SYNTHESIS AND CHARACTERISATION OF MULTI-WALLED CARBON NANOTUBES ON SUPPORTED CATALYSTS VIA CATALYTIC CHEMICAL VAPOUR DEPOSITION

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Beloved mum and dad,

just for you.

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ABSTRACT

The main hindrance to employ carbon nanotubes (CNTs) commercially is the inability to control the growth of the nanotubes and to grow bulk amounts of carbon nanotubes. However, recently the Chemical Vapour Deposition (CVD) has been modified by applying various supported metals catalysts in the production of CNTs. Therefore, in this research we focus on the effects of supported catalysts in the synthesis of CNTs via Catalytic Chemical Vapour Deposition (CCVD) method. The CCVD method was used to synthesize high quality CNTs in high yield and economical cost with controlling of the CNTs characteristics and morphologies. A practical and high performance CCVD system has been designed and built. The fixed bed flow reactor in the CCVD system is specifically fabricated to carry out the pyrolysis of hydrocarbon to produce CNTs. The supported catalysts of cobalt (Co), iron (Fe) and mixture of these metals (Co/Fe) were prepared by using the alumina (Al_2O_3), molecular sieves (MS) and anodic aluminium oxide (AAO) template as supports. All supported catalysts were prepared by impregnation method. The as-prepared supported catalysts were subjected to calcination at 450 °C. The catalysts were characterised using X-Ray Diffraction (XRD) technique. Acetylene (C_2H_2) was selected as the carbon precursor and the reaction was performed at 700 °C for 30 minutes. The yields of the reaction collected as black depositions on the catalysts. The characterisations of the yield were carried out using Scanning Electron Microscopy (SEM), Field-Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) as well as Energy Dispersive X-Ray Analysis (EDAX) techniques. Catalysts prepared were active in the production of CNTs. The most active catalysts were identified as Al-Co/Fe(3.0)Cal, AAO-Co/Fe(1.0)Cal and MS-Co/Fe(3.0)Cal as they generated high carbon contents of 72.00, 64.03 and 48.50 wt.% respectively. The as-grown CNTs over various catalysts showed high degree of graphitisation, purity and density with configurations of bundles, arrays and coils. The CNTs yields were classified as multi-walled carbon nanotubes (MWNTs). The best MWNT consists of 11 layers of turbostratic graphene wall with inner diameter of 3.57 nm and outer diameter of 11.43 nm as well as distance between layers of 0.33 nm. The CNTs grown over Al_2O_3 supported catalysts followed the tip growth mechanism whereas the CNTs grown over MS supported catalysts followed the base growth mechanism.

ABSTRAK

Halangan utama dalam menggunakan nanotiub karbon (CNTs) secara komersial adalah ketidakupayaan untuk mengawal pertumbuhan nanotiub karbon dan tidak dapat menghasilkan nanotiub karbon dalam jumlah yang banyak. Walau bagaimanapun, kebelakangan ini kaedah Pemendapan Wap Kimia (CVD) telah diubahsuai dengan menggunakan pelbagai jenis mangkin logam berpenyokong dalam penghasilan CNTs. Oleh itu, kajian ini menfokuskan kepada kesan mangkin berpenyokong ke atas sintesis CNTs melalui teknik Pemendapan Wap Kimia Bermangkin (CCVD). Teknik CCVD ini digunakan untuk mensintesis CNTs berkualiti tinggi dengan hasil yang tinggi, kos yang ekonomik dan dapat mangawal ciri-ciri dan morfologi CNTs terhasil. Sistem CCVD yang praktikal dan berkeupayaan tinggi telah direka bentuk dan dibina. Reaktor pengaliran dasar tetap dalam CCVD sistem ini dibina khas untuk proses pirolisis hidrokarbon untuk menghasilkan CNTs. Mangkin berpenyokong jenis kobalt (Co), ferum (Fe) and campuran kedua-dua logam ini (Co/Fe) telah disediakan dengan menggunakan alumina (Al_2O_3), penapis molekul (MS) dan templat anodik aluminium oksida (AAO) sebagai penyokong. Kesemua mangkin berpenyokong telah disediakan dengan kaedah pengisitepuan. Mangkin berpenyokong tersedia telah dikalsinkan pada suhu 450 °C. Semua mangkin berpenyokong telah dicirikan dengan teknik Pembelauan Sinar-X (XRD). Asetilena (C_2H_2) telah dipilih sebagai bahan asas karbon. Tindak balas telah dijalankan pada suhu 700 °C selama 30 minit dan hasil daripada tindak balas dikumpul sebagai serbuk hitam yang termendap atas mangkin. Pencirian hasil ini telah dilakukan dengan menggunakan teknik Mikroskopi Imbasan Elektron (SEM), Mikroskopi Imbasan Elektron Pemancaran Medan (FE-SEM) dan Mikroskopi Transmisi Elektron (TEM) serta Analisis Penyerakan Tenaga Sinar-X (EDAX). Mangkin berpenyokong yang disediakan adalah aktif dalam penghasilan CNTs. Mangkin yang teraktif dikenalpasti sebagai Al-Co/Fe(3.0)Cal, AAO-Co/Fe(1.0)Cal dan MS-Co/Fe(3.0)Cal kerana ia menghasilkan kandungan karbon yang tinggi, iaitu masing-masing 72.00, 64.03 and 48.50 % berat. CNTs tersedia atas pelbagai jenis mangkin menunjukan darjah grafitasi, ketulinan dan kepadatan yang tinggi dengan konfigurasi jenis gumpalan, teratur and lingkaran. Hasil CNTs itu telah diklasifikasikan sebagai nanotiub karbon dinding berganda (MWNTs). MWNTs yang terbaik terdiri daripada 11 lapis dinding grafin turbostratik dengan diameter dalaman 3.57 nm dan diameter luaran 11.43 nm serta jarak antara lapisan 0.33 nm. Pertumbuhan CNTs bagi mangkin berpenyokong Al_2O_3 adalah melalui mekanisma pertumbuhan hujung, manakala mangkin berpenyokong MS melalui mekanisma pertumbuhan pangkal.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAO	-	Anodic Aluminium Oxide template
Al_2O_3	-	Alumina support
C	-	Carbon
Cal	-	Calcination
CVD	-	Chemical Vapour Deposition
CCVD	-	Catalytic Chemical Vapour Deposition
C_2H_2	-	Acetylene
CNFs	-	Carbon Nanofibers
CNTs	-	Carbon Nanotubes
Co	-	Cobalt
Cu	-	Copper
EDX	-	Energy Dispersive X-Ray Analysis
FE-SEM	-	Field Emission-Scanning Electron Microscopy
Fe	-	Iron
MgO	-	Magnesium Oxide
Mo	-	Molibdenum
MS	-	Molecular Sieves support
MWNTs	-	Multi-Walled Carbon Nanotubes
Ni	-	Nickel
sccm	-	Standard cubic centimetres per minute
SEM	-	Scanning Electron Microscopy
SiO_2	-	Silica
SMSI	-	Strong Metal-Support Interaction
SWNTs	-	Single-Walled Carbon Nanotubes
TEM	-	Transmission Electron Microscopy
V	-	Vanadium
XRD	-	X-Ray Diffraction

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

The past decade has witnessed tremendous effort and progress in the field of carbon nanotubes. Ever since the discovery of carbon nanotubes by Iijima (1991), it has captured the attention of researchers worldwide. Understanding their unique properties and exploring their potential applications have been a main driving force for this area.

Throughout history, the allotropes of carbon have played a number of important roles in technology. In ancient times, diamond was celebrated for its hardness and beauty, and carbon black was used as a colorant. The industrial age brought greater interest in graphite and related carbon materials as a source of carbon vapour in arc-lamps and as clean-burning fuels. Graphite-like carbon materials are now widely used for their unique mechanical, electrical and thermal properties.

Very small diameter (less than 10nm) carbon filaments were prepared in the 1970's and 1980's by the decomposition of hydrocarbons at high temperatures (Dresselhaus and Avouris, 2001). Direct stimulus to study carbon filaments of very small diameters more systematically came from the discovery of fullerenes by Kroto and Smalley.

In December 1990 at a carbon-carbon composites workshop, papers were given on the status of fullerene research by Smalley, the discovery of a new synthesis method for the efficient production of fullerenes and a review of carbon fibers research by M.S. Dresselhaus. Discussions at the workshop stimulated Smalley to speculate about the existence of carbon nanotubes of dimensions comparable to C_{60}. These conjectures were later followed up in August by an oral presentation at a fullerene workshop by Dresselhaus on the symmetry proposed for carbon nanotubes capped at either end by fullerene hemispheres (Saito *et al.*, 1998).

However, the real breakthrough on carbon nanotube research came with the experimental observation of carbon nanotubes in 1991 by Iijima of the NEC Laboratory in Tsukuba, Japan using High-Resolution Transmission Electron Microscopy (HRTEM) (Iijima, 1991). It was this work which bridged the gap between experimental observation and the theoretical framework of carbon nanotubes in relation to fullerenes and as theoretical examples of 1D system. Since the pioneering work by Iijima, the study of carbon nanotubes has progressed rapidly.

1.2 Problem Statement

The main hindrance to employing carbon nanotubes (CNTs) in real world is the inability to control the growth of the nanotubes and to grow bulk amounts of carbon nanotubes. There are three main techniques to grow carbon nanotubes: arc-discharge, laser ablation and chemical vapour deposition (CVD). The first two methods are high temperature processes that produce high quality CNTs, but they cannot grow mass quantities of nanotubes within a reasonable amount of time. The CVD technique is able to grow bulk amounts of nanotubes and arrays of multi-walled carbon nanotubes (MWNTs). However, these nanotubes contain a vast amount of defects along the length of the tubes due to the relatively low synthesis temperature of 600 – 1200 °C.

Nevertheless, some progress has been recently obtained, the chemical vapour deposition (CVD) has been modified by applying various supported metals catalysts in the production of CNTs. The catalytic chemical vapour deposition (CVD) method supplies CNTs in high yield and low costs, but also at controlling the CNTs characteristics and morphologies. Being a catalytic process, the combinations of transition metals and support can be changed depending on the characteristics required, such as the alignment and diameter of the nanotubes. The CCVD synthesis of CNTs can be carried out at low temperature and ambient pressure.

1.3 Research Objectives

This research is intended to synthesize carbon nanotubes (CNTs) of high yield and purity at economical cost. Therefore, this research is conducted to achieve the following primary objectives:

1. To produce carbon nanotubes (CNTs) using Catalytic Chemical Vapour Deposition (CCVD) method.

2. To study the effects of supported catalysts in the synthesis of carbon nanotubes (CNTs).

3. To characterise the supported catalysts and carbon nanotube yields chemically and physically.

4. To identify the best catalyst-support combination to catalyze the carbon nanotubes growth.

1.4 Scopes of Study

In order to achieve the objectives, this research is focusing on the following scopes:

(i) Designing and fabricating an effective Catalytic Chemical Vapour Deposition (CCVD) system contains a fixed bed flow reactor which facilitates the production of CNTs.

(ii) Preparing supported catalysts by using alumina (Al_2O_3) beads, molecular sieves (MS) beads and anodic aluminium oxide (AAO) template as catalyst supports and cobalt (Co) or ferrum (Fe) as metal catalysts with impregnation or dip coat techniques. Applying calcination treatment to enhance the activity of the catalysts.

(iii) Producing CNTs through catalyze pyrolysis of acetylene (C_2H_2) at optimum temperature, reaction time and gas flow rate.

(iv) Characterising the supported catalysts and CNT yields using X-ray Diffraction (XRD) technique to reveal the active catalyst sites and effects of calcination.

(v) Investigating the morphologies and topologies of the supported catalysts and the CNT yields through Scanning Electron Microscopy (SEM), Field-Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) techniques.

(vi) Determining the surface composition of a sample (metal catalyst and carbon content) using Energy Dispersive X-Ray Analysis (EDAX) technique.

(vii) Comparing the performance of supported catalysts in the production of CNTs to figure out the best combination of support, catalyst, loading and treatment for the supported catalysts.