

## CHAPTER II LITERATURE SURVEY



### 2.1 Introduction to Carbon Nanotubes

Carbon nanotube can be viewed as a seamlessly rolled up of a single or several graphene sheets into cylindrical tubes having both ends closed by half of fullerenes. The walls of carbon nanotube may consist of one or more cylindrical layers of graphitic sheets. If the carbon nanotube contains two or more concentric walls, it is typically referred to as multi-wall carbon nanotube (MWNT), while, if the wall is only one layer of graphene, it is single-wall carbon nanotube (SWNT). The transmission electron microscope (TEM) images of these two types are shown in Figure 2.1 (Kitiyanan *et al.*, 2000).

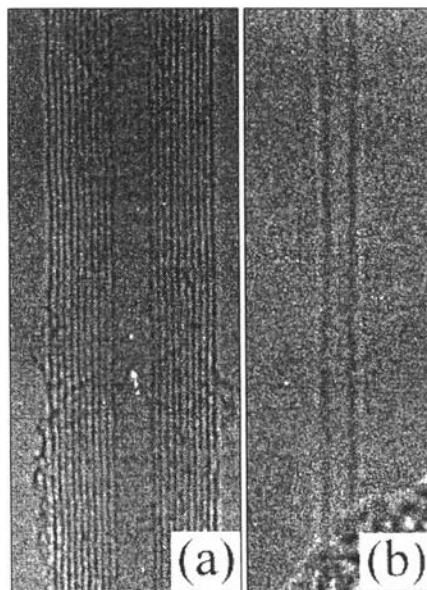
Carbon nanotube can be in various diameters and lengths. Normally, the diameter of SWNT is around 1-2 nm and the length can be up to several microns, while the outer diameters of MWNT can range from about 2.5 nm to 30 nm and the length from a few tens of nanometers to several micrometers. The spacing between each layer in MWNT closely matches the spacing between the carbon sheets in graphite that is around 0.344 nm.

### 2.2 Properties and Applications of Carbon Nanotubes

Carbon nanotubes have shown their outstanding mechanical and electrical properties, which can be used in a wide range of applications. Carbon nanotubes are predicted to have very high Young's modulus, which can be over 1 Tera Pascal, and a maximum tensile strength close to 30 GPa. Moreover, they have shown a combination of lightweight with high elastic modulus. From these properties, carbon nanotubes probably can be used as reinforcing nanofibers for composite materials. SWNTs also have outstanding electronic properties that they can be either conductor or semi-conductor depending on their helicity. Because of a very small diameter, they may be used as nanoelectronic devices. Moreover, carbon nanotubes have

demonstrated others practical applications such as advanced scanning probes for scanning probe microscope and energy storage. (Cassel, 1999).

Because of these features as mentioned above, carbon nanotubes could be a material that drastically change our way of living. In order to reach this point, it is necessary to obtain high quality nanotubes in a large scale. However, the carbon nanotubes are not in commercial market since they still can be produced in a small scale, causing very high cost of this material.



**Figure 2.1** TEM images of (a) multi-wall carbon nanotube (b) single-wall carbon nanotube (from <http://www.physics.berkeley.edu/research/zettl/projects/imaging.html>)

## 2.3 Productions of Carbon Nanotubes

Nowadays, three methods have been used for synthesis of carbon, which are arc discharge of carbon electrodes, the laser evaporation of carbon graphite and the catalytic reaction of hydrocarbon compounds.

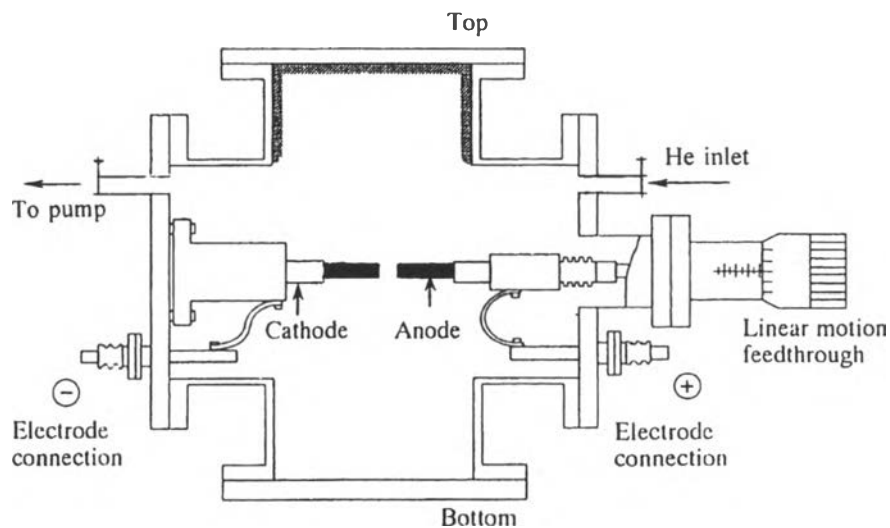
### 2.3.1 Arc Discharge of Carbon Electrodes Technique

The first production of carbon nanotubes has been operated by arc discharge technique in 1991. The carbon arc discharge apparatus is schematically illustrated in Figure.2.2. Generally, the electrical current is applying through the opposing carbon electrodes, positive and negative electrodes. Consequently, arc plasma is generated between both electrodes. Then, carbon on positive electrode (anode electrode) is vaporized and formed carbon nanotubes that deposit on the negative electrode (cathode electrode). In order to synthesize SWNTs, a transition catalyst is needed and can be done by drilling the carbon anode and filling this hole with the metal catalyst inside.

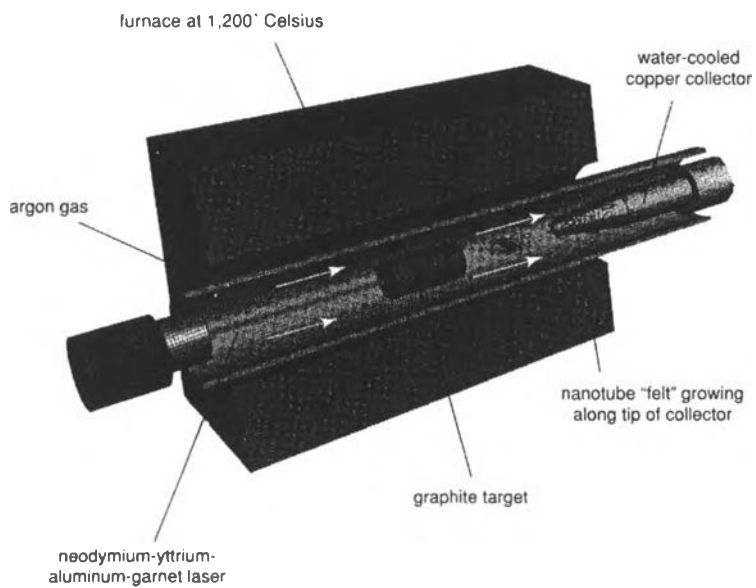
### 2.3.2 Laser Evaporation of Carbon Graphite Technique

Gou and coworkers (1995) demonstrated that it is possible to grow carbon nanotubes with a laser evaporation technique. Typically, the experiment is performed in a horizontal flow quartz tube under a flow of inert gas at controlled pressure an electrical tube furnace, as depicted in Figure 2.3. The reactor contains a graphite target usually compressed with a small amount of a transition metal such as Co or Fe. The laser is focused on the graphite target with the result that carbon in graphite is vaporized, coalesced, swept out of the furnace zone by inert gas, and then deposited as soot on a collecting zone outside the furnace zone.

Although the arc discharge and the laser evaporation techniques are the early methods for making the high quality carbon nanotubes, both of them are not suitable for mass production of SWNTs because of the limitation to scale up the processes.



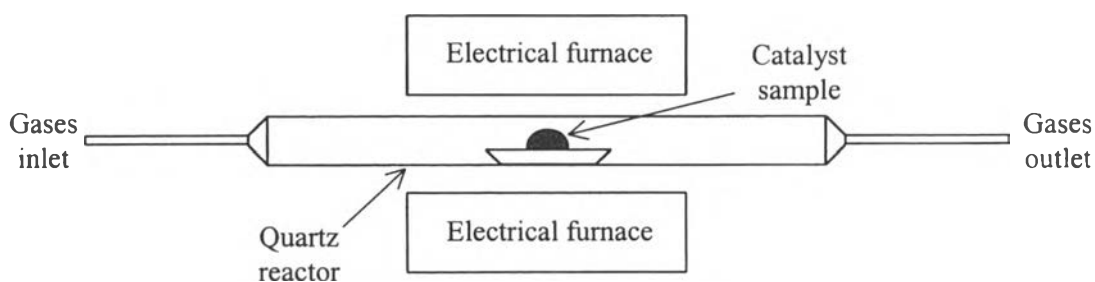
**Figure 2.2** Carbon arc discharge apparatus; from Harris (1999)



**Figure 2.3** Laser vaporization apparatus; from Harris (1999)

### 2.3.3 Catalytic Reaction of Hydrocarbon Compounds Technique

Besides the traditional arc discharge and laser ablation processes, other methods based on catalytic growth have come into play. This approach has been very successful in the large-scale production of other carbon materials such as carbon fibers and filaments. Similarly, carbon nanotubes should be produced by the decomposition of carbon-containing gases. The catalytic reaction apparatus is schematically illustrated in Figure 2.4. Normally, a carbon containing gas (mostly methane and carbon monoxides) as well as an inert gas pass 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. The carbon products may be formed in several types, such as carbon nanotubes, carbon filament, and amorphous carbon, depending on catalysts and reaction conditions. The choice of feed gas, the type of catalysts and reaction conditions are the crucial parameters to obtain the high selectivity of carbon nanotubes.



**Figure 2.4** Reactor set up for catalytically growing carbon nanotubes; from Kitiyanan (2000)

The choice of carbon feeding gas is one of the key factors to grow high quality and quantity of carbon nanotubes. Recently, there are reports of carbon nanotubes synthesis by catalytic method of benzene, carbon monoxide and methane. Among these carbon monoxide and methane are very stable molecules, which possibly eliminate self-pyrolysis that may lead to the generation of amorphous carbon.

Cheng and coworkers (1998) reported a method that employed benzene as the carbon source, hydrogen as the reducing gas and ferrocene as the catalyst precursor. The reaction temperatures were in the range of 1100-1200 °C. In this work, ferrocene was vaporized and decomposed into iron form, which was subsequently reduced by hydrogen to form atomic iron. Then the atomic iron agglomerated into iron clusters that can catalyze the growth of SWNTs. However, mostly carbon products were amorphous carbons that could be generated by the self-pyrolyzed of benzene.

Nikolaev and colleagues (1999) has developed a gas phase catalytic process to grow SWNTs. Carbon monoxide and iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) were used as carbon feedstock and the iron containing catalyst precursor. The reaction temperatures were in the range of 800-1200 °C. In this technique, catalysts were *in situ* generated by thermal decomposition of iron pentacarbonyl and form iron catalyst particles. To enhance the reaction, they have used high pressures of CO (1-10 atm) to speed up the disproportionation of CO. The disproportionation of CO or Boudouard reaction is shown in equation 2.1



It has been reported that the high yield of SWNTs was obtained in this work. However, the distributions of SWNT diameters were significantly broad, range from 0.7 to 1.4 nm. The high distribution of diameter sizes may be resulted from the uncontrolled iron particle size during the decomposition of iron pentacarbonyl.

Kitiyanan and coworkers (2000) have systematically studied the catalytic method by carbon monoxide disproportionation at different ratio of Co and Mo on silica supported catalysts. The catalyst was calcined in air at 500 °C and reduced in hydrogen at 500 °C. Then the treated catalyst was heated in helium to 700 °C and reacted with CO at this temperature. They found that Mo alone on silica support could not produce carbon nanotubes at this condition. Moreover, Co alone produces high amount of MWNTs. However, when Co and Mo metals are simultaneously presented on silica support with low Co:Mo ratio (less than 1), the products mostly are SWNTs. The highest yield of produced SWNTs is around 0.25 g/gram catalyst. The selectivity towards SWNT is better than 80% with a narrow distribution of tube diameters. In order to investigate the system of Co-Mo catalyst, a variety of characterization techniques were utilized (Herrera *et al.*, 2001). They reported that, after calcinations of catalyst, Mo is in the form of dispersed Mo<sup>6+</sup> oxide. And, the state of Co strongly depends on the Co-Mo ratio. At high Co:Mo ratios (greater than 1), Co forms a non-interacting Co<sub>3</sub>O<sub>4</sub> phase. At low Co:Mo ratios, it appears interacting with Mo in a superficial Co molybdate-like structure. During the subsequent reduction treatment in hydrogen, the non-interacting Co phases is reduced to metallic Co and converted into large metallic Co cluster upon reduction, which produced the unwanted forms of carbon during reaction. By contrast on the selective catalyst, the Co molybdate-like species remain as well dispersed Co<sup>2+</sup> ions. As the carbon monoxide starts, 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 SWNTs 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 SWNTs 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 m<sup>2</sup>/g, and large mesopore volume, around 1.4 ml/g. Using the aerogel catalyst, Su and coworkers (2000) were able to obtain around 200% yield of

SWNTs. The high yield of SWNTs 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) reported the growth 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 SWNTs could be further purified by acidic treatment to yield a product with about 70-80% of SWNTs.

Tang and coworkers (2001) studied the catalytic synthesis of SWNTs. The catalyst used in this work was Mo-Co/MgO at different ratio of Mo and Co. The carbon containing gas was a mixture of hydrogen and methane with molar ratio of  $H_2/CH_4 = 4$ . The reaction temperature was programmed from room temperature up to 1000 °C. From this study, the amount of SWNTs and MWNTs may be controlled by adjusting the cobalt and molybdenum loading. Co/MgO catalyst produced mostly MWNTs. Moreover, the addition of appropriate amount of Mo to Co/MgO could largely increase the yield of SWNTs. They explained that the addition of Mo might increase the number of Co nanoparticles, which were responsible for the growth of SWNTs. In addition, Mo is known to be a catalytic center for promoting the aromatization of methane. The addition of Mo may provide the intermediate aromatic species, which can feed into the adjacent Co sites with high efficiency, hence increase the yield of carbon nanotubes. But there was a limit to the amount of molybdenum. The addition of excess of molybdenum to Co/MgO, MWNTs would be formed.

## **2.4 Characterizations of Carbon Nanotubes**

### **2.4.1 Raman Spectroscopy**

Raman spectroscopy technique is used to characterize the types of overall carbon product. In case of carbon nanotubes, there are important three modes: graphite-like tangential mode (G-band), disordered carbon band (D-band), and the radial breathing mode frequency range (RBM).



Graphite-like tangential mode or G-band locates at around  $1570\text{ cm}^{-1}$ , which is the characteristic carbon nanotube and graphite. Disordered carbon mode or D-band occurs at about  $1350\text{ cm}^{-1}$ . This wavelength is important for determining the purity of the carbon nanotubes. Radial breathing mode or RBM locates below  $300\text{ cm}^{-1}$ . This mode can provide information about the presence of SWNT in the product and also use to estimate the diameter of SWNT, which can be related by the following equation:

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

Where  $d$  is the diameter of the tube in nanometer unit and  $\nu$  is wavelength in the  $\text{cm}^{-1}$ .

#### 2.4.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) can provide high magnification of two-dimensional images of nanomaterials. Therefore this technique is highly suitable for studying the structure of carbon nanotubes. However, TEM can only provide a qualitative description and is relative expensive and time consuming so this technique is not suitable to be applied as a routine quality control for the large-scale production.

#### 2.4.3 Temperature Programmed Analysis

Temperature programmed analysis is a technique which monitors the change in sample for examples, weight or chemical reaction as the temperature is linearly increased with time. In this thesis, a continuous flow of an oxygen-containing gas is passed over the catalyst containing the carbon deposits. At sufficient high temperature, the carbonaceous materials are oxidized resulting in the reduction of sample's weight and the evolution of gases (*i.e.*  $\text{CO}_2$ ). If the sample's weight is the monitored parameter, this technique is typically called thermal gravimetric analysis (TGA). If the emitted gas were monitored, it is usually called

temperature programmed oxidation (TPO). Quantification of the loss weight or emit gases give a direct measurement of the amount of carbon that gets oxidized.