



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Allotropes of Carbon

Allotropes of carbon are substances consisting of only carbon atom that include diamond, graphite, fullerene, amorphous and carbon nanotubes. For diamond, each carbon atom bond to four others and has tetrahedral geometry. Therefore, diamond is a very hard material and has a very high melting point.

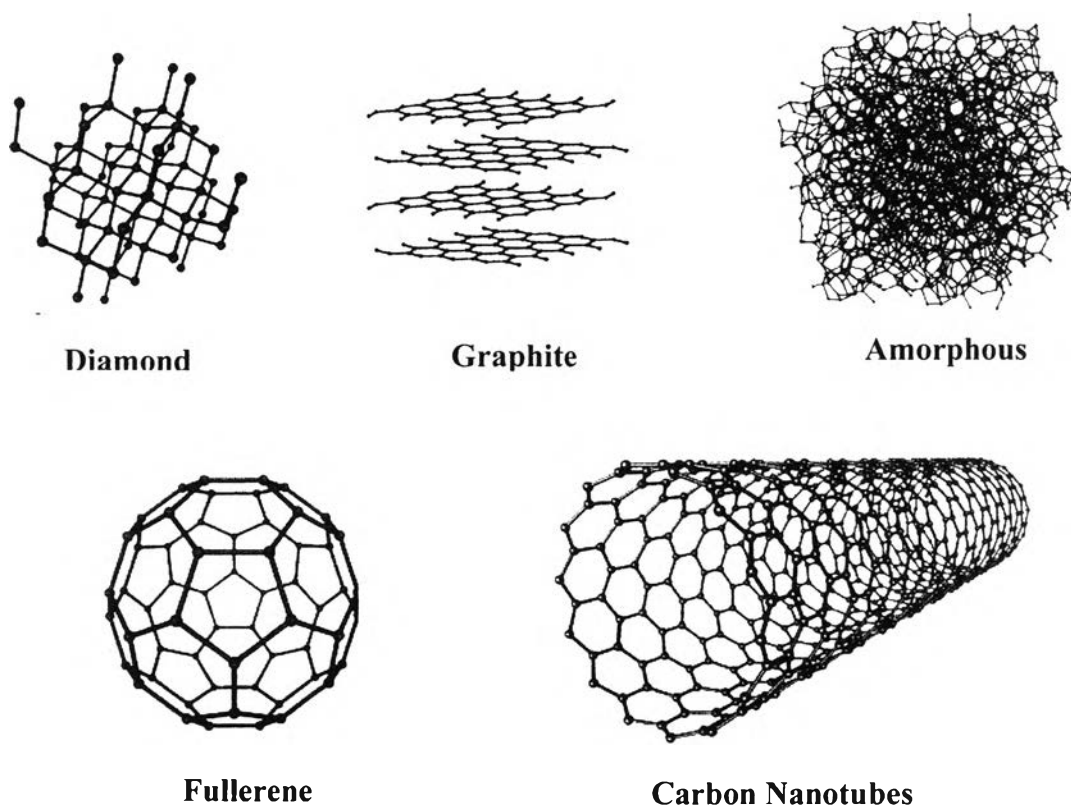


Figure 2.1 Allotropes of carbon; diamond, graphite, amorphous, fullerene and carbon nanotubes.

The most common allotrope is graphite which carbon atoms are arranged in the layers. Within the layer, each carbon atom is connected to three others to form hexagonal rings. The layers interact via only van der Waals force so graphite is a soft,

slippery substance. Amorphous carbon does not have any crystalline structure. Similar to glassy materials, some short-range order can be observed.

The fullerenes are recently-discovered allotropes. Their structure includes hollow sphere, ellipsoid, or tube. Spherical fullerenes are sometimes called buckyballs, while cylindrical fullerenes are called buckytubes or nanotubes.

Carbon nanotubes (CNTs) was discovered in 1991 by Sumio Iijima. This cylindrical nanostructure has a length-to-diameter ratio greater than 1,000,000.

2.2 Structures and Properties of Carbon Nanotubes

Single walled carbon nanotubes (SWNTs) can be observed as a long wrapped graphene sheet (Figure 2.2) with a typical diameter on the order of 1.4 nm. A multi-walled carbon nanotube (MWNT) consists of concentric cylindrical layers of graphite sheets and the interlayer distance is approximately 0.34 nm, close to the interlayer distance in graphite.

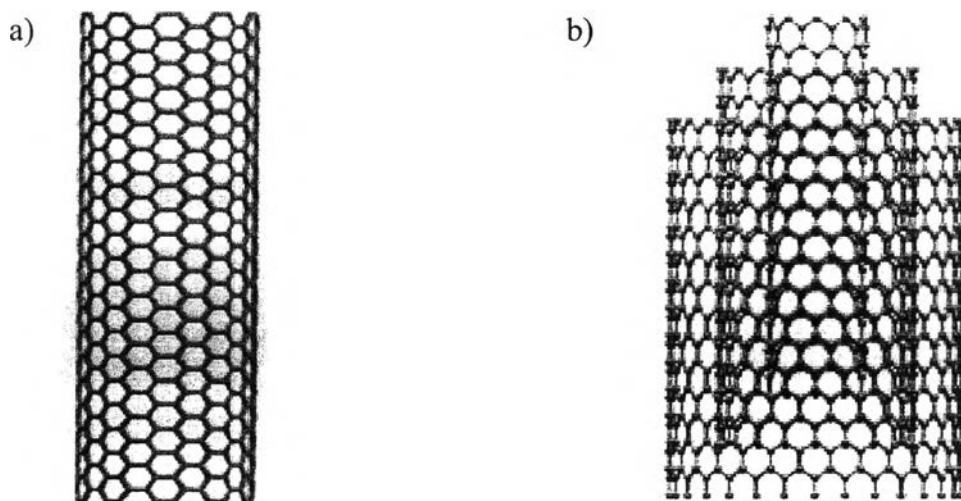


Figure 2.2 Structures of carbon nanotubes a) SWNT, b) MWNT

2.2.1 Electrical Conductivity

The difference in molecular structures result in different band structures and different band gaps, therefore electrical conducting property are different.

SWNTs with a small diameter are either semi-conductor or metallic (Cassel *et al.*, 1999). Moreover metallic carbon nanotubes have higher electrical conductivity than metal. From this property, they may be applied to nanoelctronic device.

2.2.2 Mechanical Strength

CNTs have very large Young modulus in their axial direction and very flexible. So, these substances are suitable for making a hard and flexible composite (Treacy *et al.*, 1996).

2.3 Structures and Properties of Carbon Nanofibers

Carbon nanofibers can possibly be in fishbone or platelet types. For fishbone type, the graphite sheets are stacked with an angle to the fiber axis. But for platelet nanofiber, the graphite sheets are perpendicular to the fiber axis. In nanofibers, the interlayer distance is approximately 0.335 nm, similar to the interlayer distance in graphite. The core of the fibers consists of highly disordered graphene sheets or an amorphous carbon phase.

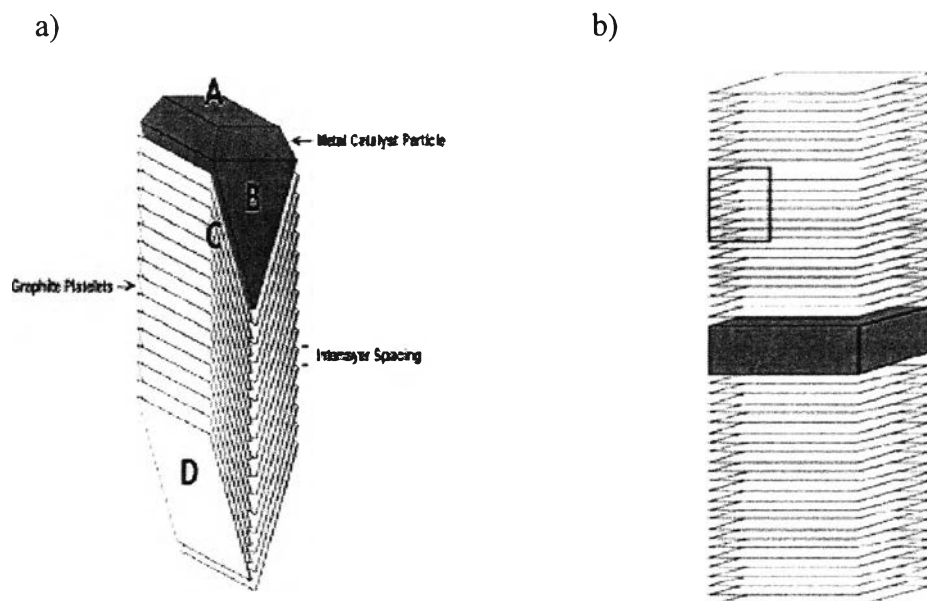


Figure 2.3 Structure of carbon nanofiber a) fishbone nanofiber, and b) platelet nanofiber.

CNF have high aspect ratio, large external surface due to edge sites exposed. It is an ideal candidate for gas adsorption. Moreover its high mechanical strength and less micro pore make them useful for catalyst support.

2.4 Production of Carbon Nanotubes

Nowadays, three methods have been developed for synthesis of CNTs, which are arc discharge of carbon electrodes, laser ablation of graphite and catalytic decomposition of carbon containing compounds.

2.4.1 Electric Arc-Discharge

The carbon arc discharge method initially was used for producing C₆₀ fullerenes. Until in 1991, Iijima observed carbon nanotubes deposited on the cathode site of electric arc apparatus, it has been developed for producing both multi-walled carbon nanotubes and single-walled carbon nanotubes. The carbon arc discharge apparatus is schematically illustrated in Fig. 2.4. Generally, the electrical current (A direct current of 50 to 100 A driven by approximately 20 V) is applying through opposite carbon electrodes, positive and negative, separated by approximately 1 mm in an enclosure that is usually filled with inert gas (helium or argon) at low pressure (between 50 and 700 mbar) (Daenen *et al.*, 2003). Consequently, arc plasma is generated between both electrodes. Carbon on positive electrode (anode electrode) is vaporized and then forms carbon nanotubes that deposit on the negative electrode (cathode electrode). In order to synthesize SWNTs, a transition metal catalyst is needed and can be done by drilling the carbon anode and filling this hole with the metal catalyst inside.

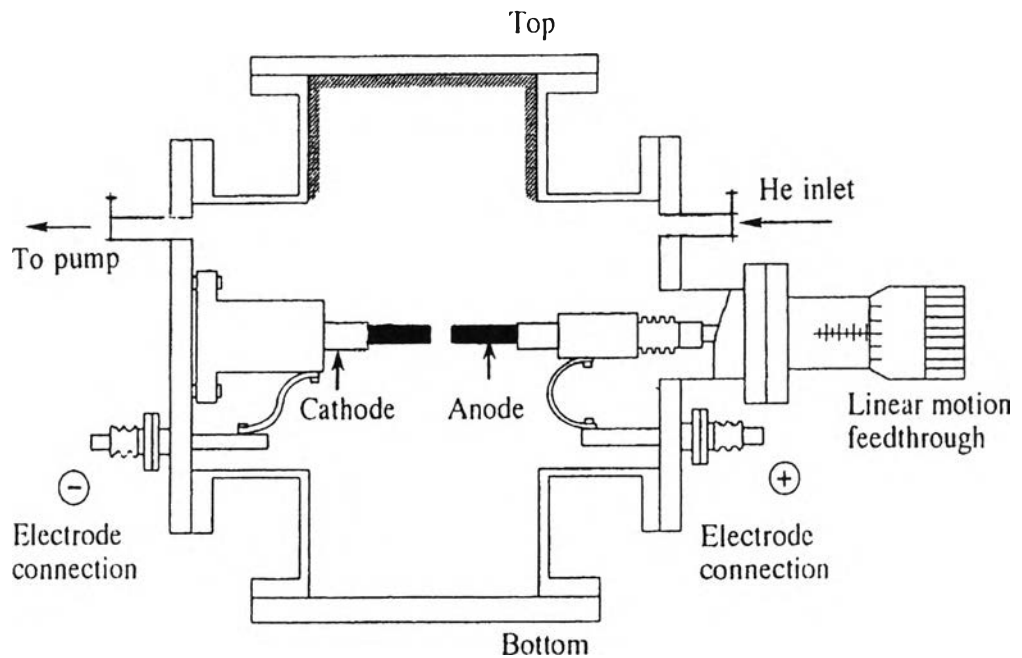


Figure 2.4 Schematic diagram of the arc discharge apparatus employed for fullerene and carbon nanotube production (Harris *et al.*, 1999).

2.4.2 Laser Ablation

The growth of high quality SWNTs at the 1–10 g scale was achieved using a laser ablation method (Thess *et al.*, 1996). As shown in Fig. 2.5, the method utilized intense laser pulses to ablate a carbon target containing 0.5 atomic percent of nickel and cobalt. The target was placed in a tube-furnace and heated to 1200°C. During laser ablation, a flow of helium or argon was passed through the growth chamber to carry the grown nanotubes downstream to be collected on an acceptor.

There are both carbon nanotubes and carbon nanoparticles depositing on the collector. If pure graphite is used as electrode, the products are MWNTs, but if a mixture of graphite with Co, Ni, Fe or Y is employed, uniform SWNTs could be synthesized.

The SWNTs from laser ablation have better properties and narrower size distribution than SWNTs produced by arc-discharge. Moreover laser ablation results in higher yield and higher purity for SWNTs (up to 90% purity) (Maser *et al.*, 1998).

Since the technique produce good quality and quantity of SWNTs, many research groups have been trying to scale up laser ablation. However the results are not yet as good as for the arc-discharge method (Daenen *et al.*, 2003).

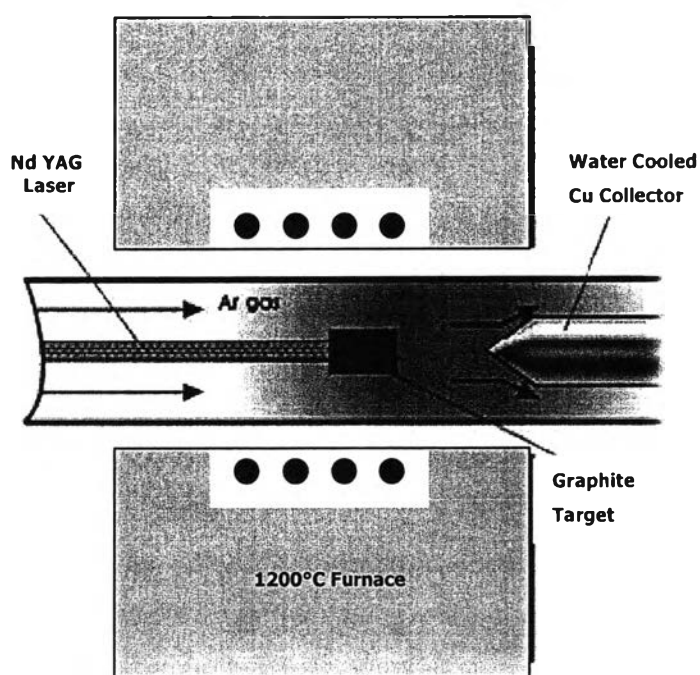


Figure 2.5 Schematic of a laser ablation apparatus (Thess *et al.*, 1996).

2.4.3 Catalytic Decomposition of Carbon-Containing Compounds

Due to limitation to scale up the arc discharge and laser ablation techniques, catalytic decomposition of carbon-containing compound technique has been developed for mass production of SWNTs. As show in Figure 2.6, reaction is performed by first place catalyst in the oven, add carbon source with an energy source such as heat, laser or plasma to break the molecules of carbon source to be reactive carbon atom that adsorb, diffuse into the catalyst, rearrange and grow as SWNTs.

Generally, carbon sources include methane, ethylene, carbon monoxide and alcohols while the catalysts are first row transition metals such as Ni, Fe and Co. The appropriate metal catalysts can preferentially grow single rather than multi-walled carbon nanotubes. First, the catalysts are prepared and then they will be used to grow SWNTs.

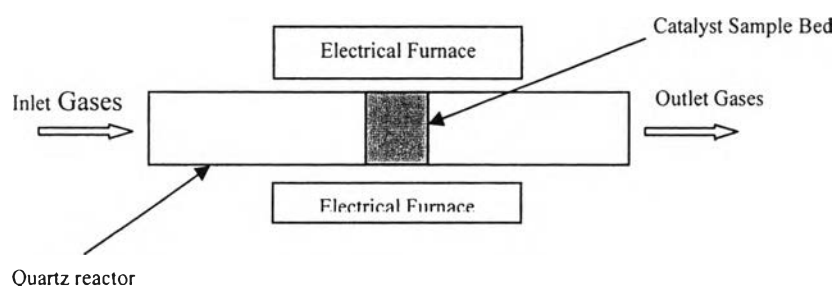


Figure 2.6 Reactor setup for catalytically growing of carbon nanotubes (Kitiyanan *et al.*, 2000).

The most accepted mechanism for carbon fibers formation called diffusion precipitation mechanism was proposed by Baker *et al.* (1989). As show in figure 2.7, the first step is the decomposition of carbon-containing gases on the metal surface at the gas-particle interface followed by dissolution of carbon in the particles, and carbon diffusion through the bulk or on the surface of the metal particles. In the final step, carbon precipitates on the form of CNFs or CNTs at the other side of the particle. This mechanism works well for the formation of CNFs and MWNTs.

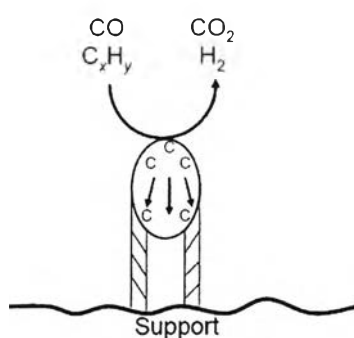


Figure 2.7 A simplified model of the CNF/CNT growth process.

Nagy *et al.* (2004) compared the activation energy for nanotube growth measured by *in situ* electron microscopy and the activation energy for carbon diffusion on Ni, α -Fe, γ -iron, Ni-Fe, Co, V, Mo, Cr, the values are always similar. Re-

sasco *et al.* (2004) concluded that in the SWNTs synthesis once the nucleation is completed, the formation rate is controlled by mass transfer.

The catalyst particle located at both the tip (tip growth) or at the base (base growth) of a CNT depending upon whether bulk diffusion or surface diffusion is dominant (Figure 2.8). Moreover, it depends on the interaction between the catalyst and substrate. If the metal-support interaction is weak, the metals detach and move up called 'tip-growth'. Whereas for the high metal-support interaction, the metal particles remain attached to the support called 'root growth'.

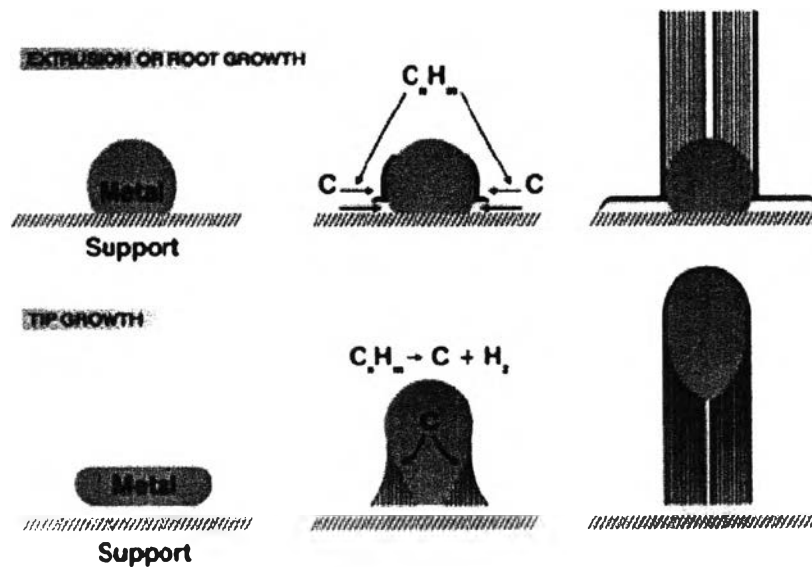


Figure 2.8 Schematic diagram of the root growth and tip growth mechanisms, after Sinnott *et al.*, 1999.

Nagy *et al.* (2004) depicted a cap formation for SWNTs (Figure 2.9): the supersaturation leads to the segregation of the carbon atoms, which move to the surface and combine to form an initial graphene. After reaching a critical size and if the system contains enough kinetic energy, it detaches from the particle surface and forms a fullerene-like cap.

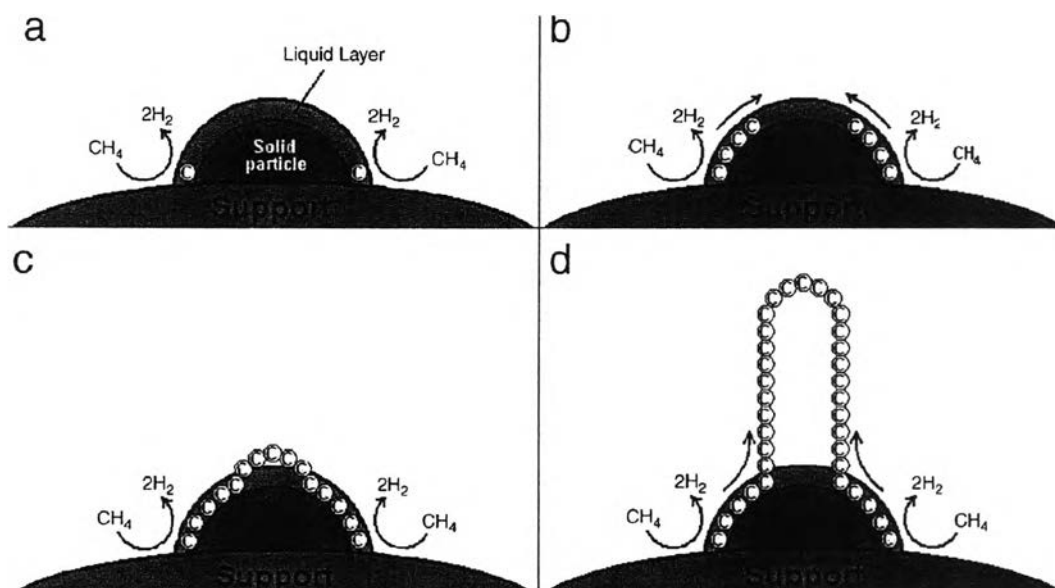


Figure 2.9 Schematic view of the nucleation of a cap and a SWNT. (a) Hydrocarbon decomposition. (b) Carbon diffusion in the surface layer. (c) Supersaturation of the surface and formation of the cap. (d) Growth of a SWNT (Nagy *et al.*, 2004).

The catalyst can be prepared by various methods, for example, impregnation, sol-gel, or reverse micelle, and then physical or chemical pretreatment will be performed. The right annealing time is essential to obtain nanoparticles of right size before growing SWNTs. Moreover, in some systems, gas pretreatment is required to change the catalyst from oxide to metallic state which is the real catalyst (Dupuis, 2005).

Anderson *et al.* (2000) demonstrated that CNFs can be produced when metals are used in a supported form than in a powder form. The support may alter the precipitation faces of the catalyst particle, which influences the structural characteristics of the CNFs. For example, CNFs grown from iron powder from CO/H₂ at 600°C possess a platelet structure, whereas CNFs grown on the silica supported iron produced a tubular structure.

Toebes *et al.* (2002) reported the CNFs production from the decomposition of CH₄, CO/H₂, or C₂H₄/H₂ over supported Ni and powder Ni catalyst at 550°C. They found that the small supported Ni particles need gases with a relatively low activity,

like CH_4 or CO to produce CNFs. The large unsupported Ni only produces CNFs using C_2H_4 .

The role of hydrogen has been described quite extensively in both the VGCF and CNT literature. Hydrogen is known to either accelerate or suppress the formation of CNTs. Jiao *et al.* (1996) found that when no hydrogen was present, only closed forms of carbon deposits such as MWNTs were produced from CO. As the hydrogen partial pressures increased to 0.1 vol%, the filament with open edges was observed. The number of open edges and the angle between the graphite sheets and the axis increased with increasing H_2 concentration.

Nolan *et al.* (1995) found that carbon deposition from CO resulted in encapsulated carbon only when hydrogen was absent. They proposed that hydrogen atoms serve to satisfy valences at the free edges of graphite sheets. Without hydrogen, carbon will deposit in closed forms such as shells and nanotubes. Equations were derived to calculate the minimum number of hydrogen atoms necessary to form a CNF. Nolan *et al.* (1998) further derived thermodynamic expressions for the relationship between filament cone angle and hydrogen partial pressure. Therefore, the orientation of graphite basal planes of carbon filaments can be tailored. The most accepted hypothesis is similar to the diffusion precipitation

2.5 Characterization of Carbon Nanotubes

Many 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, the technique that has been widely used to characterize carbon nanotube such as electron microscopy and temperature programmed analysis will be briefly discussed.

2.5.1 Scanning Electron Microscopy (SEM)

The surfaces morphology of the resulting electrospun SWNTs were observed by a JSM5800 Scanning Electron Microscope (SEM), which was operated

at 20 kV, at the Dentist Department, Chulalongkorn University. Prior to the analysis, samples were coated by a thin layer of gold with 15 mA for 3 minutes.

2.5.2 Transmission Electron Microscopy

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

2.5.3 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) technique has been developed in order to determine the distribution of 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 structure.