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SYNTHESIS OF ALKYLAMINE FUNCTIONALIZED GRAPHENE OXIDE BY GAMMA IRRADIATION

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By

NORANIZA BINTI AHMAD DAUD

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

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To them this work is dedicated.

My parents Ahmad Daud & Norbaini who gave me strength and courage throughout the journey. Brothers, sister and best friends who housed, nurtured and praying for my success. Without their understanding and support, I would never have completed this project.
Lots of love.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

SYNTHESIS OF ALKYLAMINE FUNCTIONALIZED GRAPHENE OXIDE BY GAMMA IRRADIATION

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May 2017

Chairman : Associate Professor Nor Azowa Binti Ibrahim, PhD
Faculty : Science

This research aims to alter hydrophilic GO to becomes hydrophobic. Gamma-ray (γ-ray) irradiation technique was used to functionalize GO with various alkyl chain length of an alkylamine. Functionalization of alkylchain onto the GO was confirmed by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (^{1}H NMR), and X-ray Photoelectron Spectroscopy (XPS). XRD analysis showed the diffraction peak of graphite was shifted from 2θ=26.40° to lower angle at 2θ=10.20° corresponding to an increasing the interlayer spacing from 0.34 nm of graphite to 0.87 nm of GO upon oxidation. Further increasing of interlayer up to 2.68 nm for GO-A18 was observed after functionalization suggested the long alkylchain was successful intercalated between graphene sheets. FTIR result verified the existence of oxygenfunctionalities on GO after been oxidized by modified Hummers method. Functionalization by γ-ray irradiation method was able to attach alkylchain on the surfaces of GO by the appearance of significant peaks around 2928-2863 cm^{-1} corresponding to the C-H stretching vibration of the alkyl chain (CH_2). ^{1}H NMR analysis also supported these findings by the emergence of small intensity at ~0.88 ppm (-CH_3) and the very intense signal at ~1.25 ppm (-CH_2). Simultaneously, this method showed reduction effect by removing some of the oxygen functionalities that have been confirmed by decreasing of O/C ratio in XPS analysis. The effects of various alkyl lengths functionalized-GO on morphological and thermal properties were investigated. The addition of alkylchain on GO surfaces significantly improves the thermal stability of GO, suggesting their great potential for hydrophobic material in for various applications. Scanning Electron Microscopy (SEM) analysis showed an increase in surface roughness after functionalization which gives huge influences on the wetting properties of the substance as the water contact angle of GO-A18 gives higher value up to 114.11°. Therefore, this gamma irradiation technique has been successfully functionalized GO and simultaneously reduce them to becomes hydrophobic materials.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

SINTESIS ALKILAMIN PERFUNGSIAN-GRAFIN OKSIDA MENGGUNAKAN SINAR GAMMA

Oleh

NORANIZA BINTI AHMAD DAUD

Mei 2017

Pengerusi : Profesor Madya Nor Azowa Binti Ibrahim, PhD
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Kajian ini bertujuan untuk mengubah sifat hidrofilik GO untuk menjadi hidrofobik. Teknik penyinaran sinar gamma (sinar-γ) telah digunakan untuk memfungsikan grafin oksida (GO) dengan pelbagai panjang rantai alkil daripada alkilamin. Perfungsian rantai alkil kepada GO telah disahkan oleh Sinar-X Difraktometer (XRD), Inframerah Jelmaan Fourier (FTIR), Nuklear Magnetik Resonan (^{1}H NMR), dan Spektroskopi fotoelektron Sinar-X (XPS). Analisis XRD menunjukkan puncak pembelauan grafit telah beralih daripada $2\theta=26.40^{o}$ kepada sudut yang lebih rendah di $2\theta=10.20^{o}$ sepadan dengan peningkatan jarak antara lapisan daripada 0.34 nm grafit kepada 0.87 nm GO selepas pengoksidaan. Peningkatan antara lapis yang berterusan sehingga 2.68 nm untuk GO-A18 diperhatikan selepas perfungsian mencadangkan bahwa rantai alkil panjang telah berjaya diinterkalasi antara kepingan graphene. Keputusan dari FTIR mengesahkan kewujudan kumpulan berfungsi oksigen pada GO selepas teroksida dengan kaedah Hummers yang diubah suai. Perfungsian dengan kaedah penyinaran sinar-γ dapat melekatkan rantai alkil pada permukaan GO degan kemunculan puncak yang ketara sekitar 2928-2863 cm^{-1} yang sepadan dengan C-H isyarat getaran rantai alkil (CH_2). Analisis ^{1}H NMR juga menyokong penemuan ini dengan kemunculan keamatan kecil di ~0.88 ppm ($-CH_3$) dan isyarat yang sangat kuat pada ~1.25 ppm ($-CH_2$). Pada masa yang sama, kaedah ini menunjukkan kesan penurunan dengan membuang sebahagian daripada kumpulan berfungsi oksigen yang telah disahkan dengan pengurangan daripada nisbah O/C dalam analisis XPS. Kesan pelbagai panjang alkil dalam GO-terfungsi pada sifat morfologi dan kestabilan terma telah disiasat. Penambahan rantai alkil pada permukaan GO meningkatkan kestabilan terma GO, menunjukkan potensi besar mereka sebagai bahan hidrofobik untuk pelbagai aplikasi. Mikroskop Pengimbasan Elektron (SEM) menunjukkan peningkatan kekasaran permukaan selepas perfungsian yang memberikan pengaruh yang besar terhadap sifat-sifat pembasahan bahan sebagai mana sudut sentuh air untuk GO-A18 memberikan nilai yang tinggi sehingga 114.11^{o}. Oleh itu, teknik sinaran gamma ini telah berjaya mengfungsikan GO dan pada masa yang sama menurunkannya untuk menjadi bahan hidrofobik.

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I certify that a Thesis Examination Committee has met on 22 May 2017 to conduct the final examination of Noraniza binti Ahmad Daud on her thesis entitled "Synthesis of Alkylamine Functionalized Graphene Oxide by Gamma Irradiation" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the Master of Science. The members of the Supervisory Committee were as follows:

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TABLE CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

nm	Nanometer
Sm^{-1}	siemens per meter
wt %	weight percentage
•OH	oxidative radical
•H	reductive radical
ē	Electron
λ	wavelength

CHAPTER 1

INTRODUCTION

1.1 Background of study

The usage of hydrophobic material in the recent years is very popular especially as a coating material due to the presence of desired features such as waterproof, corrosion-resistant and stable against bio-fouling and inorganic materials (in some cases). However, water is often detrimental to the materials when the surface is penetrated to moisture. This is because most of the surfaces are design to work under dry conditions. For that reason, the investigation on the synthesis and preparation of hydrophobic materials become popular among the researcher. To prepare the materials with a larger contact angle, one should combine the effect of the surface roughness which is mainly governed by both chemical composition and geometrical microstructure of the surface (Mohamed *et al.*, 2015).

Graphene has become a matter of interest in science and another research field since it was introduced in 2004. It has been exploited in various application due to the amazing properties such as high Young's modulus, strength, good mobility of charge carrier and good in thermal conductivity (Li *et al.*, 2014). However, production of graphene is quite difficult because each layer of graphene that exist in graphite is hold by strong Van der Waals forces. Graphene oxide (GO) is another derivative of graphene that consists of highly oxygen-containing functional groups on their basal planes and edges which can be synthesized by chemical oxidation of graphite. Various oxygen functionalities that exist on GO surfaces make them easily disperse in water and several polar solvents. Recently, GO has attracted much attention due to its outstanding unique and physical property such as good thermal conductivity, high mechanical strength, and also have very good electrical (Compton *et al.*, 2010) and optical characteristics (Zhu *et al.*, 2010; Loh *et al.*, 2010). This great and amazing properties makes GO suitable for use in a numerous of technological applications such as composite materials, sensors, hydrogen storage and semiconductor materials for electronic devices.

After all, very few studies have examined water–graphene interactions which could be an important study, if GO has to be used in conformal coatings. Apart from that, various functionalities on the surface of GO make it an ideal platform for chemical modification, which may generate materials with fabulous properties. The introduction of hydrophobic groups on GO surface is an attractive objective, especially when aiming for compatibilization with non-polar substances and making of coating materials. For this project, GO was used as the main materials for modification by altering its surfaces in order to improve the hydrophobicity.

Hydrophobicity can be improved by increasing surface roughness with introducing a new substance that owns hydrophobic properties with low surface energy. Various low surface energy materials have been used to modify materials surface to become hydrophobic. Fluorinated compounds, the long alkyl chain of fatty acids, and silanes are compounds that have low surface energy and the ability to attach with various substrates (Meng and Park, 2014). Intercalation of organic molecules in the gallery spacing of layered materials is one of the common modification technique since they can lead to potential applications such as catalytic supports. Numerous method had been established for modification of GO. Recently, gamma-ray (γ-ray) irradiation has attracted attention among researchers in providing not only an environmental friendly method but also feasible, cost effective and can be performed at room temperature as well.

In the present research work, an easy and efficient method will be used to synthesize functionalize-GO that possesses hydrophobic properties by using γ-ray irradiation. GO will be functionalized with a different chain length of alkylamine keeping the other parameters fixed at certain values. The chain length of alkylamine present on GO will change the surface roughness which lead to production of a good hydrophobicity materials.

1.2 Problem statement

Although graphene has attracted numerous attention from research field because of their wide-ranging in industrial and various applications, there are still some obstacles to produce graphene in large scale. GO has been seen as a trigger to the production of graphene through various methods. In fact, GO has been studied for a longer time period than graphene. However, GO somehow is difficult to be incorporated and distributed homogeneously into some of the matrices for applications, especially with hydrophobic materials. Despite focusing on their amazing properties, still, not much research has been done on hydrophobicity properties of GO. Recently, many researchers conducted the investigation on the chemically modified of GO in order to improve properties of GO such as solubility, hydrophobicity and interfacial interactivity with target matrix. However, producing functionalized-GO in large-scale and at low cost is still a challenge which should be overcome before widespread application. Most of the commonly employed modification techniques are often complex that usually possesses long reaction time, involving toxic reagents with specific reaction condition which will restrict the large-scale production. Therefore, a novel route that combines the economic benefits and convenience of chemical synthesis with possessing high reduction efficiency, has been a target for the preparation of functionalized-GO. In this research, the preparation and characterization of GO are presented at first. Subsequently, the functionalization of GO with alkylamine had been done through gamma-ray irradiation method. The investigation on the hydrophobic characteristics of functionalized-GO will be carried out and the results of this study are presented in this thesis.

1.3 Significant of study

Compared with the chemical modifications method, the use of the γ-ray radiation method for functionalized GO has been highlighted to provide a safe, shorter reaction time and environment-friendly to alter the chemical or physical properties of this materials. In addition, the capability of this technique to reduce GO makes it very effective in tuning the hydrophilic GO becomes hydrophobic.

1.4 Scope of study

Due to cheap and readily available in bulk quantities, graphite has been used as a starting material for preparation of GO. The method for preparation of GO is through modified Hummer's method. X-ray diffraction analysis (XRD) was conducted to confirm the increasing of an interlayer between graphene sheets upon oxidation process. In order to improve the hydrophobicity of GO, the resulted GO is further functionalized with various type of alkylamine through γ-ray radiation method. Nuclear Magnetic Resonance (NMR) and X-ray photoelectron Spectroscopy analysis (XPS) was performed in order to verify the formation of the new bond upon functionalization. The structure and wetting properties of functionalized-GO were observed via Scanning Electron Microscopy (SEM) and Water Contact Angle (WCA) analysis respectively. In addition, the investigation on the thermal stability of the functionalized-GO was performed using Thermogravimetry analysis (TGA).

1.5 Research objectives

The main objectives of the study are:

1) to synthesize GO using an improved Hummer's method.
2) to functionalize GO with alkylamine through gamma irradiation.
3) to investigate the effect of different chain length of alkylamine on the hydrophobicity behavior of functionalized-GO.

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