UNIVERSITI PUTRA MALAYSIA

EFFECT OF HYDROGEN FLOW RATE ON THE QUALITY OF CARBON NANOTUBES PRODUCED USING THE FLOATING CATALYST CHEMICAL VAPOR DEPOSITION METHOD

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By

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Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

February 2007

DEDICATED TO

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Abstract of thesis presented to the Senate of Universiti Putra Malysia in fulfillment of the requirement for the degree of Masters of Science

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Chairman: Associate Professor Fakhru'l-Razi Ahmadun, PhD

Faculty : Engineering

Well aligned multi walled carbon nanotubes (MWNTs) was successfully synthesized by floating catalyst chemical vapor deposition method (CVD) involving the catalytic decomposition of benzene upon the surface of iron particle. Two sources of hydrogen were employed and varied; H_2* that carried benzene vapor and H_2** that supplied fresh hydrogen into the electrical furnace to analyze the effects they had on quantity as well as the morphology and structure of the produced CNTs. Total hydrogen flow rate was kept constant to allow constant residence time. Reaction time was also varied to study the growth rate of the products. The remaining parameters such as reaction temperature (850°C), ferrocene sublimation temperature (120°C), and mass of ferrocene (200 mg) were kept constant throughout the reaction. Argon (300 ml/min flow rate) was flown into the system before reaction to provide an inert atmosphere in the furnace. It was also flown after reaction to prevent product oxidation. The quantity of CNTs produced was highest (0.08g) when the reaction time and supply of benzene were maximized (t = 50 min, H_2*=350 ml/min, and H_2**= 0 ml/min).

The structure of the selected CNT samples was then further characterized via the means of Electron Microscopy (SEM, TEM, and HRTEM) as well as X Ray Diffractometer. By using TEM, measurement of 50 tubes per sample revealed CNTs of outer diameter (OD) from 5 to 55 nm and inner diameter (ID) from 5 nm to 25 nm for all conditions studied. At H_2* = 150 ml/min, H_2** = 250 ml/min, and t = 50 min, mean OD and ID of 18.64 nm and 4.85 nm with standard deviation of 18.64 nm and 4.85 nm, respectively were obtained.

XRD results revealed formation of sharp and narrow peaks at around 26° position (2θ), which confirms the presence of highly crystallized CNTs for all samples. The values of the intershell spacing of the wall (d_{002}) are between 0.338 nm to 0.342 nm. The values of full width at half maximum (FWHM) of the peaks of 0.7144, 0.2273, and 0.0200 was obtained when H_2*=350 ml/min, H_2*=250 ml/min and H_2*=150 ml/min, respectively at 50 min reaction time. The reduction in the FWHM value indicated the CNTs exhibit more crystalline graphite as more H_2** was supplied.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KESAN ALIRAN GAS HIDROGEN KE ATAS KUALITI NANOTIUB KARBON MELALUI KAEDAH PEMANGKIN TERAPUNG-PENGURAIAN WAP KIMIA

Oleh

RAJA NOR IZAWATI RAJA OTHMAN

Febuari 2007

Pengerusi: **Profesor Madya Fakhru'l-Razi Ahmadun, PhD**

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Nanotiub karbon menjajar pelbagai dinding (MWNTs) telah berjaya disintesis dengan menggunakan kaedah pemangkin terapung-penguraian wap kimia, (*floating catalyst chemical vapor deposition (CVD)*) yang melibatkan penguraian bermangkin benzena di atas permukaan zarah ferum. Dua sumber gas hidrogen telah digunakan dan dipelbagaikan, H_2* yang membawa wap benzene dan H_2** yang membekalkan hidrogen segar ke dalam sistem untuk menganalisa kesan kadar aliran tersebut terhadap kuantiti, morfologi, dan struktur nanotiub karbon yang terhasil. Masa tindakbalas juga dipelbagaikan untuk mengkaji kadar pertumbuhan produk. Nilai parameter yang selebihnya seperti suhu tindakbalas (850°C), suhu pemejalwapan ferosin (120°C), dan jisim ferosin (200 mg) dikekalkan sepanjang tindakbalas. Gas argon (kadar aliran sebanyak 300 ml/min) digunakan sebagai gas lengai semasa tempoh pemanasan relau sebelum tindakbalas dan semasa tempoh penyejukan relau selepas tindakbalas untuk mengelakkan pengoksidaan produk. Kuantiti maksimum nanotiub karbon (0.08g)

diperolehi apabila masa tindakbalas dan pembekalan benzena adalah pada tahap maksimum (t = 50 min, H_2*=350 ml/min, dan H_2**= 0 ml/min).

Struktur CNT yang terpilih kemudiannya dicirikan dengan menggunakan mikroskopi electron (SEM, TEM, and HRTEM) dan *X Ray Diffractometer*. Dengan menggunakan TEM, pengiraan 50 tiub untuk setiap sampel menunjukkan garis pusat luar (OD) CNT diperolehi adalah dari 5 ke 55 nm dan garis pusat dalam (ID) CNT dari 5 ke 25 nm untuk semua keadaan yang dikaji. Pada H_2* = 150 ml/min, H_2** = 250 ml/min, dan t = 50 min, purata OD dan ID diperolehi adalah 18.64 nm and 4.85 nm dengan nilai piawai *deviation* masing-masing sebanyak 18.64 nm and 4.85 nm.

Keputusan XRD menunjukkan penghasilan puncak yang tajam dan sempit pada posisi 26°, iaitu 2θ. Nilai jarak di antara dinding dalaman (d_{002}) adalah di antara 0.338 nm dan 0.342 nm. Nilai *full width at half maximum (FWHM)* puncak diperolehi adalah 0.7144, 0.2273, dan 0.0200 apabila H_2*=350 ml/min, H_2*=250 ml/min dan H_2*=150 ml/min, masing-masing pada masa tindakbalas tertinggi iaitu 50 minit. Pengurangan di dalam nilai FWHM menunjukkan CNT mempunyai lebih tahap kekristalan grafit apabila lebih H_2** dibekalkan.

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I certify that an Examination Committee has met on 14 February 2007 to conduct the final examination of Raja Nor Izawati Raja Othman on her Master of Science thesis entitled "Effect of Hydrogen Flow Rate on the Quality of Carbon Nanotubes Produced Using the Floating Catalyst Chemical Vapor Deposition Method" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citation, which has been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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RAJA NOR IZAWATI RAJA OTHMAN

Date:

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LIST OF ABBREVIATIONS

Ar	Argon
C	Carbon
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
d_{002}	Interlayer spacings between walls
Fe	Iron
FeCp	Ferrocene
H_2	Hydrogen
H_2*	Hydrogen that carries benzene vapor
H_2**	Hydrogen that is supplied directly to the furnace
HRTEM	High resolution transmission electron microscopy
MWNT	Multi walled nanotubes
SEM	Scanning electron microscopy
SWNT	Single walled nanotubes
TEM	Transmission electron microscopy
VGCF	Vapor grown carbon fibers
XRD	X Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Research in finding new materials has attracted the attention of scientists all over the world due to the growing need of humankind to improve the quality of life. Research on carbon materials especially has a lot to be explored due to its unique C-C bonding that enables carbon to assume different structures such as one-dimensional nanotubes, two-dimensional graphite, three-dimensional diamond, and even zero-dimensional fullerenes.

The discovery of multiwalled carbon nanotubes (1991) and single walled nanotubes (1993), both by Iijima of NEC laboratories in Japan has stimulated researchers all over the world to explore their much-anticipated extraordinary properties. As described by Iijima (1991), multiwalled nanotubes (MWNTs) consist of two to seven concentric graphene shells. As the name implies, single-walled nanotubes (SWNTs) consist of a single graphene cylinder. Compared to MWNTs, SWNTs exhibit superior properties that emerge from the strong one-dimensionality and crystalline perfection of the structure. These two are often simply called Carbon Nanotubes (CNTs).

Realizing that these structures exhibits remarkable mechanical, electrical, and electronic properties, the focus of the CNTs research has moved to the engineering aspect of it, i.e.

the production of CNTs. In order to fully utilize of their special properties, it is important to come out with a method for synthesis that can be controlled, relatively cheap, and scaleable, so that the production of high quality of carbon nanotubes can be commercialized. Arc discharge (Iijima, 1993) and laser vaporization (Thess *et al*., 1996) methods have been used to produce CNTs of superior straightness and highly crystallized. These two methods however suffer a high cost of manufacturing since they involve with high operating temperature (>2727°C) and size constraint. Hence, these two are not economical to produce CNTs on a large scale.

Chemical Vapor Deposition (CVD) technique has gained popularity as an alternative production method due to its potential to produce CNTs on a large scale. With this method, CNTs are produced via catalytic decomposition of hydrocarbons at relatively lower temperatures, normally between 427°C to 1400°C in a furnace. Although the technology had been applied to produce vapor grown carbon fibers (VGCFs) back in 1970s, the VGCFs produced are often of low quality, which formed spaghetti-like structure (Teo *et al.*, 2004). Driven by the need to produce CNTs on a large scale, substantial and rapid progress was made in the development of CVD to establish it as a highly controlled technology for the production of CNTs.

Baker *et al.* (1972), Oberlin *et al.* (1976) and Dai *et al.* (1996) each suggested three different growth models for the formation of carbon filament or CNT. These authors however agreed that the formation occurred as a consequence of the precipitation of carbon through or on the catalyst. The growth would occur as long as the catalyst

remained active, i.e. the catalyst was not covered by amorphous carbon or the formation of carbide was prevented. Hence, the presence of catalyst deactivation agent would play an important role in determining the amount of the CNTs formed. It could also prevent catalyst poisoning that would eventually yield low purity CNTs.

Hydrogen is known to have significant effect in increasing the amount of CNTs formed during CVD process. Cui *et al.* (1999) reported that the growth of CNTs flourished as the percentage of H_2 was increased in their CVD system. Bladh *et al.* (2000) observed that the formation of SWNT was enhanced upon moderate addition of hydrogen to the $CO/Fe(CO)_5$ mixture. Both Neumayer *et al*. (2004) and Qiu *et al*. (2004) also reported the presence of H_2 in facilitating the growth of CNTs in their CVD system as well.

The presence of hydrogen also could prevent catalyst poisoning. As a result the as synthesized CNTs would be of high purity with minimal side product formation. Both Rao *et al.* (1998) and Satishkumar *et al.* (1998) observed that the use of H_2 in the gas flow with argon minimized the amorphous carbon coating on the CNT produced by their CVD. Li *et al.* (2001) also observed that low flow-rate of methane accompanied by a hydrogen co-flow could prevent amorphous formation. Venegoni *et al.* (2002) observed encapsulated iron particles in all of their samples with a greater occurrence when hydrogen was not introduced in the gas phase. Dong *et al.* (2004) reported formation of nanoparticles on the surface of the CNTs when hydrogen was not introduced in their CVD system.

Previous work in synthesizing CNT at UPM involved synthesizing CNT via floating catalyst CVD method that employed ferrocene as catalyst and benzene as hydrocarbon precursors (Atieh, 2005). Hydrogen was used to bubble benzene into the reactor to obtain CNT. Higher flow rate of hydrogen contributed to higher amount of benzene that would enhance to the formation of amorphous carbon and encapsulated nanoparticles, as highligted by this author (Atieh, 2005). Hence, the real effects exerted by hydrogen in minimizing co-formation of amorphous carbon and encapsulated nanoparticles as mentioned by other researchers (Rao *et al.,* 1998; Satishkumar *et al.,* 1998; Li *et al.,* 2001; Venegoni *et al.,* 2002 and Dong *et al.,* 2004) was not fully utilized. This study seeks to improve the previous process based on the earlier findings.

In spite of the well known effects exerted by hydrogen, not much work has been published on the CNT grown by adding fresh hydrogen to the benzene-ferrocene-horizontal-floating catalyst CVD system. Ci *et al.* (2001) added thiophene to the similar system and obtained mostly carbon nanofiber, not carbon nanotube, at unnecessarily high operating temperature (>1000°C). The products obtained were of high impurity (presence of carbonaceous product), which might be due to H_2 that didn't effectively react with excess carbon. This indicated the failure of H_2 as purification agent and the inefficiency of the parameters employed to control the CNTs growth in their system. The presence of thiophene might explain such observations.

1.2 Objectives and Scope of Work

The objectives of this research are

1) To determine the operating conditions to synthesize CNTs of no side products as well as of highest quality at a relatively low temperature.
2) To study the effects of adding fresh hydrogen into the system on the as produced CNTs in terms of morphology and growth mechanism.

The scopes of the work are directed towards assessing the effects of operating parameters on the quantity and quality of CNTs produced. The parameters considered in the study are reaction time, amount of benzene, as well as flow rates of fresh hydrogen supplied. The reaction involves catalytic decomposition of benzene at constant temperature, which is 850°C in this reactor. Benzene is chosen due to its low boiling point which is 80°C (Williamson, 1994). Hence, it is easily decomposed upon entering the low-temperature reaction zone. Ferrocene is used since it does not need to be pretreated, i.e. can be readily used upon purchase. The reaction is run under atmospheric pressure to eliminate its dependency on pressure factor. The weighted sample is characterized by using SEM, TEM, as well as HRTEM. XRD is further used to identity the crystallinity of the carbon produced.

1.3 Thesis Outline

The thesis consists of five chapters. Chapter 1 highlights the background of the problem and the significance of the research work in the field of carbon nanotubes. Chapter 2 covers the literature reviews on the subject, where extensive review, analysis and synthesis are given to the reported work of various authors. The review provides the basis for the experimental and analysis section of the thesis. Chapter 3 is on the development of the analytical methods. Chapter 4 presents the results and the discussions of the obtained results. The mass of the pure CNTs produced as well as their outer and inner diameters are reported. The optimized condition for producing high quality CNTs is suggested. Chapter 5 presents the conclusion of the work and recommendation for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Carbon is one of the three basic elements (C, H, and O) that form many kinds of organisms with other elements to constitute life on earth. Among the pure elements in the periodic table, carbon can assume different structures such as one-dimensional nanotubes, two-dimensional graphite, three-dimensional diamond, and even zero-dimensional fullerenes. The tubule morphology of carbon includes carbon fibers, whiskers, and nanotubes. Other forms of carbon are glassy carbon, carbon blacks, amorphous carbon, and liquid carbon (Dresselhaus *et al.,* 1997).

Discovered in 1991 by Iijima, CNTs has attracted attention of scientists and researchers all over the world due to its unique structure and properties. Since then, tremendous work has been extensively done to study its unique properties. Due to its wide practical application, massive work on the methods of its preparation/production has also been studied to improve its yield in terms of quantity and also quality. This literature reviews previous work on the synthesis of CNTs by different methods in details; special attention will be given to 'Chemical Vapor Deposition' technique using 'floating catalyst' type. Role of hydrogen in growth mechanism will be discussed in details.

2.2 History: Fullerenes and Carbon Nanotubes

It was the Kroto-Smalley work (Kroto *et al.,* 1985) that pioneered the field of nano-structured carbon science era and further stimulated the search of finding new carbon materials. In this experiment, graphite was laser-vaporized and a new structure was accidentally found. Fullerenes or C_{60}, a dominant structure of the product was detected by mass spectrometry. They soon realized that it was a closed cluster containing precisely 60 carbon atoms, which would have a structure of unique stability and symmetry.

Iijima was the first to discover CNTs in 1991. This was multiwalled nanotube (MWNT), which consisted of two to seven concentric graphene shells, and were embedded in the fullerene by-product soot materials produced by the arc-discharge method. Researchers and scientists were stimulated by the remarkable one dimensional quantum effects predicted for their electronic properties (Iijima, 1991). The remarkable structure and properties of CNTs also were predicted to give rise to some unique applications (Iijima, 1991).

Independently and at about the same time, Iijima (1993) and Bethune *et al.* (1993) both synthesized single walled nanotube (SWNT). Iijima's important contribution to CNTs was that he connected his nanotube work to the ongoing fullerene studies. It was observed that fullerene-like caps or hemisphere were formed at the end of nanotube. As the name implies, single-walled nanotube (SWNT) consists of a single graphene cylinder.