

# MODIFICATION OF GLASSY CARBON ELECTRODE (GCE) WITH PRUSSIAN BLUE AS A MEDIATOR ON CARBON NANOTUBE MATERIALS THROUGH SEQUENTIAL DEPOSITION

By

Abdullahi Mohamed Farah

Student number: 209041889

Dissertation submitted in fulfillment of the requirement for the degree of

MASTER OF TECHNOLOGY IN CHEMISTRY

FACULTY OF APPLIED AND COMPUTER SCIENCES

**DEPARTMENT OF CHEMISTRY** 

Supervisor: Prof. E.D. Dikio

**Co-supervisor: Prof. S J Modise** 

August 2012

### **DECLARATION**

I hereby declare that this dissertation, which I am submitting for the qualification of

### **Master of Technology in Chemistry**

To the Vaal University of Technology, Faculty of Applied and Computer Science, Department of Chemistry, is apart from the recognized assistance of my supervisor and the sources that have been acknowledged in literature survey, entirely my own work and has not been previously submitted to any other institution before for a research diploma or degree.

	On this	day of	2012
Candidate			
	On this	day of	2012
Supervisor			
	On this	day of	2012
Co-Supervisor			

# DEDICATION

I dedicate this work to my family, my mother Hawo. Dahir, my father Mohamed Farah and all my sisters and my brothers. And my wife Falastiin Ahmed hersi.

#### ACKNOWLEDGEMENTS

First I would like to thank God almighty for his guidance through all entire my life and also for giving me the strength to carry out this study to finish.

I would like to express my sincere gratitude to my Supervisor Prof Ezekiel Dixon Dikio for his great support sharing his knowledge and guidance during my degree programme and my Co-supervisor Prof Sekomeng Johannes Modise. I thank you all a million times and I remain eternally grateful for your assistance.

I also wish to thank Dr. Abdulkadir Ali Egal for his an exceptional support and guidance through all the difficult time that I have experienced.

Special thanks are also due to the Vaal University of Technology, particularly the research directorate and the Department of Chemistry for every support.

Thanks to my fellow students E.M. Laka, P.A Ngoy, F.T. Thema, A.P Mzulwini, M. Bucibo, N.D. Shotoo, I. Ledwaba, S. Ngema A.N. Pholosi, R.R Mutloane and all I might have forgotten for the good company and support.

Finaly I would like to thank Mrs. Caren Billing for her assistance during my lab work lab in the school of chemistry at Witwatersrand University.

# **PRESENTATION AND PUBLICATIONS:**

### **1. Presentation:**

 Poster presentation: A. M .Farah, J. Modise and E.D. Dikio. Synthesis of Prussian blue nanoparticles and it is modification on glassy carbon electrode promoted by carbon nanotube for determination of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The 4<sup>th</sup> international conference nanoscience and Nanotechnology University of the Free State, Bloemfontein, South Africa 1-4 April 2012.

## 2. Publication

- A.M. Farah, N.D Shooto. F.T. Thema. J. Modise and E.D. Dikio, Fabrication of Prussian blue/multi-walled carbon nanotubes modified glassy carbon electrode for electrochemical detection of hydrogen peroxide. *Int. J. electrochem. Sci.* 2012 7(5) 4302-4313.
- S. Adekunle, A. M. Farah, J. Pillay, K. I. Ozoemena, B. B. Mamba, B. O. Agboola, Electrocatalytic properties of Prussian blue supported on poly(*m*-aminobenzenesulfonic acid)-functionalized single-walled carbon nanotubes towards the detection of dopamine, *Colliod. Surf. B: Biointerfaces.* 2012, 95, 186-194.
- A.M Farah. F.T Thema and E.D .Dikio, electrochemical detection of hydrogen peroxide based on grapheme oxide /Prussian blue modified glassy carbon electrode. *Int. J. Electrochem. Sci.* 2012, 7(6) 5069-5083.
- N D. Shooto, F T. Thema, A M. Farah, and E D. Dikio. Raman and TGA study of carbon nanotubes synthesized over Mo/Fe catalyst on aluminium oxide, calcium carbonate and magnesium oxide support. *J. Mat. Chem. Phys.* 2012 SUBMITTED. Ref: Matchemphys-D-12-01003.

5. F T. Thema, **A M. Farah**, N D. Shooto, and E D. Dikio. One-step reduction, characterization and magnetic behavior of exfoliated graphene oxide with hydrazine hydrate *J. Mater. Sci. Pol.* **2012** SUBMITTED. Ref: 2012- 375.

#### ABSTRACT

Prussian blue (PB) nanoparticles were synthesized from  $FeCl_3.6H_2O$ ,  $K_4[Fe(CN)_6].3H_2O$ , and from Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O and K<sub>4</sub>[Fe(CN)<sub>6</sub>].3H<sub>2</sub>O, and then characterized by Fourier transform infrared (FT-IR), Ultraviolet-visible spectroscopy, X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS), Scanning electron microscopy (SEM), Raman spectroscopy and thermogravimetric analysis. Graphene oxide and carbon nanotubes were also synthesized and characterized. PB nanoparticles, carbon nanotubes (CNT), graphene oxide (GO) and cetyltrimethylammonium bromide (CTAB) were sequentially deposited onto glassy carbon electrode surface to form chemically modified electrode for the detection of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and dopamine. The following electrodes were fabricated, GC-PB, GC-MWCNT, GC-GO, GC-CTAB, GC-MWCNT-PB, GC-GO-PB and GC-CTAB-PB. Cyclic and Square wave voltammetric techniques were used to measure the hydrogen peroxide detectability of the electrodes at pH ranges of (3 - 7.4) in 0.1M phosphate buffer solution, in the absence or presence of 25 µL of H<sub>2</sub>O<sub>2</sub>. The GC-CNT-PB, GC-GO-PB,GC-CTAB-PB electrodes showed a good response for the detection of hydrogen peroxide in both acidic and neutral media while the GC-PB electrode only showed good response in acidic media.

# TABLE OF CONTENTS

Description	Page number
Declaration	i
Dedication	ii
Acknowledgements	iii
Presentation and Publications	iv
Abstract	vi
Table of contents	vii
List of figures	xii
List of schematics	xvii
List of tables	xvii
List of abbreviations	xviii

# **CHAPTER ONE**

# INTRODUCTION AND PROBLEM STATEMENT

1.1 Introduction	1
1.2 Problem statements	3
1.3 Objectives	3
1.4 Value of research	4

1.5 Outline of the dissertation	4
References	6
CHAPTER TWO	
LITERATURE REVIEW	
2. Introduction	9
2.1 Electrochemistry overview	9
2.2 Mass transport processes	11
2.3 Cyclic voltammeters	13
2.4 Square wave voltammeters	17
2.5 Prussian blue nanoparticle and its analogues	18
2.5.1 Prussian blue modified glassy carbon electrode	21
2.5.2 The crystal structure of Prussian blue	22
2.6 The electrochemistry of hydrogen peroxide and dopamine	24
2.6.1 Chemical property of hydrogen peroxide	26
2.6.2 Physical properties of hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	27
2.7 Graphene	27
2.7.1 Introduction	27

viii

2.8 Carbon nanotubes	28
2.8.1 Introduction	28
2.8.2 Synthesis of carbon nanotubes	30
References	31

# **CHAPTER THREE**

# **EXPERIMENTAL METHODS**

3.1 Introduction	37
3.2 Materials and reagents	37
3.3 Synthesis of Prussian blue	38
3.4 Electrode modification and pretreatments	38
3.4.1 Electrode cleaning	38
3.4.2 Electrode modification	39
3.4.2.1.1 Drop-dry/ electrodeposition methods	39
3.4.2.1.2 Sequential deposition methods	39
3.4.2.2.1 Drop-dry/ electrodeposition methods	40
3.4.2.2.2 Sequential deposition methods	40
3.4.2.3.1 Drop-dry/ electrodeposition methods	41

3.4.2.3.2 Sequential deposition methods	41
3.5 Equipments	42
3.5.1 Cyclic voltammetry	42
3.5.2 Square wave voltammetry	42
3.6 Spectroscopy and microscopy techniques	43
3.6.1 Spectroscopy	43
3.6.1.1 Infrared spectroscopy (IR)	43
3.6.1.2 Ultraviolet-visible spectroscopy	44
3.6.1.3 X-ray Diffraction spectroscopy	45
3.6.1.4 Energy Dispersive Spectroscopy (EDS)	46
3.6.1.5 Thermogravimetric analysis (TGA)	48
3.6.1.6 Raman spectroscopy	49
3.6.2 Microscopy	50
3.6.2.1 Scanning Electron Microscopy (SEM)	51
References	53

## **CHAPTER FOUR**

## **RESULTS AND DISCUSSION.**

4.1 Introduction	54
4.2 Characterization of Prussian blue nanoparticles	54
4.3 Cyclic voltammetry investigation	66
4.4 Square wave voltammetry investigation	78
4.5 Cyclic voltammetry investigations	88
4.6 Square wave voltammetry investigation	91
References	94
CHAPTER FIVE	
CONCLUSION.	

95
Ģ

LIST OF FIGURES	Page number	
2.1 A type of electrochemical cell used in voltammetry is three electrode c	cells. 10	
2.2 The three ways of mass transport processes: Diffusion controlled (A),		
Migration controlled (B) and Convection controlled (C).	12	
2.3 Cyclic voltammetry potential waveform.	13	
2.4 Typical cyclic voltammogram for reversible process.	114	4
2.5 A typical excitation signal for square wave voltammetry.	18	
2.6 Face-centered lattice adopted by the Prussian blue structure.	19	
2.7 Representative cyclic voltammogram of Prussian blue modified		
glassy carbon electrode.	20	
2.8 Structures of soluble Prussian blue (A) and insoluble Prussian blue (B)	). 23	
2.9 The structure of dopamine.	26	
2.10 (A) single –walled carbon nanotubes (B) multi-walled carbon nanotubes	bes. 29	
3.1 Infra-red (IR) spectroscopy setup.	44	
3.2 Ultraviolet-visible spectroscopy.	45	
3.3 X-ray diffraction pattern formed when x-rays are focused on		
a crystalline material.	46	

3.4 Simple representation of first three shells presentation, (a) the formation of

energy dispersive X-ray resulting in (b) a distinctive spectrum.	47
4.1 Fourier Transform infrared (FTIR) spectra of (a) Prussian blue,	
before and after drying.	55
4.2 Fourier transforms infrared (FT-IR) spectra of MWCNT-PB (a), GO-PB (b)	
and CTAB-PB (c) composites.	57
4.3 UV- visible spectra of PB (a) GO-PB (b) CNT-PB(c) CTAB-PB (d).	59
4.4 The XRD Spectra of Prussian blue nanoparticle iron(III) Chloride (A)	
and iron(III) nitrate (B).	60
4.5 The EDS Spectra of Prussian blue iron(III) chloride (A) and iron(III) nitrate (B).	61
4.6 The SEM Spectra of Prussian blue nanoparticles iron(III) chloride (A)	
and iron(III) nitrate (B).	62
4.7 The Raman Spectra of Prussian blue nanoparticles iron(III) chloride (A)	
and iron(III) nitrate (B).	64
4.8 The thermogravimetric Spectra of Prussian blue nanoparticles iron(III) chloride (A)	
and iron(III) nitrate (B).	65
4.9 Cyclic voltammograms of bare-GC electrode (a) absence and (b) presence of	
$25\mu l H_2O_2$ in 0.1M PBS and (c) overlay of the two.	67

4.10 Cyclic voltammograms of GC-PB electrode (a) in the absence and (b)	
in the presence of $25\mu l H_2O_2$ in 0.1M PBS.	68
4.11 Cyclic voltammograms of GC-CNT electrode (a) before and (b)	
after injection of 25µl $H_2O_2$ in 0.1M PBS pH 7.4 (c) Overlay of the two.	70
4.12 Cyclic voltammograms of GC-MWCN-PB electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	71
4.13 Cyclic voltammograms of GC-GO electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS pH 7.4 (c) Overlay of the two.	73
4.14 Cyclic voltammograms of GC-GO-PB electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	74
4.15 Cyclic voltammograms of GC-CTAB electrode (a) before and (b)	
after injection of 25µl $H_2O_2$ in 0.1M PBS pH 7.4 (c) Overlay of the two.	76
4.16 Cyclic voltammograms of GC-CTAB-PB electrode (a) in the absence and (b)	
in the presence of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	77
4.17 Square wave voltammograms of GC-CNT electrode (a) before and (b)	
after injection of $25\mu$ l H <sub>2</sub> O <sub>2</sub> in 0.1M PBS pH 7.4 (c) Overlay of the two.	79

4.18 Square wa	ve voltammogram	ns of GC-GO	electrode (a	) before and (	(b)
				,	< - /

after injection of $25\mu$ l H <sub>2</sub> O <sub>2</sub> in 0.1M PBS pH 7.4 (c) Overlay of the two.	81
4.19 Square wave voltammograms of GC-CTAB electrode (a) before and (b)	
after injection of 25µl $H_2O_2$ in 0.1M PBS pH 7.4 (c) Overlay of the two.	82
4.20 Square wave voltammograms of GC-PB electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	83
4.21 Square wave voltammograms of GC-CNT-PB electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	85
4.22 Square wave voltammograms of GC-GO-PB electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	86
4.23 Square wave voltammograms of GC-CTAB-PB electrode (a) before and (b)	
after injection of $25\mu l H_2O_2$ in 0.1M PBS with different pH.	87
4.24 Cyclic voltammograms of Bare-GC (a) and GC-PB (b)	
in 0.01M dopamine solution.	88
4.25 Cyclic voltammograms of GC-CNT-PB (a), GC-GO-PB (b), and GC-CTAB-PB(c)	
in 0.01M dopamine solution.	90
4.26 Square wave voltammograms of GC-PB (a) and GC-CNT-PB (b)	

in 0.01M dopamine solution.

4.27 Square wave voltammograms of GC-GO-PB (a) and GC-CTAB-PB (b)

in 0.01M dopamine solution.

93

92

# LIST OF SCHEMATICS

# Page number

LIST OF TABLES	Page number	
3.6 Schematic diagram of an SEM.	51	
3.5 Shows the scheme of a thermogravimetric analyzer.	49	
3.4 Scheme of a TGA furnace.	49	
in the presence of graphene oxide.	41	
3.3 Electrode modification procedure with Prussian blue (PB) nanoparticle	es	
in the presence of CTAB.	40	
3.2 Electrode modification procedure with Prussian blue (PB) nanoparticle	es	
in the presence of MWCNT.	39	
3.1 Electrode modification procedure with Prussian blue (PB) nanoparticles		

2.1 A summary of factors for the diagnosis of the reversible, quasi-reversible	
and irreversible cyclic voltammetric processes.	17
4.1 Selected FT-IR bands of MWCNTPB, GO-PB and CATAB-PB.	56

# LIST OF ABBREVIATIONS

GCE	-	Glassy carbon electrode
GC	-	Glassy carbon
CNTs	-	Carbon nanotubes
SWCNTs	-	Single wall carbon nanotubes
MWCNTs	-	Multi-wall carbon nanotubes
OMC	-	Ordered mesoporous carbon
GO	-	Graphene oxide
СТАВ	-	Cetyltrimethylammonium bromide
PB	-	Prussian blue
PLV	-	Pulsed laser-vaporization
CVD	-	Chemical vapour deposition
W.E	-	Working electrode
R.E	-	Reference electrode
C.E	-	Counter electrode
Ag/AgCl	-	Silver/silver electrode
CV	-	Cyclic voltammetry
SWV	-	Square-wave voltammetry
A.A	-	Ascorbic acid
U.A	-	Uric acid
DA	-	Dopamine
DW	-	Deionized water
DMF	-	Dimethylformamide

Min	-	Minutes
FT-IR	-	Fourier transform infrared
UV-VIS	-	Ultraviolet-visible
XRD	-	X-ray diffraction
EDS	-	Energy dispersive spectroscopy
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis
PBS	-	Phosphate buffer solution

# **CHAPTER ONE:**

# **INTRODUCTION AND PROBLEM STATEMENT**

### **1.1 Introduction**

Carbon nanotubes (CNTs) have been the focus of the scientific research since their discovery in 1991 [1] due to their good electric conductivity, chemical stability, high mechanical strength and attractive properties of being particle carriers [2-5]. However, there are two types of CNT materials, single walled and multi walled, and both of them have been considered to have interesting properties towards electrochemical modification of electrodes and sensors [6-7]. Carbon nanotubes can be produced by three common methods, namely electric arc- discharge, pulsed laser vaporization (PLV) and chemical vapour deposition (CVD) [8-9].

Graphene, a two-dimensional single layer of graphite and one-atom-thick sheet material with interesting physical properties, has been considered as the mother of all graphitic structures [10-11]. Graphene also is an ideal material for electrochemistry due to its very large 2D electrical conductivity, large surface area and low cost [12]. Recently, studies have highlighted the ability of CNTs, cetyltrimethylammonium bromide and graphene materials to enhance the electrochemical properties of some important polycrystalline molecules such as Prussian blue (PB) [13-15]. Prussian blue is an inorganic polycrystalline substance which has popular electrochromic, electrochemical, photophysical, magnetic properties and potential application [16-17]. It is a classical mixed valence compound which has a chemical formula of  $Fe_4^{111}[Fe^{II}(CN)_6]_3$  and well known as an artificial per-oxidase [18-20]. Prussian blue nanoparticles can be easily synthesized by simple method addition of aqueous solution of iron(III) to an aqueous ferrocyanide solution in ambient condition [21-22].

Prussian blue could be deposited on solid electrodes such as gold electrode [23], graphite electrode [24], basal plane pyrolytic graphite electrode, edge plane pyrolytic graphite electrode

[12], carbon paste electrode and glassy carbon electrode [25], but during modification process it is necessary to use binders or wax to fix PB on the surface of these electrodes. These binders' materials could cause the Prussian blue to develop poor conductivity during electrochemical detection. It is important to use an electroactive material such as ordered mesoporous carbon, Chitosan [26] carbon nanotubes and graphene materials which improves the electrochemical properties of PB-modified electrodes. The function of the electroactive material is to facilitate the charge transfer between the analyte and the electrode [27]. There are several electrode deposition processes that have been used for electrode depositions of Prussian blue nanoparticles on electrode surfaces. These processes include electrochemistry deposition [28], chemistry deposition [29], self-assembling method [30] and sequential deposition method [31]. Electrochemistry deposition is the widely used method in the deposition of Prussian blue on electrode surface by cycling different number of cycles using cyclic voltammetry [32-33]. Therefore, among these methods, the sequential deposition method is the most appropriate to use for making effective film on the surface of the electrode.

Studies have shown that PB modified electrode have weak electrochemical stability with neutral and alkaline solutions pH but only effective with a lower pH solution or acidic solution. In this study Prussian blue nanoparticles will be synthesized from FeCl<sub>3</sub>.6 $H_2O$ , K<sub>4</sub>[Fe(CN)<sub>6</sub>].3 $H_2O$  and Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, K<sub>4</sub>[Fe(CN)<sub>6</sub>].3H<sub>2</sub>O and was characterized we will investigated the enhancement Prussian of blue with multi-walled carbon nanotubes. graphene oxide and cetyltrimethylammonium bromide as mediators and determination of their electron transfer reaction using both cyclic and square voltammetry.

We will determine the electrocatalytic activity of Prussian blue modified glassy carbon electrode and Prussian blue promoted by the above mentioned materials and their ability to detect hydrogen peroxide in different pH solution. It is also to determine their ability to oxidize dopamine hydrochloride.

#### **1.2 Problem statements**

Recent studies have shown coating of electrode surfaces with various electroactive materials have gained research interest in electrochemical sensors [34-36]. The combination between PB with carbon nanotubes or graphene has received more attention to scientific researchers due to their unique physical and chemical properties and their much wider range of potential applications [37-40]. Since the majority of studies relating to the PB modified electrodes have focused on different materials such as ordered mesoporous carbon (OMC), carbon nanotubes and graphene as a promoter. In this study we will focus on the use of multi-walled carbon nanotubes, graphene oxide and cetyltrimethylammonium bromide as mediators for PB modified electrodes to enhance it is detection of hydrogen peroxide.

### **1.3 Objectives**

- To synthesize Prussian blue nanoparticles and characterize them with different techniques: Fourier transform infrared (FT-IR), Ultraviolet-visible spectroscopy (UV-Vis) X-ray diffraction spectroscopy (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), thermogrametric analysis (TGA) and Raman spectroscopy.
- 2. To determine the improvement of Prussian blue modified on glassy carbon electrodes promoted by multi-wall carbon nanotubes, graphene oxide and cetyltrimethylammonium bromide to fix the Prussian blue on the surface of electrode to enhance it is electrochemical stability for a wide range of pH.

3. To determine the electrocatalytic ability of modified electrodes towards the detection of hydrogen peroxide and dopamine.

#### **1.4 Value of research**

This research is useful for well-designed of Prussian blue modified electrode in the presence of carbon nanotubes and graphene materials. These materials improve the electrochemical properties of Prussian blue nanoparticles and it is biosensor. Therefore taking the advantages of the unique properties of the three carbon nanotubes, graphene materials and Prussian blue nanoparticles would give great broaden application in the electrochemistry field as well as industrial sector.

### **1.5 Outline of dissertation**

Below is an outline of this dissertation

**Chapter 1** (Introduction): This chapter gives an insight into the research work that was carried out and its importance. Also presented in this chapter is the problem statements and the objectives of the study.

**Chapter 2** (Literature Review): In this chapter a review of literature relating to electrochemistry, chemical, physical and electrocatalytic properties of (PB) and its electrode modification as mediators by carbon nanotubes (CNTs), graphene oxide (GO) and cetyltrimethylammonium bromide (CTAB) and their detection of hydrogen peroxide ( $H_2O_2$ ) and dopamine hydrochloride.

**Chapter 3** (Experimentation): All analytical methods. Experimental procedures and instruments that were used in this research project are discussed in details in this chapter.

Chapter 4 (Results and discussion): Results obtained from this study are presented and discussed in chapter 4.

**Chapter 5** (Conclusion): Based on the results obtained with respect to the initial objectives and hypothesis, a conclusion is drawn and highlighted in this last chapter.

## References

- 1. S. Iijima, Nature. 1991, 354, 56-58.
- A.S. Ade kunle, B.O. Agboole, J. Pillay, K.I. Ozoemena, Sens. Actuators B. 2010, 93-102.
- 3. S. Han, Y. Chen, R. Pang, P. Wan, Ind. Eng. Chem. Res. 2007, 46, 6847-6851
- 4. M.E.G. Lyons, G.P. Keeley, Int. J. Electrochem. Sci. 2008, 3, 819-853.
- W. Yue-Rong, H. Ping, L. Qiong-Lin, L. Guo-An, W. Yi-Ming, J. Chin. Anal. Chem. 2008, 36, 8, 1011-1016.
- 6. T. Basu, P.R. Solanki, B.D. Malhotra, Sensors. 2008, 8 1-x manuscripts
- T. Vural, F. Kuralay, C. Bayram, S. Abaci, E.B. Denkbas, *Appl. Surf. Sci.* 2010, 257, 622-627.
- W. Merchan-Merchan, A.V. Saveliev, L. Kennedy, W.C. Jimenez, Prog. Energy. Combust. Sci. 2010, 36, 696-727.
- 9. C.B. Jocobs, M.J. Peairs, B.J. Verton, Analytica. Chimica. Acta. 2010, 662, 105-127.
- 10. A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183-191.
- Y. Shao, J. Wang, H. Wu, J. Liu, L.A. Aksay, Y. Lin, *Electroanalysis*. 2010, 22, No 10, 1027-1036.
- 12. Y. Zhang, X. Sun, L. Zhu, H. Shen, N. Jia, *Electrochim. Acta.* 2011, 56, 1239-1245.
- 13. E. Jin, X. Lu, L. Cui, D. Chao, C. Wang, C. Electrochem. Acta. 2010, 55, 7130-7234.
- 14. Z. Li, J. Chen, W. Li, K. Chen, L. Nie, S. Yao, J. Electroanal. Chem. 2007, 603, 59-66.
- D.J. Yang, C.Y. Hsu, C.L. Lin, P.Y. Chen, C.W. Hu, R. Vittal, K.C. Ho, Solar. *Energy*. *Mater. Solar cells.* 2012, 99, 129-134.
- 16. Y. Zhang, Y. Wen, Y. Liu, D, Li, J. Li, Electrochem. Commun. 2004, 6, 1180-1184.

- 17. S. Chen, L. Ma, R. Yuan, Y. Chai, Y. Xiang, C. Wang, *Eur. Food, Res. Technol.* 2011, 232, 87-95.
- 18. Z. Jia, G. Sun, Col. Surf. A Physicochem. Eng. Aspects. 2007,302, 326-329.
- Y. Miao, J. Chen, X. Wu, J. Miao, Col. Surf. A Physicochem. Eng. Aspects. 2007, 295, 135-138.
- 20. S.Q. Liu, H. Li, W.H. Sun, X.M. Wang, Z.G. Chen, J.J. Xu, H.X. Ju, H.Y. Chen, *Electrochem. Acta.* 2011, 56, 4007-4010.
- M. Shokouhimehr, E.S Soehnlen, A. Khitrin, S. Basu, S.D Huang, *Inorg. Chem.* Commun. 2010, 13, 58-61
- 22. J.D. Qiu, H.Z. Peng, R.P. Liang, J. Li, X. H. Xia, Langmuir. 2007, 23, 2133-2137.
- 23. P.A. Fiorito, V.R. Goncales, E.A. Ponzio, S.I. Cordoba de Torresi, *Chem. Commun.*2005, 366-368.
- N.B. Li, J.H. Park, K. Park, S.J. Kwon, H. Shin, J. Kwak, *Biosens. Bioelectronics* 2008, 23, 1519-1526.
- 25. B. Haghighi, H. Hamidi, L. Gorton, Sens. Actuators. B. 2010, 147, 270-276.
- 26. L. Cui, J. Zhu, X. Meng, H. Yin, X. Pan, S. Ai, Sens. Actuators. B. 2012, 161, 641-647.
- 27. N. Zhang, G. Wang, A. Gu, Y. Feng, B. Fang, Microchim. Acta. 2010, 168, 129-134.
- A.S. Adekunle, B.B. Mamba, B.O. Agboola, K.I. Ozoemena, *Int. J. Electrochem. Sci.* 2011, 6, 4388-4403.
- F. Ricci, G. Palleschi, Y. Yigzaw, L. Gorton, T. Ruzgas, A. Karyakin, *Electroanalysis*.
   2003, 15, 175-182.
- 30. M. Karbarz, M. Gniadek, Z. Stojek, *Electroanalysis*. 2009, 21, 1363-1368.

- L. Wang, S. Guo, X. Hu, S. Dong, Col. Surf. A Physicochem. Eng. Aspects. 2008, 317, 394-399.
- 32. Zhang, J. Li, F. Yang, B. Zhang, X. Yang, X. Sens. Actuators. B. 2009, 143, 373-380.
- J. Bia, B. Qi, J. C. Ndamanisha, L.P. Guo, *Micropor. Mesopor. Mater.* 2009, 119, 193-199.
- 34. C. Wang, L. Zhang, Z. Guo, J. Xu, H. Wang, H. Shi, K. Zhai, X. Zhuo, *Electroanalysis*.
  2010, 22, 16, 1867-1872.
- G.G. Wildgoose, C.E. Banks, H.C. Leventis, R.G. Compton, *Microchim .Acta.* 2006, 152, 187-214.
- S. Laschi, E. Bulukin, I. Palchetti, C. Cristea, M. Mascini, *ITBM-RBM*. 2008, 29, 202-207.
- P. Salazar, M. Martin, R. Roche, R.D. O'Neill, J.L. Gonzalez-Mora, *Electrochim. Acta*.
   2011, 6476-6484.
- 38. Y. Jiang, X. Zhang, C. Shan, S. Hua, Q. Zhan, X. Bai, L. Dan, L. Niu, *Talanta*. 2011, 85, 76-81.
- 39. D. Du, M.H. Wang, Y.H. Qin, Y.H. Lin, J. Mater. Chem. 2010, 20, 1532-1537.
- W. Zhang, R. Yuan, Y.Q. Chai, Y. Zhang, S.H. Chen, *Sens. Actuators*. B. **2012**, 166-167, 601-607.

# **CHAPTER TWO:**

# LITERATURE REVIEW

#### 2. Introduction

Inorganic nanoparticles are proper candidates of the subjects in the electrochemical studies for their stability and reproducibility. Prussian blue (PB) is an inorganic polycrystalline substance which is well known for its attractive photophysical, magnetic, electrochromic and electrochemical properties. The electrochemical properties of Prussian blue can further be improved by using carbon nanotube materials (CNT), graphene oxide (GO) and cetyltrimethylammoniumbromide (CTAB). This chapter is based on a survey on the literature related to the electrochemistry, physical, chemical and electrocatalytic properties of (PB) and its electrode modification as mediators by the above mentioned materials and their detection of hydrogen peroxide ( $H_2O_2$ ) and dopamine hydrochloride.

#### **2.1 Electrochemistry overview**

Electrochemistry is the study of chemical reactions used to produce electric power or alternative power, using of electricity to affect chemical processes [1]. Electrochemistry can be defined as the relationship between chemistry and electricity, specifically the measurements of electric quantities such as potential, current and charge, and their parameters. The characterization of nanoparticles such as inorganic nanoparticles is a subject in electrochemical studies owing to their stability and reproducibility. The use of these nanoparticles in electrochemistry has found research interest in the biosensors [2]. The use of electrochemistry for analytical purposes has found a wide diversity of applications in industrial quality control, pharmacy, medicinal chemistry, biomedical analysis and environmental monitoring.

Electroanalytical techniques (such as cyclic and square wave voltammetry's) and electrode processes employed in this study are discussed in this section.

All current measuring (voltammetric) techniques make use of a three electrode electrochemical cell depicted in figure 2.1.



Figure 2.1: A type of electrochemical cell used in voltammetry is three electrode cells.

This type of electrochemical cell consists of working, reference and counter electrodes. The working (or indicator) electrode, W.E., provides a surface where the electrochemical reaction being studied occurs. The selection of the WE depends on the redox behavior of the target analyte and the background current over the potential region being examined. A reference electrode R.E., and a counter electrode C.E., complete the electric circuit.

In the circuit, potential is applied between the working and reference electrodes, while current flow is measured between the working and counter electrodes. Thus a good reference electrode is the one whose potential remains stable upon the passage of a small current, in other words nonpolarizable [3]. There are several types of reference electrodes employed in electroanalytical experiments such as silver/silver chloride (Ag/AgCl) and mercury/mercury chloride (Hg/Hg<sub>2</sub>Cl<sub>2</sub>) (Calomel). Since the use of mercury became less popular, the silver/silver chloride is the most widely used reference electrode. It consists of a piece of a silver wire in contact with AgCl in a saturated KCl solution. The mostly used working electrodes include mercury, carbon (such as glassy carbon, carbon pest) and inert materials like platinum or gold. Finally the preferred counter electrodes are platinum wire and graphite rod due to the fact they are inert materials.

#### **2.2 Mass transport processes**

Mass transport processes are a fundamental movement of charged or neutral species in electrochemical cell to the electrode surface assisted by three forms which can influence an electrolysis reaction. These processes are diffusion, migration and convection [4].

**Diffusion** is mass transport resulting from spontaneous movement of analyte species from regions of high concentrations to lower concentration regions.

**Migration** is essentially an electrostatic effect which arises due to the application of a voltage on the electrode or the movement of charged particles under the influence of an electric field. However, the addition of a large quantity of the electrolyte (relative to reactants), eliminates the contribution of migration to mass transport of the target analyte [5-6].

Lastly, **Convection results** from the action of a force on the solution. This action can be achieved by stirring the whole solution, solution flow or rotation and or vibration of the electrode [6].



Figure 2.2. Shows the three different mass transport processes below.

Figure 2.2: The three ways of mass transport processes: (A) Diffusion controlled, (B) Migration controlled and (C) Convection controlled.

### **2.3 Cyclic voltammeters**

Cyclic voltammetry (CV) is the most versatile electroanalytical technique for the study of electroactive species, and it is extensively used in industrial application and academic research laboratories. However, it is used to determine electrochemical reactions as well as to give information on the reversibility and kinetics of such reactions.

During a cyclic voltammetry experiment, the potential of an electrode is scanned linearly from an initial potential to a final potential and then back to the initial potential. The important parameters (variables) in a cyclic voltammogram are the peak potential  $(E_p)$  and peak current $(I_p)$ . The peak potential is where the oxidation/reduction species has been depleted at the electrode surface and current is controlled by diffusion. The magnitude of the faradaic currents  $(I_{pa}$ - anodic peak current) or  $(I_{pc}$ - cathodic peak current), provides an indication of the rate at which the electrons are being transferred between the electrode and the redox species. The excitation wave in CV is a linear potential scan with a triangular waveform as shown in figure 2.3.



Figure 2.3: Cyclic voltammetry potential waveform.

In this case the voltage is swept between two values at a constant rate, however when the voltage reaches "b" the scan is reversed and the voltage is swept back to "a" though it is this excitation signal wave form.

There are three processes in cyclic voltammetry, reversible, irreversible and quasi-reversible.

Figure 2.4 shows a typical CV for a reversible process. The electroactive species are stable and so the magnitudes of anodic peak and cathodic peak are equal and proportial to concentration of active species.



Figure 2.4: Typical cyclic voltammograms for reversible process.

### **Reversible process:**

Reversible process is when the electron transfer process is fast compared with the other processes (such as diffusion), and peak separation is as shown in equation 1.
$$\Delta_{Ep=(E_{pa}-E_{pc})=\frac{2.303RT}{nF}} \tag{1}$$

Thus, for a reversible redox reaction at 25°C with n electrons  $\Delta_{Ep}$  should be (0.0592/n)V or about 60 mV for one electron. In practice this value is difficult to attain because of such factors as cell resistance.

# **Irreversible process:**

In an irreversible process, the rate of the electron transfer is lower than the rate of the mass transfer, due to a slow electron transfer rate results in  $\Delta_{Ep} > (0.0592/n)V$ , greater, say than 70mV for a one –electron reaction.

The ratio of the anodic to cathodic peak current  $\left(\frac{I_{pa}}{I_{pc}}\right)$  is equal to 1 for totally reversible

process for all scan rates. A linear plot of peak current versus half scan rate specifies that the current are controlled by planar diffusion to the electrode surface.

The formal reduction potential  $(E_0)$  for a reversible couples is given by equation 2.

$$E_o = \frac{\left(E_{pa} - E_{pc}\right)}{2} \tag{2}$$

At 25°C, the concentration is related to peak current by the Randlesh Sevcik equation 3 as follows.

$$I_p = (2.69x10^5)n^{3/2} A.C.D^{1/2} V^{1/2}$$
(3)

Where  $I_P$ = peak current (A) n = number of electrons transferred A= electrode area (cm<sup>2</sup>) C= concentration (mol.cm<sup>-3</sup>) D= diffusion coefficient (cm<sup>2</sup>·s<sup>-1</sup>) V= scan rate (v.s<sup>-1)</sup>

For an irreversible process (those with slow-moving electron transfer) the individual peaks are reduced in size and widely separated. The peak current is given by equation 4.

$$I_p = (2.99x10^5)n[(1-\alpha)n]^{\frac{1}{2}}A.C.D^{\frac{1}{2}}.V^{1/2}$$
(4)

Where  $\alpha$  is the coefficient of electron transfer, the rest of the symbols are mentioned above in equation 3. For a completely irreversible system,  $\Delta E_P$  can be calculated by equation 5.

$$\Delta E_p = E^{O'} - \frac{RT}{\alpha nf} \left\{ \left( 0.78 - ln \frac{k}{D^{\frac{1}{2}}} ln \left( \frac{\alpha nF}{RT} \right)^{\frac{1}{2}} \right) \right\}$$
(5)

Where k is the standard rate constant, the other symbols are defined above.

# **Quasi-reversible processes**

It is not uncommon that in an electron transfer processes; one observes that at low scan rates reversible process occurs, whereas at high scan rates irreversible process takes place. The quasi-reversible process is that which occurs in the transition zone between reversible and irreversible. Differences between these three cyclic voltammetric processes are defined in table 2.1.

Parameters	Reversible	Irreversible	Quasi-reversible
E <sub>p</sub>	Independent of V	Shift cathodically by 30/αn mv for a 10-fold increase in V	Shift with V
I <sub>pa</sub> /I <sub>pc</sub>	Equals 1 independent of V	Generally No current on the reverse side	Equals 1 only for $\alpha = 0.5$
$E_{pa} - E_{pc}$	~ 59/n mv at 25°C & independent of V		May approach 60/n mv at low V but increases as V increases
<i>I</i> <sub>p</sub> /V <sup>1/2</sup>	Constant	Constant	Virtually independent of V

Table 2.1. A summary of factors for the diagnosis of the reversible, quasi-reversible and irreversible cyclic voltammetric processes.

# 2.4 Square wave voltammeters

Square-wave voltammetry (SWV) pioneered by Barker is one widely used pulse technique that offers the advantage of great speed and high sensitivity [7]. Square-wave voltammetry is usually practiced with the square-wave being superimposed on a staircase wave form. During each square-wave cycle, the current is sampled two times, once at the end of the forward pulse ( $I_f$ ) and once at the end of reverse pulse ( $I_r$ ). The difference between the forward ( $I_f$ ) and reverse currents ( $I_r$ ) is displayed as a function of potential which results in a peak- shaped voltammogram shown in figure 2.5. This difference is directly proportional to the concentration. The potential of the peak corresponds to the voltammetric half-wave potential.



Figure 2.5: Atypical excitation signal for square wave voltammetry.

# 2.5 Prussian blue nanoparticle and its analogues

Prussian blue (PB) is the representative of the coordination polymers and a classically mixed valence compound that contains iron hexacyanoferrate with the approximate formula,  $A_4xFe_4^{III}[Fe^{II}(CN)_6]_{3+x}nH_2O$ , where A stands for a group one metal elements (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) except with francium and include thallium metal [8]. Prussian blue solid nanoparticles can be easily synthesized by addition of aqueous solution of iron(III) ions to an aqueous ferrocyanide solution [9]. The Prussian blue has a face centered cubic structure (space groups' *fm3m*) in which two different iron centers Fe<sup>3+</sup> and Fe<sup>2+</sup> are bridged by the CN-groups in figure 2.6. [10-11]. The Fe<sup>2+</sup> is carbon –bonded and has a low-spin (S=0) while the Fe<sup>3+</sup> is nitrogen –bonded and has a high –spin (S= 5/2) which gives rise to a total of five unpaired electrons per Fe<sup>2+</sup>-C=N-Fe<sup>3+</sup> unit.



Figure 2.6: Face-centered lattice adopted by the Prussian blue structure.

Prussian blue is deep blue in color at ground state. However, under a suitable applied potential it can be reduced to colorless Prussian white (PW) known as eventt salt (ES), while by oxidation the yellow form, Prussian yellow (PY) also known as Berlin Green [12-14].

The electron transfer reactions in the presence of potassium chloride as a supporting electrolyte may be formulated as expressed in equation 6&7.

$$(PB)Fe (III) 4[Fe (II) (CN)_{6}]_{3} + 4e^{-} + 4K^{+} \rightarrow (PW) K_{4}Fe (II)_{4}[Fe (II) (CN)_{6}]_{3}$$
(6)  

$$(PB)Fe (III) 4[Fe (II) (CN)_{6}]_{3} + 3Cl^{-} \rightarrow (PG) Fe (III) 4[Fe (III) (CN)_{6}]_{3}Cl_{3} + 3e^{-}$$
(7)

There are two sets of peaks (cathodic and anodic) in the cyclic voltammogram of Prussian blue modified electrode as shown in figure 2.7. The cathodic peak corresponds to the Prussian blue/Prussian white (PW) redox system with potassium as the counter cation to compensate for the transfer of electrons in the film according to the chemical equation 6. At high anodic potentials Prussian blue converts to its fully oxidized form and it's known as Prussian yellow or berlin green according to equation 7 above [15-17].



Figure 2.7: Representative cyclic voltammogram of Prussian blue modified glassy carbon electrode.

Prussian blue and its analogues have received significant attention due to their unusual electrochemical, electrochromic photophysical, magnetic properties and its potential analytical applications [18-20]. Recent investigations of PB have shown by growing interest in multifunctional materials and a revival in the chemistry of inorganic cyanide compounds. PB is an inorganic polycrystalline molecule that has been widely used as electron-transfer mediators in the fields of electrocatalysis. In 1978, Neff [21] reported for the first time the successful deposition of Prussian blue on a platinum foil as well as its electrochemical behavior [20]. A large number of studies followed and different methods for the preparation of Prussian blue modified electrodes based on a simple electrochemical reduction of a ferric- ferricyanide solution is described by Itaya *et al* [22]. So the procedure was adopted with different electrode materials such as Platinum, SnO<sub>2</sub>, gold, edge plane pyrolytic graphite electrode basal plane pyrolytic

graphite electrode and glassy carbon electrode under certain conditions. A high stability of the layer deposited through successive cycling was demonstrated.

#### 2.5.1 Prussian blue modified glassy carbon electrode

Glassy carbon electrode is very common due to its excellent mechanical and electrical properties, chemical inertness and relatively reproducible performance. But to improve its activity, modifying with electroactive species is needed. Chemically modified electrodes (CMEs) have received great significance as important analytical tools for the electrochemical determination of various analytes with the aid of electrode modification [23]. The modification of an electrode results in efficient detection of electrode active biomolecules at very low potential without major interferences. To activate the electrode, various organic and inorganic modified electrodes [16]. Prussian blue is among inorganic materials used to immobilize the electrode surface due its unusual characteristic such as electrochemical, electrochromic, electrocatalytic and magnetic properties [24].

Prussian blue modified electrode has the ability to detect hydrogen peroxide in solution but the stability of detection leaching because of the film of PB on the electrode is not stable in a neutral solution. However, it has been reported that problems caused by leakage of PB layer in solution phase after a few scans at neutral pH due to the relatively weak combination between PB and bare electrode [25-26]. Thus, how to efficiently improve the electrochemical stability of PB film becomes desirable. To overcome this problem, screen-printed electrode (SPEs) [27], ordered mesoporous carbon (OMC) [28], polyaniline (PANI), cetyltrimethylammonium bromide (CTAB) [29] and multi-walled carbon nanotubes (MWCNTs) [30] have been used to immobilize of PB.

The combination of PB and CNTs has received research interest. CNTs are considered to be good mediators for PB-modified electrodes due to their good electric conductivity and the property of being particle carriers. Several methods have been used as modification processes. These include electrochemical deposition, chemical deposition, self-assembling method [31] and sequential deposition method. Self-assembling method is a more efficient method for the modification processes but its application increases the impedance of the electrode [32]. Thus the sequential deposition method is more appropriate to use in making effective film on the surface of the electrode.

## 2.5.2 The crystal structure of Prussian blue

There are two structural forms of Prussian Blue (PB) soluble Prussian (KFe<sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>] and insoluble Prussian blue (Fe<sub>4</sub><sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub>. These two forms have similar structure, but have different extents of peptization with potassium ions. Replacement of potassium ions with ferric ions in a soluble PB would produce an insoluble PB [33-34]. The soluble form of PB has a cubic structure in which iron(II) and iron(III) are located on the face centered cubic lattice, where iron(II) ions are surrounded by carbon atoms and iron(III) ions are surrounded octahedrically by nitrogen atoms. Ludi and co-workers successfully determined the structure of insoluble form which showed some differences from that proposed by Keggin and Miles. The structures of both insoluble and soluble PB contain number of water molecules. Therefore the water molecules in the formula (Fe<sub>4</sub><sup>III</sup> [Fe<sup>II</sup> (CN)<sub>6</sub>]<sub>3</sub>.nH<sub>2</sub>O where n=14-16 per unit cell insoluble Prussian blue (IPB), while the soluble Prussian blue (SPB) KFe<sup>III</sup> [Fe<sup>II</sup> (CN)<sub>6</sub>].nH<sub>2</sub>O where n=1-5. In 1986, Iataya *et al* [22] addressed the structure depending on the row materials and the procedure adopted to crystallize PB, could contain co-precipitated ions, indefinite amounts of water hydrolyzed ferrocyanide and various vacancies in the crystal structure

Figure 2.8. depicts the structures of the two different forms of Prussian blue, i.e. the soluble Prussian blue (SPB) and insoluble Prussian blue (IPB).



Figure 2.8: Structures of soluble Prussian blue (A) and insoluble Prussian blue (B)

# 2.6 The electrochemistry of hydrogen peroxide and dopamine

The detection of hydrogen peroxide  $(H_2O_2)$  plays an important role in many areas such as clinical diagnosis, environmental protection and industries.  $H_2O_2$  is electroactive in aqueous solution that allows its electrochemical detection feasible and convenient. There are many active species present in biological fluids such as ascorbic acid (A.A), uric acid (U.A) and dopamine (DA) that are easily co-oxidized at comparable potentials and may cause interfering responses [35]. To limit the problem it is important to follow two effective protocols, (i) lowering the  $H_2O_2$ detecting potential and sensitizing the reduction of  $H_2O_2$  by using a catalyst immobilized at an electrode instead of its oxidation. (ii) taking a permselective film that diminishes the electrochemistry of the interferents, though a high penetrability for  $H_2O_2$  across the film still permits its high electroactivity at the electrode [36].

Since its discovery almost two decades ago, Prussian blue or ferric ferrocyanide, electrodeposited onto an electrode surface, could act as an electrocatalyst for hydrogen peroxide reduction [37]. Modified glassy carbon electrode with cobalt(II) hexacyanoferrate and chromium(III) hexacyanoferrate were obtained using amperometric hydrogen peroxide sensor and many other metals have been reported. Both the electrode materials (Pt, Au, graphite, carbon paste, edge plane pyrolytic graphite electrode and glassy carbon electrode) and techniques of immobilization of Prussian blue (mechanical immobilization, self-assemble, electrodeposition and sequential deposition) have been tested.

Dopamine (DA) (figure2.9) is a catecholamine neurotransmitter, which is generated in various parts of central and peripheral nervous system that plays an important role in the function of the central nervous, renal, hormonal and cardiovascular systems [38]. DA level can be as high as 50 nmolg<sup>-1</sup> in the mammalian central nervous system in a region of the brain known as the "caudate nucleus" [39]. A number of diseases found to be associated with either low concentration or abnormal metabolisms of DA are Parkinson disease, epilepsy, HIV infection and senile dementia [40-42]. To reduce these problems, it is necessary to fabricate very sensitive sensors that will determine the presence of this substance in human fluid should be the focus of neuro-scientist. So due to the interfering effect of this molecule with other biological molecules like ascorbic acid (A.A) and uric acid (U.A). Therefore many techniques have been reported in the literature for the determination of dopamin. These techniques include chromatography, fluorescence, spectrophotometry and electrochemistry. But chromatography, spectrophotometry and fluorescence are highly expensive and require long time for analysis.

Electrochemical methods have been employed with the use of different electrodes as sensors nanostructure material in polymer matrix (e.g. gold nanoparticles on polymer matrix), GC/nafion/nanoPt, carbon nanotube [43], ordered mesoporous carbon and carbon ionic liquids [44]. These carbon based materials have been reported for the electrochemical determination of DA and AA. Thus the electrochemistry based methods are preferred from others due to their simplicity, low detection limits, fast response time and relatively low costs [45]. The detection of dopamine and hydrogen peroxide is very important in several areas such as environmental, clinical diagnosis and so on.



Figure 2.9: The structure of dopamine

# 2.6.1 Chemical property of hydrogen peroxide

Hydrogen peroxide has a marked tendency to decompose to water and oxygen, liberating a large amount of heat as shown in equation 8.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \Delta H = -196.2kJ \tag{8}$$

At room temperature, it appears metastable, either in pure taste or in solution. It is stable because the first step in its thermolysis involves splitting the molecule into two HO<sup>•</sup> radical and this requires a large input of energy. The radical initiates a chain reaction. The most characteristic property of hydrogen peroxide is its oxidizing action as expressed in equation 9.

$$H_2O_2 \rightarrow H_2O + O^{-} \text{ or } H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$$
 (9)

# **2.6.2** Physical properties of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

Hydrogen peroxide is a clear and colorless liquid. It has a slightly pungent odor. Hydrogen peroxide is a versatile and environmentally friendly chemical with a wide variety of applications. It is a syrupy liquid due to extensive hydrogen bonding with boiling point of 150°C and density

at 20°C of 1.448 g.cm<sup>-3</sup>. Hydrogen peroxide and water form a eutectic mixture, exhibiting freezing-point depression. Pure water melts and freezes at approximately 273 K, and pure hydrogen peroxide just 0.4 K below that, but a 50% (by volume) solution melts and freezes at 221 K. Physiologically, it is very irritating to the skin, and especially to mucous membranes of the respiratory passages and eyes. If swallowed, hydrogen peroxide causes internal bleeding.

# 2.7 Graphene

#### 2.7.1 Introduction

Graphene, a two-dimensional single layer of graphite and one-atom-thick sheet material with interesting physical properties [46-47] has been considered as the mother of all graphitic structure. The unique properties of graphene make it a promising candidate for fundamental study as well as for potential application [48-49]. These properties include thermal, excellent electronic, mechanical and chemical stability which has shown great interest in research activities in the world for production of graphene [50-51]. Among these potential applications include energy storage, fuel cells, solar cells, transparent conducting electrodes and electronics [52]. It has been reported that well dispersed graphene could be prepared by noncovalent functionalization or covalent modification approach [53].

In the past 15 years, electrochemical biosensors based on nanomaterial's, such as metal nanoparticles, carbon nanotubes, metal oxides etc. have been an important topic in the area of sensor research [54]. There are several reported methods for the synthesis of graphene by different scholars choi *et al.*, [55] Dreyer *et al.* [56], Kuila *et al.*, [57] Park and Rouff. These include exfoliation and cleavage of natural graphite, chemical vapour deposition CVD) [58] PE-

CVD, electric arc discharge, micromechanical exfoliation of graphite, epitaxial growth on electrically insulating surface [59].

Surfactants have been generally used to improve the charge transfer between and electrode and its electroactive species. This can be divided into four groups: anionic, cationic, zwitterionic and non-ionic surfactants. Previous literature [60-61] has indicated that cetyltrimethylammonium bromide (CTAB), a cationic surfactant, supports the formation of a Prussian blue film and improves the reversibility of its oxidation reduction reactions [27, 62].

# 2.8 Carbon nanotubes

#### **2.8.1 Introduction**

Since the discovery of carbon nanotubes (CNTs) in 1991 by lijima [63] research on CNTs has progressed speedily and has become one of the most attractive parts of nanotechnology in the world [64]. CNTs possess sp<sup>2</sup> carbon units with several nanometers in diameter and many microns in length. They can be subdivided into two types of carbon nanotubes namely: singlewalled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) in Figure 2.10. The SWCNT possess a cylindrical nanostructure (with a high aspect ratio) designed by rolling single graphite sheet into a tube while MWCNT comprise of several layers of graphene cylinders that are concentrically nested like rings of a tree trunk (with an interlayer spacing of 3.4A° [65-66]. These two groups of nanotubes have attracted the attention of researchers and become the subject of intensive investigation because of their unique physical and chemical properties such as electrical conductivity, chemical stability, mechanical and tensile strength [67]. Carbon nanotubes have found many applications in different areas such as electrochemical capacitors, hydrogen storage [68], field emission, water purification and electrochemical sensors [69].

These materials receive significant attention in the subject of electrochemistry not only due to their properties as mentioned above, but they represent the world's smallest electrode allowing electrochemistry to be performed, where other electrode materials cannot penetrate. Britto and coworkers employed carbon nanotubes modified electrodes in electrochemical sensing with nanotubes dispersed in bromoform as a binder material and packed into a glass tube.

After that, CNTs application in electrochemistry has developed vastly where CNTs-modified electrodes have gained interesting catalytic properties towards electrochemical processes. It acts as electrical conducting nanowires between the electrode and the electroactive species on the surface.



Figure 2.10: (A) single –walled carbon nanotubes (B) multi-walled carbon nanotubes

# 2.8.2 Synthesis of carbon nanotubes

For a reactor to fit for the synthesis of carbon nanotubes it must have three essential components (i) a source of carbon material, (ii) a source of heat, and (iii) the presence of metal catalytic particles. The synthesis can be employed by three common methods such as electric arc-discharge, pulsed laser vaporization (PLV) and chemical vapour deposition (CVD) [70-73]. These methods are very useful and are of widespread importance, but the chemical vapour deposition has been considered to be the most appropriate method for the synthesis of CNTs produced in large quantities [72-73]. After synthesis with different methods, the CNTs are purified.

# References

- 1. J. Wang, Analytical electrochemistry. VCH Publishers Inc. New York, 1994
- 2. S.Q. Lue, J.J Xu, H.Y. Chen, Electrochem.Commun.2002, 4, 421-425.
- A.E. Kaifer, M. Gomez-kaifer, *Supermolecular electrochemistry*, Wiley-VCH, New York, 1999.
- 4. A.M. Bond, Broadening electrochemical horizons, Principles and illustration of voltammetric and related techniques. **2002**, 1<sup>st</sup> edition, page 48-49.
- D.A. Skoog, J.F. Holler, S.R. Crouch, *Principles of instrumental analysis*. 2007.6<sup>th</sup> edition.
- P. Zenello, *Inorg. Electrochem. Theory, practical & application.* 2003, The Royal society of chemistry. Page 34-36.
- D.J. Gavaghan, D. Elton, K.B. Oldham, A.M. Bond, J. Electroanal. Chem. 2001, 512, 1-15.
- A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kage, S. Okamoto, M. Ohta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Hara, H. Shiozaki, M. Yamada, M. Miyake, M. Kurihara, *Nanotech.* 2007, 18, 345609(6pp).
- 9. M. Shokouhimehr, E.S Soehnlen, A. Khitrin, S. Basu, S.D Huang, *Inorg. Chem. Commun.* **2010**, 13, 58-61.
- 10. Z. Jia, G. Sun, Col. Surf. A. Physicochem. Eng. Aspects. 2007, 302, 326-329.
- N.B. Li, J.H. Park, K. Park, S.J Kwon, H. Shin, J. Kwak, *Biosens. Bioelectron.* 2008, 23, 1519-1526.
- 12. Y. Toyoda, N. Katoh, K. Kuwabara, Mater. Sci. Eng. B 108, 2004, 271-277.

- P. Salazar, M. Martin, R. Roche, R.D. O'Neill, J.L. Gonzalez-Mora, *Electrochim.* Acta. 2010, 6476-6484.
- B. Haghighi, S. Varma, F.M. Alizadeh sh, Y. Yigzaw, L. Gorton, *Talanta*. 2004, 64, 3-12.
- 15. A.A. Karyakin, *Electroanalysis*. 2001, 13, 10, 813-819.
- C. Wang, L. Zhang, Z. Guo, J. Xu, H. Wang, H. Shi, K. Zhai, X. Zhuo, *Electroanalysis.* 2010, 22, 16, 1867-1872.
- S. Xing, H. Xu, G. Shi, J. Chen, L. Zeng, L. Jin, *Electroanalysis*. 2009, 21, 15, 1678-1684.
- 18. J. Zhang, J. Li, F. Yang, B. Zhang, X. Yang, Sens. Actuators. 2009, B143, 373-380.
- 19. B. Haghighi, H. Hamidi L. Gorton, Sens. Actuators. 2010, B147, 270-276.
- 20. F. Ricci, & G. Palleshci, Biosens. Bioelectron. 2005, 21, 389-407.
- 21. V. D. Neff, J. Electrochem. Soc. 1978, 125, 886-887.
- 22. K. Itaya, I. Uchida, I. Acc. Chem. Res. 1986, 19, 162-168
- 23. J. Zen, A.S. Kumar, D. Tsai, *Electroanalysis*. 2003, 15, 13, 1073-1087.
- 24. C. Yang, C. Wang, J. Wu, X Xia, *Electrochem.Acta*. 2006, 51, 4019-4023.
- 25. L. Lin, X. Huang, L. Wang, A. Tang, Solid. State. Sci. 2010, 12, 1764-1769.
- S. Liu, H. Li, W. Sun, X. Wang, Z. Chen, J. Xu, H. Ju, H. Chen, *Electrochem. Acta*.
   2011.56, 4007-4014.
- F. Ricci, A. Amine, G. Palleschi, D. Moscone, J. Biosens. Bioelectron. 2003, 18, 165-174.
- J. Bai, B. Qi, J.C. Ndamanisha, L.P. Guo, *Micropor. Mesopor. Mater.*2009, 119, 193-199.

- R. Vittal, K.J. Kim, H. Gomathi, V. Yegnaraman, J. Phys. Chem. 2008, B 112, 1149-1156.
- 30. N. Zhang, G. Wang, A. Gu, Y. Feng, B. Fang, Mirochim. Acta. 2010, 168, 129-134.
- 31. Y. Liu, Z. Chu, W. Jin, *Electrochem. Commun.* 2009, 11, 484-487.
- L. Wang, S. Guo, X. Hu, S. Dong, Col. Surf. A Physicochem. Eng. Aspects. 2008, 317, 394-399.
- D.J. Yang, C.Y. Hsu, C.L. Lin, P.Y. Chen, C.W. Hu, R. Vittal, K.C. Ho, Solar. Energy. Mater. Solar cells. 2012, 99, 129-134.
- 34. Y. Miao, J. Chen, X. Wu, Colliod. J. 2007. Vol. 69, No, 3, PP. 334-337.
- 35. R.K. Shervedani, H.A. Alinajafi-najafabadi, Int. J. Eelectrochem. Dio:10.4061./2011/60313
- 36. R. Garjonyte, A. Malinauskas, Sens . Actuators. 2000, B63, 122-128.
- 37. M.S. Lin, B.I. Jan, *Electrocanalysis*. 1997, 9, 340-344.
- 38. W. Zhang, R. Yuan, Y.Q. Chai, Y. Zhang, S.H. Chen, Sens. Actuators. B. 2012, 166-167, 601-607.
- 39. S. Thiagarajan, S. Chen, Talanta. 2007, 74, 212-222.
- 40. A.S. Adekunle. B.O. Agloola. J. Pillay, K.I. Ozoemena, Sens. Actuators. 2010, B148, 93-102.
- 41. R.N. Goyal, S.P. Singh, Carbon 2008, 46, 1556-1562.
- 42. E. Baldrich, R. Gomez, G. Gabriel, F.X. Munoz, *Biosens. Bioelectron.* 2011, 26, 1876-1882.
- 43. G. Xu, M. Xu, J. Zhang, S. Kim, Z. Bae, *Bioelectrochem.* 2007, 72, 87-93.

- 44. Y.F. Zhao, Y.Q. Gao, D.P. Zhan, H. Lui, Q. Zhao, Y. Kou, Y.H. Shao, M.X. Li, Q.K. Zhuang, Z.W. Zhu, *Talanta*. 2005, 66, 51.?
- 45. S. Chuekachang, V. Kruefu, S. Chaiyasit, S. Phanichphant, Proceeding of the 2010
   5<sup>th</sup> IEEE international conference on nano/micro engineered and molecular systems.
   January 20-23, Xiamen, china.
- 46. A.K. Geim, K.S. Novoselov, Nat. Mater. 2007 6, 183-191.
- X.W. Liu, Z.J. Yao, Y.F Wang, X.W. Wei, *Colloids. Surf. B. Biointerfaces.* 2010, 18, 508-512.
- 48. Y. Zhang, X. Sun, L. Zhu, H. Shen, N. Jia, N. *Electrochim. Acta.* **2011**, 56, 1239-1245.
- S. Woo, Y.R. Kim, T.D. Chung, Y. Piao, H. Kim, *Electrochim. Acta.* 2012, 59, 509-514.
- Y. Shao, J. Wang, H. Wu, J. Liu, L.A. Aksay, Y. Lin, *Electroanalysis*. 2010, 22, No 10, 1027-1036.
- 51. H. Kim, A.A. Abdala, C.W. Macosko, *Macromolecules*. 2010, 43, 6515-6530.
- 52. S. Niyogi, E. Bekyarova, M.E. Itkis, J.L. Mcwilliams, M.A. Hamon, R.C. Haddon, J. Am. Chem. Soc. 2006, 128, 7720-7721.
- 53. W. Wu, Z. Liu, L. A. Jauregui, Q. Yu, R. Pillai, H. Cao, J. Bao, Y. P. Chen, S-S Pei, *Sens. Actuators* B 2010, 150, 296-300.
- 54. E. Jin, X. Lu, L. Cui, D. Chao, C. Wang, *Electrochem. Acta.* 2010, 55, 7130-7234.
- 55. W. Choi, I. Lahiri, R. Seelaboyina, Y.S. Kang, *Critical Review. Solid. State. Mat. Sci.*2010, 35, 52-71.

- D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, Chem. Soc. Rev. 2010, 39. 228-240.
- 57. T. Kuila, S. Bose, A.K. Mishra. P. Khana, N.H. Kim, J.H. Lee, *Prog. Mat. Sci.* 2012, 57, 1061-1105.
- 58. D. Zhang, X. Lui, X. Wang, J. Inorg. Biochem. 2011, 105, 1181-1186.
- T. Kuila, S. Bose, P. Khanra, A.K. Mishra, N.H. Kim, J.H. Lee, *Biosens. Bioelectron.* 2011, 26, 4637-4648.
- 60. J. Wang, B.Z Zang, C.Fang, X.Y. Zhau, J. Electroanal. Chem. 2000, 484, 88-92.
- 61. B.X. Ye, X.Y. Zhou, *Electroanalysis*. 1996, 8, 1165-1168.
- 62. S.M.S. Kumar, K.C.J. Pillai, Electrochemical. Chem. 2006, 589, 167-175.
- 63. S. Iijima, Nature. 1991, 354, 56-58.
- W. Yue-Rong, H. Ping, L. Qiong-Lin, L. Guo-An, W. Yi-Ming, J. Chin, *Anal. Chem.* 2008, 36, 8, 1011-1016.
- 65. A.J. Saleh Ahammad, J.J. Lee, M. Aminur Rahman, Sensors. 2009, 9, 2289-2319.
- 66. J. Wang, *Electroanalysis*. 2005, 17, 1, 7-14.
- 67. M.E.G. Lyons. G.P. Keeley, Int. J. Electrochem. Sci. 2008, 3, 819-853.
- M. Valcarcel, B.M. Simonet, S. Cardenas, B. Zuarez, Anal. Bioanal. Chem. 2005, 382, 1783-1790.
- 69. M. Trojanowicz, Trends. Anal. Chem. 2006, V 25, No 5.
- 70. J.J. Gooding, *Electrochem. Acta.* 2005, 50, 3049-3060.
- W. Merchan-Merchan, A.V Saveliev, L. Kennedy, W.C. Jimenez, *Prog. Ener. Comb.* Sci. 2010, 36, 696-727.
- 72. T. Basu, P.R. Solanki, B.D. Malhotra, Sensors 2008, 8 1-x manuscripts.

- 73. S. Karthikeyan, P. Mahalingam, M. Karthik, *E.J.Chem.* 2009, 6(1), 1-12.
- 74. E. Couteau, K. Hernadi, J.W. Seo, L. Thein-nga, C. Miko, R. Gaal, L. Forro, *Chem. Phys. Lett.* **2003**, 378, 9-17.
- 75. J. Qiu, Y. An, Z. Zhao, Y. Li, Y. Zhou, Fuel. Process. Tech. 2004, 85, 913-920.

# **CHAPTER THREE:**

# EXPERIMENTAL

# **3.1. Introduction**

Experimental procedures that have been conducted for the fulfillment of this research project are discussed in this chapter. Most of the methods and experiments used for the study were done at normal conditions, at the atmospheric pressure unless stated otherwise in the procedure.

# 3.2. Materials and reagents

Glassy carbon electrodes (GCE) were purchased from BAS Inc (Tokyo Jaban), Multi-walled carbon nanotubes (MWCNT) and Grapheme oxide (GO) were obtained in our research group by Ndwandwe *et al* [1], cetyltrimethylammoniumbromide (CTAB), Sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>), potassium hexacyanoferrate (K<sub>4</sub>[Fe (CN)<sub>6</sub>]<sub>3</sub>.H2O, iron(III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, iron(III) chloride hexahydrate FeCl<sub>3</sub>.6H<sub>2</sub>O, alumina oxide (AlO<sub>3</sub>) and Dopamine hydrochloride (DA) were purchased from Sigma-Aldrich. Acetone (C<sub>3</sub>H<sub>6</sub>O), *N*,*N*-dimethylformamide (DMF), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) nitric acid (HNO<sub>3</sub>) and hydrochloric acid (HCl) were analytical grade and obtained from Sigma – Aldrich and Merck respectively. All solutions were prepared with deionized water (DW).

## **3.3.** Synthesis of Prussian blue (PB)

Prussian blue nanoparticles were synthesized as follows:

a) An aqueous solution of 0.5M of FeCl<sub>3</sub>.6H<sub>2</sub>O was added to an aqueous solution of equimolar mass of  $K_4$ [Fe(CN)<sub>6</sub>].3H<sub>2</sub>O. The reaction mixture was vigorously stirred for 10 min. the product dark blue precipitate was centrifuged, washed with distilled water three times and with methanol once , and then dried under oven at 80°C to yield the insoluble Prussian blue nanoparticles [2].

b) An aqueous solution of 1M Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O was added to an aqueous solution of an equimolar mass of  $K_4$ [Fe(CN)<sub>6</sub>].3H<sub>2</sub>O. The reaction mixture was vigorously stirred for 10 min. the product dark blue precipitate was centrifuged, washed with distilled water three times and with methanol once , and then dried under oven at 80°C to yield the insoluble Prussian blue nanoparticles [2].

# **3.4. Electrode modification and pretreatments**

#### **3.4.1 Electrode cleaning**

Electrodes were prepared using the following procedures. First, the glassy carbon electrode surface was cleaned by gentle polishing in aqueous slurry of alumina oxide nanopowder (Sigma-Aldrich) on a mesh paper. The electrode was then subjected to ultrasonic vibration in acetone to remove residual alumina particles that might be trapped at the surface of the electrode. Again the electrode subjected to ultrasonic vibration in deionized water. After cleaning processes the obtained electrode was used for electrochemical analysis.

## 3.4.2 Electrode modification

The following three steps in duplex format were carried out in the processes of electrode modification.

#### 3.4.2.1.1 Drop-dry/ electrodeposition methods

50 mg of MWCNTs was dispersed in 5ml of *N*,*N*-dimethylformamide (DMF) with the aid of ultrasonic mixing for 30 min to form a stable black suspension. About 20  $\mu$ L drop of MWCNTs/DMF solution was dropped on the bare glassy carbon electrode and dried in an oven at 50°C for 5 min. the modified electrode obtained is herein denoted as GC-MWCNTs.

#### **3.4.2.1.2 Sequential deposition methods**

The PB film was prepared by sequential deposition method as described by Han *et al* [3]. GC-Bare or GC-MWCNTs electrodes were immersed in Fe(NO<sub>3</sub>)3.9H<sub>2</sub>O solution for 30 min, with stirring after which the electrodes were rinsed and dried and then immersed in K4[Fe(CN)6].3H<sub>2</sub>O solution and stirred for another 30 min, followed by a re-rinsing and a re-drying processes to complete the deposition cycle. The obtained electrodes were described as GC-PB and GC-MWCNTs-PB respectively.





## 3.4.2.2.1 Drop-dry/ electrodeposition methods

50 mg of cetyltrimethylammoniumbromide (CTAB) was dispersed in 5 ml of *N*,*N*-dimethylformamide (DMF) with the aid of ultrasonic mixing for 15 min to form a homogenous suspension. About 20  $\mu$ L drop of CTAB/DMF solution was dropped on the bare glassy carbon electrode and dried in an oven at 50°C for 5 min. the modified electrode obtained is herein designated as GC-CTAB.

# 3.4.2.2.2 Sequential deposition methods

GC-CTAB was deposited  $Fe(NO_3)_3.9H_2O$  and  $K_4[Fe(CN)_6].3H_2O$  solutions with same concentration were used for the deposition experiment Han *et al* [3]. The GC-CTAB electrode was first immersed in stirred  $Fe(NO_3)_3.9H_2O$  solution for 30 min, after the electrode was rinsed and dried it was then immersed in  $K_4[Fe(CN)_6].3H_2O$  solution and stirred for another 30 min, followed by a re-rinsing and a re-drying processes to complete the deposition cycle. The obtained electrode was described as GC-CTAB-PB.





## 3.4.2.3.1 Drop-dry/ electrodeposition methods

50 mg of graphene oxide (GO) was dispersed in 5 ml of *N*, *N*-dimethylformamide (DMF) to dissolve in the absence of ultrasonic mixing for 5 min to form a homogeneous solution. About 20  $\mu$ L drop of GO/DMF solution was dropped on the bare glassy carbon electrode and dried in an oven at 50°C for 5 min. the modified electrode obtained is herein denoted as GC-GO.

## 3.4.2.3.2 Sequential deposition methods

GC-GO was deposited  $Fe(NO_3)_3.9H_2O$  and  $K_4[Fe(CN)_6].3H_2O$  solutions with same concentration were used for the deposition experiment Han *et al* [3]. The GC-GO electrode was first immersed in stirred  $Fe(NO_3)_3.9H_2O$  solution for 30 min, after the electrode was rinsed and dried it was then immersed in  $K_4[Fe(CN)_6].3H_2O$  solution and stirred for another 30 min, followed by a re-rinsing and a re-drying processes to complete the deposition cycle. The obtained electrode was described as GC-GO-PB.



## (Stirring for 30 mins)

Scheme.3.3: Electrode modification procedure with Prussian blue (PB) nanoparticles in the presence of graphene oxide.

# **3.5. Equipments**

The convectional three electrode cell with a Ag/AgCl (3 MKCl) electrode as a reference electrode, Platinum wire as a counter electrode, bare, Prussian blue modified electrode and Prussian blue promoted by (multi-walled carbon nanotube, graphene oxide, and cetyltrimethylammonium bromide) as a working electrode was used for all the measurements. The pH of the buffer solution was measured with digital pH 780 meter model. All electrochemical experiments were carried out using an autolab potentiostat (663VA stand metrohm Swiss mode) driven by the general purpose electrochemical systems (GPES) windows version 4.9.

# 3.5.1 Cyclic voltammetry

All cyclic voltammetry measurements were recorded in the potential ranges from -250 to 500 mV with scan rate of 100 mV/s.

# 3.5.2. Square wave voltammetry

All square wave voltammetry measurements were recorded in the potential ranges 700 to 700 mV with amplitude of 10 mV.

# **3.6.** Spectroscopy and Microscopy techniques

## **3.6.1.** Spectroscopy

Spectroscopy is the study of interaction between radiation and matter as a function of wavelength frequency or energy which is usually in the form of photon of light and represented asE = hv, where *h* is the Planck constant. A plot of the response as a function of wavelength is denoted to as a spectrum.

#### 3.6.1.1. Infrared spectroscopy (IR)

Infrared spectroscopy (IR) is a well-known analytical technique which deals with the infrared region of the electromagnetic spectrum, which is light with a longer wavelength and lower frequency than visible light. It can be used to identify functional groups that are present in a molecule or compound. The infrared spectroscopy is a simple and reliable technique broadly used in both organic and inorganic chemistry, in research as well as industry, due to its reliability for measurements such quality control and monitoring [4-5]. It is also used in forensic analysis in both civil and criminal cases, enabling identification of polymer degradation for example. The infrared portion of the electromagnetic spectrum is commonly divided into three regions; these are near, mid and far infrared. Where in this figure 3.1. Presents an IR apparatus showing the different components. The IR spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. These resonances frequencies are determined by the shape of the molecular potential energy surface, so the masses of the atoms and by the associated vibronic coupling.

The analysis was done on a Perkin Elmer instrument, spectrum 400 FTIR/FT-NIR spectrometer. The particularity of this instrument is that no sample holder (KBr plate) is needed or a particular substance such as nujol. The sample was analyzed by placing it directly placed on top of the detector.



Figure 3.1: Infra-red (IR) spectroscopy setup.

# **3.6.1.2.** Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy (UV-VIS) involves the spectroscopy of photons in the uv-visible region. It allows one to determine the wavelength and maximum absorbance of compounds. When a molecule absorbs a photon of light, electrons in the molecule are promoted to a higher energy level. UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic

compounds, and biological macromolecules [6]. In figure 3.2 presents schematic of wavelength selectable single –beam uv-vis spectroscopy.



Figure 3.2: Ultraviolet-visible spectroscopy.

# **3.6.1.3.** X-ray diffraction spectroscopy

X-ray diffraction discovers the geometry or shape of a molecule using X-ray diffraction techniques which is based on the elastic scattering of X-rays from structures that have long range order. The single-crystal X-ray diffraction is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules such as proteins. Powder diffraction (powder or polycrystalline X-ray diffraction, PXRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data [7]. Powder diffraction is also a common method

for determining strains in crystalline materials. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper K $\alpha$ 1 radiation of wavelength ( $\lambda = 1.540598$ ) and K $\alpha$ 2 radiation of wavelength ( $\lambda = 1.544426$ ). Scan speed of 1 s/step and a step size of 0.03°. Figure 3.3. Displayed the X-ray diffraction pattern formed when X-rays are focused on a crystalline material, and a representative spectrum obtained.



Figure 3.3: (a) X-ray diffraction pattern formed when x-rays are focused on a crystalline material.

# **3.6.1.4.** Energy dispersive spectroscopy (EDS)

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the study of an interaction of some source of X-ray excitation and a sample. Its depiction capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be recognized individually from one another.

To excite the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons is focused into the sample being studied. Initially an atom within the sample contains ground state electrons in discrete energy levels or electron shells bound to the nucleus. When the incident beam excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole. The difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. Therefore this allows the elemental composition of the specimen to be measured. The EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope.



Figure 3.4: Simple representation of first three shells presentation, (a) the formation of energy dispersive X-ray resulting in (b) a distinctive spectrum [8].

## 36.1.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterize an extensive variety of materials. TGA is a widely used analytical method for determining changes in the mass of a material as a function of temperature. It provides a measure of the reaction kinetics associated with structural decomposition, oxidation, corrosion, and moisture adsorption/desorption, and gas evolution [9]. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent.

TGA comprise an automatic balance onto which the sample is loaded. The pan containing the sample is encapsulated by a furnace as shown in scheme 3.4, which is heated from room temperature to about 1000°C at a heating rate of 5-10°C per minute. The sample is continuously weighed while being heated to higher temperatures and the mass loss is recorded as function of temperature. The analysis was done on STA 6000 simultaneous thermal analyser from PerkinElmer. While Scheme 3.5 shows the scheme of a thermo gravimetric analyser.



Scheme 3.4: Scheme of a TGA furnace



Scheme 3.5: Shows the scheme of a thermogravimetric analyzer.
#### **3.6.1.6.** Raman spectroscopy

Raman spectroscopy is a spectroscopic technique used to study rotational, vibrational and other low-frequency modes in a system. The operation of the Raman spectroscopy is as follows, the sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line are filtered out while the rest of the collected light is dispersed onto a detector.

There are a number of advanced types of Raman spectroscopy, including surface-enhanced Raman, resonance Raman, tip-enhanced Raman, polarized Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially-off set Raman, and hyper Raman.

The Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40 attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected by means of back scattering geometry with an acquisition time of 50 seconds

#### **3.6.2.** Microscopy

Microscopy is the technical field of using microscopy to view objects or sample surfaces. There are three common branches of microscopy such as optical, electron and scanning probe microscopy. Optical and electron microscopy involve the diffraction, reflection or refraction of electromagnetic radiation/ electron beam interaction with the study, and the subsequent collection of this scattered radiation in order to build up an image. While the scanning probes microscopy involves the interaction of a scanning probe with the surface or object of interest.

In the microscopy techniques, the scanning electron microscopy (SEM) is discussed with further details due to it is used in this study but the transmission electron microscopy (TEM) and atomic force microscopy are not given any further discussion.

### 3.6.2.1. Scanning electron microscopy (SEM)

A scanning electron microscopy (SEM) is a potent microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity [10].



Scheme 3.6: Schematic diagram of an SEM

The operation of SEM is as follows: at the top of a SEM column an electron beam is emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. The electron beam, has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot with 0.4 to 5nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface [11]. After that the image may be captured by photography from a high- resolution cathode ray tube, or computer monitor. The surface morphology measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope.

The results obtained for the analysis of these instruments mentioned above will be discussed in chapter four.

## References

- 1. S. Ndwandwe, P. Tshibangu, E.D. Dikio, Int. J. Electrochem. Sci. 2011, 6, 749-760.
- M. Shokouhimehr, E.S. Soehnlen, A. Khitrin, S. Basu, S.D. Huang, *Inorg. Chem.* Commun. 2010, 13, 58-61.
- 3. S. Han, Y. Chen, R. Pang, P. Wan, Ind. Eng. Chem. Res. 2007, 46, 6847-6851
- A.O. Gorman, G. Downey, A.A. Gowen. C. Barry-Ryan, J. Frias, J. Agri .Food. Chem.
  2010, 58, 13, pp 7770-7776.
- F.R. Van de voort, J. Sedman, A.A. Ismail, *Food. Chem.* 1993, Volume 48, Issue 2, 213-221,
- The Free Encyclopedia, http://en.wikipedia.org/wiki/Ultraviolet spectroscopy (accessed online) 24 April 2012.
- The Free Encyclopedia, http://en.wikipedia.org/wiki/x-ray-diffraction (accessed online) 16 Jan, 2012.
- L. Corbari, M.A. Cambon-Bonarita, G.J. Long, F. Grandjean, M. Zbinden, F. Gaill, P. Compere, *Biogeoscience*. 2008, 5, 1295-1310.
- 9. E. Mansfield, A. Kar, T.P. Quinn, S.A. Hooker, Anal. Chem. 2010, 82, 9977-9982.
- 10. The free Encyclopedia, http://en.wikipedia.org/ scanning electron microscopy (accessed on line) 30 Jan, 2012.
- C.A. Gervasi, P.E. Alvarez, M.V. Fiori Bimbi, M.E. Folquer, J. Electroanal. Chem. 2007, 601, 194-204.

# **CHAPTER FOUR:**

# **RESULTS AND DISCUSSION**

## **4.1 Introduction**

Results obtained from this study are presented and discussed in this chapter. This includes the results for the characterization of Prussian blue nanoparticles using Fourier transform infrared spectroscopy (FT-IR), Ultraviolet-visible spectroscopy (UV-Vis), X-ray diffraction spectroscopy (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and thermogravimetric analysis. Electrochemical determinations of hydrogen peroxide and dopamine hydrochloride using modified electrodes as a working electrode employed both cyclic and square wave voltammetry are presented.

### 4.2 Characterization of Prussian blue nanoparticles

Prussian blue nanoparticles were synthesized from iron(III) chloride or iron(III) nitrate and potassium ferrocyanide. The Fourier transform infrared spectra of synthesized Prussian blue nanoparticles before and after drying are presented in figure 4.1. The analysis were confirmed on a Perkin Elmer instrument, spectrum 400 FTIR/FT-NIR spectrometer. The particularity of this instrument is that no sample holder (KBr plate) is needed or a particular substance such as nujol. The sample was analyzed by placing it directly on top of the detector. The spectra were measured in the range of 4000.0 -650.0 cm<sup>-1</sup>. The spectrum of Prussian blue before drying shows a strong broad band at 3336 cm<sup>-1</sup> which is assigned to stretching modes of O-H group and H-O-H bending mode of water. This band shows that water molecules in the Prussian blue is coordinated in the shell of high spin iron or occupying interstitial positions as uncoordinated water. The sharp peak at 2077 cm<sup>-1</sup> is a characteristic of Fe-CN bond and it is also linked to the stretching vibration of Fe-CN. The strong peak at 2057 cm<sup>-1</sup> is a characteristic vibrational peak of PB which is attributed to the stretching vibration of the CN group. The FT-IR of dried PB nanoparticle show a reduced broad band at 3325 cm<sup>-1</sup> indicating the removal of water



Figure 4.1: Fourier Transform infrared (FTIR) spectra of (a) Prussian blue, before and after drying.

The Fourier transforms infrared spectra of the PB/MWCNT, PB/CTAB and PB/GO composites were presented in figure 4.2 (a, b and c). Figure 4.2, (a and b) shows a broad band centered at 3350 cm<sup>-1</sup> and a sharp peak at 1637 cm<sup>-1</sup>. So the two peaks are assigned to the presence of OH and CN group in the nanocomposites respectively. While figure 4.2, (c) Shows a broad band centered at 3325 cm<sup>-1</sup> and sharp peak at 1637 cm<sup>-1</sup> which is also assigned the presence of OH and CN group in the nanocomposite formed. Therefore the presence of these two bands in the three composite further demonstrates the successful formation of the composites.

Selected FT-IR bands of MWCNT-PB, GO-PB and CTAB-PB in wave number (cm<sup>-1</sup>) were show in the table 4.1.

MWCNT-PB	GO-PB	СТАВ-РВ	Assignment
3350.87cm <sup>-1</sup>	3350.54cm <sup>-1</sup>	3325.89cm <sup>-1</sup>	<i>V</i> (OH group) of water
1637.43cm <sup>-1</sup>	1637.11cm <sup>-1</sup>	1637.22cm <sup>-1</sup>	V(CN group)







Figure 4.2: Fourier transforms infrared (FT-IR) spectra of MWCNT-PB (a), GO-PB (b) and CTAB-PB (c) composites.

Ultraviolet-visible absorption spectroscopy is used for the analysis of molecules that absorb ultraviolet and visible light (photons). The UV visible spectra of Prussian blue (PB), GO-PB, CNT-PB and CTAB-PB are presented in figure 4.3 (a, b, c & d). The spectra of Prussian blue shows that the characteristic absorption band of Prussian blue at 720 nm is due to charge transfer between Fe<sup>3+</sup> and Fe<sup>2+</sup> ions. Figure 4.3 (b & c), the composite spectra of GO-PB and CNT-PB show two peaks at 430 nm and 720 nm. The absorbance of the GO-PB and CNT-PB at 710 nm is lower suggesting that the presence of graphene oxide and carbon nanotube materials within the composite affect the absorbance of PB. The composite spectra of CTAB-PB, figure 4.3, show a peak at 430 nm due to Prussian blue has disappeared. The absorbance of Prussian blue is shifted downfield after using those materials.









Figure 4.3: UV- visible spectra of PB (a) GO-PB, (b) CNT-PB, (c) CTAB-PB, (d)

X-ray diffraction (XRD) spectra of Prussian blue nanoparticles are presented in figure 4.4. The X-ray diffraction discovers the geometry or shape of a molecule using X-ray diffraction techniques based on the elastic scattering of X-rays from structures that have long range order. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper Ka1 radiation of wavelength ( $\lambda = 1.540598$ ) and Ka2 radiation of wavelength ( $\lambda = 1.544426$ ). Scan speed of 1 s/step and a step size of 0.03°. The spectra show diffraction peaks at 17.38, 24.60, 35.18 and 39.25 which can be allocated to the Prussian blue phase (200, 220, 222 and 400) crystal planes respectively. These peaks can be related into face-centered cubic structure of PB with space group *Fm3m*. the result has agreement with literature. The two spectra have shown same space group.





Figure 4.4: The XRD Spectra of Prussian blue nanoparticle iron(III) Chloride (a) and iron(III) nitrate (b).

Energy dispersive spectroscopy (EDS) spectra of Prussian blue nanoparticles are presented in figure 4.5. The Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDS spectra of synthesized Prussian blue nanoparticles figure 4.5 (a), indicate the presence of elemental carbon, oxygen, potassium, iron and chlorine for the Prussian blue nanopartciles synthesized  $K_4$ [Fe(CN)<sub>6</sub>].3H<sub>2</sub>O with FeCl<sub>3</sub>.6H<sub>2</sub>O and carbon, oxygen, potassium, iron for the nanoparticles prepared  $K_4$ [Fe(CN)<sub>6</sub>].3H<sub>2</sub>O with Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O figure 4.5 (b). This confirms the successful synthesis of Prussian blue nanoparticles.





Figure 4.5: The EDS Spectra of Prussian blue iron(III) chloride (a) and iron(III) nitrate (b)

Scanning electron microscopy (SEM) is a potent microscope that images a sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. Scanning electron microscopy (SEM) image of Prussian blue nanoparticles is presented in figure 4.6. The SEM was used to determine the particle size distribution of the as-synthesized Prussian blue nanoparticles. The SEM images at 100  $\mu$ m show the PB as aggregates of nanoparticles of high dimension with no precise shape. The two spectra differ with respect to the particle size distribution. In spectrum (a), unordered crystals are observed, while spectrum (b) shows little uniformed particles.





Figure 4.6: The SEM Spectra of Prussian blue nanoparticles iron(III) chloride (a) and iron(III) nitrate (b)

Raman spectroscopy is a spectroscopic technique used to study rotational, vibrational and other low-frequency modes in a system. Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40 attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected by means of back scattering geometry with an acquisition time of 50 seconds. The Raman spectra of synthesized Prussian blue nanoparticles are presented in figure 4.7. The spectra of Prussian have shown a strong vibrational band at 2154.96 cm<sup>-1</sup> caused by the stretching vibration of carbon nitrogen triple bond group of Prussian blue. Where the other peaks at 1254.35, 507.47 and 275.49 cm<sup>-1</sup> are expected to have relation to the presence of co-precipitated ferricyanide ion. The both spectra have similar identification peaks which support the synthesis of Prussian blue was done in a good condition.





Figure 4.7: The Raman Spectra of Prussian blue nanoparticles iron(III) chloride (A) and iron(III) nitrate (B)

Thermogravimetric spectra of Prussian blue synthesized from iron(III) chloride or iron(III) nitrate are presented in figure 4.8 (a and b). TGA is a widely used analytical method for determining changes in the mass of a material as a function of temperature. It provides a measure of the reaction kinetics associated with structural decomposition, oxidation, corrosion, and moisture adsorption/desorption, and gas evolution. The TGA measurements show three weight loss regions, the first region started at 65°C and continued to 160°C. Due to this temperature range is characteristic for the evaporation of water molecules at different position in the PB structure. The second region ranges from 480 to 530°C which can be assigned to the cyanide decomposition of PB. While the last regions at 624°C and above could be due to the decomposition of sample impurities.





Figure 4.8: The thermogravimetric Spectra of Prussian blue nanoparticles iron(III) chloride (a) and iron(III) nitrate (b).

# 4.3. Cyclic voltammetry investigations

Electrochemical properties of bare-GC, GC-PB, GC-WMCNT, GC-MWCNT-PB, GC-GO, GC-GO-PB, GC-CTAB and GC-CTAB-PB electrodes were studied in 0.1M phosphate buffer solution at different pH values, recorded between -250 to 500 mV at scan rate of 100 mV/s. The cyclic voltammograms of bare GC electrode in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.9 (a and b). The overlay of the electrode response in the absence or presence of hydrogen peroxide is presented in figure 4.9 (c). as can be seen a small anodic response is observed. The bare GC electrode does not have the ability to detect hydrogen peroxide.







Figure 4.9: Cyclic voltammograms of bare-GC electrode (a) absence and (b) presence of  $25\mu l H_2O_2$  in 0.1M PBS and (c) overlay of the two.

Cyclic voltammograms of Prussian blue modified glassy carbon electrode (GC-PB) in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution at pH 3, pH 5.12 and pH 7.4 are presented in figure 4.10. It is well known that Prussian blue has certain intrinsic peroxidase activity due to its close similarity with peroxidase, thus it can be engaged to catalyze the reduction of hydrogen peroxide. The GC-PB electrode in the absence of hydrogen peroxide is in figure 4.10 (a). does not show any electrochemical response at pH 5.12 and pH 7.4, while at pH 3 anodic and cathodic responses are observed. In the presence of hydrogen peroxide, in figure 4.9 (b), responses are observed at all mediums. The highest response at pH 3 and the lowest response are observed at pH 7.4. The high response at pH 3 is due to the fact that at high pH range, Prussian blue diminishes its stability. However it has been reported that problems caused by leaching of PB in to solution phase will always be encountered after a few scans at neutral pH because of the relatively weak combination between bare electrode and PB [1-2]. To

overcome this problem, it is important to enhance the electrochemical stability of PB film. It is desirable to use some electroactive materials to stabilize the electrochemical properties of PB.





Figure 4.10: Cyclic voltammograms of GC-PB electrode (a) in the absence and (b) in the presence of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS.

The cyclic voltammograms of glassy carbon electrode modified carbon nanotubes (GC-MWCNT) in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.11 (a and b). The overlay of the electrode response in the absence and presence of hydrogen peroxide is presented in figure 4.11 (c).the voltammograms show no significant change in response resulting from the modification of GC electrode with carbon nanotube.







Figure 4.11: Cyclic voltammograms of GC-CNT electrode (a) before and (b) after injection of 25µl H<sub>2</sub>O<sub>2</sub> in 0.1M PBS pH 7.4. (c) Overlay of the two.

Cyclic voltammograms of GC-MWCNT-PB electrode in the absence or presence of hydrogen peroxide in 0.1M phosphate buffer solution at pH 3, pH 5.12 and pH 7.4 are presented in figure 4.12. In the absence of hydrogen peroxide, figure 4.12(a), electrochemical responses are observed at pH 5.12 and 7.4 with a very negligible response observed at pH 3. The anodic response at pH 5.12 and 7.4 are very significant with the peak at pH 5.12 higher than at pH 7.4. The cathodic responses at pH 5.12 and 7.4 are very significant but less than the anodic response. On the other hand, in the presence of hydrogen peroxide, figure 4.12(b), electrochemical cathodic and anodic response is observed at pH 7.4. These results indicate that the presence of multi-walled carbon nanotubes have significantly enhanced the electrochemical stability of PB as well as its detection of hydrogen peroxide. The extraordinary stability of the MWCNT/PB hybrid composite film could be due to the  $\pi$ - $\pi$  stacking interaction between carbon atoms in the carbon nanotubes (carboxyl moieties) through ionic interaction [3].





Figure 4.12: Cyclic voltammograms of GC-MWCN-PB electrode (a) before and (b) after injection of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

Cyclic voltammograms of glassy carbon electrode modified graphene oxide (GC-GO) in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.13 (a & b). The overlay of the electrode response in the absence and presence of hydrogen peroxide is presented in figure 4.13 (c), as can be seen no response is observed. This is because graphene oxide modified GC electrode does not detect hydrogen peroxide at low potentials.







Figure 4.13: Cyclic voltammograms of GC-GO electrode (a) before and (b) after injection of 25μl H<sub>2</sub>O<sub>2</sub> in 0.1M PBS pH 7.4. (c) Overlay of the two.

Cyclic voltammograms of GC-GO-PB electrode in the absence or presence of hydrogen peroxide in 0.1M phosphate buffer solution at pH 3, pH 5.12 and pH 7.4 are presented in figure 4.14. In the absence and presence of hydrogen peroxide, anodic and cathodic responses are observed at pH values. The highest response is observed at pH 7.4 and lowest in acidic medium at pH 3. The cathodic response on the other hand is more pronounced at pH 5.12. In the presence of hydrogen peroxide figure 4.14 (b), GC-GO-PB electrodes produce both anodic and cathodic responses. Two anodic and cathodic peaks are observed at pH 7.4 indicating two electron transfer reactions taking place. At pH 5.12 the electron reaction fizzled away showing that the presence of hydrogen peroxide has adversely affected the anodic response previously observed. For GC-GO-PB electrode, this is a conversion of a  $sp^2$  to  $sp^3$  bond in graphene. These results indicate that the presence of graphene oxide is considerably enhanced the electrochemical stability of PB film and its detection of hydrogen peroxide in wide range of pH.





Figure 4.14: Cyclic voltammograms of GC-GO-PB electrode (a) before and (b) after injection of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

Cyclic voltammograms of glassy carbon electrode modified cetyltrimethylammonium bromide (GC-CTAB) in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.15 (a and b). The overlay of the electrode response in the absence and presence of hydrogen peroxide is presented in figure 4.15 (c). In the absence and presence of hydrogen peroxide two redox peaks are observed in the voltammograms which indicates transfer that electron took place in the processes. This indicates cetyltrimethylammonium bromide modified glassy carbon electron has the ability to detect hydrogen peroxide at low potentials value.







Figure 4.15: Cyclic voltammograms of GC-CTAB electrode (a) before and (b) after injection of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS pH 7.4 (c) Overlay of the two.

Cyclic voltammograms of GC-CTAB-PB electrode in the absence or presence of hydrogen peroxide in 0.1M phosphate buffer solution at pH 3, pH 5.12 and pH 7.4 are presented in figure 4.16. In the absence of hydrogen peroxide, two redox pair of responses are observed at pH 7.4, while at pH 5.12 and pH 3 show one redox response. In the presence of hydrogen peroxide, in figure 4.16 (b), GC-CTAB-PB electrodes show redox responses at all pH values. pH 7.4 has best value of redox responses. Cationic surfactant of cetyltrimethylammonium bromide have influence the formation of Prussian blue film and improves the reversibility of its redox reaction. So these results are in agreement with previous literature [4].





Figure 4.16: Cyclic voltammograms of GC-CTAB-PB electrode (a) in the absence and (b) in the presence of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

# 4.4. Square wave voltammetry investigations

Electrochemical properties of GC-MWCNT, GC-GO, GC-CTAB, GC-PB, GC-MWCNT-PB, and GC-GO-PB and GC-CTAB-PB electrodes were studied in 0.1M phosphate buffer solution at different pH values, using square wave voltammetry recorded between -700 mV to 700 mV with amplitude of 10 mV.

Square wave voltammograms of glassy carbon electrode modified carbon nanotubes (GC-MWCNT) in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.17 (a and b). Their overlay is in figure 4.17 (c). Therefore these results are in agreement with cyclic voltammetry results presented in figure 4.11. For GC-CNT, electrode no responses were observed, both in the absence and presence of hydrogen peroxide.







Figure 4.17: Square wave voltammograms of GC-CNT electrode (a) before and (b) after injection of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS pH 7.4. (c) Overlay of the two.

Square wave voltammograms of glassy carbon electrode modified graphene oxide (GC-GO) before and after injected  $H_2O_2$  in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.18 (a and b). Their overlay is in figure 4.18 (c). These results are in agreement with cyclic voltammogram results presented in figure 4.13, for GC-GO, in which no responses were observed both in the absence and presence of hydrogen peroxide.







Figure 4.18: Square wave voltammograms of GC-GO electrode (a) before and (b) after injection of 25µl H<sub>2</sub>O<sub>2</sub> in 0.1M PBS pH 7.4 (c) Overlay of the two.

Square wave voltammograms of glassy carbon electrode modified cetyltrimethylammonium bromide (GC-CTAB) in the absence and presence of hydrogen peroxide in 0.1M phosphate buffer solution pH 7.4 is presented in figure 4.19 (a and b). Their overlay is in figure 4.19 (c). In the absence and presence of hydrogen peroxide two redox responses are observed in the process. For GC-CTAB electrode which shows electron transfer took place. These results are in relation with cyclic voltammetry results presented in figure 4.15, due to cetyltrimethylammonium bromide modified on glassy carbon electrode has ability to detect hydrogen peroxide at that potential.







Figure 4.19: Square wave voltammograms of GC-CTAB electrode (a) before and (b) after injection of  $25\mu l H_2O_2$  in 0.1M PBS pH 7.4 (c) Overlay of the two.

Square wave voltammetry of Prussian blue modified glassy carbon electrode (GC-PB) before and after injected  $H_2O_2$  in 0.1M PBS at pH 3, pH 5.12 and pH 7.4 are presented in figure 4.20 (a and b). GC-PB electrode in the absence of hydrogen peroxide is figure 4.20 (a). Does not show any significant electrochemical response at pH 5.12 and pH 7.4 while at pH 3, a high anodic responses is observed. The high response current at pH 3, is observed around 0.12V while at pH 5.12 and pH 7.4 no responses were observed at 0.03 and -0.06V respectively. In the presence of hydrogen peroxide, figure 4.20 (b), anodic response is observed at pH 3 giving rise to a small shoulder peak.





Figure 4.20: Square wave voltammograms of GC-PB electrode (a) before and (b) after injection of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

Square wave voltammetry of GC-CNT-PB before and after injection of  $H_2O_2$  in 0.1M PBS at pH 3, 5.12 and 7.4 are presented in figure 4.21 (a and b). In figure 4.21 (a), in the absence of hydrogen peroxide, show anodic response at pH 3, pH 5.12 and pH 7.4, at pH 7.4, two peaks are observed at -0.1V and 0.19V respectively. At pH 3 one peak is observed at 0.12V, while at pH 5.12 a very small peak is observed at 0.26V. In the presence of hydrogen peroxide, anodic responses are observed at pH 3 and pH 7.4 but very small at pH 5.12. At pH 7.4, the peak at -0.1V did not change while the peak at 0.19V show a reduced current. At pH 3 the anodic peak at 0.12V increased, while at pH 5.12 there was no change in potential. These results indicate that GC-CNT-PB could detect the presence of hydrogen peroxide at all mediums but significantly at pH 3 and pH 7.4.




Figure 4.21: Square wave voltammograms of GC-CNT-PB electrode (a) before and (b) after injection of 25µl H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

Square wave voltammetry of GC-GO-PB before and after injection of  $H_2O_2$  in 0.1M PBS at pH 3, 5.12 and 7.4 are presented in figure 4.22 (a & b). In the absence of hydrogen peroxide, figure 4.22 (a), anodic and cathodic current responses are observed. The highest response is observed at pH 7.4, while at pH 3 and pH 5.12, low anodic responses are observed respectively. At pH 5.12, a small but significant cathodic response is observed at potential of 0.6V. In the presence of hydrogen peroxide, figure 4.22 (b), the GC-GO-PB electrode again produces a high current response with a peak at about -0.1V. Two anodic peaks at 0.15Vand 0.4V are observed at pH 3. The cathodic peak at a voltage of 0.5 at pH 5.12 is seen to have increased.





Figure 4.22: Square wave voltammograms of GC-GO-PB electrode (a) before and (b) after injection of  $25\mu$ l H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

Square wave voltammetry of Prussian blue modified glassy carbon electrode (GC-CTAB-PB) before and after injection of  $H_2O_2$  in 0.1M PBS at pH 3, pH 5.12 and pH 7.4 are presented in figure 4.23 (a and b). In figure 4.23(a), in the absence of hydrogen peroxide anodic responses are observed at all pH values, (0.05, 0.17 and 0.1) V at pH (7.4, 5.12 and 3) respectively. The strongest anodic response was observed at pH 7.4. In the presence of hydrogen peroxide, in figure 4.23 (b) also show anodic responses at all pH values, but the potential values and current

were changed by a small value. At pH 5.12 the potential is decreased from 0.17V to 0.07V, at pH 7.4 is increased from 0.05V to 0.07, while pH 3 is unchanged. These results indicate that the cationic surfactant at cetyltrimethylammonium bromide was successful coated on Prussian blue film at the electrode surface. Therefore GC-CTAB-PB electrode could detect hydrogen peroxide at all pH mediums.





Figure 4.23: Square wave voltammograms of GC-CTAB-PB electrode (a) before and (b) after injection of 25µl H<sub>2</sub>O<sub>2</sub> in 0.1M PBS with different pH.

### 4.5. Cyclic voltammetry investigations

Electrochemical determination of dopamine using different modified glassy carbon electrode Bare-GC, GC-PB, GC-GO-PB, GC-CNT-PB and GC-CTAB-PB electrode using 0.01M dopamine solution recorded between -250 mV to 500 mV at scan rate of 100 mV/s.

Cyclic voltammograms of bare-GC and glassy carbon electrode modified with Prussian blue (GC-PB) are presented in figure 4.24 (a and b). The cyclic voltammograms obtained on the bare GC electrode show electron transfer kinetics for redox reaction of dopamine (DA). Small anodic peaks are observed. After modification of the electrode with Prussian blue the electrochemical response to dopamine at GC-PB show a redox couple which is shown in figure 4.21 (b). This indicates that the bare-GC is a poor electrode compared to GC-PB for detection purpose.



Figure 4.24: cyclic voltammograms of Bare-GC (a) and GC-PB (b) in 0.01M dopamine solution.

Cyclic voltammograms of GC-CNT-PB, GC-GO-PB and GC-CTAB-PB are presented in figure 4.25 (a to c). The voltammograms obtained for GC-CNT-PB electrode, in figure 4.25 (a), show two small anodic and cathodic peaks at -0.1 and 0.4 V as anodic response, while -0.08 and 0.48 V as cathodic. This indicate a two electron transfer process, the possibility of the two electron redox process is envisaged from the  $sp^2$  hybridized carbon of the carbon nanotubes. This could also be due to the  $\pi$ - $\pi$  stacking interaction between carbon atoms in the carbon nanotubes and the –CN group of Prussian blue. The voltammogram obtained for GC-GO-PB electrode, figure 4.25 (b), show a broad anodic peak centered at 0.0 V and two small cathodic peaks at 0.1 V and 0.5 V respectively. The voltammogram obtained for GC-CTAB-PB electrode, figure 4.25 (c), indicate that anodic and cathodic responses are observed.







Figure 4.25: Cyclic voltammograms of GC-CNT-PB (a), GC-GO-PB (b), and GC-CTAB-PB(c) in 0.01M dopamine solution.

### 4.6. Square wave voltammetry investigations

Electrochemical determination of dopamine using different modified glassy carbon electrode GC-PB, GC-GO-PB, GC-CNT-PB and GC-CTAB-PB electrode using 0.01M dopamine solution were recorded between -700 mV to 700 mV with amplitude of 10 mV.

Square wave voltammograms of glassy carbon electrode modified with Prussian blue (GC-PB) and GC-CNT-PB are presented in figure 4.26 (a and b). The voltammograms obtained for GC-PB electrode show two small peaks at -0.6V and 0.2V which indicates two electron transfers took place in the process. These electrons could originate from lone pairs of electrons on the CN group on nitrogen atom of PB. This confirms the observed two electron process in the CV of GC-PB. The voltammograms obtained for GC-CNT-PB electrode also show two peaks at 0.2V and 0.6V.





Figure 4.26: Square wave voltammograms of GC-PB (a) and GC-CNT-PB (b) in 0.01M dopamine solution.

Square wave voltammograms of GC-GO-PB and GC-CTAB–PB are presented in figure 4.27 (a and b). The voltammogram, figure 4.27 (a), show two anodic peaks which are centered at -0.5V and 0.1V. The observation of peaks in this square wave-voltammogram is in agreement with our observation of two peaks in cyclic voltammogram of GC-GO-PB, figure 4.25(b).

The voltammogram for GC-CTAB-PB figure 4.27 (b) shows a single peak centered at 0.2V. The presence of one peak indicates a one electron reaction in the process. This observation is in agreement with our previous observation in figure 4.25 (c).





Figure 4.27: Square wave voltammograms of GC-GO-PB (a) and GC-CTAB-PB (b) in 0.01M dopamine solution. .

## References

- 1. L. Lin, X. Huang, L. Wang, A. Tang, Solid. State. Sci. 2010, 12, 1764-1769.
- J. Bai, B. Qi, J.C. Ndamanisha, L.P. Guo, *Micropor. Mesopor. Mater.*2009, 119, 193-199.
- 3. J. Zhang, J.K. Lee, Y. Wu, R.W. Murry, Nano. Lett. 2003, 3, 403-411.
- D.J. Yang, C.Y. Hsu, C.L. Lin, P.Y. Chen, C.W. Hu, R. Vittal, K.C. Ho, Solar. Energy. Mater. Solar cells. 2012, 99, 129-134.

# **CHAPTER FIVE:**

# CONCLUSION

#### 5.1 Conclusion

The objectives of this research were to synthesize Prussian blue nanoparticles, to characterize it using by Fourier transform infrared spectroscopy, Ultraviolet-visible spectroscopy (UV-Vis) X-ray diffraction spectroscopy (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA). To determine the improvement of Prussian blue modified on glassy carbon electrodes, and when promoted by multi-wall carbon nanotubes, graphene oxide and cetyltrimethylammonium bromide coated the Prussian blue on the surface of the electrode to enhance its electrochemical stability for a wide range of pH. To determine the electrocatalytic ability of modified electrodes towards the detection of hydrogen peroxide and dopamine hydrochloride. This study was successfully done and the following conclusions have been drawn from the results obtained.

The synthesis of Prussian blue nanoparticles was done by a simple method at ambient condition.

- The spectra obtained from Fourier transform infrared spectroscopy (FT-IR) confirmed that the functional groups of the synthesized Prussian blue nanoparticles have OH group at 3336 cm<sup>-1</sup> and CN group at 2077 cm<sup>-1</sup> in agreement with previous literature record
- The X-ray diffraction (XRD) confirmed that the crystallographic structure of Prussian blue nanoparticle which has a face centered cubic structure with space group of *fm3m* while the energy dispersive spectroscopy (EDS) indicated the presence of elemental composition of the synthesized Prussian blue nanoparticles.
- > SEM image has shown aggregated nanoparticle of high dimension with no precise shape.
- The TGA data shows, three weight loss regions which indicates characteristics of evaporation of water molecules at different position in the PB structure and cyanide decomposition.

All these results obtained from different techniques show that Prussian blue nanoparticles were successful synthesized.

The improvement of Prussian blue modified on glassy carbon electrode was investigated taking the following steps.

- Layers of PB were successfully deposited by a sequential deposition method on glassy carbon electrode surface and used as mediators with carbon nanotubes (CNT) graphene oxide (GO) and cetyltrimethylammonium bromide (CTAB). The applicability of GC-PB, GC-CNT-PB, GC-GO-PB and GC-CTAB-PB electrodes for their detection of hydrogen peroxide was examined at different pH of 0.1M phosphate buffer solution in the presence or absence of hydrogen peroxide. The results show that GC-PB electrode provided better responses in the absence or presence of hydrogen peroxide in acidic media (pH 3) than the neutral (pH 5.12 and pH 7.4) for both cyclic and square wave voltammetry. PB in basic or neutral media loses its stability resulting in the Prussian blue leaching into the analyte.
- Carbon nanotubes (CNTs), graphene oxide (GO) and cetyltrimethylammonium bromide (CTAB) were used to stabilize Prussian blue on the surface of glassy carbon electrode. GC-CNT-PB, GC-GO-PB and GC-CTAB-PB electrodes gave good responses for the detection of hydrogen peroxide in acidic and neutral mediums. The use of these substances enhanced the property of the electrode to detect hydrogen peroxide. The stability of Prussian blue at pH 3, 5.12 and 7.4 with a high response current for the detection of hydrogen peroxide were achieved. GC-CTAB-PB electrode produced a significant detection of hydrogen peroxide with respect to the other electrodes.