SYNTHESIS OF GRAPHENE NANOPLATELETS USING CHEMICAL VAPOUR DEPOSITION AND WASTE COOKING OIL AS CARBON FEEDSTOCK

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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Sesi Pengajian: **2016/2017 Semester 2**

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I hereby, declared this report entitled "Synthesis of Graphene Nanoplatelets using Chemical Vapour Deposition and Waste Cooking Oil as Carbon Feedstock" is the result of my own research except as cited in references.

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Date : 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons).
The member of the supervisory committee is as follow:

……………………….................................

(Assoc. Prof. Dr. Mohd Asyadi 'Azam bin Mohd Abid)

ABSTRAK

Tujuan kajian ini adalah untuk menilai potensi menggunakan sisa minyak masak (WCO) sebagai bahan mentah karbon alternatif untuk menggantikan gas berbahaya dan berasaskan alkohol yang tersedia dalam mensintesis Grafin Platelets Nano komersil. Sisa minyak masak dipilih kerana ianya murah dan banyak terdapat di Malaysia, ia juga mempunyai kandungan karbon di dalamnya. Grafin Platelets Nano (GrNPs) yang dihasilkan dari eksperimen ini disintesiskan oleh kaedah pemangkin Pemendapan Wap Kimia (CVD) dan pirolisis cecair WCO bercampur dengan serbuk nikel oksida (NiO). Kajian Raman menunjukkan puncak G lebih tinggi berbanding dengan puncak 2D, menandakan kehadiran lapisan berganda Grafin Platelets Nano (GrNPs). Medan Emisi Imbasan Mikroskop Elektron (FESEM) menunjukkan dominasi Grafin Platelets Nano (GrNPs) dalam bentuk lapisan berganda, manakala Grafin Platelets Nano (GrNPs) berbentuk lapisan tunggal juga dicerapkan. NiO berbentuk serbuk digunakan dalam kajian ini berbanding menggunakan substrat. Analisis Termogravimetri (TGA) menunjukkan pengurangan berat bahan yang boleh diterima iaitu sebanyak 22% sepanjang proses pemanasan sampel. Teknik yang digunakan untuk membentuk lapisan berganda GrNPs dari WCO boleh diguna pakai dan berpotensi untuk digunakan dalam aplikasi haba. Semua analisis ini mengesahkan bahawa WCO berpotensi untuk digunakan sebagai sumber karbon untuk pertumbuhan grafin.

ABSTRACT

The aim of this study is to evaluate the potential in using waste cooking oil (WCO) as an alternative carbon feedstock to replace existing hazardous, Alcohol-based gases in synthesizing Graphene Nanoplatelets (GrNPs) Nanoplatelets (GNPs). 6 ml of WCO utilize in this experiment is extracted from cooking oil use for fried chicken, while as much as 0.2 grams Nickel Oxide (NiO) in powder form is use as catalyst. Both materials are mixed together in alumina crucible and stirred approximately for 15 minutes. Following by synthesizing process inside catalytic chemical vapour deposition (CVD) furnace; with temperature variables of 850 °C, 875 °C and 900 °C in growth time of 5 minutes. Based on Raman spectroscopy analysis, results from those three temperature show a significant 2D peak around 2670 to 2680 cm^{-1}, which signified the presence of Graphene material. Whilst, peak of G-band show 50 to 700 cm^{-1} more higher intensity than 2D-band peak with an I_{2D}/I_G ratio less than 1, indicates that the GrNPs obtained are in multilayer form. It is verified by the surface morphological results of FESEM taken from two localized spots, where the sample appeared in different shapes, and distributed irregularly in stacking form. At magnification of 200k, spot 1 demonstrate rectangular shape at certain part of its layers while spot 2 show broken piece of rectangular layers. Thermogravimetic analysis show the acceptance of the GrNPs towards heat, where the sample was heated up from 25 °C to 900°C with heat flowrate of 20 °C per minutes. During the 45 minutes of heating, the weight of GrNPs decrease 22% from initial weight. Deduce that the amount of oxidizes oxygen/moisture residues in the GrNPs content is acceptable. The technique to fabricate multilayer GrNPs from WCO is viable and scalable for potential thermal critical applications. All of this analysis confirming the potential of using WCO as a carbon source for Graphene Nanoplatelets (GrNPs) growth.

DEDICATION

To my late father and beloved families, your supports and prayers will always keep me going. Thank you for all sacrifices and extensive loves received.

ACKNOWLEDGEMENT

Alhamdulillah, praise to Allah swt upon His blessings, I managed to finish my Bachelor Degree project. A number of people who have made significant contributions in the accomplishment of this project earned more than gratitude from me. Their advices, insights and suggestions helped me a lot, especially from my Supervisor, Assoc. Prof. Dr. Mohd Asyadi 'Azam bin Mohd Abid for his time, money, tolerance and encouragement which without him, I may not completed my project. Not to forget, Miss Raja Nor Amalina bt Raja Seman and Miss Nor Najihah Zulkapli for their supports, commitments and technical help by illuminating views on issues related to the project.

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TABLE OF CONTENTS

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

APPENDICES

LIST OF TABLE

LIST OF FIGURES

LIST OF ABBREVIATIONS

GrNPs	-	as grown Graphene Nanoplatelets
NiO	-	Nickel Oxide
Ni	-	Nickel
WCO	-	Waste Cooking Oil
CO	-	Cooking Oil
FTIR	-	Fourier Transform Infrared Spectroscopy
TGA	-	Thermogravimetric Analysis
XRD	-	Xray Diffraction
CVD	-	Chemical Vapor Deposition
FESEM	-	Field Emission Scanning Electron Micsroscopy
GNPs	-	Graphene Nanoplatelets
C	-	Carbon
Si	-	Silicon
Mn	-	Manganese
P	-	Phosporus
S	-	Sulphur
Cr	-	Chromium
Ni	-	Nickel
N	-	Nitrogen
Cu	-	Copper
CO2	-	Carbon Dioxide
Ar	-	Argon

LIST OF SYMBOLS

cm	-	Centimetre
nm	-	nanometre
m	-	Metre
µm	-	micron metre
%	-	Percent
mm	-	Millimetre
MPa	-	Mega Pascal
GPa	-	Giga Pascal
°C	-	Degree Celsius
kV	-	kilo Voltage

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

This study is conducted to acknowledge the material use in this project, in order to assist student's understanding about the title given and enhance the knowledge on the processes involved in producing Graphene Nanoplatelets (GrNPs).

GrNPs have been remark as a new high potential material in enhancing and replacing current hazardous materials, which can be applied into numerous field of application especially in energy and environmental area. Its extraordinary performance of various properties showed that GrNPs could compete with other developed nanomaterial as well. Even there are extensive synthesis method have been established, yet, the need for green and inexpensive technique are preferable to ensure the sustainability of the carbon nanomaterial.

Recent researches succeeded to grow carbon nanomaterial by embedded natural carbon feedstock acquired from hydrocarbon-based plants, biomass waste, plastic & industrial waste, etc., in their experiment. This presentation would focus on development of waste cooking oil as carbon feedstock to synthesis GrNPs material. The aim of the research is to exploit the after-use of waste cooking oil as future prospect of GrNPs production, parallel with enforcement on decreasing environmental issues in Malaysia. GrNPs is an allotrope of carbon packed into a 2D honeycomb lattice to become GrNPs (Wolf, 2014), as to differentiate it from other type of carbonaceous material such as CNT, Fullerenes and Graphite who had different shapes and structures. It can be obtained in single layer or multi-layer form, depending on the success able of the synthesis processes and other parameters.

1.2 PROBLEM STATEMENT

GrNPs is one of future materials that need to be further investigate in Material Science field because of the promising properties it have. Limited production capacity (Warner, 2013) is the main constraint especially if the growth is conducted on a substrate base material. But as the world knows, GrNPs have a high demand in development of various high end technology applications. Yet, most of the GrNPs produce in industry are very limited and can be very expensive based on their quality.

While in the other hand, the existing processing technique to synthesis GrNPs which applicable in the industry is utilizing hazardous and explosive precursor such as Methane, Ethylene and other alcohol-based gases. This processes need complex facilities arrangement and energy intensive process, for example; after-process disposal, utilize high temperature process, and special material handling, that lead to the increasing in cost and time (Nandamuri, Roumimov, & Solanki, 2010). Another problem arise is the application of catalyst in synthesizing GrNPs, which the commercial GrNPs were growth using metal catalyst such that Nickel and Copper; mostly in substrate form.

Therefore, this research is conduct to utilize a natural carbon feedstock; waste cooking oil, as precursor to synthesis GrNPs by applying much more low cost process; catalytic Chemical Vapour Deposition (CCVD). In order to obtain high production of GrNPs, the synthesize process utilized powder-form Nickel Oxide instead of substrate in order to increase the possibility of growing much smaller nanoscale size platelets with high surface area as the carbonaceous product incorporated on the surface of NiO particles.

1.3 OBJECTIVE

The objectives of this research are:

- To synthesize Graphene Nanoplatelets by utilising waste cooking oil as carbon feedstock.
- To grow Graphene Nanoplatelets from Nickel Oxide powder as catalyst.
- To investigate the thermal properties of synthesized Graphene Nanoplatelets.

1.4 SCOPE OF STUDY

This research study featured about the synthesis of the GrNPs on a powdered-form Nickel Oxide surface by using catalytic chemical vapour deposition (CCVD) method which conducted using faculty facility located in Polymer Material Lab, Blok B. The CVD processing parameter is fixed in term of time and varied in temperature, due to the limited period of study. This experiment is conducted in duration of 5 minutes for the growth time and at temperature, 850°C, 875°C, and 900°C.

Nickel Oxide used as catalyst with a weight of the catalyst used is 0.2 gram for one time mixing ratio. The carbon feedstock used in this experiment is waste cooking oil (WCO) with the amount of 6 ml per mixing ratio. The WCO obtained from chicken frying oil, and Fourier Transform Infrared Spectroscopy (FTIR) were used to check the molecular structure of the WCO. Pristine cooking oil is also checked using FTIR, but only as comparison purpose to differentiate the molecular structure of WCO and pristine CO.

The surface morphological analysis of the GrNPs is performed using Field Emission Scanning Electron Microscopy (FESEM) technique which held at High Tech Instrument, Ampang. Raman Spectroscopy technique located at FKP Blok B is used to characterize the as-grown GrNPs, along with characterization of commercial single-layer graphene nanoplatelets (SLG-GNPs) act as a reference to determine the existence of graphene peak in the samples. As for thermal properties, the GrNPs is brought to FKM, UTeM and undergone Thermogravimetric analysis (TGA) process in order to investigate the relationship between oxidation and heating process.

CHAPTER 2

LITERATURE REVIEW

This chapter consists of revisions regarding each topic and subtopic stated, based on the review from various journals in attempt to gather better understanding of this research. In order to accomplish this topic, contents and information from a lot of journals have been extracted out to be analyzed and understand in knowledge manner.

2.1 OVERVIEW OF GRAPHENE

Since the first discovery of Graphene material in 2004, there are tremendous scientific investigation conducted to explore deeply into the behavior of the Graphene until there are more than thousands of research paper had been published (Savage, 2012, Novoselov et al. 2004, Bunch et al. 2007, Novoselov et al. 2008, Becerril et al. 2008).

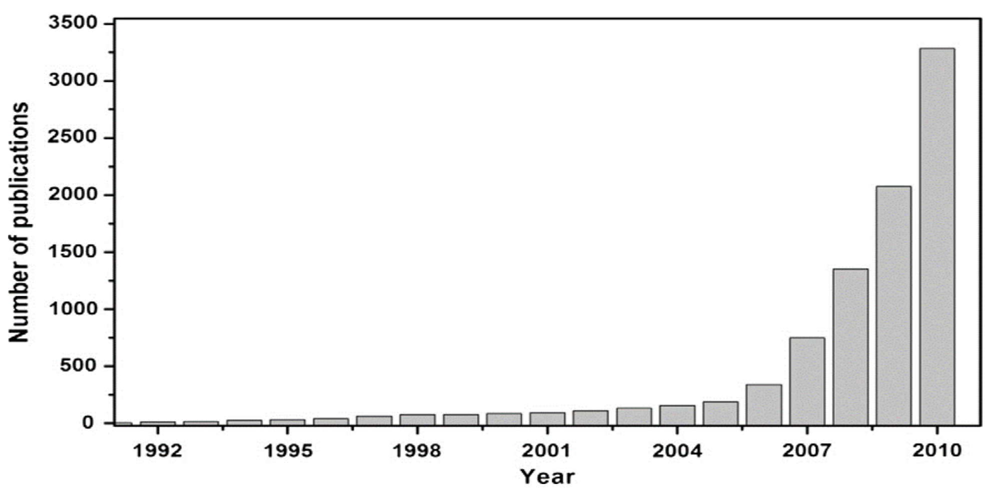

Figure 2.1: Journal of Graphene published in past 20 years (Singh et al., 2011).

Graphene is known as a carbon derived material with abundance of impressive properties in a way it can be commercialized to improve or replace existing material in so many potential applications, such as in composite materials, energy storage, optical film and so on (Mertens 2016, Terrones et al. 2019, Gupta et al. 2012). All of the properties of this super material obtained are based on its unique 2-dimension flat monolayer crystal structure and honeycomb lattice in hexagonal pattern where it could be differentiate from another type of carbon allotropes such as in Figure 2.2 (Abergel et al. 2010, Zhu et al. 2010, and Avouris & Dimitrakopoulos 2010). Graphene's physical form; nanoparticle form, nanoplatelets form, nanocrystal form, etc., and its number of layers; single-layer, bilayer, few layer and multilayer, also give affects to the properties and chemical structure (James & Tour, 2013). The sole focus of this research study is on Graphene Nanoplatelets.

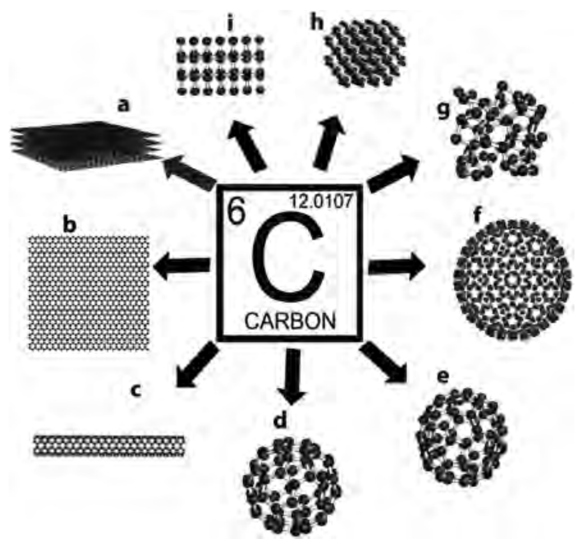

Figure 2.2: Carbon allotropes and its structure: (a) graphite, (b) graphene, (c) carbon nanotube, (d) C_{60}, (e) C_{70}, (f) C_{540}, (g) amorphous carbon, (h) lonsdaleite, and (i) diamond (Ravula et al, 2015).

2.1.1 Properties and application of Graphene Nanoplatelets

The influence from phonons gives direct effect on Graphene Nanoplatelets thermal conductivity, where the energy quanta of lattice vibration waves, gives much lower charge carrier density in Graphene Nanoplatelets than in copper (Sadeghi et al, 2012). The electrical properties of Graphene Nanoplatelets happen due to the zero band gaps; as in Figure 2.3, since it have honeycomb lattice structure. Figure 2.3 explain about the different band gap could be occur based on the lattice structure of different layer Graphene Nanoplatelets. Because of the different properties could be obtained from Graphene Nanoplatelets, the material could be use and apply to enhance various potential application in this world such as in conductive ink, in super capacitor and battery, in composite reinforcement or filler, and also in transparent film for smart phone etc., as in Figure 2.4 and Table 2.1.

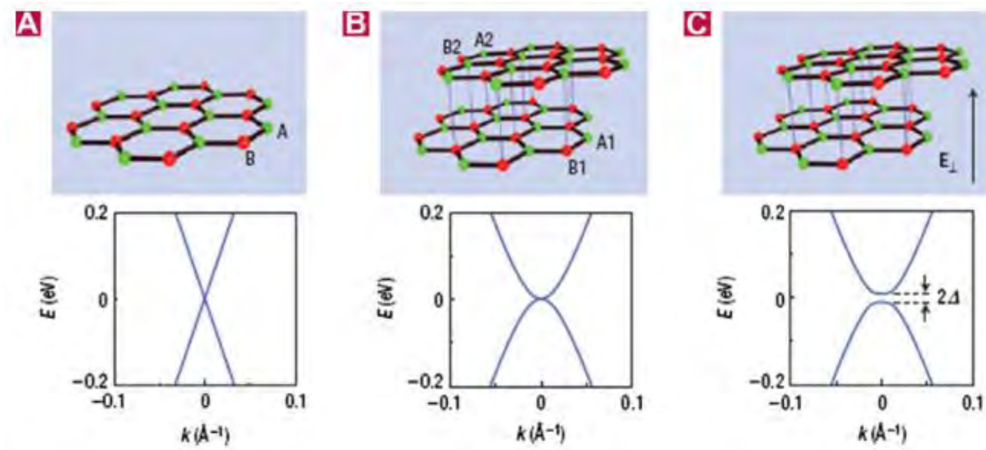

Figure 2.3: Schematic diagrams of the lattice structure of (A) monolayer and (B) bilayer Graphene Nanoplatelets. (C) When an electric field is applied perpendicular to the bilayer, a band gap is opened in bilayer Graphene Nanoplatelets (Liu et al. 2008).

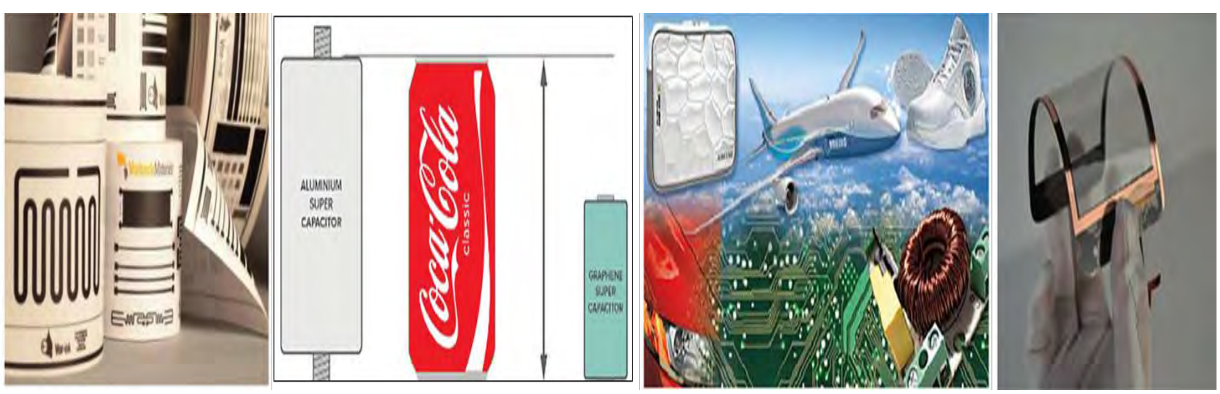

Figure 2.4: Application of Graphene Nanoplatelets in commercial use (Mertens 2016).

Table 2.1: Application and properties of Graphene Nanoplatelets (Allen & Warner, 2013; Giannazzo et al, 2004; Rao et al, Maitra, & Matte, 2013)

High Electrical conductivity	**High electron carrier mobility**	**High mechanical strength**	**Good optical properties**
Conductive Ink	Energy Storage	Composite	Transparent film

2.2 OVERVIEW OF NATURAL CARBON FEEDSTOCK

In this subtopic, a further discussion about the functionality of multiple natural carbon feedstocks as an alternative carbon sources replacing existing materials.

2.2.1 Natural Carbon Feedstock from Waste Material

Waste can be classified into three forms, first one is in liquid form, second is in solid form, and lastly in gaseous form. All of this waste came from numerous sources such as in industrial, residential and medical area, etc. Growing amount of waste in those areas, lead to a bigger problem in disposal process, which contribute to the increasing of funding needed for enlargement of Waste Disposal Center in Malaysia (Jabatan Pengurusan Sisa Pepejal Negara, 2012). Figure 2.5 Shows disposal center in all over Malaysia.

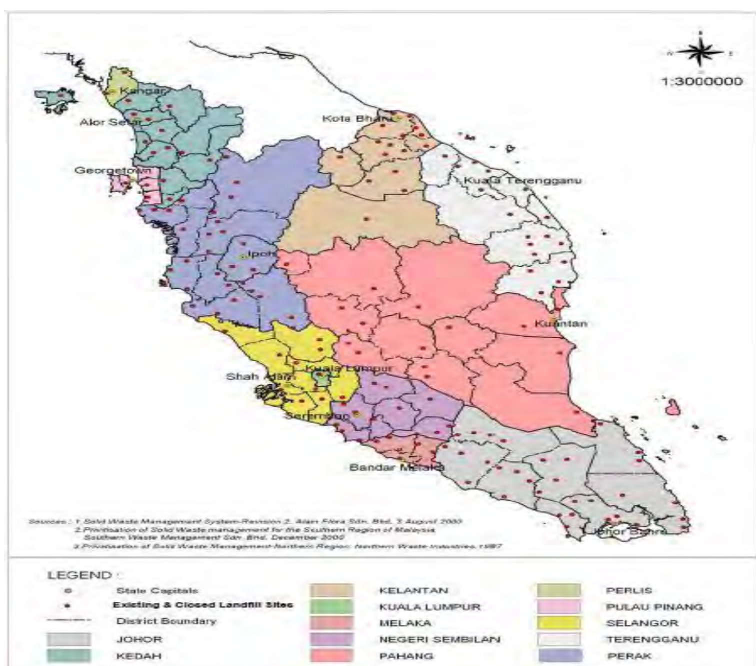

Figure 2.5: Map of disposal center in Malaysia (Jabatan Pengurusan Sisa Pepejal Negara, 2012)

Recycle program and its legal act in Malaysia have been established since 2007, many kiosk and collecting center were built in all over Malaysia but a fully utilization of that facilities are still in lower stage (Sisa, Awam, Pengurusan, & Pepejal, 2007). Most of the recycled material consists of popular waste such as steel, paper, plastic bottle, glass, etc. There are so many waste that could be extracted, yet, ample knowledge from manufacturer and in-situ recycling program in certain area cause limitation of the waste-based nanomaterial's production in large capacity.

Figure 2.6: Type of recycle material.

All of this unworthy materials was actually a source of cash to some waste developer, especially in biomass energy and polymer manufacturer. As in this nanomaterial field, most probably 90% of the waste material could be change into carbonaceous material. Recently, various researches were conducted and managed to prove a necessity in converting waste into abundance sources of carbon. Some researchers succeeded in grew Graphene Nanoplatelets, some succeeded in obtained carbon nanotubes, and some succeeded in gained another type of nanomaterials, by utilizing the carbon content in waste (Deng, You, Sahajwalla, & Joshi, 2016; Kumar, Singh, & Singh, 2016).