



Universiti Malaysia
KELANTAN

HYDROTHERMAL SYNTHESIS OF SILVER-REDUCED GRAPHENE OXIDE (Ag-rGO) FOR DETERMINATION OF MERCURY ION (Hg^{2+})

by

NURUL AFIQAH BINTI MOHD MOKHTAR

A report submitted in fulfillment of the requirements for the degree of Bachelor of Applied Science (Materials Technology) with Honours

**FACULTY OF EARTH SCIENCE
UNIVERSITI MALAYSIA KELANTAN**

2017

DECLARATION

I declare that this thesis entitled “Hydrothermal Synthesis of Silver-Reduced Graphene Oxide (Ag-rGO) for Determination of Mercury Ion (Hg^{2+})” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : _____

Name : Nurul Afiqah Binti Mohd Mokhtar

Date : 5th January 2017

UNIVERSITI
MALAYSIA
KELANTAN

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful.

Alhamdulillah, all praises to Allah for the strength and His blessing in completing this final year project. Special appreciation goes to my supervisor, Mr. An'amt Mohamed Noor for his supervision and constant support. His invaluable help of constructive comments and suggestions throughout the thesis works have contributed to the success of this research. Not forgotten his invaluable comments, sharing of knowledge on experimental method and theory of this topic have helped me to complete this final year project.

Moreover, I am also bond to offer my gratitude to Dr Azwadi Sulaiman and Mrs. Nik Alnur Auli Nik Yusuf for their guidance to assist me as an examiner in fulfilling my task. Their willingness and support by sharing their knowledge to carry out my study help to complete my final year project.

Last but not least, my deepest gratitude goes to my beloved parents Mr. Mohd Mokhtar Abd Latif and Mrs. Roslawati Alias for the endless love, prayers and encouragement. Special thanks to those who indirectly contributed their time, idea, energy and more in this research, your kindness means a lot to me. Thank you very much.

Hydrothermal Synthesis of Silver-Reduced Graphene Oxide (Ag-rGO) for Determination of Mercury Ion (Hg^{2+})

ABSTRACT

This study describes the hydrothermal treatment synthesis of a silver-reduced graphene oxide (Ag-rGO) for the determination of mercury (II) ion (Hg^{2+}). The nanocomposite was analysed by using UV-visible absorption spectra, fourier transform infrared spectroscopy (FTIR), X-ray Diffraction (XRD) and transmission electron microscope (TEM) analyses. The results indicate that the silver nanoparticles were successfully composited on the graphene sheets after the given hydrothermal treatment which distributed randomly on the surface of the graphene oxide (GO). The crystalline nature of nano silver within the composites was evidence through X-ray Diffraction (XRD) analysis which also showed that the GO for the AgNP-graphene oxide (Ag-GO) sample was completely reduced during the hydrothermal treatment of silver nanoparticles. While the surface morphology of prepared silver-reduced graphene oxide nanocomposites was characterized through transmission electron microscope (TEM). Mercury detection method was performed for the optical determination of Hg^{2+} . The color changes of the cloudy nanocomposite solution were observed during the determination of Hg (II). The Ag-rGO nanocomposite exhibited good selectivity towards the determination of Hg (II) in the presence of color changes compared to other environmentally relevant heavy metal ions.

UNIVERSITI
MALAYSIA
KELANTAN

Sintesis Hidroterma Perak-Grafen Oksida yang dikurangkan (Ag-rGO) untuk Penentuan Ion Merkuri (Hg^{2+})

ABSTRAK

Kajian ini menerangkan mengenai sintesis rawatan hidroterma daripada perak dan grafen oksida yang dikurangkan (Ag-rGO) bagi menentukan ion merkuri (II) (Hg^{2+}). Komposit nano yang diperolehi dianalisis dengan menggunakan analisis spektroskopi ultraungu-nampak, jelmaan fourier spektrometer inframerah (FTIR), pembelauan sinar-x (XRD) dan mikroskop elektron penghantaran (TEM). Keputusan eksperimen menunjukkan bahawa nanopartikel perak telah berjaya digubah dalam lembaran grafen selepas rawatan hidroterma yang diberikan serta diedarkan secara rawak pada permukaan grafen oksida (GO). Sifat nano kristal perak dalam komposit dapat dibuktikan melalui analisis pembelauan sinar-x (XRD) yang juga menunjukkan bahawa GO pada sampel nano partikel grafen oksida-perak (Ag-GO) telah dikurangkan sepenuhnya semasa rawatan hidroterma nanopartikel perak. Selain itu, morfologi permukaan nano komposit graphene oksida-perak yang dikurangkan dicirikan melalui mikroskop elektron penghantaran (TEM). Kaedah pengesanan merkuri telah dilaksanakan untuk penentuan optik ion merkuri. Perubahan warna nano komposit berwarna keruh diperhatikan dan dicatat semasa penentuan ion merkuri. Nano komposit grafen oksida-perak mempamerkan pemilihan yang baik ke arah penentuan Hg (II) dengan perubahan warna yang diberikan berbanding dengan ion logam berat lain.

UNIVERSITI
MALAYSIA
KELANTAN

TABLE OF CONTENTS

TITLE	PAGE
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iii
ABSTRAK	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	ix
LIST OF SYMBOLS	xi
CHAPTER 1 INTRODUCTION	
1.1 Background of Study	1
1.2 Problem Statement	5
1.3 Research Objectives	6
1.4 Expected Outcomes	7
1.5 Scope of Study	7
CHAPTER 2 LITERATURE REVIEW	
2.1 Fundamental of Graphene	8
2.1.1 Properties of Graphene	10
2.1.2 Preparation of Graphene	11
2.2 Graphene Oxide	12
2.2.1 Properties of Graphene Oxide	13
2.2.2 Preparation of Graphene Oxide	15
2.3 Reduced Graphene Oxide (rGO)	16
2.3.1 Processing Method of reduced Graphene Oxide (rGO)	17
2.3.2 Characterization of reduced Graphene Oxide (rGO)	17
2.4 Optical Sensor Application Towards Mercury Ion (Hg^{2+})	20
CHAPTER 3 MATERIALS AND METHODS	
3.1 Materials	22
3.2 Methods	22

3.2.1	Production of Graphene Oxide	22
3.2.2	Preparation of Ag-rGO by Hydrothermal Method	25
3.2.3	Optical Detection of Hg ²⁺	26
3.2.4	Analytical Method	26
CHAPTER 4 RESULT AND DISCUSSION		
4.1	Choice of Materials	28
4.2	Ultra Violet Visible Spectroscopy	28
4.3	FTIR Studies of Ag-rGO Nanocomposite	30
4.4	XRD Studies of Ag-rGO Nanocomposite	32
4.5	Transmission Electron Microscopy	34
4.6	Optical Determination of Hg ²⁺	35
CHAPTER 5 CONCLUSION		
5.1	Conclusion	37
5.2	Recommendation	38
REFERENCES		40
APPENDIX A		43
APPENDIX B		46

LIST OF FIGURES

No.	TITLE	PAGE
1.1	Schematic illustration of the reduction process of graphene and graphene/silver nanocomposites	3
1.2	FESEM images of GO/Ag nanocomposites with different Magnification	4
2.1	The two graphene sub-lattices (red and blue) and unit cell	9
2.2	Single crystal of CVD graphene on Cu	9
2.3	SEM images of Graphene Oxide	12
2.4	Oxidation of graphite to graphene oxide and reduction to reduced graphene oxide	16
2.5	Aberration-corrected TEM image of a monolayer of RGO	19
2.6	SEM images of rGO	19
2.7	Optical sensor observed for GO-Ag nanocomposite solution with the addition of 100 μM Hg(II) and 500 μM other heavy metal ions individually	20
3.1	Preparation of Graphene Oxide (GO)	23
3.2	The mixtures are put evenly into the centrifuge bottles	23
3.3	HCl is added to the mixture and balanced before put it into the centrifuge	24
3.4	The mixtures is washed with HCl followed by distilled water in the centrifuge until it reach pH value of 5	24
3.5	Stirred solution	25
3.6	Mixture of Ag and GO	25
3.7	The mixtures is put in the autoclave for hydrothermal treatment	26
3.8	Procedures that were conducted in this experiment	27
4.1	UV-visible absorption spectra of GO solution and Ag-rGO nanocomposite	30
4.2	FTIR patterns of GO and Ag-rGO nanocomposite	32

4.3	XRD patterns of GO and Ag-rGO nanocomposite	33
4.4	TEM images of GO-Ag nanocomposite with different magnifications (a–c) and particle size histogram (d)	34
4.5	TEM images of Ag-rGO nanocomposite at 100 nm magnification	35
4.6	Optical determination of mercury ion with GO-Ag nanocomposite (a) the colour before the addition of 200 μl Hg(II) ion (b) the color after the addition of 200 μl Hg(II) ion	36
4.7	The color of before and after addition of 200 μl metal ions; (a) Pb^{2+} , (b) Zn^{2+} and (c) Ni^{2+} into 2 ml of Ag-rGO nanocomposite solution	36

LIST OF ABBREVIATIONS

GO	Graphene Oxide
rGO	Reduced Graphene Oxide
Ag-rGO	Silver-reduced Graphene Oxide
AgNPs	Silver Nanoparticles
Hg ²⁺	Mercury(II) ion
Pb ²⁺	Lead(II) ion
Zn ²⁺	Zinc(II) ion
Ni ²⁺	Nickel(II) ion
PVC	Poly(vinyl chloride)
TDMAPP	Tetra(<i>p</i> -dimethylaminophenyl)porphyrin
LEED	Low Energy Electron Diffraction
CVD	Chemical Vapor Deposition
DGU	Density Gradient Ultracentrifugation
FGO	Functional Graphene Oxide
PC	Professional Component
EPD	Excessive Posting Disorder
GRM	Graphene-related Materials
FLG	Few Layered Graphene
XRD	X-Ray Diffraction

SEM	Scanning Electron Microscope
UV-Vis	Ultraviolet-Visible Spectroscopy
FT-IR	Fourier-transform Infrared
FE-SEM	Field Emission Scanning Electron
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
XPS	X-Ray Photoelectron
SPR	Surface Plasmon Resonance
rpm	Revolutions per minute

LIST OF SYMBOLS

$^{\circ}\text{C}$	Degree Celsius
θ	Theta
$^{\circ}$	Degree
μM	Micro Molar
mM	Milimolar
M	Molar
μl	Micro Litre
ml	Millilitre
L	Litre
nm	Nanometre
cm	Centimetre
$\%$	Percentage

UNIVERSITI
MALAYSIA
KELANTAN

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The usage of graphite had started 6000 years ago. It was started when the American in the Europe used it as pottery decoration and the research about graphene essentially an isolated single-atom plane of graphite, where it dates back to the 1960s when higher basal-plane conductivity of graphite intercalation compounds were discovered compared to the original graphite. In the late 20th century, the research of graphene has grown slowly with the hope to observe electrical properties from thin graphite or known as graphene layers while obtaining graphene was considered to be a formidable task in both theoretical and experimental aspect (Singh, Joung, Zhai, & Das, 2011).

Graphene is a single-atom-thick two dimensional carbon layer, comprised of sp^2 hybridized carbon. It has aroused considerable interest in developing a variety of novel composites due to its high surface area, high flexibility, high mechanical strength, electrical conductivity and exhibits great promise for potential applications in the fields of nanoelectronics, nanocomposites, super-capacitors and much electronics device. Furthermore, a polymeric matrix can significantly improve polymer properties such as mechanical, thermal, and flame retardancy by adding some graphene even at a very low concentration level (usually less than 5 %) (Han, Wang, Gao, Li, & Zhang, 2016). While

Avouris & Dimitrakopoulos (2012), stated that high hopes have been placed on graphene for technological applications in many areas because of its unique properties.

In 2004, the existence of graphene as the first freestanding 2D crystal is announced by a significant experiment based on an extremely simple principle. Since then, graphene has become one of the most important nanomaterials and already attracted worldwide attention in fundamental condensed matter physics and materials extending from the nano to macro-scopic scale (Xu & Gao, 2015). Recently, the chemically reduced graphene oxide (rGO) has been found to be a promising substrate for a uniform distribution of metal oxide nanoparticles. While it also been demonstrated to have excellent electrochemical conductivity, superior mechanical flexibility and remarkable stability that can be helpful for the fabrication of an efficient platform (Kumar, Sharma, Maji, & Dhar, 2016).

According to Sahu, Sarkar, Sahoo, Mohapatra, & Swain (2015), to explore the potential application of graphene-based materials, the metal nanoparticles (NPs) are explore to decorate grapheme sheets forming graphene-metal. It has already revealed that when incorporated into polymer or ceramic matrices, graphene can remarkably improve the properties of these host materials. In order to investigate the potential applications of graphene-based materials, graphene/inorganic nanocomposites, derived from the designing of graphene sheets with inorganic nanoparticles (NPs) such as metal, metal oxide and sulphide; are attracting more and more interest. While nano-sized inorganic particles and their composites display very interesting chemical and physical properties behave as a messenger for a new class of materials towards the development of novel devices, which have a wide range of applications.

In this way, introduction of various nanoparticles into a graphene-based matrix is an important study for the investigation of their properties and applications. Among these various nanoparticles, silver (Ag) nanoparticles have attracted much more research attention due to their wide applications and unique properties in biosensing, catalysis, chemical sensing, electronics, and photonics (Lin-jun et al., 2016). There are also been a considerable interest on the synthesis of silver (Ag) nanoparticles (NPs) because of their various applications and unique properties in catalysis, chemical sensing, antibacterial, pharmaceutical and biosensing (Noor, Rameshkumar, & Huang, 2015).

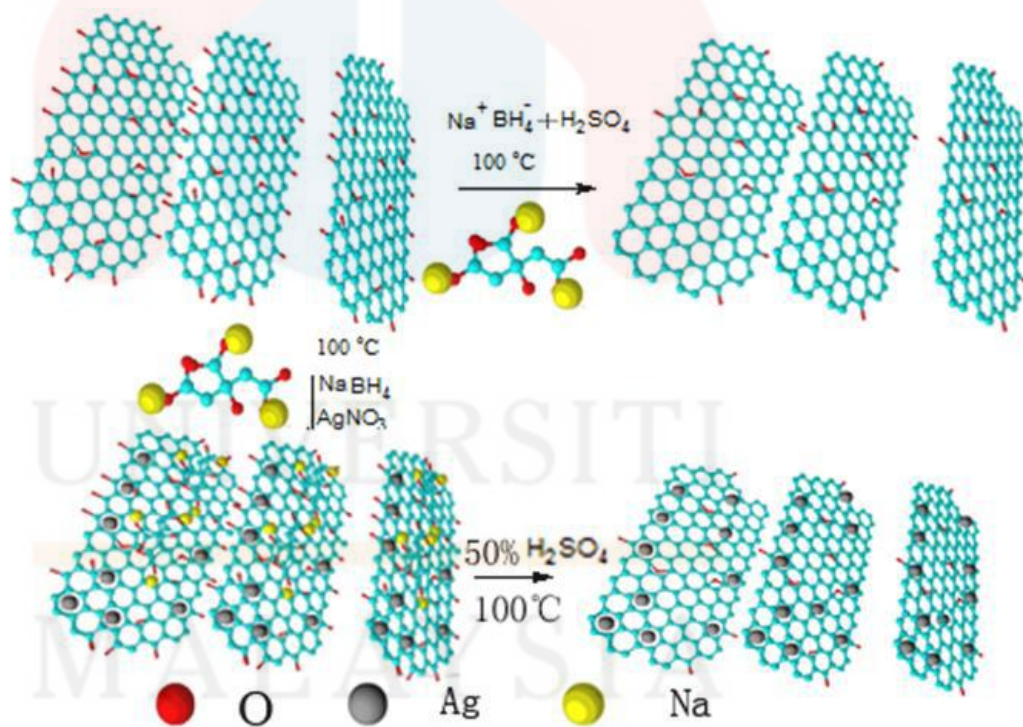


Fig. 1.1 Schematic illustration of the reduction process of graphene and graphene/silver nanocomposites (Lin-jun et al., 2016)

Nowadays, the reduction of GO by chemical reducing agents is the most usual method to obtain rGO. However, considering the toxicity of chemical reducing agents for human and environment, it is significant to explore green and facile strategies for the effective reduction of GO. Recently, our group found that hydrothermal treatment can efficiently reduce GO to rGO for the synthesis of rGO-coupled photocatalysts without adding reducing agents, which provides new insights into the fabrication (Sun, Wang, Yu, & Wang, 2016). Therefore, hydrothermal method has been applied to synthesize nanosized materials since the products prepared by this method have well crystalline phase, which also benefits to thermal stability of the nanosized materials (Zhu, Zheng, He, Zhang, & Anpo, 2004). In this study, we proposed a method called hydrothermal synthesis to produce Ag-rGO nanocomposite because of its environmental friendly behaviour. Compared to chemical reduction method by using chemical reducing agents such as hydrazine hydrate which is very harmful to human and environment.

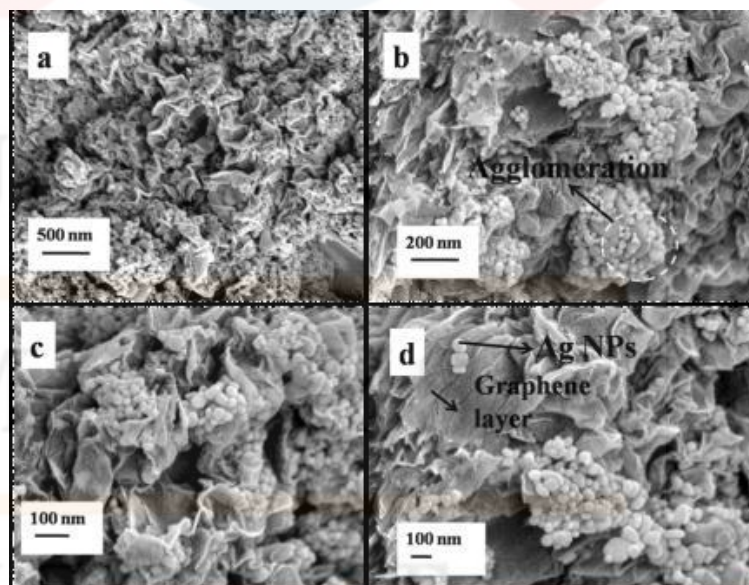


Fig. 1.2 (a, b, c and d) FESEM images of GO/Ag nanocomposites with different magnification (Sahu et al., 2015)

Besides that, mercury (Hg) is of great concern because of its deleterious effects to human and environment. It exists in metallic, inorganic and organic forms. Mercuric ions (Hg^{2+}), the most stable form of inorganic mercury, are present mostly in surface water due to its high water solubility and it can cause serious health problems in human mainly in brain, nervous system, kidneys, and endocrine system. Therefore, it is critical to be able to detect and measure the level of Hg^{2+} with high sensitivity and selectivity in the presence of other heavy metal ions (Noor et al., 2015).

This study is conducted to produce silver-reduced graphene oxide (Ag-rGO) by hydrothermal synthesis from graphite powder for the detection of mercury ion (Hg^{2+}) in optical sensor applications.

1.2 Problem Statement

In this advanced technology of century, graphene is known to have excellent properties that can produce high quality of product and can be commercializing widely. However, a few problems during the synthesis process such as use of highly toxic reducing agent, need special skill, expensive instrument become such a drawback to the productions. Also, did the production of silver-reduced graphene oxide from graphene can detect mercury ion (Hg^{2+}) that known to be widely used in optical sensor application.

As we all know, heavy metals is one of the most hazardous classes of pollutants in water sources due to their nonbiodegradability, have cause widespread water endangerment, contamination of fish, and serious health problems. Mercury is one of the known toxic metals. Its toxicity is attributed to its harmful effects on the central nervous

system disturbing haemin synthesis as well as causing neuropsychiatric disorder. Mercury is usually present at low concentrations in environmental samples as inorganic, free or complex with inorganic and organic ligands or as organomercury compounds. Therefore, determination of trace amounts of mercury in environmental samples is of great interest due to increasing public concern about environmental pollution and their high toxicity and accumulative and persistent character in the environment and living organisms. In recent years, several fluorescent sensors have been developed for the determination of (Hg^{2+}) (Yang, Jiang, Shen, & Yu, 2009) and a detection through a bare eyes need to be study for further enhancement of the sensor.

1.3 Research Objectives

In general, there are three main objectives of this study:

- i) To synthesize graphene oxide (GO) from the graphite powder by using simplified Hummer's method.
- ii) To produce silver-reduced graphene oxide (Ag-rGO) by hydrothermal method.
- iii) To determine the presence of mercury ion (Hg^{2+}) by using Ag-rGO nanocomposite.

1.4 Expected Outcomes

From the research objectives stated, this study is expected to produce graphene oxide (GO) by using simplified Hummer's method and the production of silver-reduced graphene oxide (Ag-rGO) by hydrothermal method to determine the mercury ion contained in optical sensor application.

RGO will be synthesized from graphite powder by using simplified Hummer's method while Ag-rGO nanocomposite will be synthesized using hydrothermal method. Besides that, the microstructure of the rGO can be observed under the transmission electron microscope (TEM) and the AgNPs will decorated onto the rGO layers. Meanwhile, Ag-rGO shows an extremely high limit detection of mercury ions.

1.5 Scope of Study

This experiment is conducted by using well-known method but has been simplified, which is simplified Hummer's method which collects the graphene oxide from the graphite powder. It is started with a very basic raw material which is graphite powder that usually obtained from the carbon of pencil or a charcoal. Meanwhile, in this experiment, the graphite powder is purchased and the experiment will be conducted at the materials science laboratory, UMK Jeli Campus. For the determination of mercury ion (Hg^{2+}), it will be conducted using the X-Ray Diffraction (XRD) machine and Fourier Transform Infrared Spectroscopy (FTIR) located at the materials science lab, UV-vis spectrometer and transmission electron microscope (TEM) located at the University of Malaya (UM), Kuala Lumpur because of insufficient of utilities in UMK Jeli campus.

CHAPTER 2

LITERATURE REVIEW

2.1 Fundamental of Graphene

The unit cell of graphene contains two carbon atoms and graphene lattice can be viewed as formed by two sub-lattices. Figure 2.1 shows the two graphene sub-lattices (red and blue) and unit cell. Graphene was first exfoliated mechanically from graphite in 2004. The study and elucidation of graphene properties have been invaluable by using graphene flakes. This technology is expected to have limited relevance to commercial high-end electronic applications. The first evidence of “single layer graphite” on metals was found in low energy electron diffraction (LEED) patterns from Pt surfaces. However, they are mostly might be available at several size (microns or tens of microns at best), have irregular shapes and their azimuthal orientation is not deterministically controlled (Avouris & Dimitrakopoulos, 2012).

Graphene had reach the status of exceptional material with a huge potential in a number of technological uses, which include electronics device, sensors, composite materials, energy generation and storage or biomedicine since the subsequent discovery of unusual phenomena and its unsurpassed electronic, mechanical, thermal and optical properties (Paredes, Guardia, & Tascón, 2012). Chen *et al.* (2016), discovered that the presence of multi-layer graphene could greatly decrease the friction coefficient and wear rate of composites.

Furthermore, other carbon allotropes such as graphite, charcoal, carbon, and fullerenes have the basic structural element of graphene. Besides, increasing studies in graphene material because of its 2D honeycomb-structured lattice that improves the movement of charge carriers (Low, Lai, Bee, & Hamid, 2015). Figure 2.2 shows single crystal of CVD graphene on Copper (Cu).

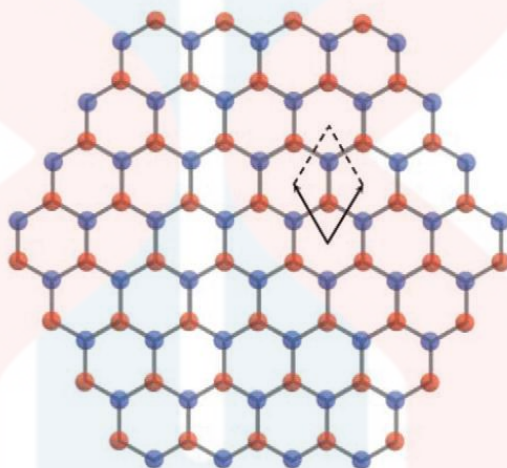


Fig. 2.1 The two graphene sub-lattices (red and blue) and unit cell (Avouris & Dimitrakopoulos, 2012)

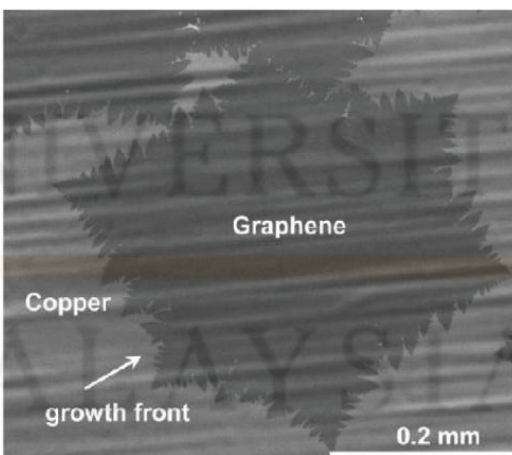


Fig. 2.2 Single crystal of CVD graphene on Cu (Avouris & Dimitrakopoulos, 2012)

2.1.1 Properties of Graphene

Graphene has a polycrystalline structure in 2D on polycrystalline metal substrate. Chemical Vapor Deposition (CVD) graphene may exhibit electrical transport properties similar to those of exfoliated graphene flakes (e.g., high mobility) and this explains CVD graphene is often observed by its variability and mobility. While the structure and properties of the kinetics of graphene formation depend on the reactor pressure and the type of gas atmosphere (Avouris & Dimitrakopoulos, 2012).

Moreover, graphene are one- and two-dimensional independent carbon crystal with long-range order up to the millimetre scale. Because of the intrinsic covalent connection of sp^2 -hybridized carbon atoms, it has extremely high mechanical strength, tensile strength and elastic modulus together with the valuable flexibility to accommodate deformation and transcendental conductivity for electrical current and thermal flow (Xu & Gao, 2015). While incorporating graphene alone into any polymers matrix, it will exhibited improved flame retardant and mechanical properties (Han *et al.*, 2016) and the microwave absorption properties of graphene and its related derivatives are closely related to their high dielectric loss and low density (Liu, Yao, & Zhou, 2015).

However, at the same time, graphene's integrity, properties and performance affect negatively by the transfer process. Wrinkle formation, impurities, graphene tearing and other structural defects can occur during transfer. Graphene production is enables at a large scale and lowers the cost per unit area because graphene not necessarily grow on a flat substrates with limited size only by the size of reactor, or in a continuous roll-to-roll process (Avouris & Dimitrakopoulos, 2012).

2.1.2 Preparation of Graphene

Graphene can generally be produced by several disruptive technologies such as mechanical approach, mechanical cleavage of graphite, epitaxial growth on a single crystal silicon carbide, and thermal expansion of graphite. The feasible method for the preparation of graphene is chemical oxidation of graphite. This method involves oxidation of graphite to graphite oxide (GO) using highly oxidizing agent (KMnO_4) and subsequently reducing GO to graphene using hydrazine solvent (Low *et al.*, 2015).

Besides, graphene mostly produced from chemically synthetic methods in large area such as chemical vapor deposition (CVD) and the huge mass graphene obtained from graphite is significant to the scalability of graphene macroscopic materials (Xu & Gao, 2015). At the same time, physical exfoliation approaches are desirable where it required to maintain the graphene structure where the graphite could be exfoliated in N-methyl-pyrrolidone to produce defect-free monolayer graphene (Singh *et al.*, 2011).

In addition, Avouris & Dimitrakopoulos (2012), stated that graphene grown on semi-insulating SiC can be used *in situ* without transfer to another substrate while electrical properties of CVD graphene cannot be tested *in situ* on the conductive metal substrate. Other than that, sodium cholate can also be used as surfactant to exfoliate graphite and moved further to isolate the resultant graphene sheet with controlled thickness using density gradient ultracentrifugation (DGU) which increase the buoyant density of the graphene sheet (Singh *et al.*, 2011).

2.2 Graphene Oxide (GO)

Graphene oxide (GO) can be seen as a single graphene layer densely decorated with oxygen functional groups with different type. Epoxides and hydroxyls are located on both sides of the graphene basal plane which are the dominant functionalities, whereas some minority groups (carbonyls and carboxyls) can be also found at the sheet edges, which are established by extensive spectroscopic studies (Paredes *et al.*, 2012). SEM images of Graphene Oxide are shown in Figure 2.3 below. Besides, chemical conversion of graphite to graphene oxide has emerged to be a viable route to afford graphene-based single sheets in considerable quantities and GO is a monolayer material produced by the exfoliation of graphite oxide which the chemical prepared by the sonication are clear, homogenous and stable indefinitely (Singh *et al.*, 2011).

Graphene-related materials (GRM), including graphene, few layered graphene (FLG), graphene oxide (GO) and reduced graphene oxide (rGO), are multifunctional nanostructured building blocks with extraordinary properties which may contribute to many fields of science and technology (Diba, Fam, Boccaccini, & Shaffer, 2016).

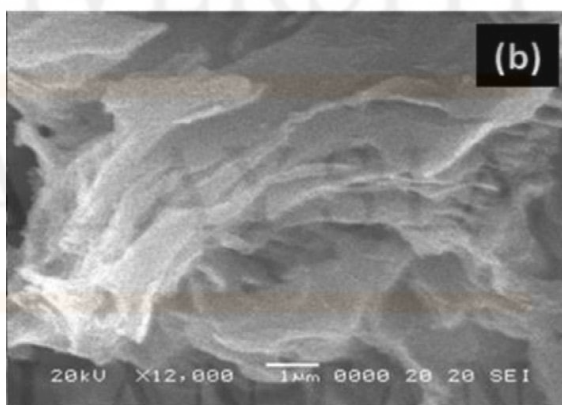


Fig. 2.3 SEM images of Graphene Oxide (Mohan, Vinodh, Sundaravel, & Abidov, 2016)

2.2.1 Properties of Graphene Oxide (GO)

Nanomaterials are cornerstone of nanoscience and nanotechnology. Among all of the carbon based nanomaterials, two dimensional graphene, reduced graphene oxide (GO) or GO-supported materials appeared as the hot topic of interest to researchers because of its unusual and exotic properties. Moreover, GO is comparable to graphene in certain aspects with oxygen moieties and holds a remarkable position independent of graphene in the research field. Besides, GO is a very promising materials as it is easy to process, low cost of manufacture, good colloid condition, high surface area, unique mechanical properties, low molecular weight, optical electronic and mechanical properties, water-dispersible and chemically versatile due to the presence of oxygenated groups on its surface (Shamaila, Sajjad, & Anum, 2016).

GO suspensions generally consist of solvated single layers and highly oxidized carbon based sheets. These oxygen groups can take the form of epoxies, carboxyls and hydroxyls. In addition, the oxidative moieties are typically found randomly attached to both sides of the GO sheets. This phenomenon results in a primarily amorphous surface structure with a surface roughness of around 0.6 nm (Diba et al., 2016).

Other than that, GO is the precursor of the graphene which possesses plenty of oxygen-containing groups on its surface, hydroxyl and epoxy groups on its basal planes and carboxyl groups at the sheet edges and these reaction functional groups of GO are very useful for the further modification with long chain of organic molecules and polymers. Silane coupling agents are frequently applied to modify the GO due to it contains the reactive groups that can both combine with inorganic and organic materials.

As a result, the compatibility of the polymer matrix will be improved accordingly. While composites containing different filler loadings of GO and FGO proved that this method can improve the re-stacking, aggregation, and folding of the nanoparticles and the properties of the acrylic resin including thermal, mechanical and chemical resistance were greatly enhance (Dong & Liu, 2016).

Because of the oxygen-containing functional groups in GO nanosheets such as hydroxyls and epoxy groups on the basal plane and the carboxyl groups on the edges, they generally have a better dispersibility in water or polar solvents than other nanoparticles. GO nanosheets also have recently attracted significant attention in membrane development because of their unique nanostructure and physical and mechanical properties. Because of the different functional groups (hydroxyl, epoxide and carboxyl) in GO, there is a good compatibility between the nanosheets with the host (polymer) materials through covalent or non-covalent attachments. Besides, when GO nanosheets are embedded into a membrane matrix, the surface hydrophilicity of the membranes will be enhance, which are helpful to enhance water permeability and fouling resistance. Moreover, the embedded GO nanosheets in the membrane matrix also increases the mechanical strength and enhances the membrane stability against high transmembrane pressures (Ali, Wang, Wang, & Feng, 2016).

2.2.2 Preparation of Graphene Oxide (GO)

Mostly, Graphene Oxide (GO) was prepared by using Hummers method. It is the mixture of graphite powder and NaNO_3 which then mix with concentrated H_2SO_4 and were put into an ice bath. The mixture was stirred on a magnetic plate and KMnO_4 were slowly added in a small amount to keep the reaction temperature below $10\text{ }^\circ\text{C}$. After stirring for 1 h, the ice bath was removed and the temperature increased up to $(35\pm 5)\text{ }^\circ\text{C}$ by applying external heat and keep the stirring for another 2 h (Roteta, Fernández-martínez, Mejuto, & Rucandio, 2015). Then, the Deionized (DI) water was added to the suspension and as consequence of the hydration heat the temperature increased to $98\text{ }^\circ\text{C}$. The bath was kept at this temperature for 30 min with stirring. Finally, the reaction was then finished by adding deionized water and hydrogen peroxide. The resulting product has a brown/yellowish color and was separated by vacuum filtration from the solution. The resulting GO powders is then washed 5 times with diluted HCl solution and warm deionized water to remove the remaining salt impurities (Guerrero-contreras, 2015).

Mostly, GO is synthesized from the oxidation of graphite based on Hummer's method including three steps: oxidation, purification and exfoliation. The oxidizing agents used are concentrated H_2SO_4 , KMnO_4 and H_2O_2 . After oxidation, the products are centrifuged and then exfoliated with the aid of ultrasonic vibration to get the uniformly dispersed GO aqueous solution. Surfactants are normally used to modify the surfaces of nanomaterials to improve their dispersion property. However, concerns are raised regarding that the surfactants may impair the hydration reactions due to their incompatibility. Among the surfactants, PC is a water reducing admixture for cement materials. Choosing PC as the modifier of GO is a feasible way for addressing this issue.

Then the mixture is subjected to ultrasonic vibration to achieve randomly dispersed GO flakes (Zhao et al., 2016).

2.3 Reduced Graphene Oxide (rGO)

Reduced graphene oxide (rGO) can be said that the carbonyl and ether groups formed from the hydroxyl and epoxy groups on graphene oxide during thermal annealing (Singh *et al.*, 2011). This will improved the properties of graphene and promote a better applications using rGO. Figure 2.4 shows the flow oxidation of graphite to graphene oxide and reduction to reduced graphene oxide.

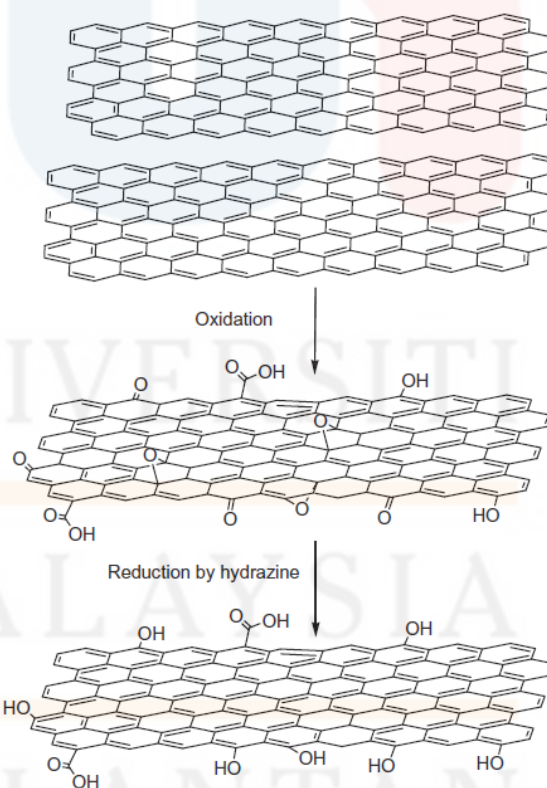


Fig. 2.4 Oxidation of graphite to graphene oxide and reduction to reduced graphene oxide (Singh et al., 2011)

2.3.1 Processing Method of reduced Graphene Oxide (rGO)

Reduction of graphene oxide has been performed with several reducing agents including hydrazine hydrate. Compared to the other strong reductants, it does not react with water and was found to be the best one in producing very thin and fine graphite-like sheets. During the reduction process, the brown colored dispersion of graphene oxide in water turned black and the reduced sheets aggregated and precipitated. The reduced graphene oxide became less hydrophilic due to the removal of oxygen atom and thus precipitated (Singh *et al.*, 2011).

In order to obtain rGO, and partially recover the desirable properties of pristine graphene, GO can be treated with a suitable reducing agent. However, in several studies, chemical reduction is employed as a post-EPD step. Many reducing agents like vitamin C (ascorbic acid), hydrazine and hydriodic acid have been explored, although hydrazine is particularly effective and popular for simplicity and cleanliness. Chemically-reduced GO sheets usually cannot form stable aqueous suspensions without using stabilizing additives, although partial reduction of GO can produce stable dispersions, depending on ionic strength, pH and rGO concentration. In several studies, partial reduction of GO has been reported as an effective way to produce stable and negatively charged rGO aqueous suspensions for EPD (Diba *et al.*, 2016).

2.3.2 Characterization of reduced Graphene Oxide (rGO)

The chemical structure of rGO can be confirmed by Fourier transform infrared spectra (FT-IR) using a spectrometer in the range of 4000-5000 cm^{-1} . While the crystalline phase structure of rGO were analysed by X-ray powder diffraction (XRD) and the morphology of rGO can also be observed by field emission scanning electron

microscope (FE-SEM) (Liu *et al.*, 2015). Moreover, various techniques are being used to images single layers of rGO such as scanning electron microscopy (SEM) and high resolution transmission electron microscopy (TEM). Often, combination of two or more techniques gives more accurate results of the imaging rGO. Figure 2.5 and Figure 2.6 shows aberration-corrected TEM image of a monolayer of RGO and SEM images of rGO respectively.

Based on Mirza-aghayan, Molaee, & Boukherroub (2016), rGO based catalyst was characterized by Fourier-transform infrared (FT-IR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray photoelectron (XPS). While for Liu *et al.* (2016), experiment, the mechanical properties and microstructure were studied and characterized via Vickers hardness, X-ray Diffraction, density measurement and scanning electron microscopy.

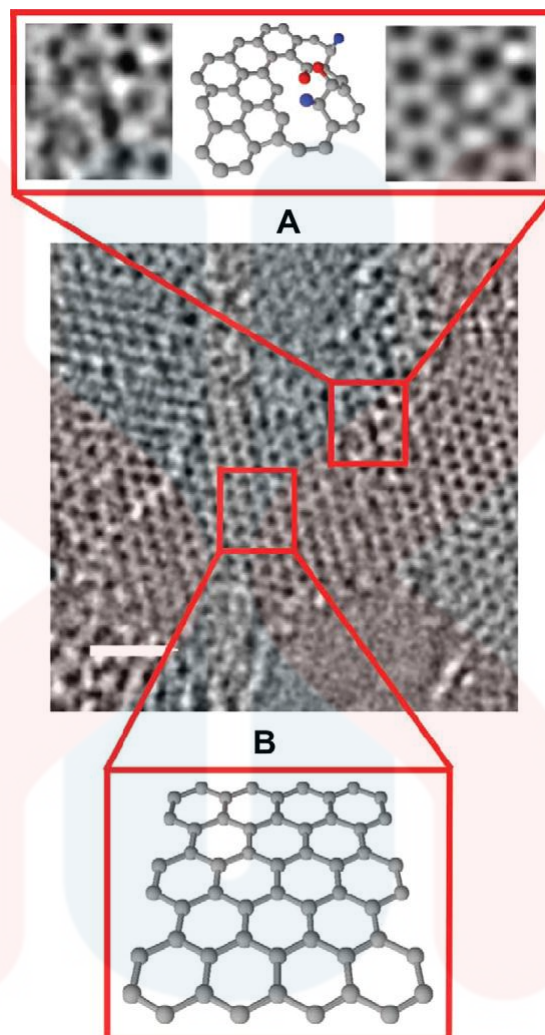


Figure 2.5: Aberration-corrected TEM image of a monolayer of rGO (Singh et al., 2011)

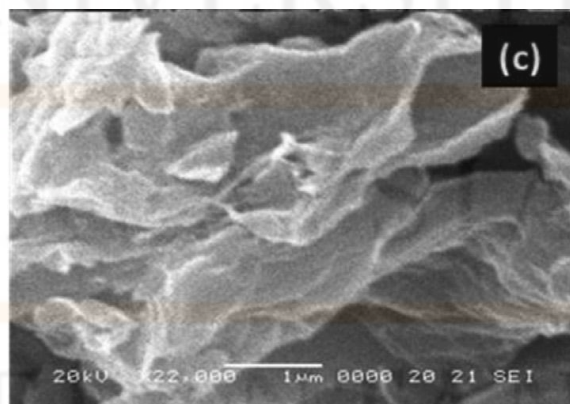


Fig. 2.6 SEM images of rGO (Mohan et al., 2016)

2.4 Optical Sensor Application Towards Mercury Ion (Hg^{2+})

A sensor measures or detects a physical parameter and converts it into a signal, which is subsequently read by an observer or an instrument. Sensors have high sensitivity and selectivity and also allow on-line, real time analysis, which have revolutionized the field of chemical analysis, particularly of blood and serum samples in critical care. Sensors with faster response times and higher selectivities are preferable in monitoring ultratrace levels of toxic-metal ions. In the past few years, numerous analytical methods have been used to detect Hg^{2+} and determine its concentration. Recently, detection or ‘sensing’ of toxic metals at the nanoscale has been intriguing development (El-safty & Shenashen, 2012).

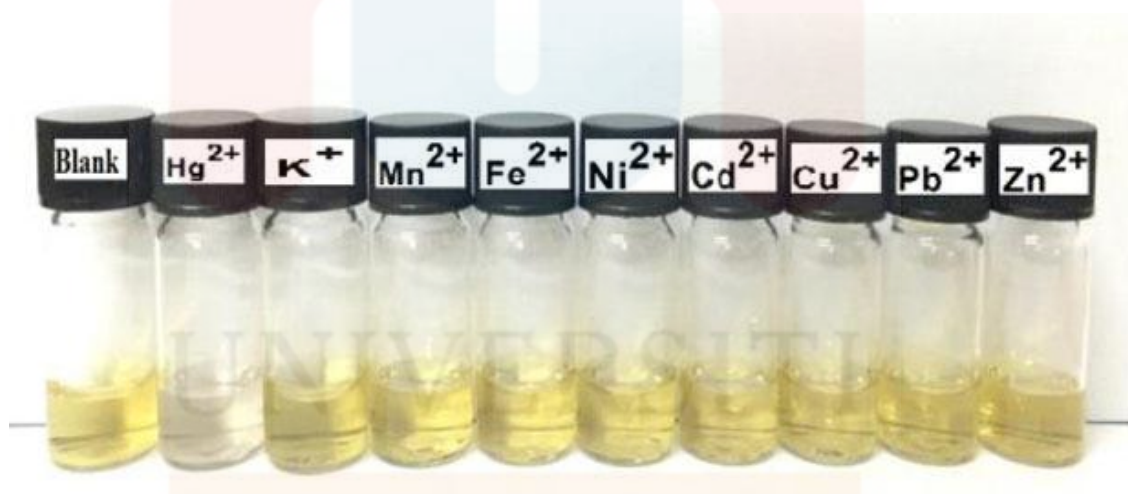


Fig. 2.7 Optical sensor observed for GO-Ag nanocomposite solution with the addition of 100 μM $\text{Hg}(\text{II})$ and 500 μM other heavy metal ions individually (Noor et al., 2015)

KELANTAN

Yang et al., (2009) also stated that noticeable decrease of fluorescence emission intensity appeared in the presence of Hg^{2+} , which was attributed to the formation of complex between TDMAPP and Hg^{2+} . Also, the fluorescence intensities of sensing membrane were gradually decreased with increasing Hg^{2+} concentrations, which have been utilized as the quantitative basis of the Hg^{2+} sensors. TDMAPP showed preferable fluorescence respond to Hg^{2+} . Thereby, a sensitive, fast and simple optical sensor for the determination of Hg^{2+} has been developed based on the fluorescence quenching of TDMAPP. The quenching of TDMAPP fluorescence was fast and the degree of the quenching was proportional to Hg^{2+} concentrations. The sensing membrane containing TDMAPP reversibly responded to Hg^{2+} and showed extremely high selectivity to Hg^{2+} in the presence of some alkali, alkaline earth and heavy metal ions.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Graphite powder will be used for the synthesis of graphene oxide in this experiment. All the reagent and chemicals were of analytical grade and used without further purification. Phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), distilled water, hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), ammonia (NH_3), silver nitrate (AgNO_3) and ethanol will be used in this experiment as the reagents.

3.2 Method

3.2.1 Production of Graphene Oxide

A mixture of H_2SO_4 (320 ml) and 80 ml of H_3PO_4 (mixture A) is stirred in a 2 L of Schott bottle with a magnetic bar on a hot plate. Then, 3 g of graphite powder is added slowly to the mixture. After a few seconds, another 18 g of KMnO_4 is slowly added into the same mixture while it is kept stirred. The mixture is left stirred for 3 days on a hot plate using magnetic stirrer (Figure 3.1).

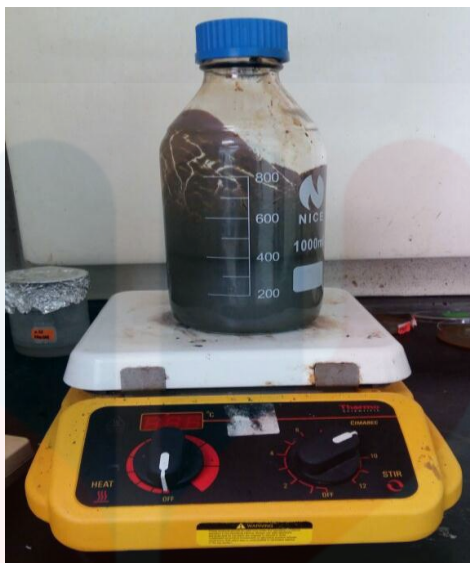


Fig. 3.1 Preparation of Graphene Oxide (GO)

After that, H_2O_2 is mixed with 500 ml of frozen distilled water and it is put in a beaker. Mixture A is then added to the beaker and mixed with the ice until it changes color. The mixture is poured evenly into the centrifuge bottles to be washed (Figure 3.2). The solid GO obtained is washed with 1 M of HCl for 3 times, followed by distilled H_2O 12 times until the pH obtained is 5 (Figure 3.3). Noor et al., (2015) mentioned that this step is crucial to ensure the excess metal ions to be removed. Centrifugation of the rGO at 10000 rpm is done for 1 week (Figure 3.4).



Fig. 3.2 The mixtures are put evenly into the centrifuge bottles

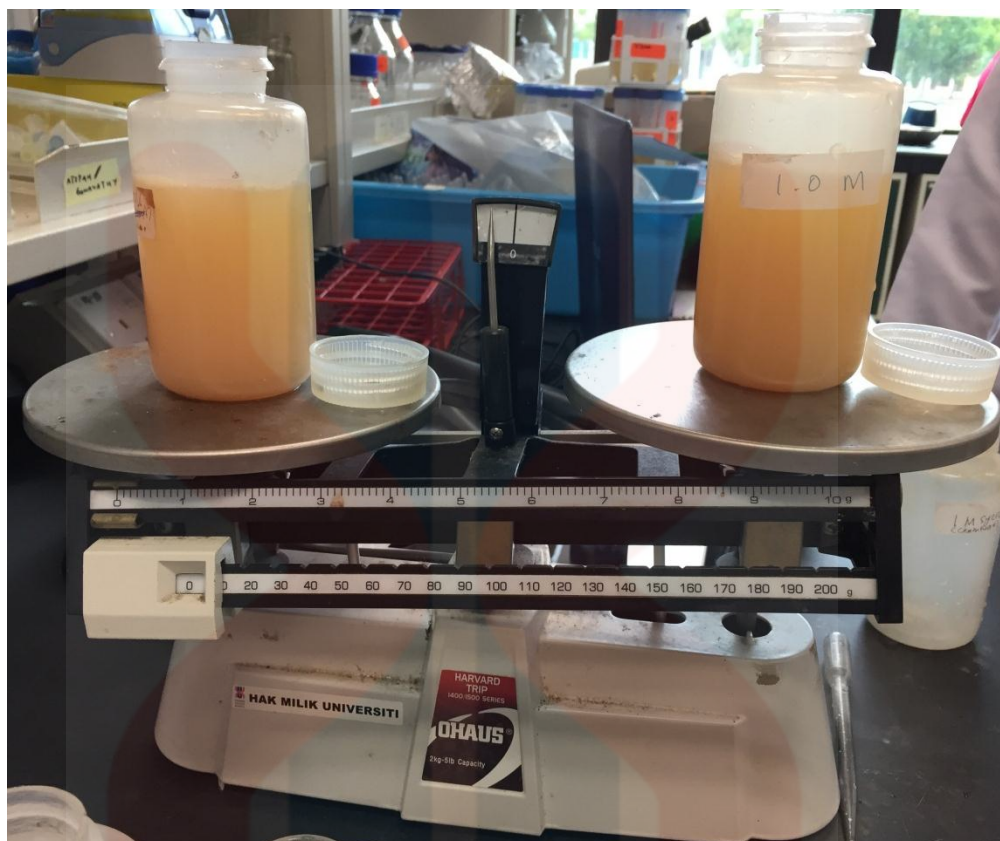


Fig. 3.3 HCl is added to the mixture and balanced before put it into the centrifuge



Fig. 3.4 The mixtures is washed with HCl followed by distilled water in the centrifuge until it reach pH value of 5

3.2.2 Preparation of Ag-rGO by Hydrothermal Method

To produce GO-Ag nanocomposite, 450 μl of NH_3 (25 %) of is added into 10 ml of AgNO_3 (10 mM) in a beaker and stirred until the solution becomes clear (Figure 3.5) to produce 1.0 M of silver complex $[\text{Ag}(\text{NH}_3)_2\text{OH}]$, while 210 μl of NH_3 (25 %) of is added into 10 ml of AgNO_3 (10 mM) to produce 0.5 M of $[\text{Ag}(\text{NH}_3)_2\text{OH}]$. After that, 10 ml of $\text{Ag}(\text{NH}_3)_2\text{OH}$ is mixed with obtained 10 ml of 0.5 M graphene oxide for hydrothermal treatment (Figure 3.6). The mixture is kept inside the oven in the autoclave (Figure 3.7) at 180 $^\circ\text{C}$ for 24 hours and allowed to cool down at room temperature. The obtained composite is washed using centrifuge at 10000 rpm for 3 times using distilled water and dried at room temperature for 24 hours.

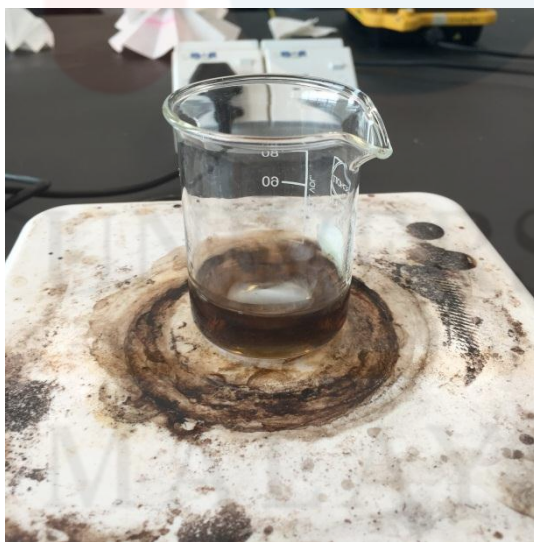


Fig. 3.5 Stirred solution

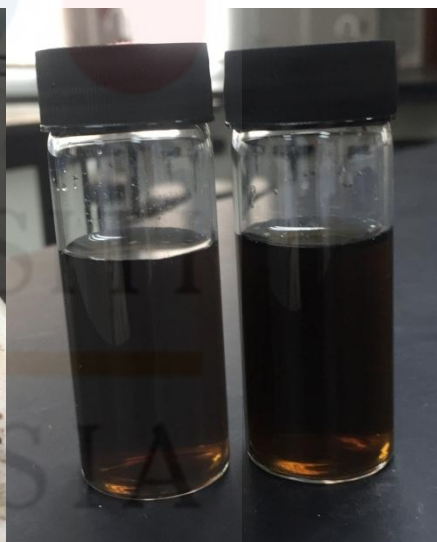


Fig. 3.6 Mixture of Ag and GO

KELANTAN



Fig. 3.7 The mixtures is put in the autoclave for hydrothermal treatment

3.2.3 Optical Detection of Hg^{2+}

The optical sensing of Hg^{2+} with the Ag-rGO is performed by recording the color changes of the solution using bare eyes. For optical detection, 200 μl of 2 μM $\text{Hg}(\text{II})$ ion, lead(II) nitrate, zinc sulphate and nickel(II) chloride solution is added into each 2 ml of Ag-rGO solution, it is shake well and subjected to a constant resting time (1 min) before the color changes of the solution was recorded.

3.2.4 Analytical Method

The impurities and percentages of carbon and silver element contained in the reduced graphene oxide (rGO) and Ag-rGO is identified by using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). While, morphology of the nanocomposite will be observe by using Transmission Electron Microscope (TEM). Also, the presence of mercury ion (Hg^{2+}) can be determined with produced silver-reduced graphene oxide (Ag-rGO). Figure 3.1 shows the procedure conducted in this experiment.

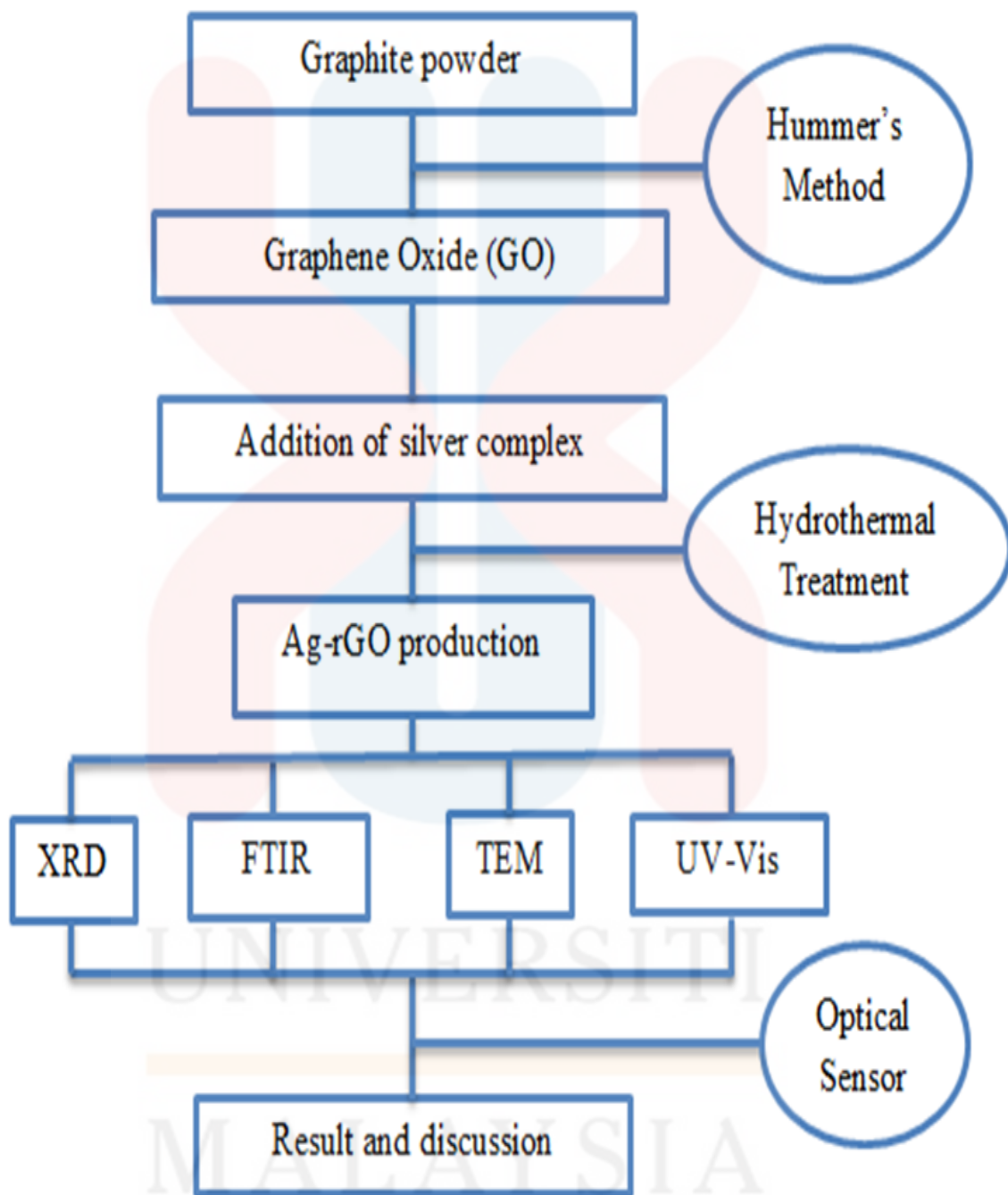


Fig. 3.8 Procedures that were conducted in this experiment

CHAPTER 4

RESULT & DISCUSSION

4.1 Choice of Materials

For this experiment, GO-Ag nanocomposite materials are used for optical detection of Hg^{2+} . Because of the presence of surface functional groups and high specific surface area of GO, it helps in host materials for the Ag nanoparticles to growth on the surface of GO. Agglomeration/aggregation of Ag nanoparticles can be prevent with the present of functional group of GO, hence the surface area of Ag nanoparticles is fully available for the interaction with Hg^{2+} . Apart than that, for bare Ag nanoparticles, a strong interparticle coupling effect may reduce the interaction of Hg^{2+} and consequently affects the detection response.

4.2 Ultra Violet Visible Spectroscopy

It is widely known that the silver nanoparticles (Ag NPs) display a Surface Plasmon Resonance (SPR) absorption band at around 420 nm of wavelength and it is very sensitive to analytes. While the positions of the SPR band depends on the Ag NP size and the local environment. Besides, the alteration in SPR spectra and color change of Ag NP solution can be easily monitored using UV-Vis absorption spectrophotometer (Noor et al., 2015).

The formation of Ag NPs was primarily confirmed by the UV-vis absorption spectrum as shown in the Fig. 4.1. As we can see, the appearance of peak at 227 nm was

proven the π - π^* transition of aromatic C—C bonds and a shoulder peak at ~300 nm corresponds to n- π^* transitions of C=O groups present in GO (Fig. 4.1 GO). After hydrothermal treatment on the mixture of the silver complex and GO solution, a new peak is appeared and visible at 420 nm which indicate the formation of SPR absorption band of the Ag NPs (Fig. 4.1 Ag-rGO). Moreover, the effect of concentration of ammonia solution on the formation of Ag-rGO nanocomposite was observed and studied. It is shown that the usage of 25 % of ammonia facilitated and gave a better formation of Ag NPs on the graphene layer. This can be understood by the appearance of intense SPR peak of Ag NPs present in the GO-Ag nanocomposite with 25 % ammonia solution. While the appearance of absorption peaks at 227 and 300 nm decrease with less intensity after the formation of Ag-rGO nanocomposite and it suggest that the partial reduction of GO might occur during the hydrothermal treatment. The single SPR absorption feature of Ag NPs indicates that the particles may probably have spherical shape with different sizes (Noor et al., 2015).

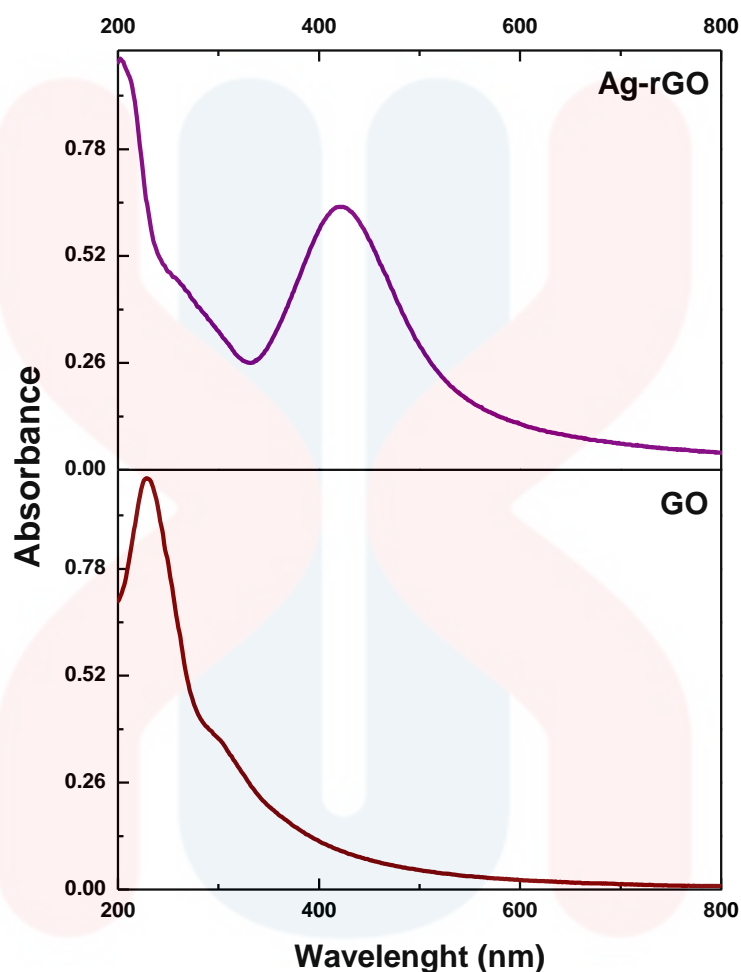


Fig. 4.1 UV-visible absorption spectra of GO solution and Ag-rGO nanocomposite

4.3 FTIR studies of Ag-rGO Nanocomposite

The Fourier Transform Infrared (FTIR) spectra measurements were carried out to investigate the interactions between GO and Ag nanoparticles. Figure 4.2 shows the FTIR spectra of GO and Ag-rGO nanocomposite. In the case of GO, the broad and intense peak are centered at 3193 cm^{-1} , which is related to the OH groups, and a really small peak are seen at 1728 cm^{-1} which corresponds to the stretching vibrations of C=O carboxylic moieties. While the presence of the adsorption band at approximately 1620

cm^{-1} corresponds to the C=C bonding of the aromatic rings of the GO carbon skeleton structure which also known as intra-molecular hydrogen bonds. Furthermore, other bands can be seen at 1419, 1225 and 1046 cm^{-1} correspond to C-O-H deformation, C-H stretching (epoxy groups), and C-O stretching vibrations (alkoxy groups), respectively. Therefore, it can be confirms that the existences of abundance of hydroxyl groups and oxygenous groups located on the surface of GO, which makes GO to be convenient for further modification with plasmonic nanoparticles, such as Ag nanoparticles. Meanwhile, there is a significant decrease in the intensity of the adsorption bands of the oxygenated functional groups for the Ag-rGO nanocomposite sample (Figure 4.2 Ag-rGO). The peak position of the functional groups on Ag-rGO is totally different compared to GO and their shapes are not that similar. In particular, the intensity of C=O carbonyl stretching is decreased, whereas the C-H stretching (epoxy groups) (1225 cm^{-1}) remain the same. This can be due probably to the existence of Ag nanoparticles on the surface of GO and also might due to the reduction of GO during the synthesis of the Ag-rGO nanocomposite by hydrothermal method. Apart from that, there are strong peaks form at 2320 cm^{-1} and 2102 cm^{-1} of GO-Ag nanocomposite samples which might due to the addition of Ag nanoparticles on the surface of GO. This change can prove that there is an interaction between Ag nanoparticles and the oxygen-containing functional groups (i.e., -COOH) of GO nanosheets by forming a chemical bond or electrostatic attraction.

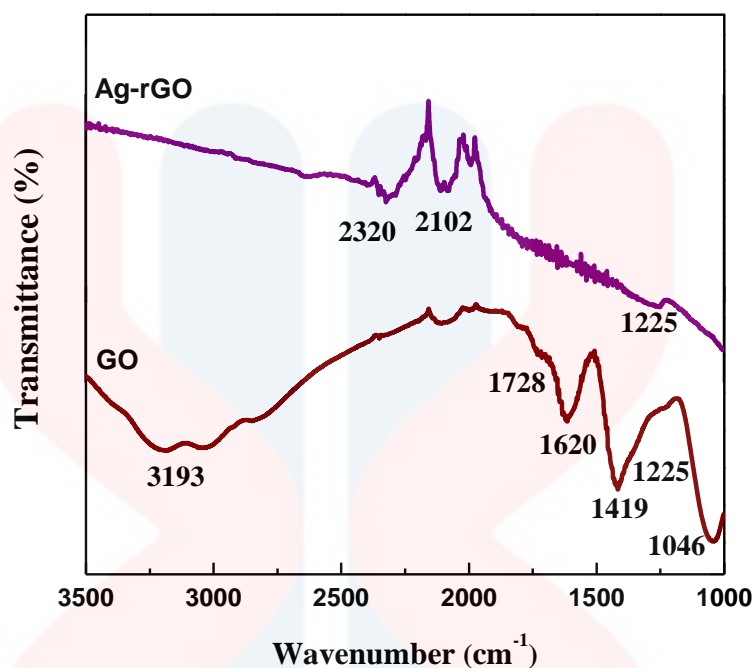


Fig. 4.2 FTIR patterns of GO and Ag-rGO nanocomposite

4.4 XRD studies of Ag-rGO Nanocomposite

The structural analysis of GO and Ag-rGO nanocomposites material is carried out by X-ray diffraction (XRD) study (Fig. 4.3). The formation of Ag nanoparticles was confirmed by the existence of diffraction patterns of Ag crystal structure which match the standard x-ray diffraction (XRD) pattern. Based on the figure, GO has shown a strong diffraction peak at 2θ (degree) value of 10.0° corresponds to the (0 0 1) reflection of GO due to its crystalline nature. After the hydrothermal treatment is given to the GO-Ag nanocomposite, a broad peak appeared at around 29.1° that shifted to the right from $\sim 20^\circ$ which shows that the reduction of GO happens after 24 hours (Fig. 4.3 Ag-rGO) and GO was completely reduced. Therefore, the functionalization of the GO surface with the Ag nanoparticles might prevent the graphene sheets from restacking. Besides that, XRD pattern of Ag nanoparticles represent several crystalline peaks at 2θ value of

38.1°, 44.1°, 64.2° and 77.2° which ascribed to the crystallographic planes (111), (200), (220) and (311) for the face-centered cubic (FCC) of the silver crystal (Fig. 4.3 Ag-rGO). The formation of Ag nanoparticles was confirmed by the existence of diffraction pattern of silver crystal structure which matches with the standard database values of X-ray diffraction (XRD) patterns (JCPDS card no. 89-3722). It shows that the intensity of Ag diffraction peaks increased with the increasing concentration of silver in the synthesis of Ag-rGO nanocomposite. These have further confirmed the complete formation of Ag nanoparticles on GO with higher silver concentration under hydrothermal treatment.

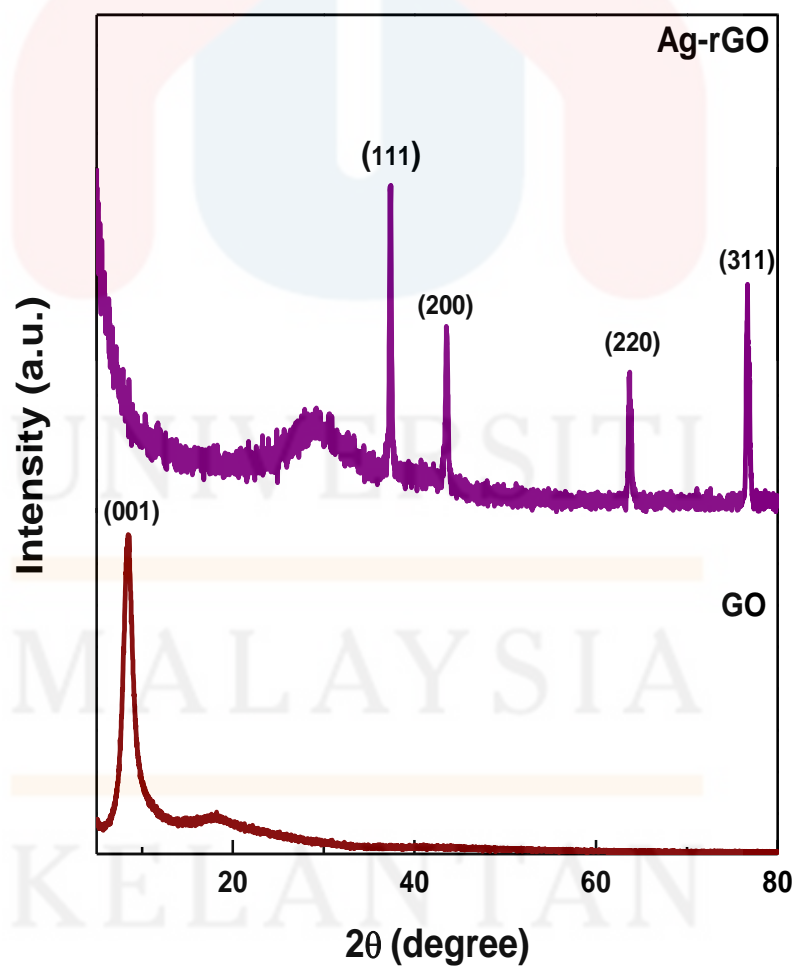


Fig. 4.3 XRD patterns of GO and Ag-rGO nanocomposite

4.5 Transmission Electron Microscopy

In this case of study, transmission electron microscopy (TEM) analysis was performed to study the morphology of the Ag-rGO nanocomposite. Figure 4.4 displays the TEM images with different magnifications recorded for GO-Ag nanocomposite. It can be seen that the successful deposition of poly-dispersed spherical Ag NPs on GO sheets (Fig. 4.3a and b) (Noor et al., 2015). As the beam of electrons is transmitted through the ultra-thin specimen, Figure 4.5 displays the TEM image of Ag-rGO nanocomposite with magnification of 100 nm is recorded. It can be seen that the deposition of poly-dispersed spherical Ag NPs is successfully located on GO sheets. Based on the image, it is proven that the spherical shape of Ag NPs relies on the single SPR absorption feature and the average particle size was found to be 12 ± 2.8 nm by taking account of 150 particles for particle size analysis.

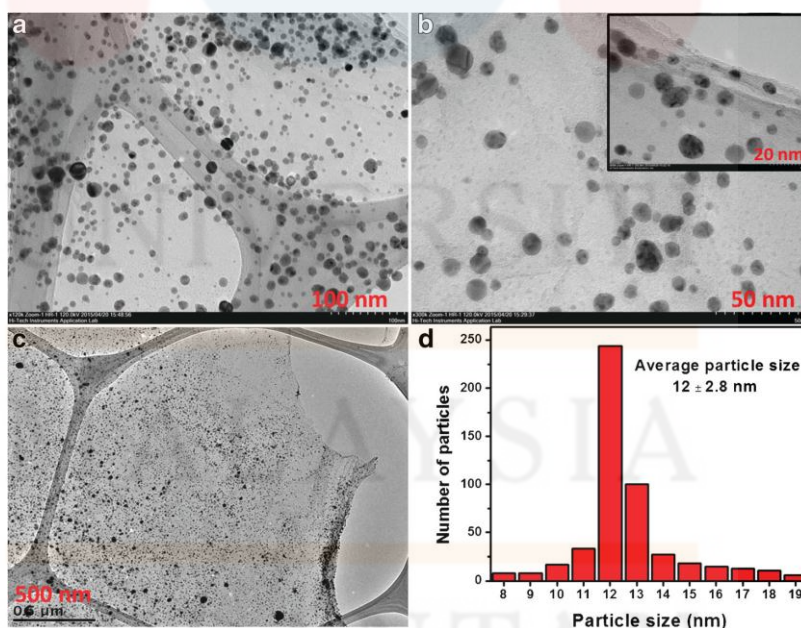


Fig. 4.4 TEM images of GO-Ag nanocomposite with different magnifications (a–c) and particle size histogram (d) (Noor et al., 2015)

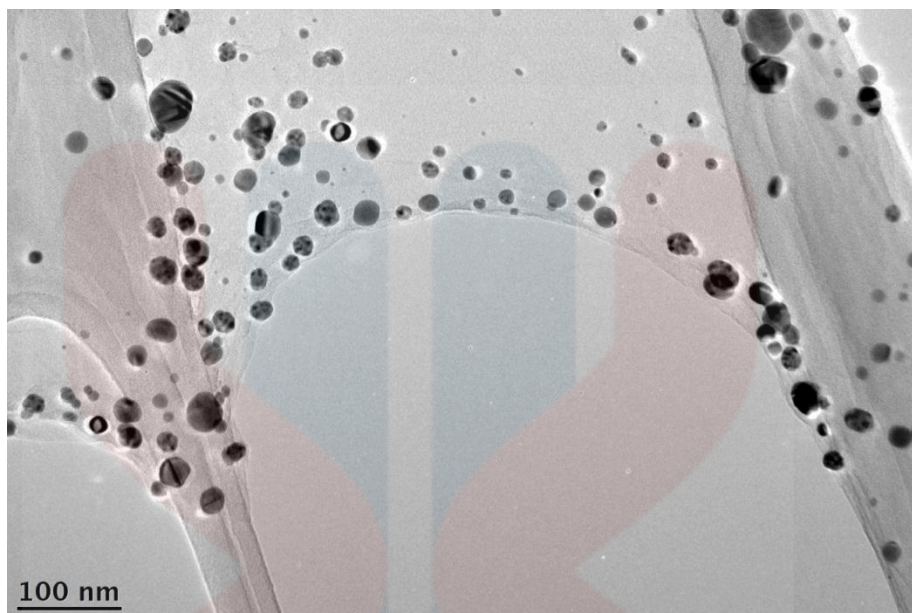


Fig. 4.5 TEM images of Ag-rGO nanocomposite at 100 nm magnification

4.6 Optical Determination of Hg^{2+}

For optical sensor of Hg^{2+} , the color changes of GO-Ag nanocomposite solution were observed and monitored after the addition of 200 μl Hg (II). It was noticed that only with the addition of Hg(II), GO-Ag turned chalky to colorless (Figure 4.6) whereas, the color of the nanocomposite did not change even after the addition of the same amount (200 μl) concentration of other metal ions such as lead(II) nitrate, zinc sulphate and nickel(II) chloride (Figure 4.7). So, this result concludes that the GO-Ag nanocomposite is highly selective toward the determination of Hg^{2+} in the presence of other common toxic metal ions. While Noor et al., (2015) stated that the Ag NP surfaces were oxidized by the interaction of Hg(II) and probably Ag amalgam occurs.

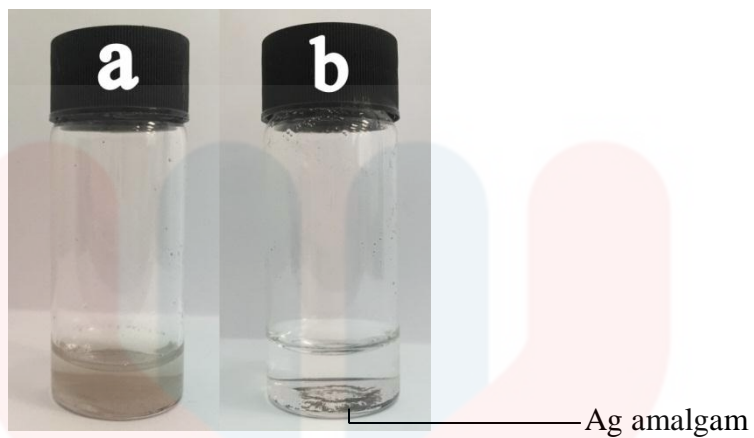


Fig. 4.6 Optical determination of mercury ion with GO-Ag nanocomposite (a) the colour before the addition of 200 µl Hg(II) ion (b) the colour after the addition of 200 µl Hg(II) ion

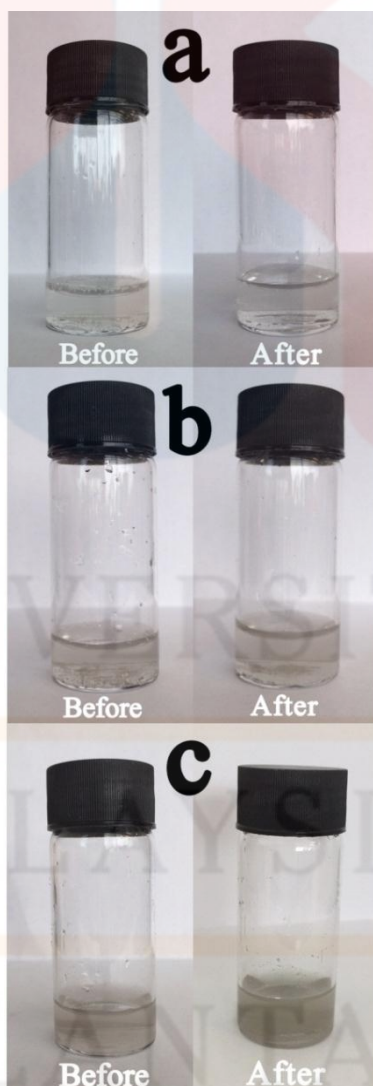


Fig. 4.7 The color of before and after addition of 200 µl metal ions; (a) Pb^{2+} , (b) Zn^{2+} and (c) Ni^{2+} into 2 ml of Ag-rGO nanocomposite solution

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This work has successfully synthesized Ag-rGO nanocomposite by using environmental friendly hydrothermal treatment and at the same time producing GO by using hummer's method that has been simplified. This study also proven the optical determination of Hg (II). The nanocomposite produced was successfully characterized by UV-visible absorption spectra, XRD, TEM and FTIR analyses. FTIR studies shows the existences of abundance of hydroxyl groups and oxygenous groups located on the surface of GO, which makes GO to be convenient for further modification with Ag nanoparticles. Meanwhile, the Ag-rGO nanocomposite sample shows existence of Ag nanoparticles on the surface of GO and the reduction of GO during the synthesis of the Ag-rGO nanocomposite by hydrothermal method.

While XRD analyses shows the formation of Ag nanoparticles which confirmed by the existence of diffraction patterns of Ag crystal structure which match the standard x-ray diffraction (XRD) pattern. After the hydrothermal treatment is given to the Ag-rGO nanocomposite, a broad peak appeared which shows that the reduction of GO happens and GO was completely reduced. The formation of Ag nanoparticles was confirmed by the existence of diffraction pattern of silver crystal structure which matches with the standard database values of X-ray diffraction (XRD) patterns and these

have further confirmed the complete formation of Ag nanoparticles on GO with higher silver concentration under hydrothermal treatment.

Last but not least, for the optical determination of Hg^{2+} , during the experiment was conducted, the color changes of Ag-rGO nanocomposite was successfully observed and recorded. The nanocomposite exhibited an excellent selectivity towards the determination of Hg(II) compared to the presence of other heavy metal ions. The present study proven that the Ag NP based nanocomposite assay can be used for the spectrophotometric determination of Hg (II).

5.2 Recommendation

Researcher can use other method to produce graphene oxide (GO) at the same time using the exact amount of reagents as the preferred method so that the product can be produce successfully. Based on the method used in this experiment, the concentration of KMNO_4 used can be increase up to certain amount to facilitate oxidation of GO. While for the production of silver complex, one's must know the most suitable concentration of silver nanoparticles (Ag NPs) to be added with GO so that the silver nanoparticles will distributed evenly on the graphene sheet. This is because, the concentration of the nanocomposite speaks will increased with the ratio increasing of silver nitrate to graphene oxide and the amount of Ag NPs will affect the optical sensor test with mercury.

Herein, for the production of Ag-rGO by using hydrothermal treatment, researchers can consider to increase the temperature and time used in the oven as this can completely reduce the production of graphene oxide which can increase the amount

of Ag NPs attached on the graphene sheets at the same time. Besides, the Ag-GO nanocomposite can be produce with the help of other agents such as sodium citrate in an aqueous GO dispersion for the reduction of silver ion (Ag^+), glucose as reducing agent and starch as stabilizer. Other than that, Ag-GO nanocomposite can also be produce by using other methods such as *in situ* hydrothermal synthesis and facile one pot method to produce various morphology of Ag-rGO nanocomposite.

For the analytical characterization testing, researchers can increase the amount of test for accurate results. Other than XRD, FTIR, TEM and UV-vis testing, one's can go for electron dispersive X-ray (EDX) analysis to determine the elemental composition of the nanocomposite, X-ray photo-electron spectroscopy (XPS) to demonstrate the nanocomposite diameter accurately, field emission scanning electron microscope (FESEM) to propose a better morphology of graphene sheet and more.

REFERENCES

- Ali, M. E. A., Wang, L., Wang, X., & Feng, X. (2016). Thin film composite membranes embedded with graphene oxide for water desalination. *DES*, 386, 67–76.
- Avouris, P., & Dimitrakopoulos, C. (2012). Graphene : synthesis and Graphene , since the demonstration of its easy isolation by the exfoliation of. *Materials Today*, 15(3), 86–97.
- Chen, Z., Yan, H., Liu, T., & Niu, S. (2016). SC. *Composites Science and Technology*.
- Diba, M., Fam, D. W. H., Boccaccini, A. R., & Shaffer, M. S. P. (2016). Electrophoretic deposition of graphene-related materials: A review of the fundamentals Department of Biomaterials , Radboud University Medical Center , Philips van Departments of Materials and Chemistry , Imperial College London , South Kensington. *JOURNAL OF PROGRESS IN MATERIALS SCIENCE*.
- Dong, R., & Liu, L. (2016). Ac ce p ip t. *Applied Surface Science*.
- El-safty, S. A., & Shenashen, M. A. (2012). Mercury-ion optical sensors. *Trends in Analytical Chemistry*, 38(3), 98–115.
- Guerrero-contreras, J. (2015). Graphene oxide powders with different oxidation degree , prepared by synthesis variations of the Hummers method. *Materials Chemistry and Physics*, 254--584.
- Han, Y., Wang, T., Gao, X., Li, T., & Zhang, Q. (2016). Preparation of thermally reduced graphene oxide and the influence of its reduction temperature on the thermal , mechanical , flame retardant performances of PS nanocomposites. *COMPOSITES PART A*, (16), 1359–835X.
- Kumar, S., Sharma, J. G., Maji, S., & Dhar, B. (2016). Biosensors and Bioelectronics Nanostructured zirconia decorated reduced graphene oxide based ef fi cient biosensing platform for non-invasive oral cancer detection. *Biosensors and Bioelectronic*, 78, 497–504.
- Lin-jun, H., Yan-xin, W., Jian-guo, T., Yao, W., Ji-xian, L., Ji-qing, J., & Wei, W. (2016). Preparation of Graphene / Silver Nanohybrid Composite with Good Surface-Enhanced Raman Scattering Characteristics, 11, 398–405.
- Liu, J., Khan, U., Coleman, J., Fernandez, B., Rodriguez, P., Naher, S., & Brabazon, D. (2016). Graphene oxide and graphene nanosheet reinforced aluminium matrix composites : Powder synthesis and prepared composite characteristics. *JMADE*, 94, 87–94.
- Liu, P., Yao, Z., & Zhou, J. (2015). Author s Accepted Manuscript. *Ceramics International*, (15), 0272–8842.

- Low, F. W., Lai, C. W., Bee, S., & Hamid, A. B. D. (2015). Author's Accepted Manuscript. *Ceramics International*, (15), 0272–8842.
- Mirza-aghayan, M., Molaee, M., & Boukherroub, R. (2016). Ultrasonics Sonochemistry Sulfonated reduced graphene oxide as a highly efficient catalyst for direct amidation of carboxylic acids with amines using ultrasonic irradiation. *ULTRASONICS SONOCHEMISTRY*, 29, 371–379.
- Mohan, C., Vinodh, R., Sundaravel, B., & Abidov, A. (2016). Fe₂O₃ / TiO₂ nanoparticles and adsorption of As (III) and As (V) from. *Journal of the Taiwan Institute of Chemical Engineers*, 0, 1–10.
- Noor, M., Rameshkumar, P., & Huang, N. M. (2015). Visual and spectrophotometric determination of mercury (II) using silver nanoparticles modified with graphene oxide, (Ii).
- Paredes, J. I., Guardia, L., & Tascón, J. M. D. (2012). Preparation , characterization and fundamental studies on graphenes by liquid-phase processing of graphite. *Journal of Alloys and Compounds*, 536, S450–S455.
- Roteta, M., Fernández-martínez, R., Mejuto, M., & Rucandio, I. (2015). Preparation of graphene thin fi lms for radioactive samples. *Applied Radiation and Isotopes*, (Cvd), 1–5.
- Sahu, D., Sarkar, N., Sahoo, G., Mohapatra, P., & Swain, S. K. (2015). Silver Imprinted Graphene Nanocomposites : Synthesis and Morphological Study, 1(July), 224–227.
- Shamaila, S., Sajjad, A. K. L., & Anum, I. (2016). Modifications in development of graphene oxide synthetic routes. *CHEMICAL ENGINEERING JOURNAL*, (February).
- Singh, V., Joung, D., Zhai, L., & Das, S. (2011). Progress in Materials Science Graphene based materials : Past , present and future. *Progress in Materials Science*, 56(8), 1178–1271.
- Sun, Q., Wang, P., Yu, H., & Wang, X. (2016). *In situ hydrothermal synthesis and enhanced photocatalytic H₂-evolution performance of suspended rGO/g-C₃N₄ photocatalysts*. *Journal of Molecular Catalysis A: Chemical* (Vol. 424). Elsevier B.V.
- Xu, Z., & Gao, C. (2015). Graphene fiber : a new trend in carbon fibers. *Biochemical Pharmacology*, 0(0), 1–13.
- Yang, Y., Jiang, J., Shen, G., & Yu, R. (2009). Analytica Chimica Acta An optical sensor for mercury ion based on the fluorescence quenching of tetra (p - dimethylaminophenyl) porphyrin, 636, 83–88.

- Zhao, L., Guo, X., Ge, C., Li, Q., Guo, L., Shu, X., & Liu, J. (2016). Investigation of the effectiveness of PC @ GO on the reinforcement for cement composites, *113*, 470–478.
- Zhu, J., Zheng, W., He, B., Zhang, J., & Anpo, M. (2004). Characterization of Fe-TiO₂ photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water. *Journal of Molecular Catalysis A: Chemical*, *216*(1), 35–43.



UNIVERSITI
MALAYSIA
KELANTAN

APPENDICES

APPENDIX A

Table A.1: Synthesizing Graphene Oxide

Concentration of GO (M)	Amount of GO needed (ml)
0.5	$M_1V_1 = M_2V_2$ $V_1 = \frac{(0.5 \text{ mg/ml}) (50 \text{ ml})}{(5 \text{ mg/ml})}$ $= 5$ <p style="text-align: center;">5 ml of GO needed to dilute into 50 ml of dH₂O to produce 0.5 M of GO</p>
0.1	$M_1V_1 = M_2V_2$ $V_1 = \frac{(0.1 \text{ mg/ml}) (50 \text{ ml})}{(5 \text{ mg/ml})}$ $= 1$ <p style="text-align: center;">5 ml of GO needed to dilute into 50 ml of dH₂O to produce 0.5 M of GO</p>

Table A.2: Synthesizing Silver Nitrate (AgNO_3) solution

Concentration of AgNO_3 (M)	Amount of AgNO_3 needed (g)
0.1	$\frac{g}{M} = \frac{MV}{1000}$ $= \frac{(0.1 \text{ M}) (10 \text{ ml}) (169)}{1000}$ $= \mathbf{0.169}$ <p>0.169 g of AgNO_3 is mixed with 10 ml of dH_2O</p>
0.5	$\frac{g}{M} = \frac{MV}{1000}$ $= \frac{(0.5 \text{ M}) (10 \text{ ml}) (169)}{1000}$ $= \mathbf{0.845}$ <p>0.845 g of AgNO_3 is mixed with 10 ml of dH_2O</p>
1.0	$\frac{g}{M} = \frac{MV}{1000}$ $= \frac{(1.0 \text{ M}) (10 \text{ ml}) (169)}{1000}$ $= \mathbf{1.69}$ <p>1.69 g of AgNO_3 is mixed with 10 ml of dH_2O</p>

Table A.3: Preparation of Silver Complex [Ag(NH₃)₂OH]

Concentration of AgNO ₃ solution (M)	Amount of 200 µl of ammonia (NH ₃) added into 10 ml of AgNO ₃ solution
0.1	2 times
0.5	7 times
1.0	15 times

Table A.4: Preparation of Mercury(II) Chloride (HgCl₂) Solution

Concentration of HgCl ₂ (M)	Amount of HgCl ₂ needed (g)
1.0	$\frac{g}{M} = \frac{MV}{1000}$ $= \frac{(1.0 \text{ M}) (10 \text{ ml}) (271.52)}{1000}$ $= \mathbf{2.7}$ <p>2.7 g of HgCl₂ is mixed with 10 ml of dH₂O</p>
0.001	$\frac{g}{M} = \frac{MV}{1000}$ $= \frac{(0.001 \text{ M}) (10 \text{ ml}) (271.52)}{1000}$ $= \mathbf{0.002}$ <p>0.002 g of HgCl₂ is mixed with 10 ml of dH₂O</p>

APPENDIX B



Figure B.1: Raw data for FTIR analyses from OMNIC software

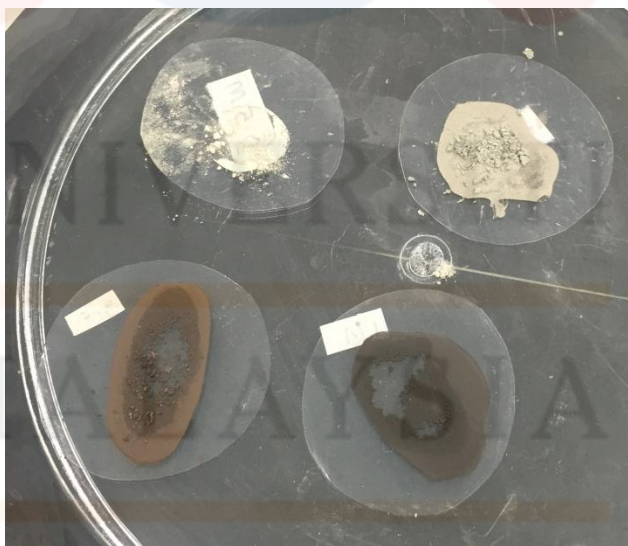


Figure B.2: Produced samples for Ag-rGO (above) and GO (below) in the form of solid