah dicirikan menggunakan voltammetri kitaran (CV), spektroskopi impedans elektrokimia (EIS), spektroskopi Raman, mikroskop imbasan elektron (SEM) dan tenaga serakan sinar-X (EDX), masing-masing. Aktiviti elektrokimia dan keupayaan penderiaan terhadap 3-nitrofenol telah dikaji menggunakan voltammetri sapuan linear (LSV). SPCE terubahsuai menunjukkan aktiviti yang luar biasa dikaitkan dengan kekonduksian yang sangat baik, luas permukaan yang besar, aktiviti elektro-mangkin dan kesan sinergi yang baik daripada filem nanokomposit terhadap 3-nitrofenol. Untuk meningkatkan kepekaan sensor yang dibangunkan parameter eksperimen seperti larutan penimbal pH, kadar imbasan, pengumpulan masa dan potensi telah dioptimumkan. Di bawah keadaan eksperimen yang optimum, ERGO/ CTAB yang dibangunkan menunjukkan dua keluk kalibrasi linear dalam julat kepekatan daripada 0.5 dan 100 µM dengan pekali regresi linear R^2 = 0,9915 dan 0,9972 dan had pengesanan 0.04 µM. Sementara SPCE terubahsuai PEDOT/ERGO memberikan keluk kalibrasi linear dalam julat kepekatan 0.3-70 µM dengan persamaan linear regresi y = 5.0042C (µM) 45.674, R^2 = 0.9934 dan had pengesanan 0.08 µM. Kaedah yang dicadangkan menunjukkan pemilihan yang baik daripada analit sasaran walaupun dengan kehadiran beberapa ion asing. Kebolehulangan yang baik telah direkodkan dengan nilai Sisihan Piawai Relatif (RSD) bersamaan 4.71 % untuk ERGO/CTAB dan 3.85 bagi PEDOT/ERGO, masing-masing.

ACKNOWLEDGEMENTS

Alhamdulillah, all glory and praises be to Allah the almighty and sustainer for the life, health, wisdom and ability to acquire this knowledge. Special thanks go to my supervisor Dr. Jaafar Abdullah who served as a pillar whenever I become weak and a guardian whenever needed throughout the research period and my stayed in Malaysia.

My appreciation also goes to my co-supervisor Dr. Yusran Suleiman and Dr. Lim Hong Ngee for their advice and guidance.

This work may not have been possible without the prayers, support and encouragement from my beloved parents Alhaji Muhammad Muazu and Hajiya Bilkisu Muhammad. Word cannot be enough to express my appreciation to my beloved wife Hauwau Sulemain Bindawa and my elegant son Musab Ibn Nafiu for their prayers and encouragement. A warm appreciation to my supporting and wonderful brothers and sisters; Malam Anas, Khalid, Maryam, Imrana, Fatima, Aisha, Hafsat, Asma'u, Ismail, Bilyaminu, Muazu, Sanusi and Abubakar Aminu, to mention few for their assistance.

I also acknowledge the assistance render to me by Sani Jibrin Gumel, Hajiya Salamatu Aliyu, Aminu Musa, Mamuda Umaru and Aliyu Muhammad toward completing this research.

I thank all my friends and colleagues Hazani, Fuzi, Aliyu Ahmad Yusuf (HOD), Sani Abubakar, Faruk Birnin Kebbi, Ibrahim Bala, Abdulaziz Kutawa, Abubakar Aisami and Hannatu Abubakar, to mention but a few, for making my stay at UPM and Malaysia a memobrable one.

Last but not the, least my profound appreciation goes to the management of Umaru Musa Yar'adua University for the encouragement and the sponsorship.

I certify that a Thesis Examination Committee has met on 6th October, 2015 to conduct the final examination of (Nafiu Muhammad) on his thesis entitled "Fabrication of Electrochemically Reduced Graphene Oxide Composite Based Electrochemical Sensor For The Detection of 3-Nitrophenol" 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 Master of Science in Environmental Chemistry.

Members of the Thesis Examination Committee were as follows:

Y. Bhg. Prof. Dr. Zulkarnain b Zainal
Chemistry Department
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Y. Bhg. Prof. Dr. Nor Azah binti Yusof
Chemistry Department
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Prof. Madya. Dr Illiyas Md Isa
Chemistry Department
Faculty Science and Mathematics
Universiti Penddidikan Sultan Idris
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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.

Members of the Supervisory Committee were as follows:

Jaafar bin Abdullah, PhD
Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Yusran Sulaiman, PhD
Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Lim Hong Ngee, Janet, PhD
Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

____

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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.

Signature: ______________________
Chairman of Supervisory Committee: ______________________

Signature: ______________________
Member of Supervisory Committee: ______________________

Signature: ______________________
Member of Supervisory Committee: ______________________

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

EC	European Commission
USEPA	United States Environmental Protection Agency
NPs	Nitrophenols
SPCE	Screen Printed Carbon Electrode
ERGO	Electro-reduced Graphene
CTAB	Cetyltrimethylammonium Bromide
PEDOT	Poly(3,4-ethylenedioxythiophene)
EDOT	3,4-ethylenedioxythiophene
AuNps	Gold Nanoparticles
CPE	Carbon Paste Electrode
GE	Graphite Electrode
GCE	Glassy Carbon Electrode
GR	Graphene
GO	Graphene Oxide
H_2O_2	Hydrogen peroxide
WE	Working Electrode
RE	Reference Electrode
CE	Counter Electrode
β-CFRGO	B-cyclodextrin Functionalized Reduced Graphene Oxide
OMC	Ordered Mesoporous carbons,
PdNps	Palladium nanoparticles,
(*p*-ABSA)	Poly(p-aminobenzene sulfonic acid)
CNT	Carbon nanotubes,
DPV	Differential Pulse Voltammetry
LSV	Linear Sweep Voltammetry,
CV	Cyclic Voltammetry,
SWV	Square Wave Voltammetry,
3-HAP	3- hydroxyaminophenol
3-NP	3-nitrophenol

CHAPTER ONE

Introduction

Since industrial revolution scientists have succeed in synthesizing different compounds that play vital role to man and his environment. However due to lack of enough attention to the fundamental and preliminary principles in planning, production of such compound may lead to inevitable catastrophic problems to the ecosystem. Some of the considerations include establishment of an industry within a residential area. This will affect the surrounding environment through discharging its waste or by sudden escape of toxic gasses which pollutes the ecosystems (Kun et al, 2013; Moradi et al., 2012) . Phenol and its derivatives are among the pollutants release by industries which caused serious health hazard ranging from headache, cancer to sudden death. Therefore monitoring these pollutants is prerequisite to healthy environment.

1.1 Phenol and its Derivatives

Phenol is widely known compound and is synonymously refer to as hydroxybenzene, carbolic acids, benzenol or phenolic acid, with a molecular formula C_6H_5OH or C_6H_6O, molar mass 94.11gmol^{-1} and structural formula as shown in Figure 1.1.

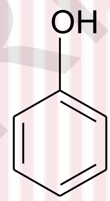

Figure 1.1: Phenol structural formula

Phenol is a transparent crystalline solid, with a sharp burning taste, sweet and tarry odour. It is soluble in water with solubility value of 8.3 g/100 mL (20 °C), melt at 40.5 °C (313.6 K; 104.9 °F) and boil at 181.7 °C (454.8 K; 359.1 °F). Phenol is a compound with benzene ring attached to hydroxyl functional group (OH). This structure makes phenol good candidate for both electrophilic and nucleophilic substitution reactions, as a result phenol becomes an important precursor to many important chemicals production such as dyes, numerous pharmaceutical drugs, cosmetics, resins, synthetic polymers, detergents, herbicides, ink, paints, rubbers, perfumes and fibers (Karim & Fakhruddin, 2012) Unfortunately with all the mentioned advantages, phenol has been classified as pollutant by United States Environmental Protection Agency (USEPA) and European Commission (EC) with environmental legislation restricting the content of phenols in the environment due to its toxicity and persistency to the environment.

Phenol has different derivatives which are either found naturally in coal tar, petroleum, lignin, cigarette, or are chemically synthesized as an intermediary in production of drugs, plastics, dyes and synthetic polymers. Not all derivatives of phenol are listed as pollutant by USEPA but those in the list include chlorophenols, nitrophenols, cresol, catechol, hydroquinone, biphenols, etc.

Nitrophenol (NP) is widely known compound with synonyms hydroxynitrobenzene, with a molecular formula $C_6H_5NO_2$, molar mass 139.11gmol^{-1} and structural formula as shown in figure 1.2. Pure nitrophenol is solid and ranges from transparent to yellowish in colour depending on the isomer, with a sharp burning taste sweet and tarry odor. It is soluble in water with solubility value of 16 g/L (25 °C), and density of 1.236 g/cm^3.

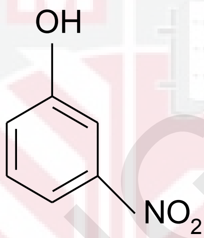

Figure 1.2: Structural formula of 3-Nitrophenol

1.2 Problem Statements

Nitrophenol is one of the derivatives of phenol, it is considered as pollutant to environment by USEPA, due to its persistence toxicity. Because of its uses, several tons are produced annually to meet the world demand, whereby certain amount escapes to the ecosystem. Therefore, facilitating its detection and presence in our ecosystem is prerequisites to healthy environment. Several methods and techniques have been developed for the effective detection of NPs. Conventional analytical methods for determination of NPs in waste water are: chromatography, capillary electrophoresis, spectrophotometry and immunoassays (Various, 1998). Though the techniques have advantages in accuracy, however, they involve complex sample pre-treatment, required well trained technician to operate, not suitable in the field, expensive instrumentation and also the analysis is time consuming (Svitel & Miertus, 1998). Therefore to overcome these challenges, a new analytical method called chemical sensor have been designed. Chemical sensor is an analytical tool which is simple, sensitive, high in accuracy, reliable and less expensive instrumentation, thus, making them ideal for environmental analysis.

1.3 Objective of the Research

The aim of this research is to develop simple, high selective and sensitive electrochemical sensor for effective detection of 3-nitrophenol (3-NP). The objective set to achieve these goals includes:

1. To prepare and characterize the screen printed carbon electrode (SPCE) modified with electro-reduced graphene oxide/cetyltrimethylammonium bromide (ERGO/CTAB) nanocomposite and electro-reduced graphene oxide/poly(3,4-ethylenedioxythiophe) (ERGO/PEDOT) nanocomposite.
2. To optimize experimental parameter of the modified SPCEs for the determination of 3-nitrophenol.
3. To evaluate the sensing capability of the modified SPCEs for the determination of 3-nitrophenol.