EFFECT OF CATALYSTS AND PRECURSORS IN THE SYNTHESIS OF CARBON NANOTUBES BY CATALYTIC CHEMICAL VAPOUR DEPOSITION

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ABSTRACT

Since the pioneering report of discovery of carbon nanotubes (CNTs) in 1991 by Iijima, scientists and researchers worldwide have carried out in depth investigations in this new family of carbon because of its myriad properties and potential applications. The synthesis of novel nanoscale material is the main target in current material science. This study investigates the effect of different types of cabon source and and catalyst on the type of CNTs formed via catalytic chemical vapour deposition (CCVD) method. Three types of carbon source *i.e*. acetylene, methane and ethanol were used for the synthesis of CNTs. The catalysts used in the synthesis of CNTs are monometallic, bimetallic and trimetallic derived from Fe, Co and Ni salts using wet impregnation method. The catalysts were characterized by scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDX). The analysis confirmed the presence of Fe, Co and Ni. The as-synthesized CNTs were characterized using SEM/field emission-scanning electron microscope (FE-SEM), EDX, Raman spectroscopy and transmission electron microscopy (TEM). This analysis also confirmed that all the prepared catalysts were active for the production of CNTs. SEM/FE-SEM analysis revealed different morphologies of CNTs were formed when different catalysts and carbon source were used. Raman spectra revealed that acetylene and methane precursor produced multi-walled carbon nanotubes (MWNTs) as indicated by the presence of G-band and D-band peaks. However, their structures were different depending on the catalysts used. Meanwhile, the presence of RBM peaks along with the G-band and D-band revealed that single-walled carbon nanotubes (SWNTs) are produced using ethanol as the carbon source. TEM micrographs obtained confirmed that acetylene and methane produced MWNTs and ethanol produced SWNTs with diameter in the range of 14.74-34.59 nm, 10.19-37.61 nm and 0.96-2.52 nm, respectively. However, Fe/Al_2O_3 catalyst selectively produced double-walled carbon nanotubes (DWNTs) when ethanol was used as the carbon source. Generally, this research has been successful in producing various types of CNTs depending on the catalyst used and the carbon source selected.

ABSTRAK

Sejak daripada penemuan tiubnano karbon (CNT) yang pertama oleh Iijima, ramai saintis dan penyelidik serantau dunia sangat berminat untuk mengkaji dengan lebih mendalam kumpulan carbon yang baru ini kerana sifat dan aplikasinya yang sangat meluas. Sintesis bahan baru dalam skala nano merupakan tumpuan utama dalam kajian sains bahan sekarang. Kajian ini menyelidik kesan penggunaan pelbagai sumber karbon dan mangkin kepada jenis CNT yang terbentuk melalui kaedah pemangkinan pemendapan wap kimia (CCVD). Tiga jenis sumber karbon iaitu asetilena, metana dan etanol digunakan untuk sintesis CNT. Mangkin yang digunakan dalam sintesis CNT ialah monologam, dwilogam dan trilogam yang dihasilkan daripada garam Fe, Co dan Ni dengan menggunakan kaedah pegisitepuan basah. Mangkin dicirikan dengan mikroskopi imbasan electron (SEM) dan analisis penyerakan tenaga sinar-X (EDX). Analisis ini menunjukkan kehadiran Fe, Co dan Ni dalam sampel mangkin. CNT yang disintesis dicirikan dengan SEM/mikroskopi imbasan elektron-sinaran medan (FE-SEM), EDX, spektroskopi Raman dan mikroskopi elektron penyerakan (TEM). Analisis SEM/FE-SEM menunjukkan pelbagai morfologi CNT terhasil apabila pelbagai mangkin dan sumber karbon digunakan. Analysis ini juga membuktikan bahawa semua mangkin yang disediakan aktif terhadap penghasilan CNT. Spektrum Raman menunjukkan bahawa asetilena and metana menghasilkan tiubnano karbon dinding berganda (MWNT) seperti yang ditunjukkan dengan kehadiran puncak jalur G dan jalur D. Walaubagaimanapun, strukturnya berbeza bergatung kepada mangkin yang digunakan. Sementara itu, kehadiraan puncak RBM bersama-sama dengan jalur G dan jalur D menunjukkan tiubnano karbon berdinding tunggal (SWNT) dihasilkan apabila etanol digunakan sebagai sumber karbon. Mikrograf TEM yang diperolehi membuktikan bahawa asetilena and metana menghasilkan MWNT dan etanol manghasilkan SWNT dengan diameter 14.74-26.08 nm, 10.19-37.61 nm and 0.96-2.52 nm. Walaubagaimanapun, mangkin Fe/Al_2O_3 secara selektifnya manghasilkan tiubnano karbon berdinding dua (DWNT) apabila etanol digunakan sebagai sumber karbon.

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LIST OF SYMBOLS/ABBREVIATIONS

A	-	ampere
Al_2O_3	-	alumina
atm	-	atmosphere
CNT	-	carbon nanotube
Co	-	cobalt
DWNT	-	double-walled carbon nanotube
Fe	-	iron
FE-SEM	-	field emission scanning electron microscopy
HRTEM	-	high resolution transmission electron microscopy
I_G	-	intensity of G-band
I_D	-	intensity of D-band
K	-	Kelvin
MWNT	-	multi-walled carbon nanotube
mW	-	milliwatt
Ni	-	nickel
NT	-	nanotube
RBM	-	radial breathing mode
SEM	-	scanning electron microscopy
Si	-	silicon
SWNT	-	single-walled carbon nanotube
TEM	-	transmission electron microscopy
^{o}C	-	degree of celcius
π	-	pi

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CHAPTER 1

INTRODUCTION

1.1 Nanoscience and Nanotechnology

The words nanoscience and nanotechnology both stem from the term nanometer, which is just a scale of measurement. A meter is about a yard, and there are 1,000,000,000 nanometers in a meter (1 nm = one billionth of a meter). If people were the size of nanometers, all of the people who ever lived on the planet could line up within a parking space. So what is a nanometer? It is about the size of a medium-sized molecule, say a molecule containing 60 carbon atoms. This is the smallest scale at which we can meaningfully study and manipulate matter as we understand it. At the nanometer length scale, the laws of physics operate somewhat differently; the classical mechanics that we encounter in everyday life give way to quantum mechanics. At the nanoscale, for example, a tablespoon is not smooth, but instead composed of discrete atoms and molecules.

Nanoscience is a broad term used for the study of materials and/or processes at the nanoscale in a variety of disciplines. Biology, chemistry, and physics have all independently converged into nanoscientific research areas, ranging from everything to understanding intracellular processes to chemical interactions to quantum mechanics.

Nanotechnology is the creation of functional materials, devices, and systems through control of matter on the nanometer (1 to 100+ nm) length scale and the exploitation of novel properties and phenomena developed at that scale. A scientific and technical revolution has begun that is based upon the ability to systematically organize and manipulate matter on the nanometer length scale. In other words, nanotechnology can be defined as a field which deals with materials and system having the following key properties:

1. They have at least one dimension of about 1 to 100 nm.
2. They are designed through process that exhibit fundamental control over the physical and chemical attributes of molecular-scale structures.

These include the design and manufacture of ever-smaller computer chips, custom-designed drugs, and materials with vastly increased strength due solely to the arrangement of their molecules (such as carbon nanotubules). All matter is made up of atoms and the property of that matter depends on how the atoms are arranged. For example, coal, carbon and graphite (pencil lead) are all made up of pure carbon. The difference in their properties (hardness of diamond vs. soft graphite) is the way the atoms are arranged. It is thought that if we can harness the movement of atoms on a molecular level we can rearrange the carbon atoms in graphite to make diamonds. This is one small example of the power of nanotechnology. This technology is still in its infancy.

Materials and devices at the nanoscale hold vast promise for innovation in virtually every industry and public endeavor including health, electronics, transportation, the environment, and national security, and have been heralded as "the next industrial revolution." Commonplace examples of nanotechnology products include some magnetic memory devices, optical, protective and decorative coatings, some sunscreens and many cosmetics. Defining the scope of the subject is difficult. Ultimately the subjects of nanoscience and nanotechnology may disappear as separate disciplines, because they describe a mode of research and application rather than a unique field of study.

1.2 Synthesis Methods of Carbon Nanotube

Many methods have been developed to synthesize carbon nanotube since it was first discovered. Generally carbon nanotubes can be produced via three common methods *i.e*. arc discharge, laser ablation and chemical vapour deposition (Dresselhaus *et al*., 2001). Each method has its strengths and weaknesses.

1.2.1 Arc Discharge

In arc discharge method, carbon atoms are evaporated by plasma of helium gas ignited by high currents passed through opposing carbon anode and cathode. Generally, the temperature in the vacuum chamber is not controlled and the walls of the chamber are cooled by water. After arching, the soot deposited on the chamber walls consists of useless metal catalyst and carbonaceous particles other than few CNTs. Most CNTs are produced in the centre of the core deposited at the head of the cathode and also around the anode rod (Journet *et al*., 1997). Arc discharge has been developed into an excellent method for producing both high quality MWNTs and SWNTs by controlling the experimental conditions.

1.2.2 Laser Ablation

Smalley and coworkers has reported the synthesis of CNTs by laser vaporization. In this method, a pulsed or continuous laser is used to vaporize a graphite target in an oven at 1200 ºC. The oven is filled with helium (He) or argon (Ar) gas in order to keep the pressure at 500 Torr (0.66 atm). A very hot vapour plume forms, then expands and cools rapidly. As the vaporized species cool, small carbon molecules and atoms quickly condense to form larger cluster, possibly including fullerenes. The catalysts also begin to condense, but more slowly at first, and attach to carbon clusters and prevent their closing into cage structures. Catalysts may even open the cage structures when they are attached to them. From these initial clusters, tubular molecules grow into SWNTs until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become that much coated with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by van der Waals forces (Daenen *et al*., 2003).

1.2.3 Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to “crack” the molecule into reactive atomic carbon. The carbon then diffuses towards the substrate, which is heated and coated with a catalyst where it will bind. CNTs will be formed if the proper parameters are maintained.

1.2.4 Mass Production of CNTs

The main problem of CNTs production is to find a way to produce CNTs in/on a large scale and at a low cost, consequently the full potential of CNTs for applications will not be realized until their growth can be further optimized and controlled. Reproducibility of the CNTs production is also another problem studied by many researchers. Among the different techniques that have been applied for the mass production of CNTs, catalytic chemical vapour deposition (CCVD) appears to be the most promising method owing to its relatively low cost and potentially high yield production. The catalytic method seems to be the best because of the lower reaction temperature (Willems *et al*., 2000). Furthermore, the purification step has been optimized to eliminate the catalyst and amorphous carbon produced during the decomposition of hydrocarbon (Colomer *et al*., 1998, Corrias *et al*., 2003, Kónya and Kiricsi, 2004). Their future use will also strongly depend on the development of simple, efficient and inexpensive technologies for large scale production.

1.3 Problem Statement

There has been great progress in both the production and application of CNTs since their discovery in 1991. Till now, CNTs has been commonly synthesized using three different methods namely, arc discharge, laser ablation and chemical vapour deposition (CVD). The CVD method has been shown to be a promising method to synthesize CNTs on a large scale. However, the problems encountered in the CVD method are the many factors that influence the production of the different forms of CNTs such as types of catalyst, types of support, carbon source, flow rate of precursors and the operating temperature (Kim *et al*., 2002, Nagaraju *et al*., 2002, Li *et al*., 2004). Among these parameters, the types of catalyst and carbon source are the most critical factors influencing the types and structures of CNTs produced. Hence, a detailed study on the effect of the types of catalyst and carbon source on the formation of different types and structure of CNTs will be undertaken.

1.4 Scope of Research

The scopes of this study are listed as below**:**

1. To prepare series of alumina supported catalysts by impregnation technique:
    a) monometallic
    b) bimetallic
    c) trimetallic

2. To synthesize carbon nanotubes from three different precursors via catalytic chemical vapour deposition (CCVD):
    a) acetylene
    b) methane
    c) ethanol

3. To characterize the prepared catalysts using:
    a) Scanning Electron Microscopy (SEM)
    b) Energy Dispersive X-ray Analysis (EDX)

4. To characterize the as-synthesized CNTs using:
    a) Scanning Electron Microscopy (SEM) and Field Emission-Electron Microscopy (FE-SEM).
    b) Energy Dispersive X-ray Analysis (EDX)
    c) Raman spectroscopy
    d) Transmission Electron Microscopy (TEM)

1.5 Research Objectives

The objectives of this research are:

1. To synthesize carbon nanotubes (CNTs) using different types of alumina supported catalyst and carbon sources by catalytic chemical vapour deposition (CCVD) method.
2. To characterize the as-synthesized CNTs.

1.7 Outline of Research

Figure 1.1 shows the flow chart of the research.

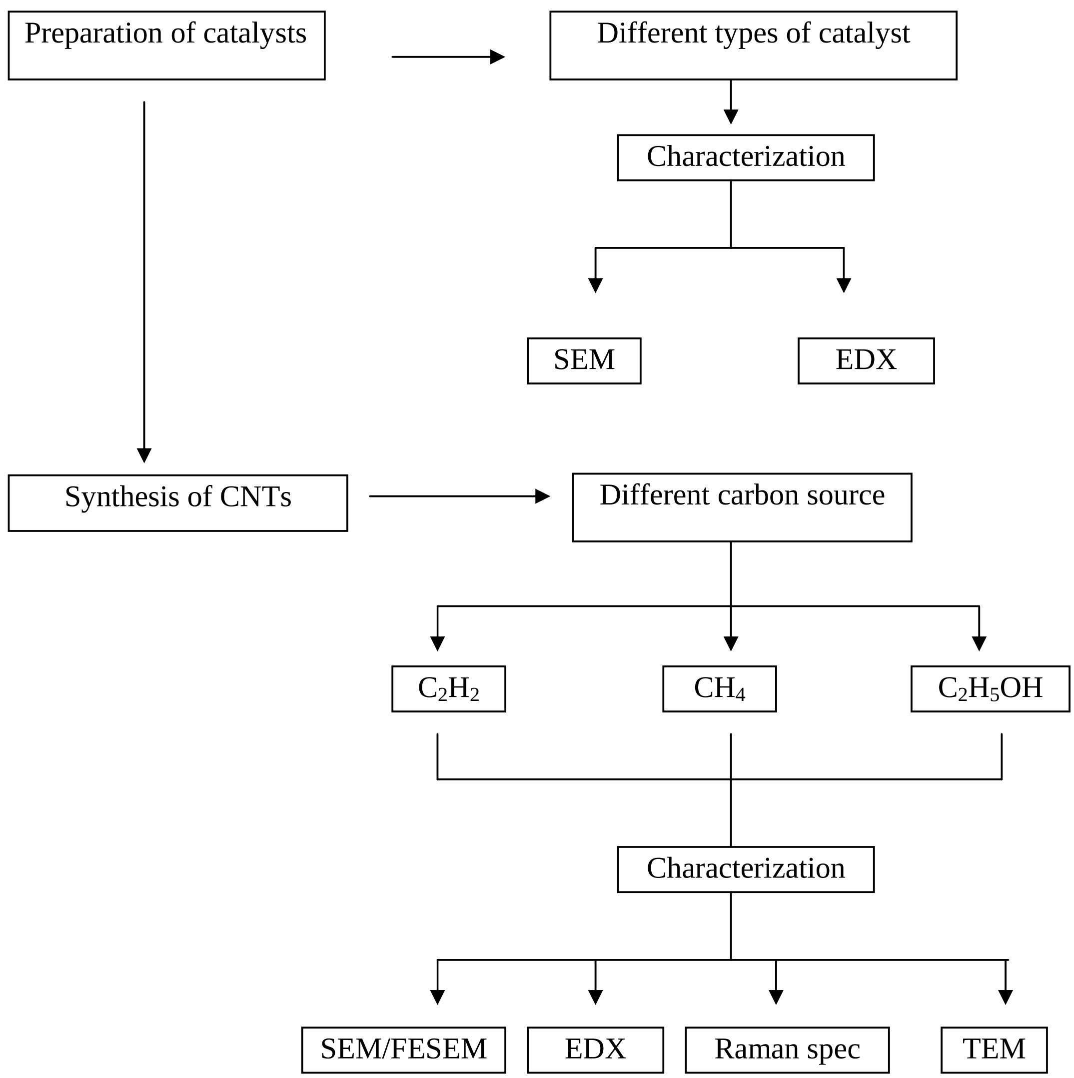

Figure 1.1: Outline of research.

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