UNIVERSITI PUTRA MALAYSIA

EFFECTS OF METAL OXIDE NANOPARTICLE CATALYSTS ON THE DIAMETER OF CARBON NANOTUBES PRODUCED VIA PULSED LASER ABLATION DEPOSITION TECHNIQUE

SAMAILA BAWA WAJE

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By

SAMAILA BAWA WAJE

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

March 2007

In appreciation of their love and sacrifices, this thesis is dedicated to Parents Malam Bawa Waje and Hajiya Hassana Bawa Waje and to my beloved wife Sadiya.

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

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Chairman: **Associate Professor Noorhana Yahya, PhD**

Faculty: **Science**

In this research work, bismuth oxide (Bi_2O_3) and nickel oxide (NiO) nanoparticles were synthesized through precipitation method, while iron oxide (Fe_2O_3) nanoparticles were synthesized via citrate pyrolysis. All the as-prepared metal oxide nanoparticles were used as catalysts for the growth of carbon nanotubes via pulsed laser ablation deposition (PLAD) technique.

Pellets were first prepared from a mixture of 90 wt% graphite and 10 wt% catalysts in each case, and used as a target. An Nd: YAG laser with wavelength of 532nm and power of 10.24W was used to ablate the target materials, using a frequency of 5 kHz and current of 25A. The target materials were evaporated and transported to the substrate under the influence of argon. The expelled carbon precipitated and diffuses through the metal oxide catalysts and condensed on the substrate as carbon nanotubes. The effect of each of the catalyst on the diameter of the as-grown carbon nanotubes was investigated and the correlation between the type and the particle size of the catalysts and the diameter of the grown CNTs were studied.

The results show that, there is a strong correlation between the diameter of the starting catalyst, with the diameter of the resulting carbon nanotubes for both Bi_2O_3 and Fe_2O_3, indicating that both catalysts serve as the nucleation point for the CNTs growth. However, the case of NiO shows a significant difference, as the diameter of the as-grown CNTs was eight times bigger than the size of the starting catalyst. This can be attributed to the aggregation of the as-prepared NiO particles to form bigger clusters, consequent to the ablation process.

Bamboo-like CNTs were observed for Fe_2O_3 and NiO, which is attributed to the high cooling rate of the reaction chamber. Further contribution to this structure is the large pulse-to-pulse width of the system (140ns). However CNTs catalyzed by Bi_2O_3 were defect free tubes which can be attributed to the lower melting point of Bi_2O_3 compare to other catalysts used, thus forming CNTs at a lower eutectic temperature. From the results, it can be concluded that, for applications that requires a short tube with relatively large diameter Bi_2O_3 is the best catalyst. For long CNTs with relatively large diameter for encapsulation purposes, NiO is the best catalyst, while Fe_2O_3 was seen to be the best catalyst for catalyzing CNTs with a narrow diameter.

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

KESAN OKSIDA LOGAM PARTIKEL NANO BAGI MANGKIN PADA DIAMETER TIUB NANO KARBON TERHASIL MELALUI CARA PEMENDAPAN ABLASI DENYUTAN LASER

Oleh

SAMAILA BAWA WAJE

Mac 2007

Pengerusi: **Profesor Madya Noorhana Yahya, PhD**

Fakulti: **Sains**

Dalam kajian penyelidikan ini partikel nano bismuth oksida (Bi_2O_3) dan nikel oksida (NiO) disediakan melalui kaedah mendakan, sementara partikel nano ferum oksida (Fe_2O_3) disintesiskan melalui pirolisis sitrat. Semua partikel nano logam oksida yang telah disintesis, digunakan sebagai mangkin bagi pertumbuhan tiub nano karbon melalui cara pemendapan ablasi denyutan laser.

Pelet telah disediakan daripada campuran 90% berat grafit dan 10% berat mangkin dalam setiap kes, telah digunakan sebagai sasaran. Pemendapan ablasi denyutan laser (PLAD) menggunakan laser Nd:YAG dengan jarak gelombang 532nm dan kuasa 10.24W digunakan untuk menyinarkan karbon dari sasaran, dengan frekuensi yang ditetapkan pada 5kHz dan arus 25A. Ia mengewapkan karbon dan produk di bawah pengaruh gas argon. Karbon yang dipercik telah termendak dan meresap melalui mangkin logam oksida dan mendap pada substrat sebagai tiub nano karbon. Kesan bagi setiap mangkin terhadap diameter tiub nano karbon dikaji dan hubungan antara saiz partikel mangkin dan diameter bagi pertumbuhan CNTs terhasil diselidik.

Hasil kajian menunjukkan, terdapat hubungan yang kuat antara diameter bagi mangkin dengan diameter bagi tiub nano karbon yang terhasil bagi kedua-dua mangkin bismuth oksida dan ferum oksida yang menunjukkan kedua-duanya bertindak sabagai titik nukleasi bagi pertumbuhan tiub nano karbon. Namun begitu nikel oksida menunjukkan perbezaan ketara, iaitu diameter yang tuhasil bagi CNTs adalah lapan kali lebih besar daripada saiz awal mangkin tersebut. Ini disebabkan oleh gumpalan partikel NiO yang membentuk kluster lebih besar akibat dari pertumbuhan pada suhu tinggi di mana laser menghentam sasaran.

CNTs berbentuk buluh diperolehi bagi Fe_2O_3 dan NiO, di mana dapat dikaitkan dengan kadar penyejukan tinggi bagi kebuk tindak balas, akibat daripada ketiadaan elemen pemanasan untuk mengekalkan suhu seragam dalam kebuk tindak balas, sebagai tambahan kepada struktur ini jarak denyutan yang besar dalam sistem ini (140ns). Walaubagaimanapun, CNTs yang dimangkinkan oleh Bi_2O_3 adalah tiub yang sempurna mungkin disebabkan oleh takat lebur mangkin yang rendah maka membentuk suatu suhu eutektik pada suhu yang rendah berbanding dengan pemangkin lain. Dari pada hasil kajian, boleh disimpulkan bahawa bagi aplikasi yang memarlukan tiub yang pendek dengan diameter yang besar, Bi_2O_3 adalah pemangkin terbaik untuk CNTs dengan tiub yang panjang dan diameter yang besar untuk tuijuan pengurungan, NiO adalah pemangkin yang terbaik, manakala Fe_2O_3 dilihat sebagai pemangkin terbaik untuk memangkinkan CNTs dengan diameter yang kecil.

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It is neither my strength nor my wisdom, but Allah's mercies that made this work a success, thus, I praise him and glorify his name. May his position continues to be exalted forever and ever, ameen.

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The crowning glory goes to my wife Sadiya for standing by me through thick and thin, may Allah reward you with the best of rewards

I cannot find the words for my parents Malam Bawa Waje and Hajiya Hassana "Oh Allah showers your mercies upon them, just as they nourish me while I was young".

Finally, I acknowledge the Ministry of Science Technology and Innovation, Malaysia (MOSTI), for the EAR grant vote number 54430, with which this research was funded.

I certify that an Examination Committee has met on 27th March 2007 to conduct the final examination of Samaila Bawa Waje on his Master of Science thesis entitled "Effects of Metal Oxide Nanoparticle Catalysts on the Diameter of Carbon Nanotubes produced via Pulsed Laser Ablation Deposition Technique" 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:

Mohd. Zobir Hussein, PhD
Professor
Faculty of Science,
Universiti Putra Malaysia
(Chairman)

Mohd. Maarof H. A. Moksin, PhD
Professor
Faculty of Science,
Universiti Putra Malaysia.
(Internal Examiner)

Mansor Hashim, PhD
Associate Professor
Faculty of Science,
Universiti Putra Malaysia.
(Internal Examiner)

Abdul Rahman Mohamed, PhD
Professor
School of Chemical Engineering,
Universiti Sains Malaysia.
(External Examiner)

HASANAH MOHD GHAZALI, PhD
Professor/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 are as follows:

Noorhana Yahya, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Irmawati Ramli, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

____
AINI IDERIS, PhD.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:17 JULY 2007

DECLARATION

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

SAMAILA BAWA WAJE

Date: 19 JUNE 2007

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LIST OF ABBREVIATIONS

Laser	Light of amplification stimulation emission radiation
Nd:YAG	Neodymium: Yittrium Aluminium Garnet
PLAD	Pulsed Laser Ablation Deposition
CNTs	Carbon nanotubes
SWNT	Single Walled Carbon Nanotubes
MWNT	Multiwalled Carbon Nanotubes
XRD	x-ray diffraction
SEM	Scanning Electron Microscopy
CVD	Chemical Vapor Deposition
EDX	Energy Dispersive X-ray
wt %	Weight percent
Ar	Argon
hkl	Miller indices
MSDS	Materials Safety Data Sheet
JCPDS	Joint Committee on Power Diffraction Standard
a.u	Arbitrary unit
HR-TEM	High resolution transmission electron microscopy

CHAPTER 1

INTRODUCTION

1.1 Background

Carbon nanotubes (CNTs) are fullerene-related structures, consisting of graphene cylinders, closed at either end with caps containing pentagonal rings (Ijima, 1991). They were discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes, of a type, which had never been previously observed (Ijima, 1991). Thomas Ebbesen and Pulickel Ajayan later from Iijima's laboratory showed how nanotubes could be produced in bulk quantities by varying the arc-evaporation conditions (Iijima and Ichihashi, 1993). These paved the way to an explosion of research into their physical and chemical properties in laboratories all over the world (Ebbesen, 1994).

Literally called the building blocks of matter, nanotubes exhibits several potentials which includes high strength, light weight, high electrical conductivity, excellent fatigue and corrosion resistance, high conductivity to mention but just a few. Another important development was the synthesis of single-wall nanotubes in 1993 (Iijima and Ichihashi 1993). The standard arc-evaporation method which initially produced only multiwall tubes was found that addition of metals such as cobalt to the graphite electrodes resulted in extremely fine tube with single-layer walls. The availability of these structures enabled scientists to test some of the theoretical predictions, which have been made about nanotubes properties (Ebbesen, 1994).

Mostly, the growth of CNT requires the use of a catalyst as shown in Figure 1.1, and the commonly used catalysts are transition metals, metal oxides or their alloys in the form of thin films or nanoparticles (Ruo et al., 2002). The role of catalysts has and is still being studied in the growth of carbon nanotubes. This is due to the complexity of the processes, involving a wide range of time and length scales. However, it is acknowledged to be very important component in the CNTs growth. This is because; the form of the resulting carbon tubules is seen closely to relate to the physical dimensions of the metal catalyst particles. When the diameter of the catalyst particle is in the range of tenths of a micron, the resulting tubules are carbon filaments of similar diameter (Sinnott et al. 1999). As the size of the catalyst particle reduces, the filament curvature increases leading eventually to the formation of multi-walled carbon nanotubes (MWNTs). If the particle size reduces still further, single-walled carbon nanotubes (SWNTs) are formed (Kong et al., 1998 and Sinnott et al., 1999).