UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF CARBON NANOTUBE AEROGEL FROM WASTE ENGINE OIL VIA FLOATING CATALYST CHEMICAL VAPOR DEPOSITION FOR OIL SPILL REMOVAL

HAYDER BAQER ABDULLAH

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By

HAYDER BAQER ABDULLAH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for Degree of Doctor of Philosophy

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October 2017

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Faculty : Science

Carbon nanotube (CNT) aerogel is a novel nanomaterial with three-dimensional (3D) macrostructure. The long CNTs assemble display high porosity, spinnability, structural stability, and good electrical conductivity. These characteristic represents a critical approach towards practical applications such as supercapacitors, gas storage, catalyst support, filtration, separation, biological sensors and oil spill removal. CNT aerogel is directly synthesized by floating catalyst chemical vapor deposition (FCCVD) using petrochemicals such as methane, cyclohexane, toluene or dichlorobenzene as a carbon source. Nevertheless, the high cost, depletion of the petrochemical products, and environmental aspects have brought the consideration of using waste engine oil (WEO) instead as a carbon source. This work is the first ever attempt to utilize WEO for CNT aerogel production. It was done via catalytic decomposition of WEO with ferrocene as a catalyst through FCCVD method. Prior to the reaction process, WEO was first filtered to remove dirt and any solid particles that might present. This was later followed by fractional distillation of the oil into different fractions which resulted in five (5) fractions. Gas chromatography-mass spectrometry (GC-MS) showed successful separation of low molecular weight hydrocarbons which was necessary for dissolving the catalyst, while Carbon-nitrogen-sulfur (CNS) analysis indicated that each fraction has more than 69% carbon, less than 0.2% nitrogen and less than 0.09% sulfur. The reaction was carried out at 1150 °C and 1200 °C in hydrogen with a flowing rate of 550 - 650 mL min^{-1}. The carbon source solution (10 mL) was continuously injected into the furnace tube at a feeding rate of 10 mL h^{-1} during one hour reaction time. It was found that all the synthesized CNT aerogel were multi-walled carbon nanotubes (MWCNTs) with 99.14% yield for CNT aerogel 3 synthesized at 1150 °C. Interestingly, CNT aerogel 2-2 and CNT aerogel 3-2 revealed graphenated carbon nanotubes (G-CNTs) structure obtained at reaction temperature 1200 °C. The CNT aerogels had a mesopore distribution with specific surface area in the range between 80.6 - 222.0 m^2 g^{-1}. Field emission scanning electron microscopy (FESEM) revealed randomly orientated to entangle thin multi-walled structure. Oil spill removal study was done by conducting benzene, toluene, and *m*-xylene (BTX) as well as kerosene, diesel oil, palm oil and waste engine oil absorption of the synthesized CNTs. Results showed that CNT aerogel 5-2 gave the highest sorption capacity (Q_e) for kerosene in both oil and oil/water system at 71.43 and 75.19 (g g^{-1}), respectively. Absorption capacity was sustained at 90% for benzene, toluene, and *m*-xylene, 93% for kerosene, 87% for diesel fuel, 68% for palm oil, and 65% for waste engine oil even after 10 absorption cycles. Therefore, it can be concluded that CNT aerogel were successfully prepared from WEO by using FCCVD method which produced MWCNT at 1150 °C and graphenated CNT aerogel at 1200 °C. The CNT aerogel showed an excellent sorption capacity for all tested solvents and oils in both oil and oil/water systems with commendable recycle performance.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN AEROGEL NANOTIUB KARBON DARI SISA MINYAK ENJIN MELALUI KAEDAH MANGKIN TERAPUNG PEMENDAPAN WAP KIMIA UNTUK PENYINGKIRAN TUMPAHAN MINYAK

Oleh

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Oktober 2017

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Aerogel nanotiub karbon (CNT) ialah bahan nano baru dengan makrostruktur tiga dimensi (3D). Himpunan CNT panjang memaparkan keliangan tinggi, kebolehan spin, kestabilan struktur, dan kekonduksian elektrik yang baik. Ciri-ciri ini merupakan pendekatan kritikal ke arah aplikasi praktikal seperti superkapasitor, penyimpanan gas, sokongan pemangkin, penapisan, pemisahan, penderia biologi dan penyingkiran tumpahan minyak. Aerogel CNT disintesis secara langsung secara mangkin terapung pemendapan wap kimia (FCCVD) menggunakan petrokimia seperti metana, sikloheksana, toluena atau diklorobenzena sebagai sumber karbon. Walaubagaimanapun kos yang tinggi, pengurangan produk petrokimia dan aspek-aspek alam sekitar telah membawa pertimbangan kepada penggunaan sisa minyak enjin (WEO) sebagai sumber karbon. Kajian ini merupakan tindakan yang pertama kali dilakukan untuk menggunakan WEO untuk penghasilan aerogel CNT. Ianya dilaksanakan melalui penguraian bermangkin WEO dengan ferosena sebagai pemangkin melalui kaedah FCCVD. Sebelum proses tindak balas, WEO ditapis terlebih dahulu untuk membuang kotoran dan sebarang zarah pepejal yang mungkin hadir. Ini diikuti oleh penyulingan berperingkat minyak menjadi pecahan-pecahan yang berbeza yang menghasilkan lima (5) pecahan Kromatografi gas-spektrometri jisim (GC-MS) menunjukkan kejayaan pemisahan hidrokarbon berat molekul rendah yang diperlukan untuk melarutkan pemangkin, manakala analisis karbon, nitrogen, dan sulfur (CNS) menunjukkan bahawa setiap pecahan mempunyai lebih daripada 69% karbon, kurang daripada 0.2% nitrogen dan kurang daripada 0.09%. Tindak balas telah dilakukan pada suhu 1150 °C dan 1200 °C di dalam hidrogen pada kadar aliran 550 - 650 mL min^{-1}. Larutan sumber karbon (10 mL) disuntik berterusan ke dalam tiub relau melalui pam picagari pada kadar suapan 10 mL j^{-1} selama satu jam masa tindak balas. Didapati semua aerogel CNT yang disintesis adalah berbilang dinding nanotiub karbon (MWCNT) dengan hasil paling tinggi, 99.14% diperolehi oleh aerogel CNT 3 yang disintesis pada 1150 °C. Menariknya, aerogel CNT 2-2 dan aerogel CNT 3-2 menunjukkan struktur nanotiub karbon bergrafen (G-CNTs) diperolehi pada suhu tindak balas 1200 °C. Aerogel CNT tersebut mempunyai taburan leliang meso dan luas permukaan spesifik sekitar 80.6-222.0 m^2g^{-1}. Mikroskopi elektron imbasan (SEM) memaparkan orientasi rawak yang mengkusutkan struktur-struktur nipis berbilang-dinding. Kajian penyingkiran tumpahan minyak telah dilakukan dengan menjalankan ujian penyerapan benzena, toluena dan *m*-xilena (BTX) serta kerosen, minyak diesel, minyak kelapa sawit dan sisa minyak enjin ke atas CNT yang disediakan. Hasil kajian menunjukkan aerogel CNT 5 mempunyai kapasiti erapan tertinggi (Q_e) terhadap kerosen bagi kedua-dua sistem minyak dan minyak/air iaitu masing-masing 71.43 dan 75.19 ($g\ g^{-1}$). Kapasiti serapan dikekalkan pada 90% untuk benzena, toluena, dan *m*-xilena, 93% untuk kerosen, 87% untuk minyak diesel, 68% untuk minyak kelapa sawit, dan 65% untuk sisa minyak enjin walaupun selepas 10 kitaran serapan. Oleh itu, dapat disimpulkan bahawa aerogel CNT telah berjaya disediakan dari WEO menggunakan kaedah FCCVD yang menghasilkan MWCNT pada suhu 1150 °C dan CNT tergrafen pada suhu 1200 °C. Aerogel CNT tersebut menunjukkan kapasiti erapan yang sangat baik terhadap pelarut dan minyak yang diuji untuk kedua-dua sistem minyak dan air/minyak, dengan prestasi kitaran semula yang dibanggakan.

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LIST OF ABBREVIATIONS AND SYMBOLS

A_S BET	Specific surface area
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CD	Carbon Deposition
CNTs	Carbon Nanotubes
DWCNT	Double-Walled Carbon Nanotubes
CVD	Chemical Vapor Deposition
EDX	Energy Dispersive X-ray Spectroscopy
FCCVD	Floating Catalyst Chemical Vapor Deposition
FESEM	Field Emission Scanning Electron microscopy
HRTEM	High Resolution Transition Electron microscopy
IUPAC	International Union of Pure and Applied Chemistry
MWCNTs	Multi-Walled Carbon Nanotubes
Po	Saturated Vapor Pressure
P/Po	Relative Pressure
SA	Surface Area
Sccm	Standard Cubic Centimeter per Minute
SWCNTs	Single-Walled Carbon Nanotubes
Vp	Total Pore Volume
WEO	Waste Engine Oil

CHAPTER 1

INTRODUCTION

1.1 Background and motivation

The discovery of multi-walled carbon nanotubes (Iijima, 1991) and single-walled carbon nanotubes (Iijima and Ichihashi, 1993), both by Iijima of NEC Laboratories in Japan has stimulated researchers all over the world to explore their remarkable properties. As described by Iijima 1991, multi-walled carbon nanotubes (MWCNTs) consist of two or more concentric graphene sheets while single-walled carbon nanotubes (SWCNTs) consist of a single graphene cylinder. Compared to MWCNTs, SWCNTs exhibit superior properties that emerge from the firm one-dimensionality and crystalline perfection of the structure. These two are often simply called Carbon Nanotubes (CNTs).

Realizing that these structures exhibit remarkable mechanical, electrical, and electronic properties, the focus of the CNTs research has moved to the engineering viewpoint of the production of CNTs. A significant limiting aspect for carbon nanotubes as a commercial material is their size which is limited to small sizes; making it very difficult in transferring their nanoscale properties to macroscale applications. Also, the limits of conventional growth processes, which can grow pristine forests of nanotubes for use in research, or as additives in another process (De Volder *et al.*, 2013). Countless papers have been published describing methods for growing longer nanotubes, some evencontinuously, but none have been able to demonstrate a material with properties even close to the theoretical limits of individual nanotubes. Up to the present time, the longest nanotubes can be grown only a few centimeters (Zhang *et al.*, 2013b), and although films (Meng *et al.*, 2014), ribbons (Nath and Sahajwalla, 2011) and aerogels (Skaltsas *et al.*, 2011) can be produced in laboratories; these are still agglomerations of individual nanotubes and not continuous structures.

While these are interesting approaches and worthy of further research, they are still under aspiration approach, where the material strength relies upon the van der Waals interactions between the nanotubes, and not on the nanotubes themselves. Even if further research improves the utility of such methods, it must be remembered that the more complicated a process is, the more difficult and expensive it will be to scale up for commercial applications.

It is of fundamental and practical distinction to scale unique properties of individual CNT into macroscopic three-dimensional (3D) porous structures, which take advantage of CNT's flexibility, excellent electrical and thermal properties, and mechanical integrity (Scarselli *et al.*, 2015). Therefore, synthesis assembly of CNTs into 3D porous architectures is of scientific and technological significance to translate the intrinsic features of individual CNT to a macroscopic level (Liu *et al.*, 2011a; Nardecchia *et al.*, 2013), thereby allowing for some unprecedented properties.

The emerging technologies, including energy storage, sensors, water treatment, etc., have driven high demand in the synthesis of lightweight, elastic and robust materials. Beside, controlled porosity are destined to provide a variety of functionalities such as high surface area, low density, mechanical integrity and great transport properties (Hashim *et al.*, 2012). The scientific and engineering challenge is to design and produce these structures in applied dimensions while manage accurate control over their chemical and physical properties at the nanoscale. Carbon nanotubes are extremely appealing with their low density and versatility in many applications. Inspired by some natural structures (Ajayan and Zhou, 2001), creating 3D porous carbon nanotubes macroscopic design, including all properties of CNTs could be a strategy for achieving promising performance for widespread applications. The main forms of the 3D macroscopic design of carbon nanotubes are carbon nanotube array (Cao *et al.*, 2013), carbon nanotube yarn (Miao, 2013), carbon nanotube ribbon (Wang *et al.*, 2014), carbon nanotube sponge (Li *et al.*, 2016a), and carbon nanotube aerogel (Bryning *et al.*, 2007). Carbon nanotube aerogel (CNT aerogel) is self-sustaining assemblies of carbon nanotube tangled well to construct 3D macroscopic design. It shows high porosity, lightweight, spin ability to yarn, structural stability, and excellent electrical conductivity. CNT aerogel exhibits promising candidate material to be employed in various critical applications such as sensors for detecting pressure, gas and chemical vapor, catalysts for chemical adsorption, photocatalysis, water treatment, electrodes in supercapacitors, microbial fuel cells, lithium-ion batteries, dye-sensitized solar cells, environmental materials for chemical removal, capacitive desalinization process, and biomaterials for tissue engineering. Therefore, these high-value applications have driven the development of reliable routes for fabrication of CNT aerogel.

The floating catalyst chemical vapor deposition (FCCVD) method is a practical process which produces CNT aerogel through the direct self-sustaining assembling of CNTs in the vapor phase (Gspann *et al.*, 2014; Mikhalchan *et al.*, 2016; Motta *et al.*, 2007). This process can create dens of CNT aerogel in one step and is considered as a promising process for large-scale productions, as well as having the ability to control the aerogel structure due to the self-assembly of pure CNTs in the vapor phase. Basically, the association of CNTs during gas flow produces an aerogel, which is formed by assembly of the grown CNTs by van der Waals attractions before condensation to a tangled CNTs (Gspann *et al.*, 2014). The previous synthesis of CNT aerogel was conducted on commercial carbon sources such as methane, ethanol, hexane, and toluene. To convey in the consideration on the depletion of fossil fuel, waste engine oil (WEO) is the preferred candidate for the imminent studies. However, control the assembly of CNTs in stable form during gas flow remains a main challenge for continuous synthesis of CNT aerogel with desired structures.

Therefore, the motivation to develop a feasible and scalable method of CNT aerogel production with controllable structures based on abundant carbon source is for emerging practical applications.

1.2 Research problems

The high cost of CNTs synthesis, which restricts its large scale in macrostructure production, is the crucial aspect to the success of the development and commercialization of CNTs industries. Practically, the CNTs are currently produced in a relatively high quality but in limited quantities. Therefore, future use of this worthwhile material strongly depends on the development of a technology for its large-scale macrostructure production. Accordingly, large-scale synthesis of CNT aerogel has been the subject of intensive researches, and many attempts have been conducted to optimize and control the CNTs growth.

The CNTs macro-assembling of individual CNTs to aerogel require implementing technologies such as pyrolysis, freeze drying, or supercritical point drying to replace trapped solvents with air (Maleki, 2016). This technique requires the use of specific chemicals, or surfactants, also, the CNT aerogels produced from these methods require the existing of additional binders such as polymers and is typically fragile. Besides, these technologies could require a thermal annealing and purification step to improve the porosity and surface area. Therefore, eventually, the process becomes extremely unfeasible and expensive.

Previous works on synthesis of CNT aerogel using Floating catalyst chemical vapor deposition method, reported that the synthesis of CNT aerogel was succeeded by utilizing methane, ethanol, hexane, and toluene (Gspann *et al.*, 2014; Mikhalchan *et al.*, 2016). Whereas, the escalate depletion of fossil fuel requires decrease dependent on such carbon source and establishes a new one for the CNT aerogel production. Therefore, this study would like to see whether waste engine oil could be used as the carbon source for CNT aerogel production.

Floating catalyst CVD systems provide a convenient space for a mixture of reactants and catalyst components in the gas phase which result in more effective production in high temperature. This feature made FCCVD as an efficient process for the synthesis of large quantities of CNT aerogel. However, the performance of a floating catalyst system toward CNT aerogel production is strongly determined by many essential features, such as the catalyst and promoter ratio, carbon source characteristic, reactor design, and operating conditions such as feedstock flow rate, gas flow rate, reaction temperature and reaction time, that all together determine the CNT aerogel quality. The entire optimization of the FCCVD process is a complicated task, especially with waste engine oil characteristics as a carbon source.

Oil spills which are leakage of petroleum onto the surface of large areas of water are a major worldwide problem. Various pollutants are entering water resources from anthropogenic activities, from conventional pollutants such as BTX (benzene, toluene, Xylene) (Guelli Ulson De Souza *et al.*, 2012), and waste engine oil (Jin *et al.*, 2015). Some of these contaminants could not be removed from water efficiently via traditional water treatment methods. Moreover, more effective and low-cost technologies to decontaminate and disinfect water for point-of-use purposes are needed, especially in rural regions.

1.3 Hypothesis

Floating catalyst chemical vapor deposition (FCCVD) method has proven as the adequate process for the CNT aerogel production. In the reported works, the researchers used commercially available carbon sources which are commonly a single component hydrocarbon and highly pure such as methane, ethanol, and toluene. These carbon sources are small size and can dissolve catalyst (ferrocene) for the FCCVD process. The process requires mixing the carbon source with ferrocene as a catalyst which must be dissolved well with the carbon source before it was introduced to the furnace chamber. However, in this work, instead of using a single component and highly pure hydrocarbon, a high density and multicomponent hydrocarbon source which is waste engine oil (WEO) was used. Chemically, WEO is a highly viscous liquid which contains long chain hydrocarbons and other impurities. To obtain the smaller size and shorter chain hydrocarbons, fractional distillation must be conducted.

Nevertheless, pre-treated WEO still contains long chain hydrocarbons with high molecular weights that would negatively affect the properties of the resultant products. Therefore, the control of FCCVD parameters such as catalyst ratio, injection rate, gas flow rate, reaction temperature, and reaction time may result with a production of CNT aerogel.

Utilizing thiophene as a promoter would prevent the catalyst particles from coarsening and aggregation. This will increase the opportunity of produce CNTs from multicomponent carbon source by enhancing the adsorbing and dissociation of carbon atoms on the growing ends of the CNTs. Moreover, adding thiophene as a promoter would produce mostly long and small diameter CNTs due to its property as a surfactant which encourages CNTs nucleation and growth and therefore prevents carbon encapsulation on the catalyst particle.

1.4 Objectives of the study

The project is primarily undertaken to synthesize CNT aerogel using waste engine oil via floating catalyst chemical vapor deposition. Under this umbrella, the objectives of the research project are then described as follows:

1- To identify and characterize the waste engine oil fractions produced by a fractional distillation process of waste engine oil in order to use them as carbon sources.
2- To synthesize CNT aerogel from WEO fractions through the floating catalyst CVD method by controlling the catalyst ratio, injection rate, gas flow rate, reaction temperature parameters.
3- To characterize the structure and properties of CNT aerogel produced from waste engine oil.

4- To evaluate CNT aerogel for oil spill removal and investigate the absorption ability for several chemicals and oils.

1.5 Scope of study

In this study, the CNT aerogels are synthesized in one step process using floating catalyst chemical vapor deposition (FCCVD) method at the reaction temperature 1150 °C and 1200 °C, and flow rate of hydrogen as a carrier gas of 550-650 sccm in a one hour reaction time. In an effort to develop a potentially feasible and efficient method for the large quantities of CNT aerogel production, the synthesis experiments focused on the design of process based on WEO as a carbon source in FCCVD method. There is no report yet declared the synthesis of CNT aerogel from WEO. The carbon source was prepared from waste engine oil by fractional distillation under nitrogen at 400 °C to attain several fractions which were used as carbon sources. The viscosity and density of the oil fractions were obtained beside CNS and GC-MS analysis, while the CNT aerogels were characterized by FESEM, EDX, HRTEM, TGA, Raman, and BET analysis.

For the ability of synthesized CNT aerogel on absorption application, it was tested for sorption study over hydrocarbons such as benzene, toluene, *m*-xylene and kerosene as well as oils which were diesel fuel, palm oil, and waste engine oil. The equilibrium sorption capacity (Q_e) was calculated by following the weight of CNT aerogel before and after absorption for comparison with other absorbents. In addition, kinetics study were considered by applying Pseudo-second-order model Fractal like - linear driving force (FL-LDF) model for oil and oil/water systems.

1.6 Thesis outline

Chapter 1 gives a motivation of the work presented in the subsequent chapters. Although each chapter briefly introduces itself, the information contained in this chapter is general to state the motivation of the thesis study and gives justification to the problems presented and briefly what measures were undertaken to address them and how that was achieved. The main objectives of the study are also presented in this chapter.

Chapter 2 is a general literature review. The chapter will be brief and will give a description of aims at providing an in-depth understanding of available synthetic methodology and routes of carbon nanotube macrostructure. Emphasis will be on carbon nanotube aerogel. The commonly used CNT synthesis procedures, relevant properties of the CNTs as well as their characteristics will be discussed briefly to reveal their role in carbon nanotube aerogel. The discussion is then shifted towards synthesis method for CNT aerogel emphasis review on floating chemical vapor deposition (FCCVD) method and the growth mechanism of CNTs using this technique.

Chapter 3 describes the experimental work completed to accomplish the goals of this study. The experiments are divided into three sections. The first section is dedicated to the fractional distillation of waste engine oil and the results characterization. The second section deals with CNT aerogel synthesis experimental via FCCVD method and the results characterization. The third section elucidates the absorption study for several chemicals and oils.

Chapter 4 discuss the results of experiments and the data collected from analysis in order to come out with the best description of the project findings. This chapter is divided into three sections. The first section is devoted to the fractional distillation of waste engine oil. Study the properties of the fractions that result from the process compare with WEO by proper characterization. The second section deals with the CNT aerogel synthesized from WEO fractions via FCCVD. Discuss the process parameters that control the CNT aerogel production. Several reaction processes were done as a preliminary study by varying the parameters involved in the formation of CNT aerogel. The parameters investigated are injection rate of reactant, temperature stability during reaction, the position and length of injection tube, sonication time of the reactants, catalyst ratio, and gas flow rate. Then study CNT aerogel production by varying several parameters such as catalyst ratio, gas flow rate, and reaction temperature have done. Morphology analysis, thermal stability, the degree of graphitization, surface area, N_2 adsorption isotherm and pore size distribution are studied. The third section exposes to the sorption study for several chemicals and oils. Investigate the sorption performance of the CNT aerogel sorption study which includes sorption capacity, kinetic study, and recyclability was conducted on various chemicals and oils were selected which are benzene, toluene, *m*-xylene, kerosene, diesel fuel, palm oil, and waste engine oil. The study has done using two system oil and oil in water (oil/water).

Chapter 5 elucidate the conclusions and recommendations for future work.

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