# SYNTHESIS OF CARBON NANOSTRUCTURED MATERIALS FROM WASTE ENGINE OIL USING THERMAL CHEMICAL VAPOR DEPOSITION METHOD

SUHUFA ALFARISA

UNIVERSITI PENDIDIKAN SULTAN IDRIS

2015

# SYNTHESIS OF CARBON NANOSTRUCTURED MATERIALS FROM WASTE ENGINE OIL USING THERMAL CHEMICAL VAPOR DEPOSITION METHOD

SUHUFA ALFARISA

THESIS SUBMITED IN FULFILLMENT OF THE REQUIREMENT
FOR THE DEGREE OF MASTER OF SCIENCE
(MASTER BY RESEARCH)

FACULTY OF SCIENCE AND MATHEMATICS
UNIVERSITI PENDIDIKAN SULTAN IDRIS

2015

UNIVERSITI PENDIDIKAN SULTAN IDRIS
اونيۏرسيتي ڤنديديقن سلطان ادريس
SULTAN IDRIS EDUCATION UNIVERSITY

Please tick (√)
Project Paper
Masters by Research
Master by Mixed Mode
PhD

**INSTITUTE OF GRADUATE STUDIES**

**DECLARATION OF ORIGINAL WORK**

This declaration is made on the ...27......day of...March...20..15..

**i. Student's Declaration:**

I, Suhufa Alfarisa / M20131000689 / SCIENCE & MATHEMATICS (PLEASE INDICATE STUDENT'S NAME, MATRIC NO. AND FACULTY) hereby declare that the work entitled Synthesis of Carbon Nanostructured Materials from Waste Engine Oil using Thermal Chemical Vapor Deposition Method is my original work. I have not copied from any other students' work or from any other sources except where due reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

Signature of the student

**ii. Supervisor's Declaration:**

I Assoc. Prof. Dr. Suriani Abu Bakar (SUPERVISOR'S NAME) hereby certifies that the work entitled Synthesis of Carbon Nanostructured Materials from Waste Engine Oil using Thermal Chemical Vapor Deposition Method (TITLE) was prepared by the above named student, and was submitted to the Institute of Graduate Studies as a * ~~partial~~/full fulfillment for the conferment of Master of Science (Material Physics) (PLEASE INDICATE THE DEGREE), and the aforementioned work, to the best of my knowledge, is the said student's work.

DR. SURIANI ABU BAKAR
Profesor Madya
Jabatan Fizik, Fakulti Sains dan Matematik
Universiti Pendidikan Sultan Idris

27/03/2015

Date

Signature of the Supervisor

## ACKNOWLEDGEMENTS

Praise to Allah S.W.T, the Almighty God for giving me the chance, strength and health to finish this study. Without Your blessing, it is impossible for me to be at this point.

First and foremost, I would like to express my sincere appreciation and thanks to my main supervisor Assoc. Prof. Dr. Suriani Abu Bakar for her support, advice, guidance and encouragement throughout my study. The experiences you shared with me are very valuable and enlightened me. May Allah repay your kindness.

Many thanks also to Dr. Mohamad Hafiz Mamat from Universiti Teknologi MARA (UiTM) and Prof. Dr. Abdul Rahman Mohamed from Universiti Sains Malaysia as my co-supervisors. Your precious advice and support are very helpful for me. My thanks also to Prof. Dr. Muhamad Rusop from UiTM for his permission to use the laboratory and equipments in NANO-SciTech Centre and NANO-Electronic Centre, UiTM. My special thanks also to Dr. Azmi Mohamed, Dr. Norhayati Hashim and Assoc. Prof. Dr. Azlan Kamari from Department of Chemistry, Universiti Pendidikan Sultan Idris (UPSI) for their kindly help on my project. I would also like to express my gratitude and appreciation to UPSI, Malaysia Toray Science Foundation and Research Acculturation Collaborative Effort Grant for the financial support on my study.

Special thanks to staffs from Faculty Science and Mathematics: Mr. Noradzman Hisham, Ms. Laili Afzan, Mr. Mohd. Faisal, Mrs. Norhayani Yusof, Mr. Noor Mazlan Mohamed, Mr. Bisyr Asfar, Mr. Mohd. Hashimi, Mr. Mohd. Zurin, Mr. Ahmad Supian and Mr. Ibrahim Saidin for their kindly help on this project. My special thanks also to Mr. Azlan Aziz, Mrs. Nurul Wahida Aziz, Mr. Sailifairus, Mr. Daniel and Mr. Suhaimi for their helping to use the equipments in NANO-SciTech Centre and NANO-Electronic Centre, UiTM Shah Alam.

Next, I would like to thanks to my lab mates, Nor Dalila Abd Rahman, Rika Noor Safitri, Nurhafizah Md Disa and Norhafizah Jusoh for their helpful discussion, support, and friendly environment in Nano Lab UPSI. My special appreciation also goes to my fellow comrades from Universitas Negeri Yogyakarta: Nur Indah Wardani, Tretya Ardyani, Mariah Raihan, Argo Khairul Anas, Wiwid Pranata Putra and Sugeng Riyanto. Thank you for your support and helpful discussion regarding to my project.

Last but not least, I dedicated this work to my parent Suherwan and Sutriyana, my sisters Sufi Inayah Perdani and Suhani Pratiwi. A million thanks to your endless love, caring, support and understanding during my entire study. I am nothing without you all. May Allah bless us always.

# ABSTRACT

This study aimed to synthesize carbon nanostructured materials from waste engine oil (WEO) as a carbon source and ferrocene as a catalyst. The method used in this study was thermal chemical vapor deposition. Several parametric studies were conducted in order to optimize the production of carbon materials from WEO. The parameters were synthesis temperatures, catalyst concentrations, precursor temperatures and volumes, synthesis times and different types of WEO. The samples were characterized using electron microscopy, energy dispersive X-ray, X-ray diffraction, micro-Raman spectroscopy and thermogravimetric analysis. Electrical and field emission properties of the selected samples were analyzed using four-point probe and field electron emission (FEE) measurements. The findings showed that two different structures of carbon materials namely carbon spheres (CS) and carbon nanotubes (CNTs) were succesfully synthesized from WEO. High density CS were produced from 3 ml of WEO mixed with 5.33 weight percent catalyst at precursor and synthesis temperatures of 450 and 800 °C, respectively. Dense quasi-aligned CNTs were also obtained from 4 ml of precursor using 17.99 weight percent catalyst at precursor and synthesis temperature of 500 and 750 °C, respectively. The composite of carbon materials with zinc oxide (ZnO) nanostructures were also fabricated using sol-gel immersion method in order to enhance their FEE performances. The growth of CNTs on ZnO nanostructures gave the best FEE performances as compared to other structures. As a conclusion, carbon materials synthesized from WEO as well as their composite materials with ZnO nanostructures were good candidates to be used in electron emission devices. Implication of the study is that it offers an environmentally friendly and economically beneficial approach for the production of carbon nanostructured materials.

# SINTESIS BAHAN KARBON BERSTRUKTUR NANO DARIPADA MINYAK ENJIN TERPAKAI MENGGUNAKAN KAEDAH PEMENDAPAN WAP KIMIA TERMA

## ABSTRAK

Kajian ini bertujuan mensintesis bahan karbon berstruktur nano daripada minyak enjin terpakai (MET) sebagai sumber karbon dan ferosena sebagai pemangkin. Kaedah yang digunakan dalam kajian ini adalah pemendapan wap kimia terma. Beberapa kajian parametrik dijalankan untuk mengoptimumkan penghasilan bahan karbon daripada MET. Parameter sintesis yang dikaji merangkumi suhu sintesis, kepekatan mangkin, suhu dan isipadu prekursor, masa sintesis dan jenis MET yang berbeza. Sampel dianalisis menggunakan mikroskop elektron, analisis tenaga sinar-X, pembelauan sinar-X, spektroskopi mikro-Raman dan analisis termogravimetri. Sifat elektrik dan pemancaran medan bagi sampel tertentu dianalisis menggunakan peralatan prob empat titik dan pemancaran elektron medan (PEM). Dapatan kajian menunjukkan bahawa dua struktur bahan karbon yang berbeza iaitu karbon sfera (KS) dan nanotiub karbon (NTK) telah berjaya disintesis daripada MET. KS dengan ketumpatan tinggi telah diperoleh daripada 3 ml MET dicampur dengan 5.33 peratus berat pemangkin pada suhu prekursor dan sintesis masing-masing 450 dan 800 °C. NTK kuasi-sejajar dengan ketumpatan tinggi juga diperoleh daripada 4 ml prekursor menggunakan 17.99 peratus berat pemangkin serta suhu prekursor dan sintesis masing-masing 500 dan 750 °C. Komposit bahan karbon dengan struktur nano zink oksida (ZnO) juga difabrikasi menggunakan kaedah rendaman sol-gel untuk meningkatkan kemampuan PEM bahan. Pertumbuhan NTK di atas struktur nano ZnO memberikan sifat PEM yang terbaik berbanding struktur yang lain. Kesimpulannya, bahan karbon yang disintesis daripada MET serta bahan komposit karbon dengan struktur nano ZnO adalah sesuai digunakan dalam peranti pemancaran medan. Implikasi kajian adalah ianya menawarkan pendekatan yang mesra alam dan bermanfaat dari segi ekonomi untuk penghasilan bahan karbon berstruktur nano.

## TABLE OF CONTENTS

CHAPTER 4 RESULTS AND DISCUSSION

# LIST OF TABLES

## LIST OF FIGURES

## LIST OF SYMBOLS AND ACRONYMS

| | | |
|---|---|---|
| CF | - | Carbon Fibers |
| CHNS | - | Carbon Hydrogen Nitrogen Sulfur |
| CNTs | - | Carbon Nanotubes |
| CS | - | Carbon Spheres |
| CVD | - | Chemical Vapor Deposition |
| CWEO | - | Car Waste Engine Oil |
| DTA | - | Differential Thermal Analysis |
| EDX | - | Energy Dispersive X-ray |
| FEE | - | Field Electron Emission |
| FESEM | - | Field Emission Scanning Electron Microscopy |
| FTIR | - | Fourier Transform Infrared Spectroscopy |
| GC-MS | - | Gas Chromatography-Mass Spectroscopy |
| HFCVD | - | Hot-filament Chemical Vapor Deposition |
| HRTEM | - | High Resolution Transmission Electron Microscopy |
| ICP-OES | - | Inductively Coupled Plasma-Optical Emission Spectroscopy |
| MgZnO | - | Magnesium Zinc Oxide |
| MWCNTs | - | Multi-walled Carbon Nanotubes |
| MWEO | - | Motor Waste Engine Oil |
| RBM | - | Radial Breathing Mode |
| PECVD | - | Plasma Enhanced Chemical Vapor Deposition |
| SWCNTs | - | Single-walled Carbon Nanotubes |
| TCVD | - | Thermal Chemical Vapor Deposition |
| TEM | - | Transmission Electron Microscopy |

| | | |
|---|---|---|
| TGA | - | Thermogravimetric Analysis |
| VACNTs | - | Vertically Aligned Carbon Nanotubes |
| WEO | - | Waste Engine Oil |
| XRD | - | X-ray Diffraction |
| ZnO | - | Zinc Oxide |
| $\beta$ | - | Field Enhancement Factor |
| $\varphi$ | - | Work Function |
| $\lambda$ | - | Wavelength |
| $\theta$ | - | Angle between Incident and Diffracted Rays |
| $\rho$ | - | Electrical resistivity |
| $\sigma$ | - | Electrical Conductivity |
| $\omega$ | - | Radial Breathing Mode Peak |
| °C | - | Degree Celcius |
| a-C | - | Amorphous Carbon |
| at% | - | Atomic Percentage |
| Al | - | Aluminum |
| Ar | - | Argon |
| Cu | - | Copper |
| D | - | Defect-Activated Peak |
| $E_g$ | - | Band Gap Energy |
| Fe | - | Iron |
| F-N | - | Fowler-Nordheim |
| G | - | Crystalline Graphite Peak |
| $I_D/I_G$ | - | Ratio of D and G peak |
| *I-V* | - | Current-Voltage |

| | | |
|---|---|---|
| *J-E* | - | Current Density-Electric Field |
| Mg | - | Magnesium |
| mins | - | Minutes |
| ml | - | Milliliter |
| µm | - | Micrometer |
| nm | - | Nanometer |
| O | - | Oxygen |
| wt% | - | Weight Percentage |
| Si | - | Silicon |
| Zn | - | Zinc |

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

Nanostructured material is closely related to nanotechnology. The term of nanotechnology is defined as the process including fabrications, characterizations and applications of a system, material or devices in the size of nanoscale which is 1 to 100 nm (Ramsden, 2009). As the size of materials is smaller, the surface area increases and resulted in the larger reaction area. At this dimension, quantum effects also influence the material properties. Their characteristics will be different with the bulk materials. Studies of nanostructured materials are becoming trend because in their small size, they still have exceptional properties and can be applied in wide range applications.

The discovery of fullerene (C60) in 1985 (Kroto, Heath, O'Brien, Curl, & Smalley, 1985) and introduction of carbon nanotubes in 1991 (Iijima, 1991) led carbon-based material as one of widely studied nanomaterials in the research area. This cannot be missed due to their great properties, easy accessible raw material and have many applications which made them interesting to be continuously studied.

## 1.2 Research Background

Carbon is an abundant element in nature and can be formed into many kind of carbon materials such as carbon nanotubes (CNTs), carbon spheres (CS), carbon fibers (CF), fullerene, carbon black nanoparticle, graphene, carbon dye and mesoporous carbon. These materials have many future applications such as solar cell (Poudel & Qiao, 2014), field emitter (Asli et al., 2013), microcable (Shanov et al., 2013), transistor (Donev, 2009), energy storage, filled composites and sensors (Ajayan & Zhou, 2001; Wilgosz et al., 2012). They also have been applied in sports equipment, automotive and textile (Nowack et al., 2013). Since the last two decades, these materials are being intensively studied due to their remarkable properties and promising applications in human life. Various synthesis methods to produce carbon materials are available such as arc discharge, laser ablation and chemical vapor deposition (CVD). This method involves the catalytic decomposition of carbon precursor on the transition metals such as iron (Fe), cobalt (Co) or nickel (Ni) (Roy et al., 2014). CVD is known as a simple method, able to control the growth direction of material and easy to scale up for mass production (Rafique & Iqbal, 2011). Due to these considerations, CVD method is used in this study.