SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

DEVELOPMENT OF BISMUTH NANOPARTICLES FOR LEAD AND CADMIUM SENSORS APPLICATION

By

TEH JIN JIAN

Supervisor: Assoc. Prof. Dr. Khairunisak Bt. Abdul Razak

Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

JULY 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: **"Development of Bismuth Nanoparticles for Lead and Cadmium Sensors Application"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Name of student : Teh Jin Jian Signature:

Date : 3 July 2017

Witnessed by

Supervisor : Assoc. Prof. Dr. Khairunisak Bt. Abdul Razak Signature:

Date : 3 July 2017

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude to my supervisor, Associate Professor Dr. Khairunisak Bt. Abdul Razak for the continuous support and guidance throughout my final year project study and research. Her extensive knowledge consistently steered me in the right direction whenever she thought I needed it about my research and thesis writing. Without her dedicated involvement in every step throughout the project, this thesis would have never been accomplished.

Second, as a Materials Engineering student, I would also like to acknowledge School of Materials and Mineral Resources Engineering and Institute for Research in Molecular Medicine (INFORMM), Universiti Sains Malaysia (USM) for providing laboratories, machines and apparatus to complete my research project smoothly.

In addition, I would like to extend my deepest thanks to Ms. Nor Dyana Zakaria, research officer at INFORMM for her wholeheartedly technical supports and helps during my laboratory work there. My sincere thanks also go to Ms. Zulfa Aiza Binti Zulkifli, Ms. Atiqah Binti Ahmad, Ms. Noorhashimah Binti Mohamad Nor and Ms. Nur Syafinaz Ridhuan, for offering me the details of the experiment and valuable assistances in leading me working on my project.

Finally, I must express my very profound gratitude to my parents and to my colleagues for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

TABLE OF CONTENTS

Contents **Page**

DECLARATION		ii
ACKNOWLEDGEMENTS		iii
TABLE OF CONTENTS		iv
LIST OF TABLES		vii
LIST OF FIGURES		ix
LIST OF ABBREVIATIONS		xv
LIST OF SYMBOLS		xxi
ABSTRAK		xxiv
ABSTRACT		xxv
CHAPTER 1 – INTRODUCTION		**1**
1.1	Introduction	1
1.2	Problem Statement	8
1.3	Research Objectives	11
1.4	Scope of Study	12
1.5	Thesis Outline	12
CHAPTER 2 – LITERATURE REVIEW		**13**
2.1	Introduction	13
2.2	Water Pollution by Heavy Metals	15
2.3	Detection of Heavy Metal Ions (Lead, Pb^{2+} and Cadmium, Cd^{2+})	18
2.4	Conventional Materials and Nanomaterials for Sensing of Heavy Metal Ions	21
2.5	Bismuth-Modified Electrodes for Heavy Metal Ions Detection	24
2.6	Types of Heavy Metal Sensors	31
2.7	Electrochemical Detection Techniques	33
2.8	Electrochemical Analysis of Trace Heavy Metals Using Screen-Printed Electrodes (SPEs)	40

2.9 Electrochemical Analysis of Trace Heavy Metals Using Indium Tin Oxide (ITO) Electrodes 42
2.10 Summary 46

CHAPTER 3 – METHODOLOGY 50
3.1 Introduction 50
3.2 Raw Materials and Chemicals 52
3.3 Synthesis of Bismuth Nanoparticles (BiNPs) Using Hydrothermal Method 53
3.4 Methodology 55
3.4.1 Preparation of Indium Tin Oxide (ITO) Glass Substrate 55
3.4.2 Preparation of BiNPs/ITO Modified Electrodes by Drop Casting of BiNPs on ITO Glass Substrates 56
3.5 Electrochemical Measurements 56
3.5.1 Procedure for Cyclic Voltammetry (CV) Analysis 59
3.5.2 Procedure of Differential Pulse Anodic Stripping Voltammetry (DPASV) Analysis 59
3.5.3 Interference Study 60
3.5.4 Application to Real Sample 61
3.6 Characterization for Synthesized BiNPs 61
3.6.1 X-Ray Diffraction (XRD) 61
3.6.2 Field Emission Scanning Electron Microscopy (FESEM) Equipped With Energy Dispersive X-Ray Spectroscopy (EDX) 61
3.6.3 Transmission Electron Microscopy (TEM) 62

CHAPTER 4 – RESULTS AND DISCUSSIONS 63
4.1 Introduction 63
4.2 The Effect of Hydrothermal Reaction Period on Formation of BiNPs 64
4.2.1 X-Ray Diffraction (XRD) Patterns of the Derived BiNPs 64
4.2.2 Morphological Analysis and Elemental Characterization 67
4.2.3 Cyclic Voltammetry (CV) Properties of BiNPs/ITO Modified Electrodes 73
4.2.4 Optimization of BiNPs Concentration Drop-Casted on ITO Electrodes 76

4.2.5 Optimization of pH Value in Supporting Electrolyte 78
4.2.6 Optimization of Deposition Potential of Target Heavy Metal Cations on BiNPs/ITO Electrodes 79
4.2.7 Optimization of Deposition Time of Target Heavy Metal Cations on BiNPs/ITO Electrode 81
4.2.8 Electrochemical Characterization of BiNPs/ITO Modified Electrodes Using Differential Pulse Anodic Stripping Voltammetry (DPASV) 82
4.2.9 Interference Studies 89
4.3 The Effect of Volume of Hydrazine Hydrate on Formation of BiNPs 93
4.3.1 X-Ray Diffraction (XRD) Patterns of the Derived BiNPs 93
4.3.2 Morphological Analysis under SEM Characterization 94
4.3.3 Cyclic Voltammetry (CV) Properties of BiNPs/ITO Modified Electrodes 96
4.3.4 Electrochemical Characterization of BiNPs/ITO Modified Electrodes Using Differential Pulse Anodic Stripping Voltammetry (DPASV) 98
4.3.5 Interference Studies 102
4.4 The Effect of Hydrothermal Reaction Temperature on Formation of BiNPs 104
4.4.1 X-Ray Diffraction (XRD) Patterns of the Derived BiNPs 104
4.4.2 Morphological Analysis under SEM Characterization 105
4.4.3 Cyclic Voltammetry (CV) Properties of BiNPs/ITO Modified Electrodes 107
4.4.4 Electrochemical Characterization of BiNPs/ITO Modified Electrodes Using Differential Pulse Anodic Stripping Voltammetry (DPASV) 109
4.4.5 Interference Studies 113
4.5 Repeatability and Reproducibility Studies 115
4.6 Application to Real Sample 117

CHAPTER 5 – CONCLUSION AND RECOMMADATIONS FOR FUTURE WORK 119
5.1 Conclusion 119
5.2 Recommendations for Future Work 120
REFERENCES 125

LIST OF TABLES

	Page
Table 1.1: Types of heavy metals and their effect on human health (Singh et al., 2011)	2
Table 1.2: Heavy metals in industrial effluents (Mahurpawar, 2015)	3
Table 2.1: Clinical Aspects of Chronic Toxicities (Mahurpawar, 2015)	16
Table 2.2: Limits, sources and effects of heavy metal ions	18
Table 2.3: Applications of bismuth nanoparticles (BiNPs) as heavy metals sensor	27
Table 2.4: Nanomaterial applications in relation to voltammetry strategies used for heavy metals detection	38
Table 2.5: Types of modified screen-printed electrodes (SPEs) for heavy metals detection	43
Table 3.1: Raw materials and chemicals being used in this study.	52
Table 3.2: Synthesis parameters optimization of BiNPs using hydrothermal method	55
Table 4.1: Average particle size of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours from SEM images	70
Table 4.2: Average particle size of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours from TEM images	72
Table 4.3: The DPASV stripping current response of different concentrations of Pb^{2+} standard solutions measured with the BiNPs/ITO electrodes synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours	88

Table 4.4: Average particle size of BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml 96

Table 4.5: The DPASV stripping current response of different concentrations of Pb^{2+} standard solutions measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml 100

Table 4.6: Average particle size of BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ 107

Table 4.7: The DPASV stripping current response of different concentrations of Pb^{2+} standard solutions measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ 112

LIST OF FIGURES

Page

Figure 2.1: Schematic illustration of general principle of electrochemical sensing of heavy metal ions (Bansod et al., 2017) 37

Figure 2.2: Screen-printed device with three-electrode configuration (Serrano et al., 2013) 41

Figure 3.1: Overview of research flow for synthesis BiNPs for heavy metal ions detection 51

Figure 3.2: Overview flow of BiNPs synthesis using hydrothermal method 54

Figure 3.3: Experimental setup of BiNPs/ITO electrodes served as the working electrode together with the counter electrode and reference electrode 57

Figure 3.4: Schematic drawing of BiNPs/ITO electrodes served as the working electrode together with the counter electrode and reference electrode 57

Figure 3.5: Experimental setup for electrochemical measurements of CV and DPASV 58

Figure 3.6: Schematic drawing of electrochemical measurements of CV and DPASV 58

Figure 4.1: XRD patterns of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: (a) 4 hours and (b) 5 hours 65

Figure 4.2: XRD patterns of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: (a) 5 hours, (b) 6 hours, (c) 8 hours, and (d) 10 hours 67

Figure 4.3: SEM images of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: (a) 5 hours, (b) 6 hours, (c) 8 hours, and (d) 10 hours 68

Figure 4.4: Elemental analysis with EDX spectrum of BiNPs powder sample synthesized using hydrothermal method 71

Figure 4.5: Elemental analysis with EDX spectrum of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate for 10 hours 71

Figure 4.6: TEM images of BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: (a) 5 hours, (b) 6 hours, (c) 8 hours, and (d) 10 hours 72

Figure 4.7: CV curves of modified ITO electrodes with BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours in 0.002 mol/L of $K_3Fe(CN)_6$ 75

Figure 4.8: Graph of current (μA) with varying hydrothermal reaction period (hours) of BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ in 0.002 mol/L of $K_3Fe(CN)_6$ 75

Figure 4.9: CV curves of modified ITO electrodes with BiNPs synthesized using hydrothermal method with varying concentrations of BiNPs drop-casted: 10 μg/L, 20 μg/L, 30 μg/L and 40 μg/L in 0.002 mol/L of $K_3Fe(CN)_6$ 77

Figure 4.10: Current (μA) versus concentrations of BiNPs drop-casted on ITO electrodes with varying concentrations: 10 μg/L, 20 μg/L, 30 μg/L and 40 μg/L in 0.002 mol/L of $K_3Fe(CN)_6$ 77

Figure 4.11: Current (μA) versus pH values of acetate buffer (NaAc-HAc) solution in electrolyte containing 100 μg/L of Pb^{2+} standard solution 79

Figure 4.12: Current (μA) versus deposition potential (V) of Pb^{2+} on BiNPs/ITO electrodes in electrolyte containing 100 μg/L of Pb^{2+} standard solution 80

Figure 4.13: Current (μA) versus deposition period (seconds) on Pb^{2+} on BiNPs/ITO electrodes in electrolyte containing 100 μg/L of Pb^{2+} standard solution 81

Figure 4.14: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours in electrolyte containing 100 μg/L of Pb^{2+} standard solution with acetate buffer solution 86

Figure 4.15: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours in electrolyte containing 100 μg/L of Cd^{2+} standard solution with acetate buffer solution 86

Figure 4.16: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours in electrolyte containing 2.5 μg/L of Pb^{2+} standard solution with acetate buffer solution 88

Figure 4.17: Current (μA) versus concentrations of Pb^{2+} standard solutions (μg/L) measured with the BiNPs/ITO electrodes synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours 89

Figure 4.18: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours 91

Figure 4.19: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method at 160 ℃ and 2.0 ml of hydrazine hydrate with varying hydrothermal reaction period: 5, 6, 8, and 10 hours with Nafion modification 92

Figure 4.20: XRD patterns of BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: (a) 1.0 ml, (b) 1.5 ml, (C) 2.0 ml, and (d) 2.5 ml 94

Figure 4.21: SEM images of BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: (a) 1.0 ml, (b) 1.5 ml, (c) 2.0 ml, and (d) 2.5 ml 96

Figure 4.22: CV curves of modified ITO electrodes with BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ for with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml in 0.002 mol/L of $K_3Fe(CN)_6$ 97

Figure 4.23: Graph of current (μA) for with varying volume of hydrazine hydrate (ml) of BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ in 0.002 mol/L of $K_3Fe(CN)_6$ 98

Figure 4.24: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml in electrolyte containing 100 μg/L of Pb^{2+} standard solution with acetate buffer solution 99

Figure 4.25: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml in electrolyte containing 100 μg/L of Cd^{2+} standard solution with acetate buffer solution 99

Figure 4.26: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0 ml, 1.5 ml, 2.0 ml, and 2.5 ml in electrolyte containing 2.5 μg/L of Pb^{2+} standard solution mixed with acetate buffer solution 101

Figure 4.27: Graph of current (μA) against concentrations of Pb^{2+} standard solutions (μg/L) measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0 ml, 1.5 ml, 2.0 ml, and 2.5 ml of hydrazine hydrate 101

Figure 4.28: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml of hydrazine hydrate 102

Figure 4.29: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method for 6 hours and 160 ℃ with varying volume of hydrazine hydrate: 1.0, 1.5, 2.0, and 2.5 ml of hydrazine hydrate with Nafion modification 103

Figure 4.30: XRD pattern of BiNPs synthesized using hydrothermal method at 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: (a) 150 ℃, (b) 160 ℃, (c) 170 ℃, and (d) 180 ℃ 105

Figure 4.31: SEM images of BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature (a) 150 ℃, (b) 160 ℃, (c) 170 ℃, and (d) 180 ℃ 106

Figure 4.32: CV curves of modified ITO electrodes with BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ in 0.002 mol/L of $K_3Fe(CN)_6$ 108

Figure 4.33: Graph of current (μA) with varying hydrothermal reaction temperature (℃) of BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate in 0.002 mol/L of $K_3Fe(CN)_6$ 109

Figure 4.34: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ in electrolyte containing 100 μg/L of Pb^{2+} standard solution with acetate buffer solution 110

Figure 4.35: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ in electrolyte containing 100 μg/L of Cd^{2+} standard solution with acetate buffer solution 111

Figure 4.36: The DPASV stripping current response measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ in electrolyte containing 2.5 μg/L of Pb^{2+} standard solution with acetate buffer solution 112

Figure 4.37: Graph of current (μA) against concentrations of Pb^{2+} standard solutions (μg/L) measured with the BiNPs/ITO electrodes synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ 113

Figure 4.38: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ 114

Figure 4.39: The DPASV stripping current response measured for interference study in electrolyte containing 100 μg/L of multi-element standard solution by using BiNPs synthesized using hydrothermal method for 6 hours and 2.5 ml of hydrazine hydrate with varying hydrothermal reaction temperature: 150 ℃, 160 ℃, 170 ℃, and 180 ℃ with Nafion modification. 115

Figure 4.40: Current (μA) versus repeatability (times) by using the BiNPs/ITO electrode in electrolyte containing 50 ug/L of Pb^{2+} standard solution 116

Figure 4.41: Current (μA) versus reproducibility by using the BiNPs/ITO electrodes in electrolyte containing 50 ug/L of Pb^{2+} standard solution 116

Figure 4.42: The DPASV stripping current response measured with the BiNPs/ITO electrode in electrolyte containing 25.0 ml of seawater mixed with 2.0 ml of 3.0 mol/L acetate buffer solutions at pH 4.5 118

LIST OF ABBREVIATIONS

$[Fe(CN)_6]^{3-}$	Ferrocyanide (III) Ion
Ag	Silver
Ag^+	Silver (I) Ion
Al^{3+}	Aluminium (III) Ion
As	Arsenic
ASV	Anodic Stripping Voltammetry
AuNPs	Gold Nanoparticles
B^{3+}	Boron (III) Ion
Ba^{3+}	Barium (III) Ion
Bi	Bismuth
Bi(III)	Bismuth (III) Ion
$Bi(NO_3)_3 \cdot 5H_2O$	Bismuth (III) Nitrate Pentahydrate
Bi_2O_3	Bismuth (III) Oxide
BiNPs	Bismuth Nanoparticles
Ca^{2+}	Calcium (II) Ion
Cd	Cadmium

Cd(II) / Cd^{2+}	Cadmium (II) Ion
CE	Counter Electrode
CH_3CO_2H	Acetic Acid
CH_3COONa	Sodium Acetate
CnP	Carbon Nanopowder
Co^{2+}	Cobalt (II) Ion
CPEs	Carbon Paste Electrodes
Cr	Chromium
Cr(II)	Chromium (II) Ion
Cr^{3+}	Chromium (III) Ion
Cu(II)	Copper (II) Ion
CV	Cyclic Voltammetry
DNA	Deoxyribonucleic Acid
DP	Differential Pulse
DPASV	Differential Pulse Anodic Stripping Voltammetry
DPV	Differential Pulse Voltammetry
EDX	Energy Dispersive X-ray

Fe^{2+}	Iron (II) Ion
FETs	Field-Effect Transistors
FWHM	Full Width at Half Maximum
Ga^{3+}	Gallium (III) Ion
GCEs	Glassy Carbon Electrodes
GO	Graphene Oxide
H^+	Hydrogen Ion
H_2	Hydrogen Gas
H_2O	Distilled Water
H_2O_2	Hydrogen Peroxide
Hg	Mercury
Hg(II)	Mercury (II) Ion
HNO_3	Nitric Acid
In^{3+}	Indium (III) Ion
IQ	Intelligence Quotient
ISEs	Ion Selective Electrodes
ITO	Indium Tin Oxide

K^+	Potassium (I) Ion
$K_3Fe(CN)_6$	Potassium Ferrocyanide (III)
KCl	Potassium Chloride
Li^+	Lithium (I) Ion
LOD	Limit of Detection
LSV	Linear Sweep Voltammetry
Mg^{2+}	Magnesium (II) Ion
Mn^{2+}	Manganese (II) Ion
MTU	Methyl-2-Thiouracil
N_2	Nitrogen Gas
N_2H_2	Diazene
$N_2H_4•H_2O$	Hydrazine hydrate
$N_2H_5^+OH^-$	Hydrazinium Hydroxide Ion
Na^{2+}	Sodium (II) Ion
NaAc-HAc	Acetate Buffer Solution
Ni(II)	Nickel (II) Ion
NO_3^-	Nitrate Ion

NPs	Nanoparticles
O_2	Oxygen Gas
OH^-	Hydroxide Ion
OTE	Optically Transparent Electrode
Pb	Lead
Pb(II) / Pb^{2+}	Lead (II) Ion
Po	Polonium
PPyBSA	Benzene Sulfonic Acid-doped with Polypyrrole
PSS	Polysodium 4-Styrene-Sulfonate
RE	Reference Electrode
RSD	Relative Standard Deviation
Sb	Antimony
Sb(III)	Antimony (III) Ion
SEM	Scanning Electron Microscope
SPEs	Screen-Printed Electrodes
Sr^{2+}	Strontium (II) Ion
SWAdCSV	Square Wave Adsorptive Cathodic Stripping Voltammetry

SWASV	Square Wave Anodic Stripping Voltammetry
SWV	Square Wave Voltammetry
TEM	Transmission Electron Microscope
Tl	Thallium
Tl(I) / Tl^{+}	Thallium (I) Ion
WE	Working Electrode
XRD	X-Ray Diffraction
Zn(II) / Zn^{2+}	Zinc (II) Ion

LIST OF SYMBOLS

%	Percentage
°	Degree
℃	Degree Celsius
A	Area of Electrode
a.u.	Atomic Unit
C	Concentration
cm	Centimeter
$cm^2\ sec^{-1}$	Centimeter Square per Second
cm^2	Centimeter Square
D	Diffusion Coefficient
e^-	Electron
g	Gram
g/cm^3	Gram per Cubic Centimeter
g/mol	Gram per Mole
h	Hour
i	Electric Current

i_p	Current Response
K	Kelvin
kV	Kilovolt
Kα	K-alpha Wavelength
M	Molarity
meV	Milli-electron Volt
mg/l	Milligram per Liter
MHz	Megahertz
ml	Milliliter
mol/L	Mole per Liter
ms	Millisecond
M_w	Molecular Weight
n	Number of Electron
ng/mL	Nanogram per Milliliter
nm	Nanometer
nM	Nanomolarity
ppb	Parts per Billion

ppm	Parts per Million
R-3m	Rhombohedral Structure Space Group
rpm	Revolutions per Minute
Sm^{-1}	Siemens per Meter
ν	Scan Rate
V	Voltage
V/s	Voltage per Second
W	Watt
wt.%	Weight Percent
β	Beta
θ	Theta
λ	Lambda
μA	Microampere
μg/L	Microgram per Liter
μM	Micromolarity
π	Pi
τ	Tau

PENGHASILAN NANOPARTIKEL BISMUT UNTUK APLIKASI SENSOR PLUMBUM DAN KADMIUM

ABSTRAK

Dalam kajian ini, nanopartikel bismut (BiNPs) telah dihasilkan dengan menggunakan kaedah pertumbuhan hidroterma dan didepositkan pada substrat indium timah oksida (ITO) untuk mengubahsuai elektrod tersebut. Pelbagai sintesis parameter telah dikaji: kesan perbezaan masa hidroterma, kesan perbezaan isipadu hidrazin hidrat, dan kesan perbezaan suhu hidroterma. Sifat-sifat BiNPs telah dikaji dengan menggunakan kaedah Belaun Sinar-X (XRD), Imbasan Elektron Mikroskop (SEM) dan Transmisi Elektron Mikroskop (TEM). Analisa XRD menunjukkan bismut tulen dengan struktur Rombohedral daripada kumpulan ruang R-3m (Kod Rujukan ICDD: 98-002-1658) telah dihasilkan bagi setiap sampel. BiNPs yang disintesis mempunyai saiz dalam julat 73.0 nm sehingga 150.0 nm dengan perubahan parameter sintesis hidroterma. Kemudian, BiNPs yang disintesis telah dititis di atas substrat ITO dan dikeringkan serta dianalisa dengan voltammetri berkitar dan pengkamiran nadi - anodik pelucutan voltametri. Elektrod yang telah diubahsuai dengan BiNPs menunjukkan prestasi yang baik dalam mengesan kepekatan logam berat dengan had pengesanan (LOD) sebanyak 2.5 µg/L bagi Pb(II). Selain itu, dengan larutan Nafion 0.1 wt.%, elektrod BiNPs/ITO telah berjaya diaplikasikan bagi mengesan Pb(II) dan Cd(II) serentak untuk kajian penggangguan. Akhirnya, elektrod BiNPs/ITO juga telah berjaya digunakan untuk mengesan Pb(II) dalam sampel air laut. Keputusan ini membuktikan elektrod yang diubahsuai dengan BiNPs berpotensi digunakan sebagai pengesan logam berat.

DEVELOPMENT OF BISMUTH NANOPARTICLES FOR LEAD AND CADMIUM SENSORS APPLICATION

ABSTRACT

In this study, bismuth nanoparticles (BiNPs) were synthesized using the hydrothermal method and deposited on Indium Tin Oxide (ITO) electrodes to modify the electrodes. Several synthesis parameters were studied: the effect of hydrothermal reaction period, the effect of volume of hydrazine hydrate and the effect of reaction temperature. The properties of BiNPs were then characterized using X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM). XRD analysis proved that pure bismuth with Rhombohedral structure of R-3m space group (ICDD Reference Code: 98-002-1658) was obtained for all samples. The synthesized BiNPs powders were in the size range of 73.0 nm to 150.0 nm with varying hydrothermal synthesis parameters. The synthesized BiNPs were then drop-casted on ITO electrodes, air dried and subjected to cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) analyses. The BiNPs/ITO modified electrodes showed good performance in terms of detecting heavy metals with limit of detection of 2.5 μg/L for Pb(II). Besides, with 0.1 wt.% of Nafion solution, the BiNPs/ITO electrode was successfully applied for simultaneous detection of Pb(II) and Cd(II) for the interference studies. Finally, the BiNPs/ITO electrode was successfully applied to the practical use for the determination of Pb(II) in seawater sample. The results showed that BiNPs modified electrodes can be used for heavy metals sensors.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Heavy metals are commonly defined as metal having a specific density of more than 5 g/cm^3 such as lead, cadmium, mercury, selenium, arsenic and nickel. Many heavy metals such as lead, cadmium and mercury are toxic materials even presence in minute of concentration. They are widely distributed in the earth's crust, but presence at very low concentrations in the human body. Their presence in the atmosphere, soil, and water can cause severe problems to all organisms. Although heavy metals are naturally occurring elements that are found throughout the earth’s crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, usages in industrial productions, domestic and agricultural use of metals, and metal-containing compounds (Verma & Gupta, 2015).

Environmental contamination can also occur through metal corrosion, soil erosion of metal ions, atmospheric deposition, leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water. Hence, water indirectly functions as the medium for the transportation of pollutants and causes serious damage to both living organisms and the environment. Heavy metals can bio-accumulate over a period of time and the concentrations become apparent and measureable (Verma & Gupta, 2015). As a result, bioaccumulation of heavy metals within target organs or tissues of organisms can ultimately threaten human health and cause death through food chains and trophic levels.

In recent years, there has been an increasing ecological and global public health concerns associated with environmental contamination of heavy metals. Furthermore, issue of human exposure has risen dramatically due to an exponential increase of heavy metals being used in several industrial, agricultural, domestic and technological applications (Jan et al., 2015). As a result, heavy metals' main impact on human health is principally through environmental contamination, occupational exposure, and accumulation in food, which mainly found in vegetables grown on contaminated soil. As shown in Table 1.1, environmental pollution is also very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations. Table 1.2 shows the types of heavy metals presence in industrial effluents and their effect on human health.

Table 1.1: Types of heavy metals and their effect on human health (Singh et al., 2011)

Heavy Metals	**Major Sources**	**Effect On Human Health**
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis, poisoning
Cadmium	Welding, electroplating, pesticide fertilizer, Cd and Ni batteries, nuclear fission plant	Renal dysfunction, lung disease, lung cancer, bone defects (Osteomalacia, Osteoporosis), increased blood pressure, kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer
Chromium	Mines, mineral sources	Damage to the nervous system, fatigue, irritability
Copper	Mining, pesticides production, chemical industry, metal piping	Anemia, liver and kidney damage, stomach and intestinal irritation
Lead	Paint, pesticide, smoking, automobile emission, mining, burning of coal	Mental retardation in children, development delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness, acute or chronic

		damage to the nervous system, epileptic, liver, kidney, gastrointestinal damage
Manganese	Welding, fuel addition, ferromanganese production	Inhalation, or contact causes damage to central nervous system
Mercury	Pesticides, batteries, paper industry	Tremors, gingivitis, minor psychological changes, acrodynia characterized by pink hands and feet, spontaneous abortion, damage to nervous system, protoplasm poisoning
Zinc	Refineries, brass manufacture, metal plating, plumbing	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane

Table 1.2: Heavy metals in industrial effluents (Mahurpawar, 2015)

Heavy metals	**Manufacturing Industries**
Arsenic	Phosphate and fertilizer, metal hardening, paints and textile
Cadmium	Phosphate fertilizer, electronics, pigments and paints
Chromium	Metal plating, tanning, rubber and photography
Copper	Plating, rayon and electrical
Lead	Paints, battery
Mercury	Chlor-alkali, scientific instruments, chemical
Nickel	Electroplating, iron steel
Zinc	Galvanizing, plating iron and steel

Generally, heavy metals may disrupt metabolic functions in two ways. Firstly, they accumulate and thereby disrupt function in vital organs and glands such as brain, heart, liver, kidneys and bone. Through bio-accumulation and bio-magnification processes in the tropic levels, concentrations of heavy metal will become noticeable and latter are known to cause adverse effects on human health. Secondly, they will displace the vital nutritional minerals from their original place, thereby indirectly hindering their biological function (Ibrahim et al., 2006). However, it is impossible to live in an environment, which is free of heavy metals. This is because there are many ways by which these toxins can be introduced into the body such as through the consumption of foods, beverages, skin exposure and the inhaled air.

In conjunction, the increase concentration of heavy metals poses many health issues either directly or indirectly. Globally, regulatory organizations have implemented some rules and regulations through the maximum permissible limits for the discharge of heavy metals into the aquatic environment and intervention in order to control the level of contamination. Federal bodies, such as the World Health Organization (WHO), The Environmental Protection Agency (EPA) and The Food and Drug Administration (FDA) keep making constant efforts in order to minimize these emissions into the atmosphere (Meyer et al., 2008). However, the heavy metals are being released at a higher concentration than the prescribed limits especially through the anthropogenic point source, thus leading to the acute health hazard and water pollution.

Among the metal contaminants, heavy metal ions such as Pb^{2+} and Cd^{2+} are two major pollutants which produce severe ailments, including mental retardation in living things. The major sources of lead arise from the burning of leaded fuel in automobiles and the industrial releases due to the activity of lead mining, smelting and refining operations. Furthermore, the other potential sources of lead in the environment include lead-acid batteries, paints and the solder in tin cans containing food. In contrast, lead is not essential as trace elements to nutrition in human or animals. It can poison organisms directly, including human being even present in low concentration as it bio-accumulates and bio-magnifies in the food chain (Ikhuoria & Okieimen, 2000). Therefore, contamination food, water, air, soil and consumer products result in the absorption of lead into human body.

On the other hand, the major sources of cadmium are from nickel-cadmium batteries, cadmium pigmented plastics, ceramics, glasses, paints and enamels (Lewinsky, 2007). Generally, cadmium is an extremely toxic heavy metal due to its stability in contaminated site and complexity of mechanism in biological toxicity. Once being absorbed in human body, cadmium can be accumulated in the body and greatly affects the human health. Even exposure to a small amount of Cd^{2+} (≥ 5 μg/L) can cause renal dysfunction, lung insufficiency, liver damage, bone degeneration and hypertension in humans with both acute and chronic toxicity (Zhao et al., 2016). Hence, the concentrations of cadmium and exposure time are key factor in cadmium toxicity measurement. Acute poisoning occurs when one is exposed to high concentration of cadmium for a short duration and the adverse effect is high and severe.

Apart from that, as entering the 21st century, the development of 'green', 'sustainable' and 'environmental friendly' analytical procedures is an active and growing research field. Thus, green analytical chemistry is especially relevant when the methodologies are intended for use in the field or in decentralized laboratories, where dangerous waste processing is available or absent. As a result, new analytical tools are required for economical and real time monitoring of environment pollutants and for prevention of toxic materials in the environment. A real time field detection system is highly desirable for continuous environmental monitoring to overcome the current limitations, such as sample collection and transport to a central laboratory, problems associated with commonly used methods for environmental pollutants (Hanrahan et al., 2004). Hence, real time methods offer a rapid return of the chemical profile with minimized errors and costs as compared to the offsite laboratory-based analyses.

Nowadays, there are many analytical techniques, including atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectrometry, and ion chromatography have been commonly used for the analysis of heavy metals in water resources, food materials and alcoholic beverages (Senthilkumar & Saraswathi, 2009). In the meantime, the detection limit reported from these commonly used laboratory instruments for heavy metal ions are very low and of analytical significance. However, these techniques need sophisticated instrumentations which are costly in term of maintenance and operation. Besides, these analytical instruments require need well-trained technicians and are inconvenience for on-site monitoring of heavy metal ions (Mafa et al., 2016).

Among the commonly used techniques for heavy metal ions detection, electrochemical techniques seem to meet the limitations of the conventional analytical stated earlier. This is because electrochemical devices offer some unique properties to address the challenges of analytical chemistry towards heavy metal ions detection. The advantages of electrochemical devices include the possibility of miniaturization and portability, sensitivity to the changes in target-species concentrations, specificity for the target species, wide linear range of detections, requires minimal space, fast response time, and cost effective (Stankovic et al., 2007). As a result, a wide range of electrochemical sensors which fulfill the requirement to be environmental friendly are commercially available.

Electrochemical sensors that rely on the measurement of current or a change in potential are being well-known nowadays. Electrochemical sensors require simple measurement protocols and employ a compact and low power instrumentation that can be operated on-site. Electrochemical methods of detection include amperometry (based on the current measurement), potentiometry (based on the voltage or potential differences) and conductometry (based on the conductivity or resistance). Among the electrochemical sensing techniques, amperometric detection is widely adopted due to its high sensitivity and applicability (Miao et al., 2009). Therefore, significant measurement time and operating cost can be saved using the portable electrochemical units for on-site metal ions monitoring. Besides, simultaneous determination of more than one metal ion is also possible (Senthilkumar & Saraswathi, 2009).

In addition, potentiometry, voltammetry and potentiometric stripping analysis are also categorized under the electrochemical techniques, which are widely applied for the traceability and determination of heavy metal ions (Buffle & Tercier-Waeber, 2005). Generally, the analytical information is obtained from the electrical signal that results from the interaction between the target analyte and the recognition layer at the sensing electrode. For instance, square wave anodic stripping voltammetry (SWASV) provides a powerful tool for the determination of heavy metal ions, which is simple instrumentation and experimental procedures, portable, low cost and high-sensitivity (Anandhakumar et al., 2013). Besides, it can also analyze several trace heavy metals at the same time. Thus, different electrochemical techniques have been developed for environmental monitoring, depending on the nature of the analyte, the characteristics of the sample matrix and the sensitivity or selectivity requirements (Rassaei et al., 2011).

Studies on nanoparticles (NPs) have increased rapidly in recent few years due to their nano-size range, shape-dependent physical and electrochemical properties, which make them extremely useful in analytical sensing applications. Generally, NPs have attractive characteristics often notably different from bulk materials in terms of both physical and chemical features (Rassaei et al., 2011). In addition to the novel of properties NPs, the combination of nanotechnology with modern electrochemical techniques also contribute to the introduction of powerful and reliable electroanalytical applications for effective process and pollution control. As compared to bulk electrodes, NPs-modified electrodes show several advantages with regard to the use of electrochemical detection of heavy metals, such as effective catalytic properties, fast mass transport, large effective sensor surface area and good control over electrode microenvironment. This is because the presence of NPs on the electrode surface enables fast electron-transfer kinetics, reduces over-potential, increases the electro-active surface area, and causes redox reactions to become kinetically feasible (Aragay et al., 2011). Lastly, particle size and size distribution are also the most important characteristics of NPs for their performance in electrochemical sensor design where the size and the distance between adjacent particles can be tuned for the deposition on the electrode surface (Rassaei et al., 2011). Thus, the defined and ordered arrangement of NPs is a promising approach for the construction of electrochemical sensors.

1.2 Problem Statement

Heavy metal elements, such as lead and cadmium always cause environmental problems during industrial procedures. As known to all, Pb^{2+} and Cd^{2+} are the most serious environmental pollutants, which are highly toxic to human immune, nervous, reproductive and gastrointestinal systems. Besides, these metals are also non-degradable and could be accumulated in ecological system in a long term, which will be definitely leading to severe pollutions for people's health (Huangfu et al., 2013). Therefore, it is necessary to develop highly sensitive, rapid and simple methods for detection of these kinds of heavy metal pollutants.

Mercury (Hg) and bismuth (Bi) are the major electrode materials used in tracing heavy metal ions by anodic stripping voltammetry due to their high sensitivity and stability through the amalgam formation on Hg electrode or the multicomponent alloy formation with Bi electrode (Wang & Hu, 2009). However, Hg is well-known to be toxic and its use is therefore being limited despite the excellent performance of mercury electrodes for heavy metal analysis. Therefore, Bi has been chosen as viable replacements of mercury based electrodes and has been widely used as an alternative sensing electrode in electrochemical detection of various heavy metals due to its similar electrochemical performance to Hg and low toxicity to environment. Moreover, another advantageous property of Bi is attributed to its ability to form a 'fused alloy' with heavy metals, which is also suitable for the sensitive detection of heavy metals (Arduini et al., 2010).

Compared with conventional modified film electrodes, the incorporation of nanoparticles onto electrode surface is also known to enhance the electroanalytical properties of the electrode, primarily due to their increased surface area to volume ratio and coupled with the enhanced mass transfer effect (Cui et al., 2015). These minuscule particles with their attractive properties have dominated the area of sensing and detection towards heavy metal ions. Moreover, nanoparticles have also presented a promising platform compared to the conventionally used approached by favoring feasible on-site detection measurements (Fenzl et al., 2016). As a result, BiNPs modified electrodes exhibits high sensitivity and selectivity over trace heavy metal ions in the analyte solution, which is comparable or even superior to that of bismuth film coated electrodes (Lee et al., 2010). Therefore, current nanotechnology presents a major breakthrough with the development of numerous nano-probes for highly favorable electroanalytical properties of metal ions detection.

Recently, several approaches that involved additional processing steps have been reported to synthesize bismuth nanoparticles (BiNPs) due to the high surface area of BiNPs, thereby resulting in the enhanced performance of sensing electrodes in heavy metal detection. BiNPs can be synthesized by using gas condensation method, chemical synthesis method, thermal plasma method, aerosol quenching, electron beam irradiation and laser ablation techniques (Hwang et al., 2009, Niu et al., 2015). However, these methods are inappropriate and impractical for mass production of nanoparticles towards the electrochemical approaches. Therefore, in an effort to obtain the benefits of easy-step fabrication process for the application of BiNPs, this work is engaged in the reliable and facile pathway of hydrothermal synthesis method of BiNPs, which can then be easily processed to the production of the electrode material for the development of electrochemical sensors that can be practical use for the on-site heavy metal analysis in diverse water sources (Gich et al. 2013).

The novelty of this work lies on the method to synthesis BiNPs using hydrothermal method as reported by Yang et al. (2013). This is because hydrothermal method is simple, cost effective, low growth temperature and energy-efficient technique to synthesis nanoparticles. Yang et al. (2013) synthesized BiNPs with dimension of about 80-90 nm claimed that the detection limit towards Pb(II) and Cd(II) is 10 ppb. However, the toxicity range set by WHO for Cd(II) is 5 ppb, which is much lower than the sensitivity detection limit by Yang et al. (2013). Therefore, further studies should be devoted on the improvement of sensitivity by varying the particle size of BiNPs towards the application as heavy metal sensor. This is because perhaps by varying the particle size of BiNPs, the sensitivity of heavy metal sensor could be further improved.

In this work, different sizes of BiNPs were synthesized using the hydrothermal reaction by changing the synthesis parameters for the purpose of optimizing the particle sizes of BiNPs for further improving of the sensitivity of heavy metal sensor. The produced BiNPs were used to modify indium tin oxide (ITO) electrodes. The produced modified BiNPs/ITO electrodes were then tested using cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV). Lastly, the qualification and quantification measurements of the sensor system will be identified in order to study the aspect of sensitivity, selectivity and limit of detection (LOD) of the analytical signal for the heavy metal ions detection.

1.3 Research Objectives

The main objectives of this research are:

i. To produce bismuth nanoparticles by using hydrothermal method.
ii. To study the sensitivity, repeatability and reproducibility of bismuth nanoparticles modified electrode as heavy metal sensor.
iii. To study the effect of interference of bismuth nanoparticles modified electrode by the addition of interfering ions.

1.4 Scope of Study

This work is aimed to synthesis high quality BiNPs with uniform size and remarkable productivity by using a hydrothermal method. In this study, different parameters for hydrothermal reaction to synthesis BiNPs were investigated, which are the effect of hydrothermal reaction period, volume of hydrazine hydrate, and effect of hydrothermal reaction temperature. The properties of the BiNPs were studied using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The prepared BiNPs were immobilized on indium tin oxide (ITO) substrate by using drop-casting method as modified electrodes, thereby forming BiNPs/ITO electrodes. The heavy metal ions sensing properties of the modified BiNPs/ITO electrodes were then analyzed using electrochemical analyses called cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV).

1.5 Thesis Outline

This thesis is organized into five chapters. Chapter 1 covers the background of the study, problem statement, objectives and scope of the work for this research. In Chapter 2, literature review of works related to synthesis of BiNPs and heavy metal sensors is presented. Moreover, experimental methodology, parameters conducted and characterization methods are laid out in Chapter 3. Chapter 4 focuses on the results and discussion of the research. Lastly, conclusion and recommendations for future work are described in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Generally, heavy metals are metallic elements with high atomic weight and density which are also highly toxic, including the transition metals, some metalloids, lanthanides and actinides elements. Heavy metals, which have widespread environmental distribution and originate from natural and anthropogenic sources, are often contributing to environmental pollution issues. In conjunction, heavy metal as the environmental contaminants can commonly be found in the air, soil and water, which indirectly pose health hazard to the human being. This is because being as metals ions, heavy metal cannot be degraded or destroyed easily, therefore their stability makes them staying as the persistent toxic substances in environment (Poreba et al., 2011).

Heavy metals occur naturally in the environment and some heavy metals are essential to carry out some daily cellular functions, such as the metabolic function in human body, thereby its concentration range has a great impact on human health. If the concentration range of metals is less than the toxicity range, then it is considered safe. However, when the concentration range goes beyond the permissible limits, it may lead to various cytological and physiological effects (Sumner et al., 2005). Apart from the direct impact on health or environmental problems, water or soil contamination can also cause considerable economic and financial damage to general public due to metals in the environment are now as widespread environmental contaminants, which directly pose a continuous threat to mankind.

Nowadays, heavy metal pollution is considered as one of the most serious environmental problems, which in-turn makes its regulations to become stricter. The main sources of heavy metals are commonly coming from human daily activities, such as industrial processes, agriculture and mining industry. Such activities may cause the release of heavy metals to the aquatic and terrestrial systems which are further transferred to the living systems including plants, animals and humans. For example, anthropogenic activities have great potential to alter the natural concentrations of a variety of heavy metals in water, thus this poses a serious threat to the ecosystems and the human health.

Besides, heavy metals are also considered as trace elements due to their presence in trace concentrations, starting from ppb range to less than 10 ppm in various environmental matrices. As a result, the detection of heavy metal levels in natural surrounding or contaminated waters is of paramount important because the persistence of these species in the environment can result in deleterious effects at different levels (Järup, 2003). The presence of heavy metal in water as the contaminants is an indication of global industrialization attributed to the large scale of illegal disposal and untreated of wastewater, which contain heavy metals from anthropogenic sources. As a result, water pollution represents the most important problems being faced by both developed and developing countries. Therefore, the development of selective and sensitive methods for the early warning pollution of trace heavy metals in different chemical systems including living systems and the whole environment is of great concern.

In conjunction, an increasing number of regulations are set by the World Health Organization (WHO), the US Environmental Protection Agency (EPA) and the European Union, including heavy metals in the list of priority substances to be monitored in order to continuously monitor the concentration levels of heavy metals and sustain the living standards of this modern world. Therefore, setting maximum concentration levels, guideline values and allowable concentrations in water are utmost important in order to enforce those industrial-based countries to follow the environmental quality standards (Jaishankar et al., 2014).

2.2 Water Pollution by Heavy Metals

Rapid acceleration of industrial growth throughout the world exerts negative impacts to the environment. Discharge of contaminated effluents without adequate treatment into the aquatic environment will directly create such implication. This is because heavy metals exhibit toxic and persistent characteristics can enter into the food chains and the ecosystem, where they can cause direct adverse impact on the biotic and abiotic components of ecosystem. Besides, they also have cumulative deleterious effects that can cause chronic degenerative changes, especially to the nervous system, liver, and kidneys. As a result, heavy metals create damaging effects on both living organisms and the environment due to the fact that water functions as a medium of transport for pollutants (Hummel et al., 2007).

Industrial wastewater which is associated with manufacturing of automobile, purification of metals, electroplating, galvanizing, coating, paint, electronics, pharmaceutical, chemicals and battery manufacturing are the most common source of heavy metal pollution (Duruibe et al., 2007). Table 2.1 shows the clinical aspects of chronic toxicities from the heavy metals. As a result, heavy metals generate many of their adverse health effects through the formation of free radicals, resulting in DNA damage, lipid peroxidation, and depletion of protein sulfhydryl (Sahu & Arora, 2008).

Table 2.1: Clinical Aspects of Chronic Toxicities (Mahurpawar, 2015)

Metal	Target Organs	Primary Sources	Clinical Effects
Arsenic	Pulmonary nervous system, skin	Industrial dusts, medicinal uses of polluted water	Perforation of nasal septum, respiratory cancer, peripheral neuropathy: dermatomes, skin, cancer
Cadmium	Renal, skeletal pulmonary	Industrial dust and fumes and polluted water and food	Proteinuria, glycosuria, osteomalacia, aminoaciduria, emphysema
Chromium	Pulmonary	Industrial dust and fumes and polluted food	Ulcer, perforation of nasal septum, respiratory cancer
Lead	Nervous system, hematopoietic system, renal	Industrial dust and fumes and polluted food	Encephalopathy, peripheral neuropathy, central nervous disorders, anemia.
Manganese	Nervous system	Industrial dust and fumes	Central and peripheral neuropathies
Mercury	Nervous system, renal	Industrial dust and fumes and polluted water and food	Proteinuria
Nickel	Pulmonary, skin	Industrial dust, aerosols	Cancer, dramatis
Tin	Nervous, pulmonary system	Medicinal uses, industrial dusts	Central nervous system disorders, visual defects Electroencephalogram (EEG) changes and pneumoconiosis.

In this 21st century, among various heavy metals, lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As) and chromium (Cr) are the most probable hazards for most of the heavy metal-related diseases. In most cases, trace levels of metals are important in the biological function of cells such as cellular transportation and cell signaling. However, if these metal ions move out from the mechanistic pathway, they will begin to interact with other regular protein sites instead of natural binding sites, thereby lead to the toxicity issue in humans (Arpadjan et al., 2008). Basically, the toxicity mechanism of heavy metal ions is through enzyme inhibition, oxidative stress and impaired antioxidant metabolism. As a result, these mechanisms show adverse health effects through free radical generation that leads to DNA damage lipid peroxidation and depletion of protein sulfhydryl (Gumpu et al., 2015).

In Malaysia, heavy metal water pollution issues have grown in large magnitude with higher complexity as compared to 30 years ago. This is attributed to the shift of the Malaysian economy from agriculture to industry based in the 1980s. From the data compiled by the Department of Environment (Malaysia), it showed that the overall trend points out to that of a slow but steady deterioration in the water quality of rivers. From the 116 monitored rivers, 36 rivers have been found to exceed the Interim National Water Quality Standard (INWQS) maximum limit of 0.01 mg/L for lead, 55 rivers exceeded the cadmium limit of 0.001 mg/L, 44 rivers exceeded the iron limit of 1.00 mg/L and 24 rivers exceeded the mercury limit of 0.0001 mg/L (Abdullah, 2011).

Wastewater contaminated with heavy metal is largely generated from electroplating, mining and metal treatment or fabrication industries. Most of these industries are located along the West coast of peninsular including Klang Valley, Penang, Ipoh and Johor Bahru (Issabayeva et al., 2008). In Klang Valley, an estimated 50 - 60 tonnes of wastes end up in the river system daily (Abdullah, 2011). The impact of industrial wastewater discharge with high concentrations of heavy metal is of great concern which warrants appropriate remediation. Therefore, the society needs to be addressed the necessity for development of strategies to decrease exposure to these metals as well as create the awareness to this issue earnestly in order to overcome their hazardous effects within the body of living organisms.

2.3 Detection of Heavy Metal Ions (Lead, Pb^{2+} and Cadmium, Cd^{2+})

Heavy metals are hazardous to human health and consequently degrade environment quality. Heavy metal elements, such as lead (Pb) and cadmium (Cd) always cause environmental problems during industrial procedures. Both of these metals are non-degradable and may be cumulated in ecological system in the long term, which definitely lead to severe pollutions for people's health. In this study, lead (Pb) and cadmium (Cd) were the selected heavy metals to be detected. Generally, each of the selected heavy metal has different characteristics.

Though metals are important to carry out cellular functions, its concentration range has a great impact on human health. If the concentration range of metals is less than the toxicity range, then it is considered to be safe. However, when it goes beyond the permissible limits, it will influence biochemical processes in a cell, thereby causes cell mutagen and cancer. Heavy metals contaminations with their toxicity range according to WHO are shown in Table 2.2. The main sources for these exposures, effluents released from electroplating and from various other industries.

Table 2.2: Limits, sources and effects of heavy metal ions

Heavy metals	**WHO limits (µg/L)**	**Common sources**	**Effects**	**References**
Cadmium (Cd)	5	Paints, pigments, electroplated parts, batteries, plastics, synthetic rubber, photographic and engraving process, photoconductors and photovoltaic cells	Renal toxicity, hypertension, weight loss, fatigue, microcytic hypochromic anaemia, lymphocytosis, pulmonary fibrosis, atherosclerosis, peripheral neuropathy, lung cancer, osteomalacia, osteoporosis, and	Ercal et al., 2001

			hyperuricemia	
Chromium (Cr)	50	Leather industry, tanning, and chrome plating industries	Reproductive toxicity, embryotoxicity, teratogenicity, mutagenicity, carcinogenicity, lung cancer, dermatitis, skin ulcers, perforation of septum, and irritant contact dermatitis	Valko et al., 2005
Lead (Pb)	50	PVC pipes in sanitation, agriculture, recycled PVC lead paints, jewellery, lead batteries, lunch boxes, etc.	Penetrates through protective Blood Brain Barrier (BBB) and is proving to be a risk factor for Alzheimer's disease and Senile Dementia. Also leads to neuro-degenerative diseases, decreases IQ, kidney damage, decreased bone growth, behavioural issues, ataxia, hyperirritability, and stupor	Patrick et al., 2006 and Liu et al., 2008
Mercury (Hg)	1	Combustion of coal, municipal solid waste incineration, and volcanic emissions	Impaired neurologic development, effects on digestive system, immune system, lungs, kidneys, skin and eyes, minamata, acrodynia, increases salivation, hypotonia, hypertension	Kobal et al., 2004

Lead (Pb) is the most common heavy metal, which exists in many forms in the natural sources throughout the world and is now one of the most widely and evenly distributed trace metals. Pb has been widely used for centuries in daily products, such as cables, paints, pipelines and pesticides, which makes it a very useful heavy metal material for human (Arduini et al., 2010). However, Pb is an environmentally persistent toxin that shows obvious neurotoxicity that may be hazard for everybody. Moreover, Pb also causes neurological, hematological, gastrointestinal, reproductive, circulatory, and immunological pathologies in human body. Since Pb^{2+} ions have shown severe health hazard to humans, which can enter the human body through water, food and air, therefore Pb is considered as one of the most potent heavy metal that poses significant threat to human health and the environment even in small concentration (Tangahu et al., 2011).

Furthermore, Pb^{2+} is found to be acute toxic to human beings when presence in high amounts. Since Pb^{2+} is not biodegradable and has a harmful effect on biological systems, it remains a long-term source of Pb^{2+} exposure, which does not undergo biodegradation. Uptake of high level of Pb^{2+} ions by human can affect the central nervous system (CNS), and cause anemia, high blood pressure and renal disease. Therefore, quantitative detection of Pb^{2+} ions in water and food is thereby utmost importance for health safety (Zou et al., 2008, Abdi et al., 2011). In conjunction, the guideline value for Pb^{2+} in drinking water has been set at 50 μg/L by WHO (Patrick et al., 2006).

In addition, cadmium (Cd) is also a heavy metal of considerable environmental and occupational concern. Cd is transferred to soil by wet or dry deposition and can enter the food chain under ambient atmosphere. Cd is released to the environment in wastewater and diffused as pollutant is caused by the contamination from fertilizers and local air pollution. Besides, Cd contamination in drinking-water may also be caused by the impurities created in zinc of galvanized pipes and solders, and some metal fittings job. Cd also easily accumulates in plants subsequently making its way through the food chain (Liu et al., 2009). Therefore, food is the main source of daily exposure to Cd. On the other hand, Cd also exerts toxic hazards on the human body, such as kidney, skeletal and the respiratory systems, which is classified as a human carcinogen. Exposure to Cd causes a wide range of disease as renal, lungs, prostate cancer and even deregulates calcium metabolism (Zou *et al*., 2008). In conjunction, the guideline value for Cd^{2+} in drinking water has been set at 5 μg/L by WHO (Ercal *et al*., 2001).

2.4 Conventional Materials and Nanomaterials for Sensing of Heavy Metal Ions

Over the last few decades, conventional materials, such as bulk materials modified film electrodes used as functionalized sensing electrodes have been employed for developing various kinds of electroanalytical sensors and detection devices. However, bulk materials modified film electrodes showed low sensitivity and less improving at the limit of detection (LOD) towards the concentration of heavy metals in order to allow for adequate miniaturization of the sensing devices. This is because bulk materials may attribute to the reason of mechanical degradation, which insufficient adhesion to create a nice thickness of film on the electrode surface, which then resulting in degradation of the modified electrodes and making difficult the deposition of heavy metal ions towards the electrode surface (Arduini et al., 2010). Hence, the less concentration of the bulk materials attached onto the electrode surface directly affect the intensity of the peak responses and easily affected by other interferences, such as adsorption of surface active compounds and intermetallic formation (Saturno et al., 2011).

In recent years, emerging research to develop better sensing strategies for trace heavy metal at the early detection stage of heavy metal pollutants in various chemical systems, including the living systems and the whole environmental ecosystem. Considering the complex and critical condition prevailing around the environment due to the toxicity of heavy metals, they must be coupled with the new approaches, such as the uses of nanomaterials for their selective detection response and the good fit of the heavy metal ions towards the nanomaterials.

In conjunction, there has been an increasing of interest towards the key point for obtaining good and reliable heavy metal sensor detection lies on the kind of material that constitutes the detection platform. In this field, nanomaterials have brought many advantages on the development of new electroanalytical transducing platforms. Besides, nanomaterials also have been used as the electroanalytical labels or tags for signal enhancement of heavy metals for the sensing technologies (Gumpu et al., 2015). Therefore, the distinctive synergy between sensors technology and nanomaterials is expecting to bring interesting achievements in the field of heavy metals detection and is thereby a promising area of research and development based on nanomaterials.

In this 21st century, nanotechnology shows a major breakthrough in this sensing response of heavy metals with the development of numerous nano-probes for the detection of heavy metal ions. The unique electronic, chemical and mechanical properties of nanomaterials make them extremely alluring for heavy metals sensor detections as compared to the conventional materials with larger particle size than nano-size range. As a result, sensing using nanostructured materials takes the advantages of the increase of electrode surface area, increase mass-transport rate, and fast electron transfer kinetics as compared to electrodes based on bulk materials between other factors, which are very apt for sensing applications (Li et al., 2013).

Nowadays, many researches show that nanomaterials are often being used for electrode modification due to the intrinsic advantages of regular structure, chemical and thermal stability, high surface reaction activity and catalytic efficiency, large surface-to-volume ratio and strong adsorption ability (Kaushik et al., 2008). In particular, metal, metal oxide, carbon and silica based on nanomaterials are the most commonly used nanomaterials in electroanalytical detection of heavy metal ions. Thus, these minuscule particles with their alluring properties have dominated the area of sensing and detection; thereby have presented a promising platform compared to the conventionally used approaches by favoring feasible on-site analysis without the need of any high voltage inputs (Jena & Raj, 2008). For an instance, the addition of metallic nanoparticles such as nanowires, nanorods and nanoparticles are beneficial in increasing the ability to trigger the specific reactions, electron transfer rate between analyte and electrode, and also helps in avoiding those undesirable sensed products (Gumpu et al., 2015).

On the other hand, semiconductor nanomaterials also contributed to improve the efficiency of photochemical reactions and are helpful in detection of heavy metals. The designing of a sensor with best suited architecture, such as nanomaterials with interconnected porous microstructures of electrode also aid in selective identification of metal ions from solutions (Katz et al., 2004). Therefore, development of sensor by coupling with the nanomaterials offers distinctive advantages such as high sensitivity, real time detection in non-destruction manner and high spatial resolution for localized detection (Liu & Guo et al., 2012). Thus, a small current can enable stripping analysis to be performed in a high resistive media with supporting electrolyte and reduces the interference effects (Li et al., 2013).

Generally, the particles size of nanoparticles can be controlled by applying different kinds of synthesis methods, including physical and chemical methods, and then being characterized through various types of devices, and lastly just applied on working electrode surfaces as sensing elements through different immobilization methods on the working electrodes surface (Wang & Hu, 2009). In addition, applying multilayers of conductive nanoparticles as the modified electrodes can provide a film with high specific surface area where the metal and semiconductor nanoparticles can be localized by crosslinking with the elements. Thus, the good surface property endues the modified electrodes with strong adsorption ability to most of substrates. As a result, analyte can further be accumulated on the surface of the modified electrodes. In addition to this accumulation effect, this kind of modified electrode may lead to specific and better selective interactions with those analytes due to corresponding large surface-to-volume ratio (Liu et al., 2007).

2.5 Bismuth-Modified Electrodes for Heavy Metal Ions Detection

Traditionally, mercury electrode has gained wide acceptance for the electrochemical stripping analysis of heavy metals. However, the toxicity of mercury makes it undesirable for sensing applications, especially for those involves food contacts. A great variety of electrode materials has been proposed as alternatives such as gold, platinum, bismuth, stannum, antimony and the others. However, among them, bismuth seems to be the most promising alternatives to mercury due to its environmentally friendly element with negligible toxicity, high sensitivity, large cathodic potential range as well as its insensitivity to the dissolved oxygen (Chen et al., 2013). Thus, bismuth is suggested as an alternative to hazardous mercury-based electrodes for the