UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF CARBON NANOTUBES IN A VERTICAL FLOATING CATALYST CHEMICAL VAPOUR DEPOSITION REACTOR

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By

THAMER H. AHMED

Thesis Submitted to the School of Graduate Studies, University Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science

October 2011

DEDICATION

This thesis is dedicated to

ALL I LOVE

Specially

MY BELOVED PARENTS

MY WIFE AND MY SONS
MY BROTHERS AND SISTERS
My friends

And

MY BLEEDING COUNTRY "IRAQ"

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

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Chairman: Mohamad Amran Bin Mohd Salleh, PhD

Faculty : Engineering

New approaches to synthesize randomly oriented MWNTs have been achieved in a vertical floating catalyst reactor. This approach based on the direct injection of the catalyst into the reactor in powder form by using a new catalyst delivery system. The catalyst was injected from the top of the reactor and simultaneously vaporized in the reactor, therefore, eliminating the need to have a traditional preheating of the catalyst.

The ethylene gas as the reactant was used to push the catalyst powder into the reactor. The new catalyst delivery system consists of three main parts. The first part is a small chamber used as a temporary container for catalyst powder and having a conical bottom end to facilitate the flow of the powder (catalyst). The top end of the chamber is a removable cover equipped with inlet gas probe. Below the chamber, there is a control valve used to control the flow of catalyst into the reactor. This valve connected to a long thin tube (5

mm ID, 6 mm OD and L=460 mm) which could be inserted into the reactor at adjustable length. This arrangement is effective to increase the residence time and provide sufficient contact between the carbon source gas and the catalyst.

Ferrocene was used as the catalyst precursor and ethylene as the carbon source. The experiments were performed at atmospheric pressure with process temperatures ranged between 650 ºC and 850 ºC under argon atmospheres. Argon was flown with flow rate of 650 ml/min through the system before the reaction to purge air from the reactor. Hydrogen and argon both are entering the reactor from the bottom. Layer of carbon nanotubes was grown on the reactor walls. The as-grown CNTs were characterized by Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscope (HRTEM) and Thermal Gravimetric Analysis (TGA).

A parametric study was made to evaluate the influence of the most crucial experimental conditions on the growth of carbon nanotubes. Reaction temperature, catalyst weight, ethylene flow rate and reaction time were systematically varied and their influence on yield, purity, and diameter distribution of carbon nanotubes were evaluated. Although hydrogen and argon may affect the properties of CNTs, it requires an entirely different scope of study.

A strong effect of the reaction temperature was found on nanotube growth. Five reaction temperatures from 650 ºC to 850 ºC were used. Both quality and quantity of CNTs synthesized were increased with the increase in synthesis temperature from 650 ºC to 750 ºC. Relatively, the highest purity and yield of CNTs deposit was obtained when reaction temperature was set at 750 ºC.

Catalyst weight strongly influenced the formation of CNTs, the appropriate catalyst weight for growing CNTs with best yield and high purity among six weights (50,100,150,200,250 and 300 mg) used was 250 mg. High catalyst content form large clusters with low activity.

Ethylene was found to play important roles in the production of CNTs, six different flow rates from 50 ml/min to 300 ml/min each 50 ml/min were used to investigate effect of ethylene on the yield, purity, diameter distribution and growth of carbon nanotubes. The optimal ethylene flow rate was 100 ml/min.

The effect of the reaction time on the purity and yield of carbon nanotubes was studied from 15 minute to 90 minutes. The maximum yield of carbon nanotubes was achieved at 30 minutes, for reaction duration longer than 30 min the growth rate was continuously suppressed and gradually the catalyst loses its activity. There was no effect of the reaction time on the average diameter.

The CNTs diameters increase with increasing these parameters under all experimental conditions. The optimum reaction have been achieved at the above conditions and the CNTs produced have yield of 148.4 wt%, purity of 89.4% and diameters from 8-53 nm.

Structure and kinetic of produced carbon nanotubes were studied using HRTEM. The CNTs display a MWNTs structure of successive graphite sheets with hollow inside.

Kinetics of MWNTs quantitatively described, the activation energy and frequency factor are calculated. The equation that fit the growth of carbon nanotubes was presented.

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

SINTESIS DAN PENCIRIAN KARBON TIUB NANO DALAM REAKTOR KIMIA PEMANGKIN LAMPUNG TEGAK BERPEMENDAPAN WAP

Oleh

THAMER H. AHMED

Oktober 2011

Pengerusi: Mohamad Amran Bin Mohd Salleh, PhD

Fakulti: Kejuruteraan

Pendekatan baru sintesis secara rawak berorientasikan MWNTs telah dicapai dalam reaktor keluli tegak dengan menggunakan kaedah pemangkin terapung. Pendekatan ini berdasarkan suntikan langsung pemangkin ke dalam reaktor dalam bentuk serbuk dengan menggunakan sistem penyampaian pemangkin baru. Pemangkin disuntik dari bahagian atas reaktor dan pada masa yang sama dipanaskan oleh tindak balas panas, oleh itu, menghapuskan keperluan untuk pra-pemanasan pemangkin.

Aliran gas etilena digunakan untuk menolak serbuk pemangkin ke dalam reaktor di mana kedua-duanya memasuki ke dalam reaktor pada masa yang sama. Sistem penyampaian pemangkin baru terdiri daripada tiga bahagian utama, semuanya diperbuat

daripada keluli. Bahagian pertama ialah ruang kecil yang digunakan sebagai bekas sementara bagi serbuk pemangkin dan mempunyai hujung bawah kon untuk memudahkan terjerumusnya serbuk (pemangkin). Hujung atas kebuk adalah penutup boleh tanggal yang dilengkapi dengan prob inlet gas. Di bawah kebuk itu terdapat injap kawalan yang digunakan untuk menyimpan pemangkin di dalam kebuk sehingga tindak balas bermula. Injap ini disambungkan kepada tiub yang panjang dan nipis (5 mm ID 6 mm OD dan L = 460 mm,) iaitu sepanjang 360 mm dimasukkan di dalam reaktor sejurus sebelum bahagian terakhir reaktor. Pengaturan ini adalah berkesan untuk meningkatkan masa kediaman dan menyediakan kenalan yang mencukupi antara sumber gas karbon dan pemangkin.

Ferrocene telah digunakan sebagai pelopor pemangkin dan etilena sebagai sumber karbon. Eksperimen telah dijalankan pada tekanan atmosfera dengan suhu proses yang berkisar antara 650°C dan 850°C di bawah atmosfera argon. Argon telah dialirkan dengan kadar aliran 650 ml/min melalui sistem sebelum tindak balas untuk membersihkan reaktor. Hidrogen dan argon kedua-duanya memasuki reaktor dari bawah. Lapisan karbon tiub nano berkembang di dinding reaktor. CNTs yang berkembang dicirikan oleh emisi Field Scanning Electron Microscopy (FESEM), Transmisi Electron Microscopy (TEM), Mikroskop Elektron Transmisi Resolusi Tinggi (HRTEM) dan Analisis gravimetrik Terma (TGA).

Satu kajian parametrik yang dibuat untuk menilai pengaruh syarat-syarat penting eksperimen pertumbuhan karbon tiub nano. Masa suhu tindak balas, berat badan pemangkin, kadar aliran etilena dan reaksi secara sistematik diubah dan pengaruh mereka ke atas pengagihan hasil, ketulenan, dan diameter karbon tiub nano dinilai. Walaupun hidrogen dan Argon boleh memberi kesan kepada sifat-sifat CNTs, ia memerlukan skop pengajian yang berbeza.

Kesan yang kuat oleh suhu tindak balas telah ditemui pada pertumbuhan tiub nano. Lima suhu tindak balas daripada 650ºC ke 850ºC telah digunakan. Kedua-dua kualiti dan kuantiti CNTs yang disintesis telah meningkat dengan peningkatan dalam suhu sintesis daripada 650ºC ke 750ºC. Secara relatif, ketulenan tertinggi dan hasil deposit CNTs telah diperolehi apabila suhu tindak balas telah ditetapkan pada suhu 750ºC.

Berat pemangkin mempengaruhi pembentukan CNTs. Berat pemangkin yang sesuai untuk perkembangan CNTs dengan hasil yang terbaik dan ketulenan yang tinggi di kalangan enam berat (50,100,150,200,250 dan 300 mg) yang digunakan adalah 250 mg. Kandungan pemangkin yang tinggi membentuk kelompok besar dengan aktiviti yang rendah.

Etilena dikenalpasti memainkan peranan yang penting dalam pengeluaran CNTs. Enam kadar aliran yang berbeza dari 50 ml/min ke 300 ml/min setiap min 50 ml/telah digunakan untuk menyiasat kesan etilena pada hasil, ketulenan, pengedaran diameter dan pertumbuhan karbon tiub nano. Kadar aliran etilena yang optimum ialah 100 ml/min.

Kesan jangkamasa tindak balas kepada ketulenan dan hasil nanotube karbon telah dikaji dari 15 minit hingga 90 minit. Hasil maksimum karbon tiub nano telah dicapai dalam 30 minit, untuk tempoh tindak balas yang lebih lama daripada 30 min kadar pertumbuhan terus ditindas dan secara beransur-ansur pemangkin kehilangan aktivitinya. Tidak ada kesan jangkamasa tindak balas pada purata diameter.

Garis pusat yang dihasilkan meningkat dengan menambah parameter ini di bawah semua keadaan uji kaji. Keadaan tindak balas yang optimum telah dicapai dan CNTs yang dihasilkan mempunyai hasil 148,4% berat, ketulenan 89,4% dan diameter 8-53 nm.

Struktur dan kinetik karbon tiub nano yang dihasilkan telah dikaji menggunakan HRTEM. CNTs memaparkan struktur MWNTs kepingan grafit berturutan dengan dalaman berongga. Kinetik MWNTs secara kuantitatif diterangkan, tenaga pengaktifan dan faktor frekuensi dikira. Persamaan yang sesuai dengan pertumbuhan karbon tiub nano telah dibentangkan.

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Finally, special thanks from me to MALAYSIA and to Malaysian people in general for their perfect hospitality in their green land during my study period.

I certify that a Thesis Examination Committee has met on 21 October 2011 to conduct the final examination of Thamer H. Ahmed on his thesis entitled "Synthesis and Characterization of Carbon Nanotubes In A Vertical Floating Catalyst Chemical Vapour Deposition Reactor" in accordance with the Universities and University Colleges Act 1971 and Universiti Pertanian Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee were as follows:

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Date: 20 December 2011

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:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations 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 other institutions.

THAMER H. AHMED
Date:

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