AGGLOMERATIO IN PREVENTING SUCCESS FOR CNTs COTINUOUS PRODUCTION IN A FLUIDIZED – BED CVD

LIM SIANG YING

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AGGLOMERATION IN PREVENTING SUCCESS FOR CNTs CONTINUOUS PRODUCTION IN A FLUIDIZED – BED CVD

By

LIM SIANG YING

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

AGGLOMERATION IN PREVENTING SUCCESS FOR CNTs CONTINUOUS PRODUCTION IN A FLUIDIZED – BED CVD

By

LIM SIANG YI NG

2011

Chair: Mohamad Amran bin Mohd Salleh, PhD

Faculty: Institute of Advanced Technology

At the first stage in this research, $Fe(NO_3)_3.9H_2O$ and Al_2O_3 was used to formed $Fe(NO_3)_3$ catalyst using wet impregnation method. Carbon nanotubes (CNTs) was then grown using the prepared catalyst introduced into fluidized-bed reactor. CNTs grown in the fluidized-bed was later purified in acid follow by thermal oxidation. After purification process, carbon nanotubes (CNTs) were characterized using scanning electron microscope (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. In this experiments, large quantity of agglomerates as much as 7 g is synthesized in a different way than other authors. This agglomerates consists of different size of CNTs and some amorphous carbon. The causes for the failure of continuous CNTs synthesizing is determined through the analysis of agglomerate formation. A new unit (g/mole) is used to measuring CNTs yields to provide a bigger picture than the commonly used percentage yields.

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

AGLOMERASI DALAM MENCEGAH KEJAYAAN UNTUK PENGELUARAN CNTs BERTERUSAN PADA LAPISAN TERBENDALIR CVD

Oleh

LIM SIANG YING

2011

Pengerusi: Mohamad Amran bin Mohd Salleh, PhD

Fakulti: Institut Teknologi Maju

Peringkat pertama dalam penyelidikan ini, $Fe(NO_3)_3.9H_2O$ dan Al_2O_3 telah digunakan untuk membentuk pemankin $Fe(NO_3)_3$ dengan menggunakan kaedah "wet impregnation". CNT kemudiannya disintesis dengan menggunakan pemangkin yang disediakan dan dimasukkan ke dalam reaktor lapisan terbendalir. CNTs yang disintesis kemudiannya direndam di dalam asid diikuti dengan pengoksidaan terma untuk penulenan. Selepas proses penulenan, CNT telah dicirikan dengan menggunakan mikroskop SEM, TEM dan spektroskopi Raman. Dalam eksperimen ini, sebanyak 7 g gumpalan CNT telah disintesis dengan cara yang berlainan daripada penulis lain. Gumpalan ini terdiri daripada saiz CNT yang berlainan dan juga karbon amorfus. Punca-punca bagi kegagalan mensintesis CNT secara berterusan telah ditentukan melalui analisis pembentukan gumpalan. Unit baru (g/mol) telah digunakan untuk mengukur hasil CNT untuk memberikan gambaran yang lebih besar berbanding unit peratusan yang biasa digunakan oleh penulis lain.

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To my father, mother & all my family members

I certify that a Thesis Examination Committee has met on 8 December 2011 to conduct the final examination of Lim Siang Ying on his thesis entitle Agglomeration in Preventing Success for CNTs Continuous Production in a Fluidized – Bed CVD in accordance with the University and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106)] 15 March 1998. The Committee recommends that the student be awarded the M.S. (Nano-materials and Nano-technology).

Members of the Thesis Examination Committee were as follows:

Prof. Dr. Azmi b Zakaria, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Dr. Azmah Hanim Mohamed Ariff, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Dr. Dayang Radiah binti Awang Biak, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Dr. Azizan bin Aziz, PhD
Associate Professor
Faculty of Engineering
Universiti Sains Malaysia
Malaysia
(External Examiner)

SEOW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Mohamad Amran bin Mohd Salleh, PhD
Dr,
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Suraya Binti Abdul Rashid, PhD
Dr,
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Jeefferie b. Abd. Razak
Faculty of Manufacturing Engineering
Universiti Teknikal Malaysia Melaka
(Member)

HASANAH MOHD GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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LIM SIANG YING

Date:

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LIST OF ABBREVIATIONS

APCVD	Atmospheric Pressure CVD
CCVD	Catalytic CVD
CNT	Carbon Nanotube
CVD	Chemical Vapour Deposition
DLC	Diamond Like Carbon
DWCNT	Double Wall Carbon Nanotube
EDX	Energy Dispersive X-Ray
FB-CVD	Fluidized-Bed CVD
GC	Gas Chromatography
I.D	Inner Diameter
LCVD	Laser assisted CVD
LPCVD	Low Pressure CVD
MOCVD	Metalorganic CVD
MWCNT	Multi Walled Carbon Nanotube
O.D	Outer Diameter
PECVD	Plasma Enhanced CVD
SEM	Scanning Electron Microscope
SWCNT	Single Wall Carbon Nanotube
TEM	Transmission Electron Microscope
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

This thesis is divided into five chapters that describe the research performed during the study. In this chapter, it serves as an introduction for continuous production of carbon nanotubes (CNTs) in a fluidized-bed chemical vapour deposition (FB-CVD). It presented a brief discussion to the background of study, research problems, objectives, scopes and benefits contribute by this research to scientific community.

1.1. Background of study

Prior to the 90's, research in CNT is mostly theoretical and did not reach to most part of the world. Following the discovery of CNT by Iijima and co-worker in 1991, research in CNT have been growing at a very fast pace ever since (Iijima, 1991). Thing fascinating about CNT that catch attention of researcher from around the world are their superior properties. A number of these properties include having a wide band gap, high melting point, high tensile strength as well as high thermal conductivity (Fischer, 2006); these properties are the results of its small size and the arrangement of carbon atom within the covalently bonded network of sp^2. Up to this date, success has been shown in the production of CNTs by authors performing the study; several methods of synthesizing CNTs have been identified and much of the research performed during this time are dedicated to the known synthesizing techniques. Much recently, continuous synthesis of CNTs has been a hot topic of discussion due to their ability of growing CNTs continuously. Several such techniques are the arc-jet plasma (Choi *et al.*, 2006), simplified carbon-arc method

(Ishigami *et al.*, 2000), floating catalyst (Mora *et al.*, 2007) and fluidized-bed (FB) (Weizhong *et al.*, 2004).

Currently, FB-CVD attracted the most attention from scientific community compared to other methods because of their capability to grow CNTs in large quantity and easy for scale-up production. Its numerous advantageous over a normal CVD method are the absence of thermal gradient, flexible operating condition and the ability of continuous manufacturing (Philippe *et al.*, 2007). This method evolves from catalytic cracking of hydrocarbons in fluidized-bed. The needs to satisfy high market demand of industrial goods such as the production of monolithic materials and fabrication of composites have made FB-CVD a new class of process in fluidized-bed technology. With the growing support from governmental and industrial sector and the needs to have huge quantity of CNTs, lots of attention has turn to FB-CVD for their potential to grow huge quantity of CNT; since research in this area do not have a long history, knowledge of growing CNTs in FB-CVD still have their lacking and further study are required before this method can be fully utilized to grow CNTs. Before the study of continuous CNTs synthesizing, other fully established techniques such as laser ablation (Kusaba *et al.*, 2006), chemical vapour deposition (Corrias *et al.*, 2003) and arc-discharge (Zhao *et al.*, 2007) are the key research topics.

1.2. Research problems

Numerous difficulties in synthesizing CNTs have been solve since its discovery up to this date by the established synthesizing techniques, but progress in growing CNTs in industrial scale have been very disappointed with the results of the research capable

of only growing CNTs in small quantity. This problem has resulted the price of CNTs to be unacceptable high; Helix Material Solutions Inc. trade a gram of purified CNTs for 210 USD while low cost CNTs are around 28 – 83 USD a gram as of 2010. Due to the high cost of CNTs, a large number of applications utilizing CNTs are unable to be realize, some of these application include but not less to ultracapacitor, air pollution filter, hydrogen storage, superconductor, artificial muscles, structural composites as well as waterproof fabrics (http://en.wikipedia.org/wiki/Potential_applications_of_carbon_nanotubes, access on 9 October 2010). Qiu *et al.* (2004) conducted a study using fixed-bed CVD method is one of the example that grow high quantity of CNTs but it contain substantial amount of impurities mainly catalyst particles and amorphous carbon. Other methods such as arc-discharge on the other hand grow high purity CNTs as compare to CVD method at the cost of lower quantity (Zhao *et al.*, 2007). Despite a lot of research conducted, these methods however, are still in their infancy of growing CNTs in commercialized scale mainly owing to the limited growth efficiency. The problem with fixed-bed CVD are inhomogeneous gas-solid mixing (Philippe *et al.*, 2007) while for arc-discharge are the evaporating of hydrocarbon feedstock at the end of graphite rod (Vittori *et al.*, 2003) which produce a very small amount of CNTs, these limitation cause scale up production of CNTs difficult to achieved. The problems however are easily overcome using fluidized bed reactor and it show to be promising in producing large quantity of CNTs by continuously synthesizing. Continuous production means CNTs are synthesize and extract continuously and need to be in loose powder form. Before the process can be scale-up for continuous production, one feature identified to have a major influence on extracting CNTs from FB-CVD are the reactor blockage during long operating hours and formation of oversize agglomerates that glued itself to the

reactor walled. The agglomerates formation are widely known to the scientific communities (Corrias *et al.*, 2003; Lan *et al.*, 2004 and Zhang *et al.*, 2009) but it is rarely research with Lan *et al.*, (2004) presented the only paper and whether any study taken into consideration the formation of carbon agglomerates adhering to the reactor wall is currently unknown. As up to this date, there are no scientific data in any peer reviews available for the problem with the closest available are the study of CNTs formations on stainless steel by a handful of authors namely Wall *et al.*, (2003) and Zhou *et al.*, (2008). Besides it is important that a method of reducing and potentially prevent the blockage of reactor and carbon agglomerates adhering to the walled during long operating hours are studied.

1.3. Objectives

- To determine the reason for CNTs adhering to the reactor surfaces.
- To observe the effects of CNTs production by manipulating the carrier gas and H_2 flow rates.
- To study the effect of catalyst amount on CNTs production.

1.4. Scope of study

This research are conducted using fluidized-bed reactor to grow CNTs using catalyst prepared from wet-impregnation method. The study on the influence of catalyst and the effect of gases used as mentioned in objectives were carried out as to determine its relationship to CNTs morphology and yields obtained from reactor surface. The most important part of this research is to study the reason behind CNTs adhearing to

the reactor wall and its effect on CNTs growth rate and morphology under different conditions. The data for mole is obtained using gas chromatography (GC). Morphology and characterization of both catalyst and synthesized CNTs were carried out using scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and raman spectroscopy.

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APPENDIX

All the calculation is made by <u>assuming spherical particles</u>

<u>Minimum fluidization,</u>

$$U_{mf} = \frac{(\rho_p - \rho_f) g D_p^2}{1502\mu}$$

Prediction error ±15%

<u>Voidage at minimum fluidization,</u>

$$Re_{mf} = \frac{D_p \rho_f U_{mf}}{\mu}$$

(*Re*, change U_{mf} into *U*)

$$Ar = \frac{D_p^3 \rho_f (\rho_p - \rho_f) g}{\mu^2}$$

$$\varepsilon_{mf} = 0.3507 Ar^{0.0387} Re_{mf}^{-0.0704}$$

Prediction error ±4%

Pressure drop,

$$\Delta P_{mf} = (1 - \varepsilon_{mf})(\rho_p - \rho_f) g H_{mf}$$

<u>Bed height above minimum fluidization,</u>

$$\varepsilon = \varepsilon_{mf} \left[\frac{Re + 0.02Re^2}{Re_{mf} + 0.02Re_{mf}} \right]^{0.1}$$

Heterogeneous fluidization (with bubbles), Todes 1981

$$\boldsymbol{H = \frac{m}{(1 - \varepsilon)\rho_p A}}$$

<u>Metal content,</u>

$$\frac{0.138x}{10} \times 100 = y\ \%\ of\ metal$$

Data at hand,

$$D_p = 125\ \mu m, 63\ \mu m, 45\ \mu m$$
$$\mu = 5.1 \times 10^{-5}\ at\ 650\ ℃$$
$$\rho_p = 3900\ kgm^{-3}$$
$$\rho_f = 0.53\ kgm^{-3}$$
$$A = 4.91\ cm^2\ (area\ of\ reactor)$$
$$m = 2\ g$$

125 µm

$$U_{mf} = 7.80 \times 10^{-3}\ ms^{-1}$$
$$\underline{Re_{mf} = 0.01}$$
$$\underline{Ar = 15.22}$$
$$\varepsilon_{mf} = 0.54$$
$$\rho_{mf} = 1794\ kgm^{-3}$$
$$H_{mf} = 0.49\ cm$$
$$\Delta P_{mf} = 193.6\ Pa$$

<u>65 µm</u>

$U_{mf} = 4.43 \times 10^{-3}\ ms^{-1}$ calculated at 29Celcius

$$\underline{Re_{mf} = 1.31 \times 10^{-3}}$$
$$\underline{Ar = 1.95}$$
$$\varepsilon_{mf} = 0.57$$
$$\rho_{mf} = 1677\ kgm^{-3}$$
$$H_{mf} = 0.56\ cm$$
$$\Delta P_{mf} = 197.4\ Pa$$

45 µm

$$U_{mf} = 1.01 \times 10^{-3}\ ms^{-1}$$
$$\underline{Re_{mf} = 4.72 \times 10^{-4}}$$
$$\underline{Ar = 0.71}$$
$$\varepsilon_{mf} = 0.60$$
$$\rho_{mf} = 1560\ kgm^{-3}$$
$$H_{mf} = 0.65\ cm$$
$$\Delta P_{mf} = 198.9\ Pa$$

Required percentage of metal content for the experiment (5 – 10 %)

$x = Fe(NO_3)_3.9H_2O$	y
7.25 g	*10 %*
6.52 g	*9 %*

5.80 g	*8 %*
5.07 g	*7 %*
4.35 g	*6 %*
3.62 g	*5 %*

Bed height achieved during particles fluidization

125 µm

$$\varepsilon = 0.63$$
$$\rho_{mf} = 1443\ kgm^{-3}$$
$$H = 0.76\ cm$$

63 µm

$$\varepsilon = 0.75$$
$$\rho_{mf} = 975\ kgm^{-3}$$
$$H = 1.67\ cm$$

45 µm

$$\varepsilon = 0.86$$
$$\rho_{mf} = 546\ kgm^{-3}$$
$$H = 5.33\ cm$$

$$\Delta P_v = \frac{2f_f \rho_f U l_v}{D} + 0.057 G l_v \sqrt{\frac{g}{D}} + \rho_p(1-\varepsilon_v) g l_v + \rho_f \varepsilon_v g l_v$$

$$\varepsilon_v^2 U_T - \left(U_T + U + \frac{G}{\rho_p}\right)\varepsilon_v + U = 0$$

Data at hand,

$$D_p = 3\ mm - CNT, 65\ \mu m - Al2O3$$

$$\mu = 5.1 \times 10^{-5}\ at\ 650\ ℃$$

$$\rho_p = 1400\ kgm^{-3} - CNT$$
$$\rho_p = 3900\ kgm^{-3} - Al2O3$$

$$\rho_f = 0.53\ kgm^{-3}$$

$$\varphi \approx 0.9$$

$$A = 4.91\ cm^2\ (area\ of\ reactor)$$
$$l_v = 0.5\ m\ (length\ of\ reactor)$$

$$Q_p = 3.33 \times 10^{-6}\ kgs^{-1} - CNT + Al2O3$$

Pneumatically transport

$$U_{salt} = \left(\frac{4M_p 10^{\alpha} g^{\beta/2} D^{(\beta/2)}}{\pi \rho_f}\right)^{1/\beta+1}$$

$$U = 1.5 U_{salt}$$

$$\alpha = 1440 D_p + 1.96$$
$$\beta = 1100 D_p + 2.5$$

Terminal velocity,

$$C_D {R_{ep}}^2 = \frac{4}{3}\left(\frac{D_p^3 \rho_f (\rho_p - \rho_f) g}{\mu^2}\right)$$

$$R_{ep} = \frac{\rho_f U_T}{\mu}$$

Calculated requirement to removed CNT

$$U = 3.64\ m/s$$
$$U_T = 0.8\ m/s$$
$$\varepsilon_v = 0.9965$$

$$\Delta P_v = 33.4\ Pa$$

Calculated requirement to removed Al_2O_3

$$U = 4.51\ m/s$$
$$U_T = 0.22\ m/s$$
$$\varepsilon_v = 1$$

$$\Delta P_v = 6.4\ Pa$$

BIODATA OF STUDENT

Author:	Lim Siang Ying
Date & place of birth:	30/04/1985; Muar, Johor
Undergraduate schools attended:	Universiti Teknikal Malaysia Melaka (UTeM)
Postgraduate schools attended:	Universiti Putra Malaysia (UPM)
Degrees awarded:	Bachelor of Manufacturing Engineering (Engineering Materials), 2009, UTeM
	Master of Science (Nano-materials and Nano-technology), 2012, UPM
Honours and awards:	Special Graduate Research Assistanceship (SGRA), UPM.
Professional experience:	Quality Assurance Engineer (2007 – 2008), Sony EMCS Sdn. Bhd, Prai, Malaysia
	Project Engineer (2011 – Current), Waterotec Sdn Bhd, Rawang, Malaysia

LIST OF PUBLICATIONS

Continuous production of carbon nanotubes – A review 2010