



UNIVERSITI PUTRA MALAYSIA

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

NAFIU MUHAMMAD

FS 2015 18



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OXIDE COMPOSITE BASED ELECTROCHEMICAL SENSOR FOR THE
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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

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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 cetyltrimethylammonium 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 LiClO₄ 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 $0.04 \mu\text{M}$. While PEDOT/ERGO modified SPCE gave linear calibration curve in the concentration range from 0.3 to 70 μM with linear regression equation $y = 5.0042C (\mu\text{M}) + 45.674$, $R^2 = 0.9934$ and detection limit of $0.08 \mu\text{M}$. 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 keperluan untuk Ijazah Sarjana Sains

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

Oleh

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Dalam kajian ini sensor elektrokimia untuk pengesanan 3-nitrofenol telah berjaya dibangunkan berasaskan elektro-turunan graphene oksida (ERGO) difungsikan dengan siltrimetilammonium bromida (CTAB) dan elektro-turunan graphene oksida difungsikan dengan poli(3,4-etilenadioksitofena) (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 $y = 5.0042C (\mu\text{M}) + 45.674$, $R^2 = 0.9934$ dan had pengesanan 0.08 μM . Kaedah yang dicadangkan menunjukkan pemilihan yang baik daripada analit sasaran walaupun dengan kehadiran beberapa ion asing. Kebolehhulangan yang baik telah direkodkan dengan nilai Sisihan Piawai Relatif (RSD) bersamaan 4.71 % untuk ERGO/CTAB dan 3.85 bagi PEDOT/ERGO, masing-masing.

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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.

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

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TABLE OF CONTENTS

ABSTRACT	Page
ABSTRAK	i
ACKNOWLEDGEMENT	ii
DECLARATION	iii
TABLE OF CONTENTS	vi
LIST OF TABLES	viii
LIST OF FIGURES	xi
LIST OF ABBREVIATION	xii
	xv

CHAPTER

1	INTRODUCTION	
1.1	Phenol and it Derivatives	1
1.2	Problem Statements	2
1.3	Objective of the Research	2
2	LITERATURE REVIEW	
2.0	Toxicity of Nitrophenol (NPs)	4
2.1	Chemical Sensor as Analytical Device	5
2.2	Electrochemical Sensor	9
	2.2.1 Voltammetry	10
	2.2.2 Linear Sweep Voltammetry	11
	2.2.3 Cyclic Voltammetry	12
	2.2.4 Screen Printed Electrode	15
2.3	Graphene	17
	2.3.1 Functionalization and Formation of Graphene Nanocomposite	19
	2.3.2 Graphene as Electrode Modifier	20
2.4	Conductive polymers	20
	2.4.1 Poly(3,4-ethylenedioxythiophene) (PEDOT)	21
2.5	Cetyltrimethylammonium Bromide(CTAB)	22
2.6	Electrochemical Methods in Electrode Modification Technique	23
3	METHODOLOGY	
3.1	Materials and Reagents	25
3.2	Instrumentation and Apparatus	25
	3.2.1 Cyclic Voltammetry (CV) Characterization	25
	3.2.2 Electrochemical Impedance Spectroscopy (EIS) Characterization	26
	3.2.3 Raman Spectroscopy Characterization	26
	3.2.4 Field Emission Scanning Electron Microscope (FSEM)	27

3.2.5	Energy Dispersive X-Ray Spectrometers (EDX)	27
3.3	Preparation of Modified Electrodes	27
3.3.1	Preparation of Electro-Reduced Graphene Oxide (ERGO) Modified SPCEs	27
3.3.2	Preparation of Electro-Reduced Graphene oxide Cetyltrimethylammonium Bromide Modified SPCE	28
3.3.3	Preparation of Poly(3,4-ethylenedioxythiophene) (PEDOT) and of PEDOT/ERGO Modified SPCE	28
3.4	Preparation of 3-Nitrophenol (3-NP) Stock Solution	28
3.5	Electrochemical Characterization of Modified SPCEs toward 3-Nitrophenol	28
3.5.1	Effect of Supporting Electrolyte	29
3.5.2	Influence of Phosphate Buffer pH On Modified SPCEs	29
3.5.3	Effect of Varying Scan Rates	29
3.5.4	Effect of Accumulation Time and Accumulation Potential	29
3.5.5	Calibration Curve of the Developed Sensors	29
3.5.6	Repeatability, Reproducibility and Stability Study of the Developed Sensors	30
3.5.7	Effect of Foreign Ions	30
3.6	Application of the Developed Sensor towards Real Sample and Validation Study	30
4	RESULT AND DISCUSSION	
4	Preparation and Characterization of SPCEs Modified ERGO and ERGO/CTAB	32
4.1	Preparation of ERGO/SPCE	32
4.2	Preparation of ERGO/CTAB/SPCE	34
4.2.1	Cyclic Voltammetry of ERGO/CTAB Modified Electrode	34
4.2.2	Electrochemical Impedance Spectroscopy (EIS)	37
4.2.3	Raman Spectroscopy Characterization	38
4.2.4	Field Emission Scanning Electron Microscope	39
4.2.5	Energy Dispersive X-Ray Spectrometers (EDX)	40
4.3	General Principle of Detection of 3-Nitrophenol	42
4.4	Electrochemical Characterization of Modified SPCEs towards 3-Nitrophenol	43

4.4.1	Effect of Supporting Electrolyte and pH	44
4.4.2	Effect of Scan Rate	46
4.4.3	Effect of Accumulation Time and Accumulation Potentials	47
4.4.4	Analytical Performance of SPCE Modified ERGO/CTAB	48
4.4.5	Interference Study	50
4.4.6	Repeatability, Reproducibility and Stability	51
4.4.7	Analysis of Spiked Real sample	52
4.5	Preparation and Characterization of SPCEs Modified PEDOT and PEDOT-ERGO	54
4.5.1	Preparation of PEDOT Electrode	54
4.5.2	Preparation of PEDOT/ERGO SPCE	54
4.5.3	Cyclic Voltammetry of Modified SPCE	55
4.5.4	Electrochemical Impedance Spectroscopy (EIS)	57
4.5.5	Raman Spectroscopy	58
4.5.6	Field Emission Scanning Electron Microscope	59
4.5.7	Energy Dispersive X-Ray Spectrometers (EDX)	60
4.6	Electrochemical Characterization of Modified SPCEs towards 3-Nitrophenol	60
4.6.1	Effect of PEDOT/ERGO Load/Thickness on SPCE toward Reduction on 3-NP	62
4.6.2	Effect of pH	62
4.6.3	Effect of Scan Rate	63
4.6.4	Effect of Accumulation Time and Accumulation Potentials	64
4.6.5	Analytical performance of SPCE Modified PEDOT/ERGO	66
4.6.6	Interference Study	67
4.6.7	Repeatability, Reproducibility and Stability	69
4.6.8	Analysis of Spiked Real sample	70
5	CONCLUSION AND RECOMMENDATIONS	
5.1	Conclusion	72
5.2	Recommendation for Future Research	72
	REFERENCES	74
	APPENDICES	82
	BIO DATA OF STUDENT	95
	LIST OF PUBLICATIONS	96

LIST OF TABLES

Table		Page
2.1	Summary of Reported Electrochemical Sensor for Detection Nitrophenols	6
2.2	Chemical Sensor Classification Based on Transducer	8
2.3	Some Reported Methods of SPCE Modification	16
2.4	Several Techniques of Reducing Graphene Oxide to Graphene	18
2.5	Electrochemical Techniques used in the Reduction of Graphene Oxide	19
3.1	The Interferants Used in the Analysis	30
4.1	The peak Current Obtained at Different Accumulation Potential	48
4.2	Comparison Performance of Different Electrochemical Sensor for the Detection 3-NP	50
4.3a	Effect inorganic foreign ions on the response of the developed sensor	51
4.3b	Effect organic foreign ions on the response of the developed sensor	51
4.4	Comparison study of Spiked Real Sample between the Developed Sensor and the APHA Method	53
4.5	The Effect of Different Accumulation Potential towards Peak Current	65
4.6	Comparison of Several Modified Electrode for Detection 3-NP	67
4.7a	Effect of some organic foreign ions on the response of the developed sensor	67
4.7b	Effect of Some inorganic Foreign Ions on the Response of the Developed Sensor	68
4.8	Analytical Performance of PEDOT/ERGO for 3-NP and 4-NP	69
4.9	Comparison of Real Sample Analysis between the PEDOT/ERGO/SPCE and Spectrophotometer	71

LIST OF FIGURES

Figure		Page
1.1	Phenol Structural Formula	1
1.2	Structural Formula of Nitrophenol	2
2.1	Structure of 3-Nitrophenol	4
2.2	Production of Nitrophenol	5
2.3	Process of Analyte Detection Using Chemical Sensor	8
2.4	Schematic Diagram of Electrode Arrangement of in Electrochemical Sensors	9
2.5	Schematic Diagram of an Electrochemical Sensor	10
2.6	Electro-reduction of 3-nitrophenol to 3- hydroxyl aminophenol	11
2.7	Example of Linear Sweep Voltammogram	12
2.8	Excitation Signals for Cyclic Voltammetry showings Triangle Potential Waveform With Switching Potential at -0.2 and -0.6 V	13
2.9	Cyclic Voltammetry of ERGO/SPCE in $K_3Fe(CN)_6$ for single scan redox	14
2.10	Screen Printed Carbon Electrode	15
2.11	Structure of Graphene	18
2.12	Structure of 3,4-ethylenedioxythiophene (EDOT)	21
2.13	Structure of Cetyltrimethylammonium Bromide	23
3.1	Schematic diagram of experimental setup	26
4.1	Cyclic Voltammogram of Electrochemical Reduction of GO in 0.1 M KCl at Scan Rate of 100 mV/s at potential range -1.5 to 0.4 V vs AgCl	32
4.2	A) Cyclic voltammetry of different ERGO modified SPCEs in 5 mM $K_3[Fe(CN)_6]$ /0.1 M KCl with scan rate of 100mV/s. B) EIS of different ERGO modified SPCE with frequency of 100 KHz to 0.1 Hz and amplitude of 0.01 V in 5 mM $K_3[Fe(CN)_6]$ /0.1 M KCl.	33
4.3	Cyclic Voltammogram of Electrochemical Reduction of GO/CTAB to ERGO/CTAB in 0.1 M KCl, potential range – 1.5 to 0.4 V with scan rate of 100 mV/s	34
4.4	Cyclic voltammetry behaviour of bare, GO and ERGO in 5 mM $K_3[Fe(CN)_6]$ /0.1 M KCl with scan rate 100 mV/s, potential range of -0.2 to 0.7 V	35
4.5	A) Effect of scan rate on ERGO/CTAB/SPCE in 5mM $K_3[Fe(CN)_6]$ /0.1M KCl from 25 to 175mVs at potential range of – 0.2 to 0.7 V B) Correlation between Current and Square Root of Scan Rate	36
4.6	The EIS of bare, GO, GO/CTAB, ERGO, CTAB and ERGO/CTAB in 5 mM $K_3[Fe(CN)_6]$ / 0.1 M KCl with frequency 100 KHz to 0.1 Hz and amplitude 0.01 V	38
4.7	Raman Spectra of GO and ERGO	39
4.8	The FESEM of (A) GO Modified SPCE (B) GO/CTAB Modified SPCE (C) ERGO modified SPCE (D) ERGO/CTAB modified SPCE	40

4.9	The EDX Spectra of the Modified SPCE with A) GO B) GO/CTAB C) ERGO D) ERGO/CTAB	41
4.10	LSV of Bare SPCE and the Modified SPCEs in the absence and presence of 0.1mM 3-NP with a scan rate of 100 mV/s and potential range of -0.2 to -0.9 V	43
4.11	LSV of influence of Acetate, Citric and PBS Buffers of equal strength and pH (0.1M, pH 6) on the Modified SPCEs Response towards 0.1 mM 3-NP at scan rate of 100 mV/s potential -0.2 to -0.9 V	45
4.12	A) PBS pH response on the Modified SPCEs towards detection of 0.1 mM 3-NP (pH from 3 to 9) C) Correlation of Reduction Potential with change in pH	45
4.13	A) LSV of ERGO/CTAB/SPCE towards 0.1m M 3-NP in PBS (pH 6.5) at potential range -0.2 to -0.9 V at different scan rate b) correlation of reduction peak current against scan rate	46
4.14	The reduction peak current of 0.1 mM 3-NP in 0.1M PBS (PH=6.5) at Different Accumulation Time	47
4.15	A) Dynamic behaviour of ERGO/CTAB at Different Concentration of 3-NP in 0.1 M PBS (pH 6.5) Scan Rate of 100 mV/s at Potential Range of 0.0 to -0.9 V B) Calibration curve of the Developed Sensor	49
4.16	The Stability Study of ERGO/CTAB Modified SPCE in 4°C Temperature and Room Temperature	52
4.17	The Cyclic Voltammogram of Electrodeposition of PEDOT on SPCEs with Potential Range -0.9 to 1.1 V, scan rate 100mVs 0.01 M LiClO ₄	54
4.18	The Cyclic Voltammogram of Electrodeposition of PEDOT/ERGO on SPCEs with Potential Range -1.5 to 1.1 V, scan rate 100mVs 0.01 M LiClO ₄	55
4.19	Comparison of CV behaviour of bare, ERGO/SPCE, PEDOT/SPCE and PEDOT/ERGO/SPCE in 5 mM K ₃ [Fe(CN) ₆]/0.1 M KCl with scan rate 100 mV/s at potential range of -0.2 to 0.6 V	56
4.20	Effect of Scan Rate and Correlation between Peak Current and Scan rate of a) Bare SPCE b) ERGO/SPCE c) PEDOT/SPCE d) PEDOT/ERGO/ERGO in 5mM K ₃ [Fe(CN) ₆]/0.1M KCl scan rate of 10 mV/s to 50 mV/s	56
4.21	The Nyquist Plot of Bare SPCE, and SPCE modified with ERGO, PEDOT, PEDOT/ERGO in 5 mM K ₃ [Fe(CN) ₆]/ 0.1 M KCl, at a Frequency of 100 KHz to 0.1 Hz and Amplitude of 0.01 V	58

4.22	Raman spectrum of SPCE modified with ERGO, PEDOT, and PEDOT/ERGO	59
4.23	The FESEM of Modified SPCE with a). PEDOT (b) PEDOT/ERGO	59
4.24	The EDX Spectrum of Modified SPCE with (a) PEDOT (b) PEDOT/ERGO	60
4.25	LSV of bare SPCE and modified SPCE with PEDOT, ERGO and PEDOT/ERGO towards 3-NP, potential ranges of 0 to – 0.9 V with scan rate 100 mV/s	61
4.26	The effect of PEDOT/ERGO thickness on detection of 1 mM 3-NP with scan rate 100 mV/s in 0.1M PBS (6.0)	62
4.27	Influence of pH on the PEDOT/ERGO response to 0.1mM 3NP in PBS different PH (from 4 to 8)	63
4.28	The behavioural response of modified SPCE towards 0.1 mM 3-NP in PBS (pH 6.5) a) at different scan rate b) Correlation of Reduction Peak Current with Scan Rate	64
4.29	The Current Peak of 1 mM 3-NP in PBS (pH 6.5) at Different Accumulation Time	65
4.30	Dynamic Behaviour of PEDOT/ERGO at Different Concentration of 3-NP in 0.1 M PBS (pH 6.5) Scan Rate of 100 mV/s at Potential Range of -0.2 to -0.9 V B) Calibration curve of the Developed Sensor.	66
4.31	Behaviour of 1 mM 4-NP in PBS a) at different scan rate b) Correlation of Reduction Peak Current with Scan Rate	68
4.32	Dynamic behaviour of PEDOT/ERGO at Different Concentration of 4-NP in 0.1 M PBS (pH 6.5) Scan Rate of 100 mV/s at Potential Range of 0.0 to -0.9 V B) Calibration curve of the Developed Sensor	69
4.33	The Stability Study of PEDOT/ERGO Modified SPCE at 4°C and room temperature	70

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 ₂ O 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,
(<i>p</i> -ABSA)	Poly(<i>p</i> -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.

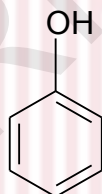


Figure 1.1: Phenol structural formula

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 139.11g mol^{-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 ($25\text{ }^\circ\text{C}$), and density of 1.236 g/cm^3 .

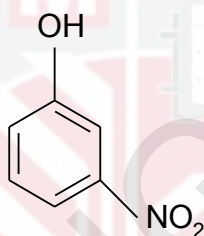


Figure 1.2: Structural formula of 3-Nitrophenol

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-ethylenedioxythiophene) (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.

