PHYSICAL PROPERTIES OPTIMIZATION OF CARBON NANOTUBES FROM PALM OIL PRECURSOR

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DECLARATION

I hereby declare that the work in this dissertation is my own work except for quotation and summaries which have duly acknowledged.

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ABSTRACT

Carbon nanotubes (CNT) were synthesized from palm oil as carbon source using thermal chemical vapor deposition method (TCVD). The parametric studies were carried out to determine the optimum parameters to produce CNT with the optimum physical properties. The parameters comprise of synthesis temperature, catalyst concentration, substrate positions, precursor amount, synthesis time, carrier gas and variety of bio-hydrocarbon precursors. The physical properties of CNT were analyzed using electron microscope, energy-dispersive X-ray analysis, micro-Raman and Fourier transform infrared (FTIR) spectroscopy, thermogravimetric (TGA) and CHNS-O analyser as well as four point probe for *IV* measurement. The carbon precursor was also analyzed using TGA, FTIR spectroscopy and gas chromatography mass spectrometry (GC-MS) in order to optimize the physical properties of CNT. The findings revealed that the synthesis parameters have significant influence on the synthesized CNT. Based on the analysis, well-aligned CNT with uniform diameters (23.4-28.4 nm), high purity (85.93 %) and crystallinity (I_D/I_G = 0.54) were successfully produced from 6 ml of palm oil precursor at 750 ^oC synthesis temperature, 5.33 wt% catalyst concentration at P3 substrate positions within 60 minutes synthesis time in argon ambient. The formulation of CNT growth mechanism produced from palm oil on the important parameters such as the effect of synthesis temperature, catalyst concentrations as well as the effect of carrier gas were proposed. In term of electrical properties, the CNT from palm oil has the highest conductivity of 3612.59 $S.cm^{-1}$ as compared to other samples produced from variety of bio-hydrocarbon precursors. From the *IV* characteristics, it shows that the metal contact helps to increase the electrical conductivity of the samples. The field electron emission (FEE) equipment was used to determine the FEE properties of CNT. From the FEE analysis, the CNT from palm oil was able to emit electrons at the lowest fields of 2.64 $V.\mu m^{-1}$ and reach highest maximum current of 15.07 $mA.m^{-2}$. It can be concluded that the optimum physical properties of palm oil based CNT were successfully produced by TCVD method with potential application as field emitting devices.

PENGOPTIMUMAN SIFAT FIZIKAL TIUB NANO KARBON DARIPADA PREKURSOR MINYAK KELAPA SAWIT

ABSTRAK

Nano tiub karbon (CNT) telah disintesis menggunakan minyak sawit sebagai sumber karbon dengan kaedah pengenapan wap kimia terma (TCVD). Kajian berparameter ini dijalankan untuk mendapatkan parameter yang optimum bagi menghasilkan CNT dengan sifat fizikal yang optimum. Parameter yang dikaji merangkumi suhu sintesis, kepekatan mangkin, kedudukan substrat, kuantiti prekursor, masa sintesis, gas pembawa dan pelbagai bio-hidrokarbon prekursor. Sifat fizikal CNT dianalisis menggunakan mikroskop elektron, analisis penyerakan tenaga sinar-X, spektroskopi mikro-Raman, spektroskopi inframerah transformasi Fourier (FTIR), termogravimetri (TGA), penganalisis unsur CHNS-O serta probe empat titik bagi mengukur arus dan voltan (*IV*). Prekursor karbon juga dianalisis menggunakan TGA, FTIR dan kromatografi gas-spektrometer jisim (GC-MS) dalam usaha untuk mengoptimumkan sifat fizikal CNT. Dapatan kajian menunjukkan bahawa CNT yang disintesiskan dipengaruhi oleh parameter yang dinyatakan. CNT yang tersusun secara sejajar, mempunyai diameter yang seragam (23.4-28.4 nm), ketulenan (85.93 %) dan tahap kehabluran yang tinggi (I_D/I_G = 0.54) telah berjaya dihasilkan daripada 6 ml prekursor minyak kelapa sawit pada suhu sintesis 750 ^oC dengan kepekatan pemangkin sebanyak 5.33 w% pada kedudukan substrat di P3 dalam tempoh masa sintesis selama 60 minit di dalam persekitaran argon. Perumusan mekanisma pertumbuhan CNT yang dihasilkan daripada minyak kelapa sawit juga dicadangkan mengikut parameter penting seperti kesan suhu sintesis, kepekatan pemangkin serta kesan gas pembawa. CNT berasakan minyak sawit menunjukkan kekonduksian elektrik yang tinggi sehingga mencapai 3612.59 $S.cm^{-1}$ berbanding dengan CNT yang dihasilkan daripada bio-hidrokarbon prekursor yang lain. Berdasarkan sifat *IV*, ia menunjukkan bahawa logam penghubung membantu meningkatkan kekonduksian elektrik pada sampel. Sifat pemancaran elektron medan (FEE) CNT ditentukan menggunakan alat FEE. Ia menunjukkan CNT berasaskan minyak sawit mampu untuk memancarkan elektron pada medan permulaan yang rendah iaitu 2.64 $V.\mu m^{-1}$ dan mampu mencapai nilai arus yang maksimum sehingga mencecah 15.07 $mA.m^{-2}$. Kesimpulannya, sifat fizikal CNT yang optimum berjaya dihasilkan daripada minyak sawit prekursor dengan menggunakan kaedah TCVD dengan potensi aplikasi sebagai peranti pemancar medan.

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LIST OF SYMBOLS AND ACRONYMS

ACNT	-	Aligned Carbon Nanotubes
CNT	-	Carbon Nanotubes
CVD	-	Chemical Vapor Deposition
EDX	-	Energy-Dispersive X-Ray
FCCVD	-	Floating Catalyst Chemical Vapor Deposition
FEE	-	Field Electron Emission
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
GC-MS	-	Gas Chromotography Mass Spectroscopy
HRTEM	-	High Resolution Transmission Electron Microscopy
IBM	-	International Business Machines Corporation
MWCNT	-	Multi-Walled Carbon Nanotubes
RBM	-	Radical Breathing Mode
PECVD	-	Plasma Enhanced Chemical Vapor Deposition
SWCNT	-	Single-Walled Carbon Nanotubes
TCVD	-	Thermal Chemical Vapor Deposition
TEM	-	Transmission Electron Microscopy
TGA	-	Thermogravimetric Analysis
VACNT	-	Vertically Aligned Carbon Nanotubes
μ	-	Carrier Mobility
a-C	-	Amorphous Carbon

Ar	-	Argon
C	-	Carbon
Co	-	Cobalt
d	-	Diameter
D	-	Defect-Activated Peak
E_g	-	Energy Band Gap
Fe	-	Ferum
G	-	Crystalline Graphite Peak
G’	-	Second-Order Raman Peaks
H	-	Hydrogen
I_D/I_G	-	The Integrated Intensity Ratio of the D and G peaks
IV	-	Current-Voltage
Mg	-	Magnesium
ml	-	Milliliters
Ni	-	Nickel
nm	-	Nanometer
O	-	Oxygen
ϖ	-	Radical Breathing Mode peak position
^{o}C	-	Degree Celcius
q	-	Charge of an Electron
R	-	Resistance
wt%	-	Weight Percentage
ρ	-	Electrical Resistivity
σ	-	Electrical Conductivity

Si	-	Silicon
t	-	Sample Thickness
mm	-	Millimeters
β	-	Field Enhancement Factor
β_L	-	Low Electric Field Enhancement Factor
β_H	-	High Electric Field Enhancement Factor
F-N	-	Fowler-Nordhem
J-E	-	Current Density-Electric Field

CHAPTER 1

INTRODUCTION

1.1 Introduction

The word "nano" is originally taken from Greek which means too small. It cannot be seen by the naked eyes as its size is in the range of 1 to 100 nm (Pradeep, 2007). It is 1000 times smaller compared to the thickness of a strand of hair.

Basically, nanotechnology is one of the science fields which study and use nano-sized materials. The most important criterion in nano-scaled materials is that the material has large surface area to volume ratio which possibly creates new quantum mechanical effects. For instance, the quantum size effect becomes dominant when the material is in the nanometer size, where a great reduction in material size altered the electronic properties of substances. This enhances the catalytic activities and lead to aggressive chemical reactions. There are many fascinating applications and benefits of nanotechnology in human life such as in the world of medical; the nano-scale molecule has multifunctional properties which can be used to detect cancer cells. It can be directly targeted into cancer cells with high solubility and therefore it can be easily absorbed as well as digested. These increases the healing time due to nutrients are being delivered more efficient and quick. From the point of textile and clothing, it provides waterproof and stain proof materials, where the materials will stay clean longer and easily cleaned. Nanoparticles are also introduced into sport equipments and car's body to make them stronger and durable. The titania nanoparticles coating are used in paints, tiles and glasses to provide a self-cleaning effect via photo-catalysis.

Carbon nanotubes (CNT) are among the materials that are being studied in nanotechnology which has interesting and unique properties. In general, CNT is divided into two categories; single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Due to its extraordinary physical properties, CNT has been classified as a unique and remarkable material in the nanotechnology field. Nowadays, it has also caught the attention of the top electronics companies like International Business Machines Corporation (IBM) (Perebeinos, Tersoff, & Avouris, 2004), Samsung (Lee et al., 2001) and Intel (Plombon, OBrien, Gstrein, Dubin, & Jiao, 2007) to invest in the development of products based on these unique materials.

1.2 Background of Study

Over the past decades, the applications of CNT were extensively increased in various fields especially in the field of electron emission (Robertson, 2004), nanocomposites (Robertson, 2004; Zhan et al., 2007), biosensor and energy storage (Baughman, Zakhidov, & de Heer, 2002). CNT is a long chain of carbon atoms which are attached to each other in a hexagonal shape to form a cylindrical structure with a diameter in nanometer range and length of a few centimeters (Deck, 2009). Due to its perfect arrangement of carbon atoms, CNT is a strong and conductive material. To fulfill this demand, the CNT need to be produced in large scale.

There are a lot of methods to synthesis CNT such as arc discharge (Cadek et al., 2002), laser ablation (Rode et al., 2005) and chemical vapor deposition (CVD) (Suriani et al., 2011). However, CVD is the most economical method and easily scalable for the mass production of CNT as compared to the other methods. CVD is used in various formats. The processes is different in term of chemical reactions initiated such as using thermal and plasma approach, variety of operating pressure and physical characteristics of vapor introduced into the system. Nevertheless, thermal CVD (TCVD) is commonly used to synthesize CNT because of several reasons including simple preparation set-up (Deck, 2009), CNT can be produced under a wide range of conditions and its furnace can be operated in 24 hours (Yeoh, Lee, Mohamed, & Chai, 2012).

Conventionally, CNT is synthesized from fossil fuels such as methane, acetylene and ethanol. The price of these precursors are expensive and are expected to increase in the future. Moreover, these raw materials will be expected to decrease in several decades time. Therefore, an effort by utilizing carbon from green source have been extensively studied. The use of bio-hydrocarbon precursors such as camphor oil (Kumar, & Ando, 2005), turpentine oil (Afre et al., 2006; Awasthi, Kumar, Tiwari, & Srivastava, 2010; Ghosh, Soga, Afre, & Jimbo, 2008), eucalyptus oil (Ghosh, Afre, Soga, & Jimbo, 2007), palm oil (Mohd Zobir et al., 2012; Suriani et al., 2009; 2011), waste cooking palm oil (Suriani, Roslan Md Nor & Rusop, 2010), neem oil (Kumar, Tiwari, & Srivastava, 2011), castor oil (Kalpana Awasti et al., 2011) and coconut oil (Paul, & Samdarshi, 2011) have been widely reported. The main factor of utilizing plant based precursor as carbon source is its sustainable features which act as renewable and cheap raw materials for large-scale CNT production.

Palm oil has molecule structure of $C_{55}H_{100}O_6$ and has an advantage of lower H:C (2:1) ratio as compared to methane gas (4:1) (Suriani, 2011). Based on its molecule structure, it was expected that CNT produced using palm oil precursor have minimal impurities as well as amorphous carbon (a-C) content. At the same time, palm oil could be better than other fossil fuel precursor due to the existence of 6 oxygen atoms in the palm oil molecule which can assist oxidation process of impurities (Suriani, 2011). Furthermore, Malaysia is the second largest producer and exporter of palm oil to more than 150 countries (Pakiam, 2013). This promises an adequate supply of palm oil as carbon precursor to produce CNT at large scale. In 2012, it has been reported that 18.79