UNIVERSITI TEKNIKAL MALAYSIA MELAKA

CARBON NANOTUBE GROWTH FROM SOLUTION PROCESSED COBALT CATALYST

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

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DECLARATION

I hereby, declared this report entitled ―Carbon Nanotube Growth from Solution Processed Cobalt Catalyst" is the results of my own research except as cited in the references

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow

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(Dr Mohd Asyadi Azam bin Mohd Abid)

ABSTRAK

Tesis ini membincangkan tentang persediaan, kajian berparameter dan pencirian pertumbuhan Nanotiub karbon (CNTs) daripada proses larutan mangkin kobalt. Proses yang terlibat dalam pertumbuhan CNT bermula dengan kaedah penyediaan mangkin menggunakan proses larutan dan diikuti oleh pertumbuhan sebenar CNTs dengan menggunakan kaedah alkohol pemangkin pemendapan wap kimia (ACCVD). Pemangkin kobalt dipilih untuk pertumbuhan CNT dan akan dimendapkan ke atas substrat oleh kaedah pusingan salut untuk menghasilkan lapisan nipis yang seragam. Selepas substrat menjalani pemanasan untuk pembentukan zarah pemangkin, morfologi, pengesahan unsur bahan dan bentuk zarah nano pemangkin diperolehi menggunakan pengimbasan mikroskop electron beresolusi tinggi (HR-SEM). CNT telah ditumbuhkan menggunakan kaedah ACCVD dengan suhu pemprosesan CVD yang dikawal dan kesimpulan mengenai kesan suhu CVD terhadap CNTs telah dibuat. CNTs yang tumbuh telah dianalisis menggunakan spektroskopi Raman untuk mengesan kehadiran CNT dan melakukan kualiti analisis terhadap CNT yg telah tumbuh. Didapati bahawa proses larutan mangkin adalah salah satu alternatif yang terbaik untuk menggantikan kaedah pemendapan wap fizikal (PVD) dalam menghasilkan lapisan nipis yang seragam untuk pertumbuhan CNT di mana CNT telah berjaya tumbuh dengan suhu optimum 700 °C dengan menggunakan kaedah ACCVD dengan nisbah I_G/I_D dikira 6.46 menunjukkan kualiti kristal baik CNTs dengan struktur graphitic sangat tersusun berkembang pada suhu ini dengan memiliki peratusan tertinggi CNTs kira-kira 83% di atas sampel dengan dominan kehadiran SWCNTs dengan diameter dalam lingkungan 0.907-0.914 nm.

ABSTRACT

The thesis discusses about the preparation step, parametric study and characterization of carbon nanotubes (CNTs) growth from solution process cobalt catalyst. The process involve in CNT growth start with catalyst preparation step that was by solution process and followed by actual growth of CNTs by using Alcohol Catalytic Chemical Vapor Deposition (ACCVD) method. Cobalt catalyst was selected for CNT growth and was deposited onto the substrate by spin coating method to create uniform thin film. After the substrate undergo heat treatment for catalyst particle formation, the elemental confirmation, morphology and shape of the catalyst nanoparticles were obtained using high resolution-scanning electron microscopy (HR-SEM). CNT was growth using ACCVD method with control of the CVD processing temperature in order to deduce the effect of CVD temperature on the as-grown CNTs. As-grown CNTs were analyse using Raman spectroscopy in order to detect the presence of CNT and make qualitative analysis on as-grown CNTs. It was found that solution processed is a good alternative to replace physical vapour deposition method in producing catalyst thin film for CNT growth where CNTs have been successfully grown with optimum growth temperature of 700 °C using ACCVD method with calculated I_G/I_D ratio of 6.46 indicates good crystalline quality of CNTs with highly ordered graphitic structures grown at this temperature with the highest percentage of CNTs about 83 % on the sample with dominant SWCNTs presence with diameter in the range of 0.907 to 0.914 nm.

DEDICATION

To my beloved parents, Marsini binti Bukari and Ithnin bin Jaman.

Your guiding hand on my shoulder will remain with me forever.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

%	Percent
ACCVD	Alcohol catalytic chemical vapor deposition
°C	Degree Celcius
CNT	Carbon Nanotube
Co	Cobalt
Co_3O_4	Cobalt(iii) Oxide(iv)
CVD	Chemical vapor deposition
D	Disodered
G	Graphite
HR-SEM	High resolution scanning electron microscope
Ie	Effective let-through amperes
JAIST	Japan Advanced Institute of Science and Technology
MWCNT	Multi-walled carbon nanotube
nm	nanometer
PVD	Physical vapour deposition
RBM	Radial breathing mode
rpm	Revolution per minutes
s	Second
SERC	Science and Engineering Research Centre
SWCNT	Single-walled carbon nanotube
T_{CVD}	Chemical vapor deposition processing temperature
t_{CVD}	Chemical vapor deposition processing time
UTeM	UniversitiTeknikal Malaysia Melaka

CHAPTER 1

INTRODUCTION

The purpose of this project is to grow carbon nanotube (CNT) from solution process at once to clarify the temperature dependence on the as-grown CNT by chemical vapor deposition (CVD) technique. The first chapter of this thesis is about to define what is CNT and their properties. Besides that, the objectives, problem statement and scope of this research also being discussed in this chapter.

1.1 Background

Researchers realized that when things getting smaller, they will act in extraordinary manner and today's labs around the world are competing to gain advantages on CNTs excellent properties. CNTs can be visualized as thick sheets of carbon that have been rolled into tubes and posses novel properties that look set to revolutionize the technological landscape in the near future. Although the CNT is promising to enhance the technology apply nowadays, but because of the high cost of the process and the presence of impurities in CNTs, the application of CNTs is still limited. In order to solve the problem, solution process and CVD technique is being intensively developed for the possibility of production of high quality CNTs in a large scale at low cost. Unfortunately, CVD method is still generally suffers from a lack of growth parameter control in order to yield high quality of CNTs. Earlier study found out that CNT growth does depend on the CVD process parameters especially the CVD processing temperature (Bronikowski, 2006; Sivakumar et al., 2010).

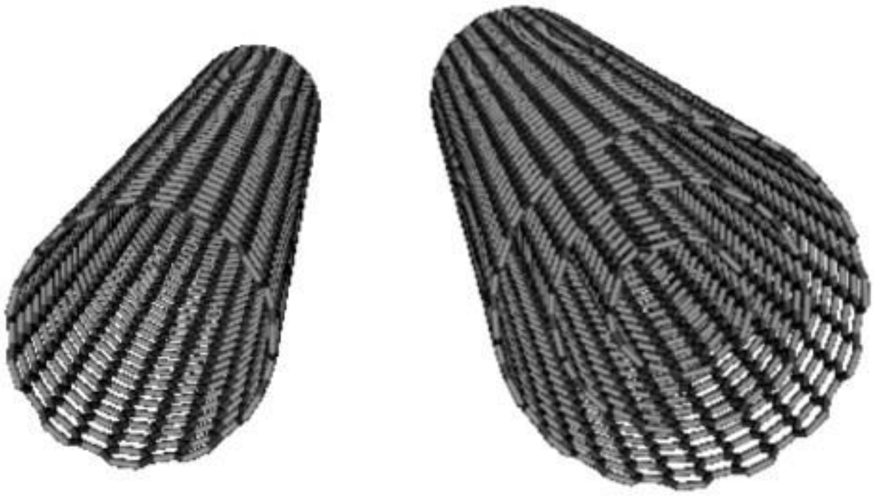
1.1.1 Carbon Nanotubes

The CNT is an unique structure of carbon material. Right from its finding, CNT has been extensively studied due to its excellent mechanical, chemical, thermal and electrical properties (Berlanga et al., 2011; Katz & Willner, 2004). Based on the dimensions and structures, CNTs are basically classified into two different groups that are multi-walled (MWCNT) and single-walled (SWCNT) (Dupuis, 2005; Sivakumar et al., 2010). Figure 1.1 shows the types of carbon nanotubes available at present, which are SWCNT and MWCNT. A SWCNT is one tubular structure of grapehene either capped at both ends or not and it contains only surface carbon atoms while its diameter is in the range of 1-2 nm. A MWCNT is consist of two or more coaxial tubes of SWCNTs with range of diameter 10-50nm.

The comparison between SWCNT and MWCNT are presented in table 1.1. CNT has been an assuring candidate in a wide range of applications, especially in nanoelectronics devices and biomedical sensors. A various of multi-scale electronic devices have been developed based on CNTs or CNT thin films and used as field-effect transistors (Mitzi et al., 2003), sensors (Yan et al., 2007), conductive interconnects (; Zhong et al., 2013), and energy storage systems (Azam et al., 2013; Bistamam & Azam, 2014; Neyts & Bogaerts, 2014). A critical step in order to grow CNT is to deposit the catalyst on to the substrate and to control the processing temperature to grow the CNTs. Not long ago researchers have developed several methods to grow CNT, however many of these methods have restrictions and limitations as all of them require either intensive devising processes or support materials with excellent properties. Thus, their applications are rather limited.

Table 1.1: Comparison between MWCNT and SWCNT (Rajkumar et al., 2013)

MWCNT	SWCNT
Composed of multi-layer of graphene	Composed of single layer of graphene
Able to be produced without presence of catalyst.	Catalyst is needed in production.
Homogenously dispersed with no apparent bundled formation.	Not fully dispersed and form bundled structure.
Contain high purity.	Having poor purity.
Typical MWCNT content in prepared samples by CVD method is about 35-39 wt%.	Typical SWCNT content in prepared samples by CVD method is about 30-50 wt%.
Low possibilities of defect.	High possibilities of defect during fictionalization.
High structure complexity.	Low structure complexity (easy to characterize and evaluate).
Cannot be twisted easily.	Easily twisted and more pliable.



a) SWCNT b) MWCNT

Figure 1.1: Types of carbon nanotubes (a) SWCNT and (b) MWCNT (Purohit et al., 2014)

1.2 Problem Statement

There have been great advances in the CNT research as many initial problems have been solved at both theoretical and experimental levels. CNT formation is not easy as picking up a graphene sheet and rolling it up without the aid of special tools and equipment. Instead, CNT must be grown like a plant that needed lots of heat, a carbon source and catalyst particles that act like a seeds to grow the CNT in appropriate manner. CNT growth is essentially a two steps process begin with the catalyst preparation step for thin film production, followed by actual CNT growth.

In CNTs production, physical vapour deposition (PVD) method is the most commonly used methods for the thin film coating since through the deposition time and the thickness of the thin film produces can controlled the size of the catalyst particles. Unfortunately, PVD is a costly method that required advanced equipment, vacuum and high temperature for catalyst deposition thus make it high energy consumption method (Seah, Chai, & Mohamed, 2011). Furthermore PVD is a time consuming method because of the slow rate of coating. In order to solve the problem, solution process method have been developed as one of alternative method to produce catalyst thin film on flat substrate with lower cost, large deposition area, simple tools and equipment, easier to operate and possible to be done in normal atmosphere as compared to PVD method (Mitzi et al., 2003; Seah et al., 2012; Seah et al., 2011; Tyona, 2013).

There are various techniques used to grow CNTs and the three common methods used are laser ablation, arc discharge & CVD. Among all of the technique, CVD technique is the most promising one which is well-known for its attractive technique to grow high quality CNTs in a large scale thus make it low cost, broad selectivity of substrates and highly yielding catalytic reaction to grow the CNTs. However, a fundamental question that remaining to date is: what is the optimum temperature for CNT growth in CVD? Even though CVD is a promising technique in CNT growth, unfortunately the process is still lacking in growth parameter control to get uniformity of the CNT growth. Systematic investigation of the influence of growth temperature on the synthesis of CNTs by the CVD method have been performed and it is stated that CNTs can be grown at temperatures as low as 450 °C (Unalan & Chhowalla, 2005) up to 1000 °C. Previous research proved that low temperature could limit the decomposition of hydrocarbon gas which is leading to the formation of amourphous carbon and highly defective structures while too high in temperature resulted in bundle form of CNTs appear and most of the CNTs posses disordered walls (Kumar & Ando, 2010; Unalan & Chhowalla, 2005).

Therefore this work is existed in order to grow CNT from solution processed cobalt catalyst at once to clarify the temperature dependence on the CNT growth by alcohol catalytic CVD technique.

1.3 Objectives

The objectives of this research project are:-

i. To grow CNT from solution processed cobalt catalyst.
ii. To investigate the effect of temperature on the CNT growth using alcohol catalytic CVD method.
iii. To characterize the CNT grown by using Raman Spectroscopy.

1.4 Scope

The main aim of this study is to grow CNT from spin coated cobalt catalyst, and to investigate the effect of temperature on the CNT growth using CVD method. In order to remove distraction from other factors, this research will be based on several scopes. For the first objective, the experiment used cobalt acetate tetrahydrate ($(CH_3COOH)_2$ Co-$4H_2O$) and ethanol (C_2H_5OH) in precursor solution preparation to form the cobalt catalyst precursor. Spin coating process was used for thin film formation with speed of 8000 rpm for 60 s and heat treatment was done using a MTI vacuum furnace for 10 minutes at temperature of 450 °C.

The characterization of the thin film was done using high-resolution scanning electron microscopy (HR-SEM; Hitachi S-5200) available at Japan Center for Nano Materials and Technology (JAIST). For the second objective, CNTs are grown using ultra-high-vacuum CVD furnace (MILA-3000) for 15 minutes with constant pressure of 2 until 2.7 kPa and gas flow rate at temperature of 650 °C, 675 °C, 700 °C, 725 °C and 750 °C. All the equipment needed for CNT growth is available at UTeM Polymer Laboratory. The characterization on grown CNTs was done using Raman spectroscopy located at Metrology laboratory, UTeM.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 describes a literature review regarding the process involve in Carbon nanotube (CNT) growth that started with catalyst preparation step that is by solution process and followed by actual growth of CNTs by using chemical vapor deposition (CVD) method. Firstly, in this section, reliable catalyst preparation (solution process) and stable growth conditions are determine to enable robust and reproducible growth result, as these should be satisfied prior to the experimental observation of the CNT growth. Various growth models especially the effect of catalyst upon the growth will be described. Chapter 2 also covers the detailed parametric study of the various factors influencing the growth of the CNTs specifically the effects of temperature to further emphasize their effects on the properties of CNTs.

2.1 Solution Process

Usually, nano-sized metal particles, such as nickel, iron, cobalt, molybdenum and copper are well known as catalyst for the growth of CNT (Dupuis, 2005). However, bulk of iron need to be dispersed in order to be able to catalyze the decomposition of alcohol to form carbon filament (Azam et al.,2013). In order to obtain CNT, methods to prepare catalyst nanoparticles need to be defined. The sol-gel process is defined as formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid (Huang et al., 2001). The sol-gel method has been extensively used in the preparation of supported metal catalysts because it typically results in highly homogeneous materials with high degree of metal dispersion (Palacio et al., 2014).

A sol is a colloidal particles that has been dispersed and stable in a solvent in the form of amorphous or crystalline structure where the particles may possessed by Van der Waals forces or hydrogen bonds. A gel consists of a three dimensional continuous network, that encloses a liquid part that the network is built from colloidal particles agglomeration. Therefore, process in sol-gel involves the transition of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). It is possible to fabricate advanced materials in a wide variety of forms especially thin film coatings for CNT growth purposes by utilizing the sol-gel process. The sol-gel technology is well known as the process is simple and allows the control of the distribution of the components in molecules, through a pre-orientation of the network (Milea & Bogatu, 2011).

Sol-gel process is a technique to produce thin bond-coating that can give remarkable adhesion between the substrate and the top coat as the fabrication can have low temperature sintering capability, usually 200-600 °C and does not need expensive apparatus or machinery. In addition, sol-gel process also provides a high flexibility and high degree of uniformity over the large area with controlled thickness also ability to produce multi-layer coatings and permitting the fabrication of layers with widely varying optical characteristics.

2.1.1 Sol-gel Process

The sol-gel process has been widely employed in the supported metal catalysts preparation as a result of it generally ends up in extremely high degree of metal dispersion with homogeneous materials (Palacio et al., 2013). Sol-gel processing can be divided into two types that are either an aqueous-based or an alcohol-based system. As the name suggests, aqueous-based systems basically are carried out in the presence of water, whereas alcohol-based systems exclude water build-up until the hydrolysis stage. On the other hand, there are additionally non-hydrolytic sol-gel processes which do not require the presence of solvents at all.

Equivalently, sol-gel precursors can additionally be divided into either alkoxides or non-alkoxides. Metal salts can also be used as alternative of other compounds instead of metal alkoxides although metal alkoxides more preferable for sol-gel process because of their greater volatility. An alternative to alkoxides is provided by the utilization of metal salts. This only applies if the metal salts can be converting readily into their respective oxides by thermal or oxidative decomposition. It is more preferable for such salts to be soluble in organic solvents. The most ideal inorganic salts are nitrates, chlorides and sulphates are thermally more stable and their removal may prove to be difficult. The utilization of nitrates in amounts more preponderant than a few hundred grams on the other hand should be avoided, as nitrates are very vigorous oxidizing agents and can lead to uncontrollable exothermic reactions and even explosions during drying. Acetates are a suitable alternative to nitrates, reducing the possibility of explosions.

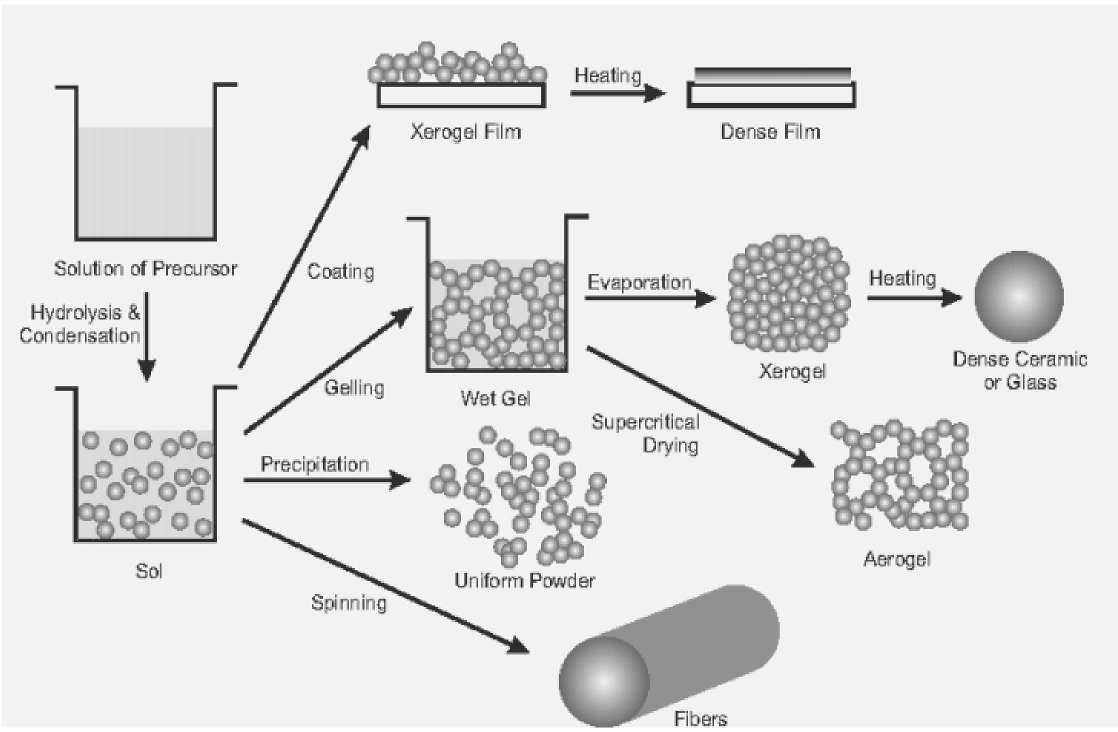


Figure 2.1: Various steps within the sol-gel process to control the final morphology of the product (Niederberger and Nicola 2009)

Nowadays, several developments in precursor solutions, coating processes and equipments have widened the application of the sol-gel technique. In sol-gel method, many ways can be apply to produce sol-gel coatings (refer to Figure 2.1) to create a