MASS PRODUCTION OF CARBON NANOTUBES FROM WASTE COOKING PALM OIL VIA MODIFIED THERMAL CHEMICAL VAPOR DEPOSITION AND ITS APPLICATION

NORHAFIZAH BINTI JUSOH

UNIVERSITI PENDIDIKAN SULTAN IDRIS

2021

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ABSTRACT

This study is aimed to synthesize carbon nanotubes (CNTs) for the large scale production (in term of high volume production around 500 mg per day) by utilizing the novel waste cooking palm oil (WCPO) as carbon feedstock. The method used were modified thermal chemical vapor deposition (TCVD) that equipped with a peristaltic sprayer in order to continuously supply the precursor and catalyst into the system. Various synthesis parameters, such as effect of vaporization and synthesis temperature, synthesis time interval, precursor flow rate, post annealing treatment, nozzle diameter, and catalyst concentration were conducted in order to find out the optimum parameter to produce high quantity and good quality of CNTs. The total amount of 1000 ml WCPO precursor was sprayed continuously during the experiment with ferrocene as catalyst via modified TCVD system. The samples were characterized using field emission scanning electron microscopy, energy dispersive X-ray, high resolution transmission electron microscopy, micro-Raman spectroscopy and thermogravimetric analysis. The optimum samples were then used as nanofiller for supercapacitor application and as an adsorbent material for adsorption heavy metal ions application. The findings showed that the total of ~433 g CNTs were produced with high carbon conversion rate of 56 %. Growth of dense CNTs with a high purity of ~90 % and good crystallinity (I_D/I_G ratio ~0.43) occurred at combination temperature of 500 and 800 °C of vaporization and synthesis temperature, respectively, time interval between spraying process of 15 min, precursor flow rate of 30 mLmin^{-1}, annealing treatment at 500 °C for 4 h, nozzle diameter of 0.25 mm and catalyst concentration of 5.33 wt% using modified TCVD system. The CNTs/natural rubber-latex (NRL) nanocomposite exhibited a good capacitance performance with a specific capacitance of 81.82 F/g. Meanwhile, CNTs from WCPO shows an excellent ability in order to remove heavy metal ion from aqueous solutions which match well with the Langmuir isotherm model with higher correlation coefficient and maximum adsorption capacity metal ions of 0.9894 and 31.25 mg/g, respectively. In conclusion, this study determined that a high production of WCPO based-CNTs using modified TCVD method provided benefits for its utilization as composite and adsorbent materials especially for supercapacitor and adsorption of heavy metal ions application. The implication of this study is used a simple method, economical and green approach in order to produces higher production and good quality of CNTs.

PENGELUARAN BESARAN NANOTIUB KARBON DARIPADA MINYAK MASAK TERPAKAI DENGAN KAEDAH PEMENDAPAN WAP KIMIA TERMA YANG DI UBAH SUAI DAN APLIKASINYA

ABSTRAK

Kajian ini bertujuan untuk mensintesis nanotiub karbon (NTK) untuk pengeluaran secara besaran (dengan jumlah pengeluaran yang tinggi iaitu sekitar 500 mg sehari) dengan menggunakan pendekatan baharu minyak masak terpakai (MMT) sebagai bahan mentah karbon. Kaedah yang digunakan adalah pemendapan wap kimia terma (TCVD) yang diubah suai dilengkapi dengan penyembur peristaltik untuk membekalkan prekursor dan pemangkin secara berterusan ke dalam sistem. Pelbagai kajian parametrik seperti kesan pengewapan dan suhu sintesis, selang masa sintesis, kadar aliran prekursor, rawatan pasca penyepulih-indapan, diameter nozel, dan kepekatan pemangkin telah dijalankan untuk mengetahui parameter yang optimum bagi menghasilkan kuantiti yang banyak dan kualiti NTK yang baik. Sebanyak 1000 ml MMT prekursor disembur secara berterusan semasa eksperimen dengan ferosena sebagai pemangkin melalui sistem TCVD yang telah diubahsuai. Sampel tersebut dicirikan menggunakan mikroskopi pengimbas pancaran medan elektron, analisis tenaga sinar-X, mikroskopi pengimbas pancaran medan elektron, spektroskopi mikro-Raman dan analisis termogravimetri. Sampel yang optimum kemudiannya digunakan sebagai pengisi-nano untuk aplikasi superkapasitor dan bahan penyerap bagi aplikasi penjerapan ion logam berat. Penemuan menunjukkan bahawa jumlah ~433 g NTK dihasilkan dengan kadar penukaran karbon tinggi iaitu sebanyak 56%. Pertumbuhan NTK yang padat dengan kemurnian tinggi ~90% dan kristaliniti yang baik (nisbah I_D / I_G ~0.43) berlaku pada suhu gabungan 500 dan 800 °C pengewapan dan suhu sintesis, masing-masing, selang masa antara proses semburan selama 15 minit, kadar aliran prekursor pada 30 mLmin-1, rawatan penyepulindapan pada 500 ° C selama 4 jam, diameter muncung penyembur 0.25 mm dan kepekatan pemangkin sebanyak 5.33 peratus berat pemangkin dengan menggunakan sistem TCVD yang diubahsuai. Nanokomposit NTK / getah asli-latek mempamerkan prestasi kapasitans yang baik dengan nilai kapasitan khusus sebanyak 81.82 F/g. Sementara itu, NTK dari MMT menunjukkan keupayaan yang sangat baik untuk menyingkirkan ion logam berat daripada larutan akueus dan sepadan dengan model isoterm Langmuir dengan pekali korelasi yang lebih tinggi dan kapasiti ion penjerapan yang maksimum dengan masing-masing 0.9894 dan 31.25 mg/g. Kesimpulannya, kajian ini mendapati bahawa pengeluaran tinggi NTK berasaskan MMT dengan menggunakan kaedah TCVD yang diubahsuai memberikan faedah untuk kegunaannya sebagai bahan komposit dan penyerap terutama untuk superkapasitor dan penjerapan aplikasi ion logam berat. Implikasi kajian ini adalah menggunakan pendekatan kaedah yang mudah, ekonomi dan hijau bagi menghasilkan pengeluaran NTK yang lebih tinggi dan kualiti yang baik.

TABLE OF CONTENTS

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LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CNTs	Carbon Nanotubes
CVD	Chemical Vapor Deposition
DTGA	Differential Thermal Analysis
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
MWCNTs	Multi-walled Carbon Nanotubes
RBM	Radial Breathing Mode
SWCNTs	Single-Walled Carbon Nanotubes
TCVD	Thermal Chemical Vapor Deposition Method
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
WCPO	Waste Cooking Palm Oil
WEO	Waste Engine Oil
Å	Armstrong
ºC	Degree Celcius
a-C	Amorphous Carbon
Cu	Copper

D	Defect-activated Peak
Fe	Iron
G	Crystalline Graphite Peak
g	Gram
ID/IG	Ratio of D and G peak
I-V	Current-Voltage
min	Minute
M	Molar
ml	Mililitre
µm	Micrometer
nm	Nanometer
wt%	Weight Percentage

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter discusses the research background of the large scale carbon nanotubes (CNTs) using natural sources and waste materials as carbon precursor by thermal chemical vapour deposition method (TCVD), as well as the application of CNTs as nanocomposites and adsorbent materials in supercapacitor and adsorption of heavy metal ions, respectively. The research background and problems are extensively discussed in this chapter. The next section of this chapter covers the research objectives, scope and limitation of study. At the end of this chapter, thesis organisation is also presented.

1.2 Research Background

CNTs have become the building blocks for the nanoscience and nanotechnology field. They have various potential applications that range from electrical, mechanical, and chemical applications, and are conventionally produced by using fossil fuel-based precursors. Potential applications of CNTs include batteries for engine powered hybrid-electric and fuel cell powered vehicles (Burke, 2007), chemical sensors for security systems (Perkins, E. S. Snow & Robinson, 2006), hydrogen storage for electrochemical devices (Chen et al., 2008), electron field emitter for flat panel displays (Bonard, 2002), scanning probe for atomic force microscope (AFM) (Bunch, Rhodin & McEuen, 2004), wires for quantum electronics (Dekkar, 1999), electrodes for discharge tubes (Miao, Lue & Ouyang, 2006), adsorbent materials (Song et al., 2015) and electrochemical capacitor for energy storage (De Volder, 2013). Therefore, the up-scale production of CNTs in abundant amount is highly needed.

To date, one of the companies that successfully produce large-scale CNTs is Shenzhen Nano-Technologies Port. Co., Ltd., which is based in China (Eklund et al., 2007). They produce 40 kg CNTs per day using a cycled vertical CVD system. Production of ~3 kg/h aligned CNTs from ethylene as carbon source via fluidized bed CVD reactor was reported by Fei et al. (Zhang, Zhao, Huang, Nie & Fei, 2010). However, the use of fossil fuel-based carbon sources is not preferable because these resources will not be renewable in the coming decades. Large-scale production of CNTs (1 kg/h) from natural precursor camphor powder using CVD reactor has been successfully achieved by Meijo Nano Carbon Co. Ltd., Japan (Kumar & Ando, 2010).

Catalytic decomposition using conventional precursors such as methane (Latorre et al., 2011), benzene (Frusteri et al., 2013), acetylene and xylene (Raza et al., 2016), have been studied for mass production of CNTs. However, other than expensive, they are also non-renewable sources. Hence, their availability is expected to be limited in the next future.

However, the use of natural precursors, such as camphor (Kumar & Ando, 2010; Asli, Shamsudin, Suriani, Rusop & Saifollah, 2013], palm (Suriani, Azira, Nik, Md Nor, & Rusop, 2009; Zobir et al., 2012), olive, corn, sesame, and coconut oil (Azmina et al., 2012; Paul & Samdarshi, 2011) for large-scale production of CNTs is unfavorable because this approach opposes the main usage of the precursors in the food sector and medical industries (Suriani et al., 2015). This approach may also contribute to environmental damage as the precursors are grown on land converted from rainforests, peatlands, savannas, and grasslands (Fargione, Hill, Tilman, Polasky & Howthorne, 2008). Therefore, the use of waste material such as waste cooking palm oil (WCPO), waste engine oil (WEO), waste chicken fat (WCF) and gutter oil (GO) as carbon feedstock for bulk CNTs production is a more economical and greener practice. These precursors served as renewable sources and low cost raw materials for large scale CNTs production.

There are several methods for large scale production of CNTs including TCVD (Mukul & Ando, 2010), laser ablation (Scott, Arepalli, Nikolaev & Smalley, 2001) and arc discharge (Senthil Saravanan, 2010) method. The laser ablation method is able to produce CNTs with high purity and good graphitization degree of CNTs (Zhang et al., 2014) but the operating cost is very expensive for large scale production. Meanwhile, arc discharge method can yield large scale CNTs but this method produce CNTs in low quality with a lot of impurities. The TCVD method is the most commonly used method for synthesis of CNTs. This method represents simplest preparation set-up where the CNTs can be grown under mild synthesis condition (such as normal pressure and low growth temperature), simple facility, and low cost as the use of high quality substrate and chemicals is not required (Zhang et al., 2006). This method also considered to be an economic and practical process for large scale production of high purity CNTs (Prasek et al., 2011).

There have been a lot of studies on the application of CNTs in supercapacitor devices (Ajayan & Zhou, 2001; Trassati & Kurzweil, 1994; Zheng et al., 2012). Supercapacitor is also called as ultracapacitors or electrochemical capacitors with unique characteristics such as cost effective storage, long cycle life, safe in operation, high specific power and environmentally friendly (Trassati & Kurzweil, 1994). Zheng et al. (2012) reported the low performance of activated carbon as electrode have brought CNTs to this application. While, Chen et al. (2014) reported the fabrication of electrode materials for supercapacitor using CNTs composited with potassium hydroxide as electrolyte. It was found that the high specific capacitance of 166 Fg^{-1} at current density 0.3 Ag^{-1} was obtained. This showed that CNTs can improve the performance of supercapacitor due to their high surface area and conductivity (Boyea, Camacho, Turano & Ready, 2007). Research in this area has led to the development of energy storage devices which can replace the existing batteries and fuel cells for the development of nanotechnology.

Meanwhile, the removal of heavy metals from the water was main issues today. Various techniques have been explored for the removal of these heavy metals from the polluted water such as chemical precipitation, ion-exchange, electrodialysis, reverse osmosis and adsorption (Ahmadpour, Efekhari & Ayati, 2014; Bernard & Jimoh, 2013; Kouakou, Ello, Yapo & Trokourey, 2013). Most of the methods become ineffective and uneconomical when the concentrations of heavy metals are raised up to 500 mg/L then the permissible limits of ~1 mg/L (Balintova, Holub & Singovszka, 2012). Considering from economy and effectiveness, adsorption process is regarded as one of the promising and widely used methods to solve this problems (Adeli, Yamini & Faraji, 2012; Siddiqa, Shahid, Gill, 2015).

Qu et al. (2008) developed CNTs filled with Fe_2O_3 particles for removal heavy metal from aqueous solution. Meanwhile, Tang et al. (2012) reported magnetic CNTs as adsorbent for removal heavy metals of atrazine and Cu (II) from aqueous solution simultaneously. However, the method involved some modification and functionalization for production magnetic CNTs. The present methods for synthesizing magnetic CNTs have drawback such as expensive, time-consuming, environmentally friendly, fussy method and leading to a low yield (Wright et al., 2012; Bollen et al., 2016; Liu et al., 2010). Hence, the introduction of metal catalyst by TCVD method was the simple technique in order to produced CNTs with filled metal nanoparticles as an adsorption of heavy metal ions in solution.

1.3 Problem Statement

In the previous work, the CNTs from waste precursor namely WCPO (Suriani, Md Nor & Rusop, 2010; Suriani et al., 2015; Suriani et al., 2016), WEO (Suriani et al., 2015), WCF (Suriani et al., 2013; Suriani et al., 2016) and GO (Suriani, Dalila, Mohamed, Soga & Tanemura, 2015) have successfully synthesized. synthesis was carried out in a TCVD furnace. A wide range of synthesis parameters were optimized (Suriani et al, 2015; Suriani, Md Nor & Rusop, 2010; Suriani et al., 2015; Suriani et al., 2013; Suriani, Dalila, Mohamed, Soga & Tanemura, 2015) to synthesize CNTs with desired characteristics. The effect of varying synthesis parameters was studied in detail by using electron microscopy, micro-Raman spectroscopy, and thermogravimetric analysis (TGA), among others. The CNTs produced from WCPO, WCF, WEO, and GO showed a high purity between 81–89% with good graphitization of 0.52–0.66 I_D/I_G ratio. The samples also demonstrated good field electron emission (FEE) characteristic (Suriani et al, 2015; Suriani, Md Nor & Rusop, 2010; Suriani et al., 2015; Suriani et al., 2013; Suriani, Dalila, Mohamed, Soga & Tanemura, 2015).

The measured FEE properties from the cathodes of the CNTs structure achieved a current density range of a few $mAcm^{-2}$ orders at reasonable fields; the attained range is suitable for application in flat panel displays and flat lamps (Hu et al., 2015; Madani et al., 2015). However the problem of the current TCVD system used for WCPO-based CNTs production was low/batch-by-batch CNTs production because of non-continuous supply of both catalyst and carbon feedstock. The existing furnace can produce only a maximum of 19.7 g of CNT in a day with a maximum furnace input of 45 ml oil (Suriani at al., 2009; Suriani, Md Nor & Rusop, 2010; Suriani et al., 2015; Suriani et al., 2013;

Suriani, Dalila, Mohamed, Soga & Tanemura, 2015). To achieve high-volume CNTs production, the growth of CNTs needs to be repeated continuously; batch production is discouraged because of difficulty in controlling the quality of CNTs.

Here, we report the first scaled-up prototype of a CNTs production system by utilizing WCPO as a carbon feedstock. In contrast to existing systems (Asli, Shamsudin, Suriani, Rusop & Saifollah, 2013; Suriani et al, 2015; Suriani, Md Nor & Rusop, 2010; Suriani et al., 2015; Suriani et al., 2013; Suriani, Dalila, Mohamed, Soga & Tanemura, 2015), the modified TCVD system is equipped with a peristaltic sprayer to ensure a continuous supply of oil and catalyst to the furnace; this approach helps to prevent carbon source shortages and poisoning of individual catalysts because the catalyst is replenished constantly during the synthesis. The continuous addition of both oil and catalyst produces a large amount of CNTs for use at industrial level with a high carbon conversion rate (56%).

Although the utilization of the sprayer, including medical nebulizer for fossil fuel-based CNTs (Yang et al., 2008), reportedly produces good-quality CNTs, the use of a sprayer for highly viscous precursors, such as WCPO, is challenging and requires a special nozzle. Our prototype is the first feeding system that uses a peristaltic sprayer to produce oil-based CNTs in bulk, and such CNTs are comparable to conventional CNTs products, with a high purity, minimal non-tubular carbon structures, and good crystallinity of loose CNTs powder. The first scaled-up prototype of a CNTs production system by utilizing WCPO as a carbon feedstock is economical and environmentally beneficial. The zero cost of WCPO reduced the price of 1 gram of CNTs from a range of USD 20–100 (Lu, Drzal, Worden & Lee, 2007) to USD 5, and the use of WCPO offers a "green" alternative as a cheap and renewable raw material for industrial volume CNTs production.

The bulk CNT produced through this work was then used as a nanofiller in natural rubber-latex (NRL) for the fabrication of CNT/NRL nanocomposite, and we demonstrate its potential use as an electrode material for supercapacitor devices. In addition, CNTs from waste i.e. WCPO has not been systematically studied as adsorbent material for removal heavy metal ions application. In this work, we reported the high production of CNTs by TCVD method using ferrocene as catalyst and WCPO as carbon source. We find that, the Fe nanoparticles encapsulated by CNTs tube, which indicate as good adsorbent material for removal heavy metal ions. This method were simple, economically and high yield production of CNTs as adsorbent material.

1.4 Research Objectives

i. To develop a scaled-up prototype of WCPO based-CNTs by using modified TCVD system assisted peristaltic sprayer.
ii. To optimize the structure properties of WCPO based-CNTs by modified TCVD system.
iii. To investigate the growth mechanism of WCPO based-CNTs using modified TCVD system.
iv. To investigate the potential application of WCPO based-CNTs for supercapacitor electrode and adsorbent materials.

1.5 Scope and Limitations of Study

The synthesis of CNTs was done using WCPO as carbon precursor by modified TCVD system assisted peristaltic sprayer. Various synthesis parameters were optimized in order to produce WCPO based-CNTs with desired physical characteristics which includes the effect of temperature combination of vaporization and synthesis temperature (450-550 °C and 750-850 °C), the effect of time interval between spraying process (5-25 min), the effect of precursor flow rate (10-50 $mLmin^{-1}$), the effect of post annealing treatment (range temperature: 400-600 °C; duration time: 2-6 h), the effect of nozzle diameter (0.25 and 0.50 mm) and the effect of catalyst concentration (2.33 – 7.99 wt%).

For direct observation of nanotubes length, diameter size, degree of lateral alignment, shape and structure of WCPO based-CNTs, the field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) were used. For element identification such as the presence of contaminants or catalyst in the specific region in the sample, it was determined using energy dispersive X-ray (EDX) while micro-Raman spectroscopy and TGA were used to study crystallinity and purity of the samples, respectively. Vibrating sample magnetometer (VSM) was used to determine the magnetization of the prepared sample. Fourier transform infrared spectroscopy (FTIR) and inductively coupled plasma – optical emission spectrometer (ICP-OES) was employed to investigate the physical and chemical properties of WCPO based-CNTs as an adsorbent material before and after adsorption process. Current-voltage (I-V), cyclic voltammetry (C-V) and charge discharge (C-D) measurements were also conducted for electrical properties investigation and capacitance measurements for the supercapacitor application.

1.6 Thesis Organization

This thesis is written in five chapters. Chapter 1 is the introduction, background of study, research problems, objectives and scope and limitation of studies. A review of CNTs is discussed in Chapter 2. Its discovery, general CNTs material properties were explained and its physical structure was also described. The various carbon source, synthesis method, mass production and the growth mechanism of CNTs were also discussed. In concluding Chapter 2, some common characterization techniques used to investigate the CNTs structure and potential application for adsorption and supercapacitor application of CNTs were also explained in detail. The experimental work, the modification TCVD system and characterizations were presents in chapter 3. At the end of Chapter 3, the procedure of preparing the samples as an adsorbent material in adsorption of metal ions and nanocomposites in supercapacitor application were also discussed. The overall flow chart of the experimental work were presented. Chapter 4 were discusses the results and findings of WCPO based-CNTs produced. In Chapter 4, the WCPO based-CNTs as an adsorbent materials in adsorption of metal ions and the fabrication of electrode from WCPO based-CNTs latex nanocomposite in supercapacitor application which were done on selected samples. Finally, the findings were summarized in Chapter 5 and some suggestions were also described for future work.