



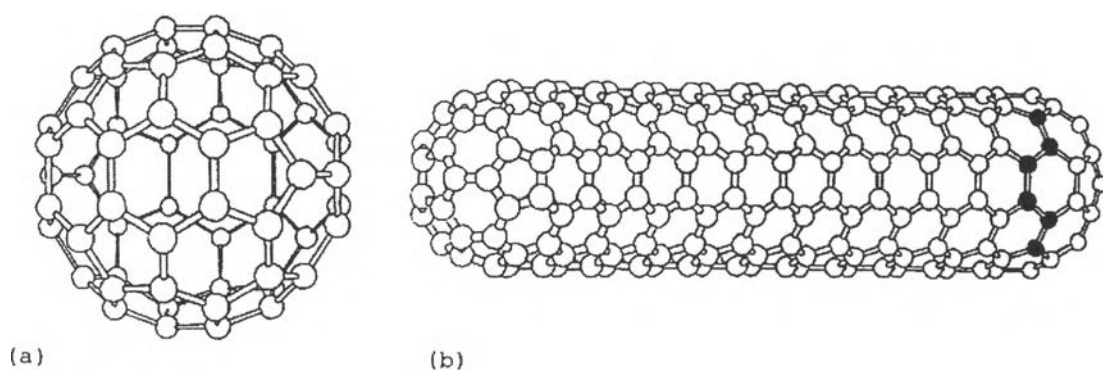
## CHAPTER II LITERATURE REVIEW

### 2.1 Introduction to Carbon Nanotubes

Carbon nanotube can be visualized as a graphite layer rolled up into a cylinder, which each end either open or capped with the half a fullerene as shown in Figure 2.1.

Normally, carbon nanotubes can be divided into two types, which are multi-wall carbon nanotubes (MWNT) and single-wall carbon nanotubes (SWNT).

MWNT composes of two or more cylindrical layers of graphitic sheets. Iijima (1991) discovered this type of carbon nanotube by using cathode deposit from carbon arc discharge experiment. Subsequently, in 1993, Iijima discovered SWNT containing only one concentric layer by using in the same experiments. In general, the diameter of SWNT is around 1–2 nm and length about 5–10 micron, while MWNT's diameter typically ranges around 2.5–30 nm and length from a few tens of nanometers to several micrometers.



**Figure 2.1** Carbon nanostructures (a) a spherical molecule, fullerene (b) a hollow cylindrical tube, carbon nanotube (Tang, 2001).

## 2.2 Properties and Applications of Carbon Nanotubes

Carbon nanotubes have been demonstrated their potentially useful mechanical and electrical properties. For mechanical properties, carbon nanotubes are predicted to have very high Young's modulus (Treacy *et al.*, 1996), which can be over 1 Tpa., and a maximum tensile strength close to 50 Gpa., about 50 times higher than steel. Moreover, they have shown a combination of lightweight (density = 1.3 g/cm<sup>3</sup>) with high elastic modulus. From these properties, carbon nanotubes probably can be used as reinforcing nanofibers for composite materials. Furthermore, SWNT also has outstanding electronic properties that they can be either metallic or semiconductor depending on their helicity. For example, the armchair nanotubes are metallic, while, zig-zag nanotubes are semiconductor. Because of a very small diameter, they may be used as nanoelctronic devices. Furthermore, carbon nanotubes have been claimed others practical applications such as field emission, biosensor, advanced scanning probes for scanning probe microscope, and energy storage. (Cassel *et al.*, 1999).

## 2.3 Production of Carbon Nanotubes

Currently, there are three techniques to synthesize carbon nanotubes, the arc discharge of carbon electrodes, the laser ablation of carbon graphite and the catalytic reaction of hydrocarbon compounds.

### 2.3.1 Arc Discharge of Carbon Electrodes Technique

In 1991, the first production of carbon nanotubes has been operated by arc discharge technique. This technique is to introduce an inert gas through the reactor, which consists of anode and cathode graphite electrodes inside the chamber. After carbon anode is drilled and filled with the transition metal, the electrical current is applying through the opposite carbon electrodes, positive and negative, with the result that arc plasma is generated between both electrodes. Consequently, the carbon atoms in carbon anode are vaporized and formed carbon products, depositing on the carbon cathode or inside the reactor chamber, as shown in Figure

2.2. The obtained carbons have several forms such as SWNT, MWNT, carbon nanoparticles, carbon amorphous, and graphitic carbon. Iijima *et al.*(1993) and Bethune *et al.*(1993) reported that an arc discharge with a cathode containing metal catalysts (Co, Fe, Ni) mixed to graphite powder results in a deposit containing SWNT. SWNT is usually assembled in ropes or bundle, but some single tube can also be found in the deposits.

### 2.3.2 Laser Evaporization of Carbon Graphite Technique

The method utilized intense laser pulses to ablate a carbon target containing 0.5 atomic percent of nickel and cobalt. As illustrated in Figure 2.3, the target gas was placed in a tube-furnace heated to 1,200 °C. During laser ablation, a flow of inert gas is introduced to the growth chamber to carry the grown nanotubes downstream to be collected at a collecting zone. The produced SWNT is mostly in the form of ropes consisting of tens of individual nanotubes packed with hexagonal crystals via van der Waals interactions. The growth of high quality SWNT was demonstrated by Gou *et al.*(1995) and the optimization of SWNT growth was achieved by Journet *et al.*(1997) using a carbon anode containing 1.0 atomic percentage of yttrium and 4.2 % of nickel as catalyst.

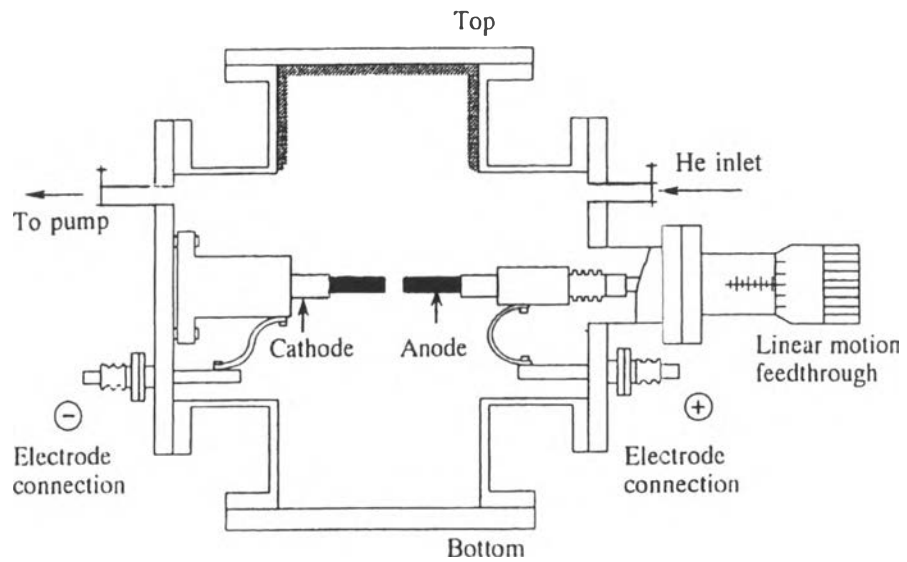


Figure 2.2 A carbon arc discharge apparatus (Harris, 1999).

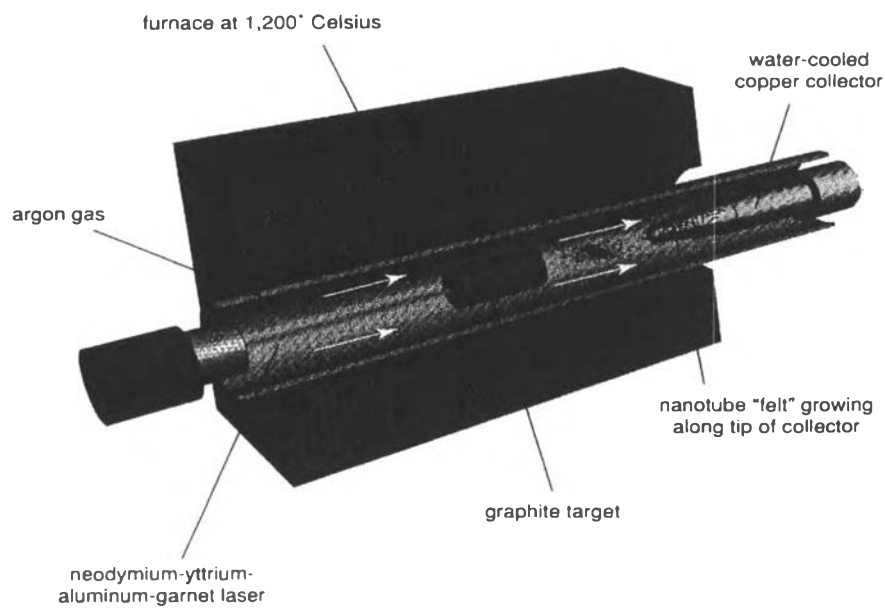
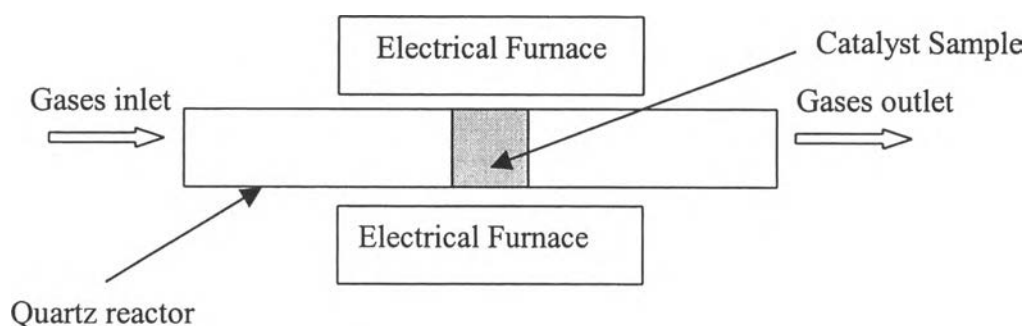


Figure 2.3 Laser vaporization apparatus (Yakobson and Smalley, 1997).

### 2.3.3 Catalytic Reaction of Hydrocarbon Compounds Technique

The arc discharge and laser ablation techniques are the traditional methods for obtaining the high quality nanotube materials. Nevertheless, both of them are not suitable for mass production of SWNT because of the limitation to scale up the processes.

The catalytic decomposition of a carbon-containing molecule on a solid catalyst or CVD (Chemical Vapor Deposition) has been the best alternative to the large-scale production of SWNT. Normally, carbon-containing gases (mostly methane and carbon monoxides) are passed over transition catalysts at elevated temperature for a period of time. At sufficiently high temperature, these gases are catalytically decomposed, and as a result, carbon products are generated on the catalyst surfaces, as depicted in Figure 2.4. The carbon products may be formed in several types, such as carbon nanotube, carbon filament, and amorphous carbon, depending on catalysts and reaction conditions. To obtain the high quality and quantity of carbon nanotubes, the variation of catalyst composition, supporting materials, hydrocarbon gases and synthesis conditions are the crucial parameters



**Figure 2.4** Reactor setup for catalytically growing carbon nanotubes.

Recently, there are many reports of carbon nanotubes synthesis by catalytic method of carbon monoxide and methane.

Hafner and coworkers (1998) improved the yield of SWNT by decomposition of ethylene over molybdenum and iron-molybdenum on alumina catalysts (1:9:90 by weight). They affirmed that pure SWNT could be produced with no MWNT containing by limiting the carbon supplied to the reaction. The partial pressure of ethylene was lowered to 0.5 torr (0.06 %). Recently, the same researcher group has produced SWNT by thermal decomposition of iron pentacarbonyl in a flow of CO at elevated pressure (1–10 atm) and at temperature 800–1,200 °C. The yield of SWNT was increased with temperature and pressure of the system, while the diameter of SWNT was decreased as the pressure is increased. As a result, the diameter as small as 0.7 nm, which is the same as diameter of fullerene (C<sub>60</sub>), can be achieved at the system pressure of 10 atm. These researchers also discovered that, by adding a little amount of methane (CH<sub>4</sub>) in the feed stream, the amount of deposited carbon was significantly enhanced. However, the considerably amount of amorphous carbon would overcoat SWNT when the concentration of methane was increased more than 1.4%, unless the reaction temperature was decreased from 1,200 °C to 1,100 °C.

Kong and coworkers (1998) demonstrated the growth of SWNT from methane (CH<sub>4</sub>) with supported catalysts at 1,000 °C. The high temperature was required in growing SWNT in order to overcome high strain energy of small diameter SWNT and to obtain defect-free SWNT. They explained that methane is a critical choice for feeding gas to prevent the amorphous carbon formation because of high temperature stability of methane so that methane will not go self-pyrolysis. They observed that iron oxide (Fe<sub>2</sub>O<sub>3</sub>) on alumina or silica support yielded abundant of SWNT, while cobalt oxide (CoO) on alumina or nickel oxide/cobalt oxide (NiO/CoO) on silica delivered moderate amount of SWNT; however, nickel oxide (NiO) did not generate SWNT in their report.

Cheng and coworkers (1998) reported a novel synthesis method for SWNT using an improved floating catalyst approach in which benzene was catalytically pyrolyzed at 1,100–1,200 °C. Benzene was used as carbon feedstock, hydrogen as

the carrier gas and ferrocene as the catalyst precursor. In this work, ferrocene was vaporized and decomposed into iron form, subsequently reduced by hydrogen to form atomic iron. Then, the atomic iron agglomerated into iron clusters that can catalyze the growth of SWNT. However, most of the carbon products were amorphous carbons that could be generated by the self-pyrolyzed of benzene.

Nikolaev and colleagues (1999) developed a gas phase catalytic process to grow SWNT. Carbon monoxide was feed as carbon feedstock and the growth temperature was in the range of 800–1,200 °C. In this technique, catalysts were *in situ* generated by thermal decomposition of iron pentacarbonyl [Fe (CO)<sub>5</sub>] to form iron catalyst particles. To enhance the reaction, they used high pressures of CO (1–10 atm) to speed the disproportionation of CO molecules into carbon. The high yield of SWNT was obtained in this work. However, the distributions of SWNT diameters were significantly broad, range from 0.7 to 1.4 nm.

Flahaut and colleagues (1999) employed the oxide spinels containing binary transition metals of iron, cobalt and nickel catalyst, particularly with iron and cobalt, can fabricate high quality SWNT by catalyzing mixture of hydrogen and methane gases at 1070 °C. They believed that the reduction of oxide spinels renders relatively small metal nanoparticles with narrow size distribution leading to good quality SWNT product in terms of yield, size distribution and cleanness.

Kitiyanan and coworkers (2000) developed a catalytic method (CoMoCAT) to produce SWNT. They systematically studied the catalytic method by carbon monoxide disproportionation at different ratios of Co to Mo on silica supported catalysts. The catalysts were calcined in air at 500 °C for 3 h. After calcination, Mo is in the form well-dispersed Mo<sup>6+</sup> oxide while Co strongly depends on the Co-Mo ratio. In case of high Co:Mo ratios (greater than 1), Co forms a non-interacting Co<sub>3</sub>O<sub>4</sub> phase. On the other hand, at low Co:Mo ratios, it appears interacting with Mo in a superficial Co molybdate-like structure. After that the calcined catalysts were reduced in hydrogen at 500 °C. During the reduction treatment in hydrogen, the non-interacting Co phase was reduced to metallic Co and converted into large metallic Co clusters upon reduction, which produced the unwanted forms of carbon during reaction i.e. MWNT, carbon filaments, graphite, etc. By contrast on the selective

catalyst, the Co molybdate-like species remain as well dispersed  $\text{Co}^{2+}$  ions. Then the reduced catalyst was heated in helium to 700 °C and reacted with CO at this temperature. In the presence of carbon monoxide, Mo is converted into Mo carbide. This transformation breaks up the Co molybdate-like structure, allowing for the reduction of Co by CO and releasing of extremely small metal Co clusters into the gaseous CO. These small Co particles seem to be favorable for the production of SWNT instead of the large metal particles that mostly occur in the high Co:Mo ratio catalysts.

Su and coworkers (2000) studied the catalytic synthesis of SWNT with methane. The catalyst used in this work was a Mo-Fe catalyst (0.16:1 mole ratio) supported on aerogel alumina. The catalyst exhibited an ultra-high surface area, around 540  $\text{m}^2/\text{g}$ , and large mesopore volume, around 1.4 ml/g. Using the aerogel catalyst, they were able to obtain around 200% yield of SWNT. The high yield of SWNT is possibly due to the high surface area and large pore volume of the catalyst support that may facilitate the diffusion of methane to the catalytic sites.

Colomer and coworkers (2000) recently reported the growth of bulk quantities of SWNT by catalytic decomposition of methane. The catalyst used in this work was a cobalt catalyst supported on magnesium oxide. This group found that the produced SWNT could be further purified by acidic treatment to yield a product with about 70-80% of SWNT.

Tang and coworkers (2001) studied the catalytic synthesis of SWNT. The catalyst used in this work was Mo-Co/MgO at different ratios of Mo and Co. The carbon-containing gas was a mixture of hydrogen and methane with a molar ratio of  $\text{H}_2/\text{CH}_4 = 4$ . The reaction temperature was programmed from room temperature up to 1000 °C. From this study, the amounts of SWNT and MWNT may be controlled by adjusting the cobalt and molybdenum loads. Co/MgO catalyst produced mostly MWNT. Moreover, the addition of appropriate amount of Mo to Co/MgO could largely increase the yield of SWNT.

Xuto (2002) studied catalytic synthesis of carbon nanotubes by methane decomposition. The catalysts were CoMo and FeMo in different ratios of 1:1, 1:2 and 2:1 mole ratios on  $\text{SiO}_2$  and MgO supports. All catalysts were prepared by using



incipient wetness impregnation technique with 6% total metal loading and calcined in dried air with a flow rate 100 sccm at temperature 500 °C. The experiment was conducted into two approaches, which were methane alone with fixing reaction temperature and the mixture of hydrogen and methane with scanning reaction temperature.

First approach, a 0.1–0.5 g of calcined catalyst was loaded into the ceramic boat and placed at the middle of reactor. The catalyst was reduced by heating in 100 sccm of hydrogen stream up to 500 °C and held at this temperature for 30 minutes. Then, the methane stream was turned on at the range of reaction temperature, typically 700–1,000 °C.

Second approach, a 0.1–0.5 g of calcined catalyst was loaded into the ceramic boat and placed at the middle of reactor. Next, the mixture of hydrogen and methane with constant flow rates of 100 and 25 sccm, respectively, was passed over the catalysts, while the reactor temperature was linearly increased at a rate of 5 °C/min up to 1,000 °C and held at this temperature for 2 min.

For this result, carbon products obtained from Co-Mo/SiO<sub>2</sub> and methane mostly were MWNT, while carbon from Co-Mo/SiO<sub>2</sub> and carbon monoxide mostly consisted of SWNT. Among the studied catalysts, only Fe-Mo/MgO (2:1 mole ratio) produced SWNT; nevertheless, the selectivity towards SWNT was still very low compared with Co-Mo/SiO<sub>2</sub> with CO.

Hornyak and coworkers (2001) investigated the growth of SWNT from methane on alumina-supported metal catalysts with narrow temperature window from 680–850 °C. The SWNT growth occurs at the low temperature side of the window and appears free of amorphous or nanocrystalline carbon impurities.

Qingwen and coworkers (2002) studied a scalable CVD synthesis of high-purity SWNT with porous MgO as support material. In their work, they found that porous MgO prepared by thermal decomposition of its salts was an eminent support material for CVD growth of SWNT compared with other kind of supports such as SiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

Harutyunyan and coworkers (2002) studied a series of Fe and Fe/Mo catalyst on alumina support by using Chemical Vapor Deposition (CVD) method.

They investigated under low methane flow ( $40 \text{ cm}^3/\text{min}$ ) and the temperature range around  $600\text{--}900 \text{ }^\circ\text{C}$ . They found that the Fe/Mo oxide catalyst was active at soft condition, temperature  $680 \text{ }^\circ\text{C}$  and methane flow rate of  $40 \text{ cm}^3/\text{min}$  while the Fe-oxide catalyst (without Mo) was not active, but it could be active by an in situ reduction to metal in flowing He/10%  $\text{H}_2$ . For this growth condition, the tube diameters were in the range  $0.7\text{--}1.7 \text{ nm}$ .

Alvarez and coworkers (2002) studied the disproportionation of CO over Co-Mo /  $\text{SiO}_2$  catalysts with low Co/Mo ratios. To obtain high selectivity of SWNT, the reaction was conducted between  $700$  and  $950 \text{ }^\circ\text{C}$  in a flow of pure CO at total pressure between 1 and 5 atm. The Raman spectroscopy, TPO, and TEM were used to characterize the products. Moreover, they showed that the product of this process had a high concentration of SWNT and they concluded that the nanotubes produced at  $750 \text{ }^\circ\text{C}$  with an average diameter of  $0.9 \text{ nm}$ .

## 2.4 Characterization of Carbon Nanotubes

There are a large number of techniques have been employed for carbon nanotube characterization: Raman spectroscopy, Electron microscopy, Temperature-programmed analysis, Scanning probe microscopy, X-ray diffraction and etc. In this section, we will briefly discuss certain techniques that have been widely used to characterize carbon nanotube such as Raman spectroscopy, electron microscopy, and temperature programmed analysis.

### 2.4.1 Raman Spectroscopy

Raman scattering is an interaction between photon and electron cloud of the molecule or crystal. The difference in energy between the incoming and the outgoing photons corresponds to the energy of vibrations of the materials. Typically, the Raman technique allows for a systematic screening the type of overall carbon products. It is a powerful technique for the characterization of the structure of carbon nanotubes. Moreover, It can provide formation about the distribution of tube diameters, electronic properties, and analysis of disordered carbon. Firstly, the

distribution of tube diameters was shown in the radial breathing mode frequency range (RBM), i.e. below  $300 \text{ cm}^{-1}$ . It has been shown that for all tube symmetries and SWNT are appeared, there is common linear relationship between the breathing mode frequency and the inverse of the tube diameter as can be shown by the following equation:

$$\nu = 238 / (d)^{0.93} \quad (2.1)$$

where  $d$  = Diameter of the tubes in nanometer unit

$\nu$  = Wavelength in  $\text{cm}^{-1}$ .

Secondly, the electronic properties, metallic or semiconductor, were shown in the tangential mode (TM) range, i.e.  $1,400\text{--}1,700 \text{ cm}^{-1}$ . Finally, the level of disorder carbon, amorphous carbon, was showed in D-band at around  $1,350 \text{ cm}^{-1}$ .

#### 2.4.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) gives the two dimensional images of carbon nanotubes. It is able to give sub-nanometer resolution; therefore, it is highly suitable for studying structure of nanotubes, for instance, diameters of both SWNT and MWNT, diameter of SWNT bundle, graphitic layer of MWNT as well as crystallinity of carbon sample.

#### 2.4.3 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) technique has been developed in order to determine the distribution of the different forms of carbonaceous deposits presenting on the catalyst. In other words, carbon with different morphology is burnt at different temperature; consequently, temperature program analysis is a technique that is suitable to study carbon structures.