CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Introduction of Carbon Nanotubes (CNTs)

Since 1991, carbon nanotubes were first discovered by Sumio Iijima, an electron microscopist from the NEC laboratories in Japan. These 'molecular carbon fibers' consist of graphite that is closed at each end with caps containing precisely six pentagonal rings. Their structures in the form of the two 'archetypal' carbon nanotubes can be formed by cutting a C_{60} molecule in half and placing a grapheme cylinder between the two halves. The structure of carbon nanotubes can be formed and classified in three categories. First, dividing C_{60} parallel to one of the three-fold axes, it results in the zig-zag nanotubes. Second, bisecting C_{60} along one of the five-fold axes produces the armchair nanotubes. The terms of 'zig-zag' and 'armchair' refer to the arrangement of hexagons around the circumference. The third class of structure can be formed by arranging hexagons arranged helically around the tube axis. This structure is generally known as chiral, since it can exist in two mirror-related forms.
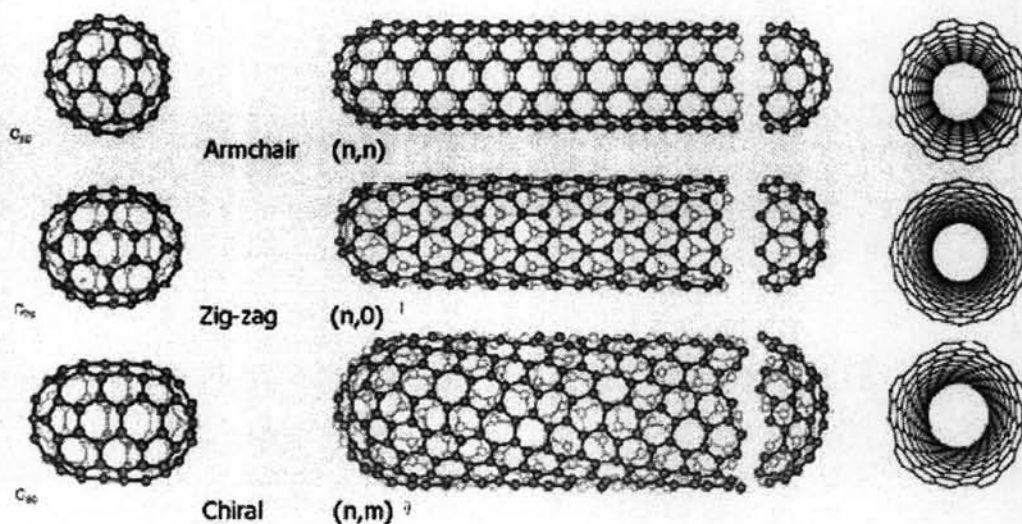

Figure 2.1 Structure of carbon nanotubes

Carbon nanotubes (CNT) can be visualized as a seamless role up of a single or several graphene sheets into cylindrical tubes having both ends closed by half of fullerence. The walls of carbon nanotubes 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 as multi-wall carbon nanotube (MWNT), while, if the wall is only one layer of graphene, it is named single wall carbon nanotube (SWNT). CNT can possess various diameters and lengths. Typically, the diameter of SWNTs is around 1-2 nm and the length can be several micrometer, while the outer diameter of MWNTs can range from 2.5-30 nm and the length is from a few ten of nanometers to several micrometer. The spacing between each layer in MWNT is around 0.344 nm. These structures of carbon nanotubes are shown in Figure 2.2.
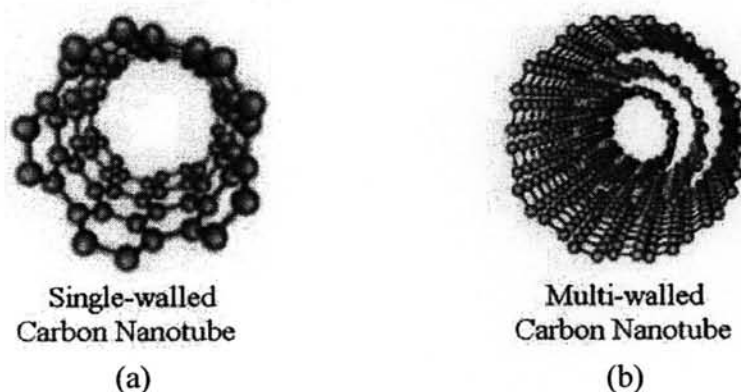

Single-walled
Carbon Nanotube
(a)

Multi-walled
Carbon Nanotube
(b)

Figure 2.2 Structural arrangement of carbon nanotube. (a) SWNTs, (b) MWNTs.

2.2 Single-Walled Carbon Nanotubes (SWNTs)

In 1993, Iijima and Toshinari Ichihashi of NEC, and Donald Bethune and colleagues of the IBM Almaden Research Center in California independently reported the synthesis of SWNTs. This discovery is considered to be an extremely important development, because of fascinating electrical and mechanical properties of SWNTs. In early 1993, several groups reported that foreign materials could be encapsulated inside carbon nanoparticles or nanotubes by carrying out arc-evaporation using modified electrodes. After that, in 1996 Smalley's group described an alternative method for preparing SWNTs. This method is the laser-

vaporization of graphite, obtaining a high yield of SWNTs with unusually uniform diameters.

The catalytically produced SWNTs have a number of interesting features. Kitiyanan *et al.,* (2000) reported that SWNTs were first produced by the catalytic decomposition of carbon-containing molecules. First, the catalytic tubes generally had small metal particles attached to one end. The SWNT diameter was found to be in a relatively wide range (approximately 1-5 nm). Finally, the synthesized SWNTs were generally isolated rather than grouped into bundles as always found with the SWNTs synthesized by arc-evaporation. This technique was claimed to be suitable for scaling up and for achieving a 'controlled production' of the SWNTs.

2.3 Production of SWNTs

Currently, there are three techniques to synthesize SWNTs: arc discharge, laser ablation, and the chemical vapor deposition. Moreover, the properties of SWNTs strongly depend on the synthesis conditions i.e. temperature, pressure, feed gas or carrier gas, ratio and types metallic catalysts; however, numerous techniques have been developed to achieve possibilities of scale up and feasible economics.

2.3.1 Arc Discharge of Carbon Electrode Technique

Arc discharge of carbon electrode technique was firstly performed to produce carbon nanotubes in 1991. Typically, the electrical current is applied through the opposing carbon electrodes (positive and negative electrodes). The result shows that arc plasma generated between electrodes, creates a high temperature. Therefore, the carbon atoms in the anode are vaporized, and then carbon nanotubes are produced and deposited on the negative electrode (cathode electrode). The apparatus of carbon arc discharge is schematically illustrated in Figure 2.3. This technique has been used for the synthesis of single-walled nanotube and multi-walled nanotubes (Iijima *et al.,* 1993) and (Bethune *et al.,* 1993). A use of catalysts can be done by drilling the carbon anode and filling this hole with a metal catalyst inside. Moreover, efficient water cooling of the cathode is essential for producing good quality nanotube. (Physical properties of CNT)
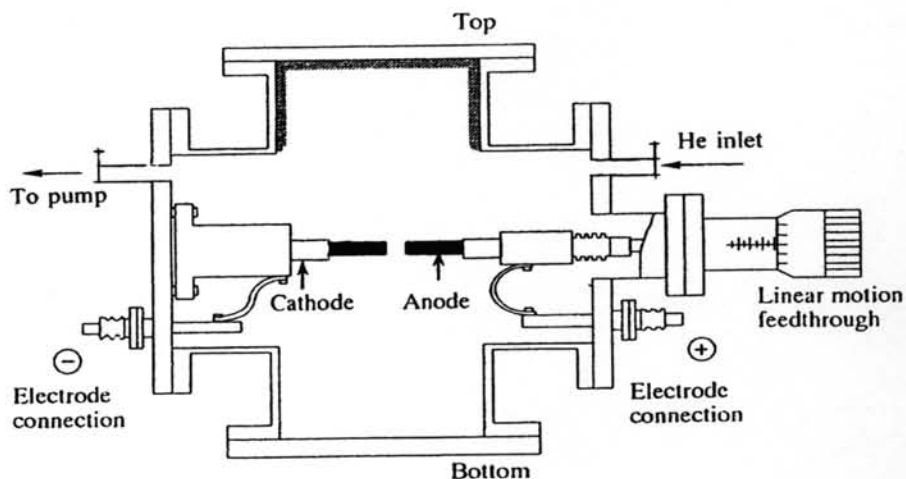
Figure 2.3 Production carbon nanotubes by arc discharge apparatus (Harris, 1999).

2.3.2 Laser Ablation of carbon

In 1995, Smalley's group (Gua *et al.*, 1995) reported the synthesis of carbon nanotubes by using laser vaporization technique. Figure 2.4 shows the laser ablation apparatus. The method utilized intense laser pulses to ablate a carbon target in an oven at 1200°C. During laser ablation, laser was injected to the growth chamber which contained a graphite target compressed with a small amount of a transition metal. Consequently, most carbon atoms were vaporized, coalesced, also swept out of the furnace zone by inert gas, and then deposited as soot on a collecting zone outside the furnace zone. The SWNTs formed in laser vaporized are bundled together with hexagonal crystal by van der Wall force (Scott *et al.*, 2001).

This technique can provide not only the highest yield > 70-90% with unusually uniform diameter but also extraordinary quality but require high energy which limits the large scale production.
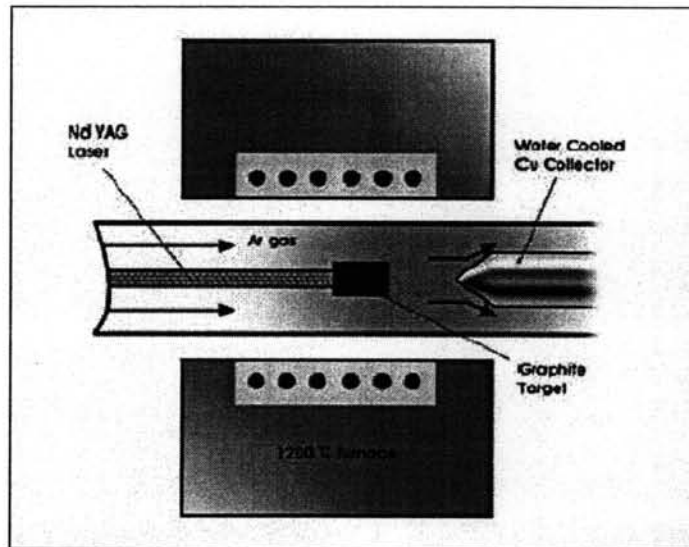
Figure 2.4 Schematic of the Laser ablation apparatus producing carbon nanotubes.

2.3.3 Catalytic Chemical Vapor Deposition Technique

The synthesis of carbon nanotubes using chemical vapor deposition was first reported by Endo Shinshu of University Nagano in Japan. The chemical vapor deposition (CVD) shows advantages over other traditional methods to provide high quality nanotubes material. The catalytic reaction apparatus is schematically depicted in Figure 2.5.
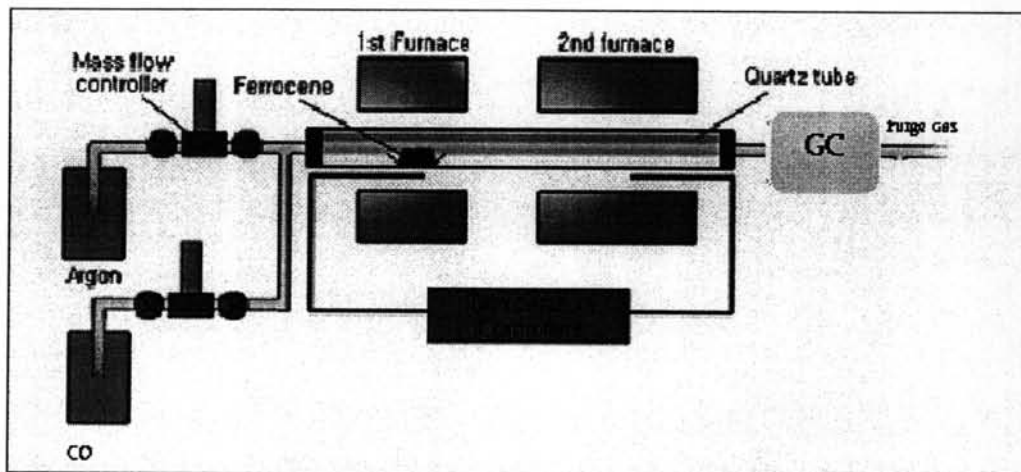

Figure 2.5 Reactor setup for catalytically growing carbon nanotubes (Kitiyanan, 2000).

Typically, a carbon containing-gas (methane, carbon monoxide and acetylene) is passing over transition catalyst which the reactant is catalytically decomposed into reactive atomic carbon, resulting in forming several forms of carbon nanotubes. The carbon nanotubes may be formed in several types, depending on catalyst and reaction conditions. Beside that, catalyst composition, supporting material and carbon source were also reported to affect quality and quantity of carbon nanotubes. Table 2.1 summarized the comparisons of three basic synthesis methods for carbon nanotubes.

Table 2.1 Summary of most common techniques producing carbon nanotubes

Method	Arc discharge method	Chemical vapor deposition	Laser ablation
Process	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWNT	MWNT Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.

Advantage	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Disadvantage	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique requires expensive lasers and high power requirement, but is improving

2.4 Properties and Application of Carbon Nanotubes

Carbon nanotubes have been focused in recent research because of their potential in a variety of applications. Single-walled carbon nanotubes (SWNTs), having fullerene structure with a typical diameter of one nanometer (nm) have received considerable interest because of their exceptionally mechanical, electrical and thermal properties. SWNTs exhibit excellent mechanical properties greater than IM7 carbon fiber, tensile strength as high as 100 GPa~200 GPa and modulus of ~ 1.4 TPa. SWNTs claimed to be the strongest fiber and have about 50 times stronger than steel. Moreover, they possess both lightweight (density~1.33-1.40 g/cm^3) and high elastic modulus. Moreover, a number of researchers believe that SWNTs will be a ultimate reinforcement material for the next generation due to high structural performance with multi-function properties. SWNTs can be a metallic or semiconductor material, depending on their spiral conformation (charity); for instance, armchair nanotubes are metal while zig-zag nanotubes are a semiconductor. According to SWNTs having a very small diameter, they may be used as nanoelectronic devices. Interestingly, SWNTs exhibit 2~3 times higher thermal conductivity than diamond. Nanotubes have unique electrical properties giving

nanotubes a very high electrical conductivity similar to that of copper. Yet the structure of nanotubes is such good conductivity that they can withstand much higher currents than copper. Furthermore, the strength of the carbon bonds in nanotubes makes them had an ability to withstand high temperatures. This unique combination of electrical and thermal properties has the tremendous implications for computing. Besides that, carbon nanotubes are believed to have others practical applications such as field emission, biosensor, energy storage and advanced scanning probes for scanning probe microscope (Cassel *et al.*, 1999).

2.5 Purification of Single-Walled Nanotubes

A large problem with nanotubes application is not only to have high production cost but also to have high impurities derived from the production. Typically, the main impurities of SWNTs are amorphous carbon, metal catalysts and solid support. Therefore, several techniques to purify SWNTs have been intensively studied.

Matarredona *et al.*, (2003) studied a new purification technique of SWNTs which were synthesized by the catalytic decomposition over silica supported Co-Mo. The SWNTs quality obtained from this synthesis method was found to depend on the Co-Mo ratio and the catalyst treatment conditions. The SWNTs produced still contained the spent catalyst (Co and Mo species) and silica support as unwanted material. In this study, the chemical treatments using concentrated NaOH and HF were investigated. Subsequently, anionic surfactant sodium dodecybenzenesulfonate the surfactant itself was not capable for suspending the carbon nanotubes effectively without the aid of vigorous sonication. The acid treatment could not open the graphictic shell without attacking their nanotubes, causing the structure change of the purified SWNTs.

Chiang *et al.* (2001) investigated the stability and characteristic of SWNTs obtained from the gas phase decomposition of CO (HiPCO) over the Fe metal catalyst. The SWTNs was first treated by air oxidation in order to convert the metallic catalyst to the metal oxide form (densities for Fe and Fe_2O_3 are 7.86 and 5.18 g/cm^3). The SWNT samples were further purified with concentrated HCl solution with sonication overnight to dissolve the ferric oxide. Then, SWNTs were

washed several times with water and methanol. After drying in a vacuum oven at approximately 100°C for 1 h, the dried SWNTs sample was annealed at 800°C. The studied treatment method could reduce the catalyst to 0.2% as compared to the original content of 3.5%. However, a significant amount of carbon loss was also reported.

Younghyun and Devid et al. (2005) developed a magnetic filtration technique to remove the metal catalyst from SWNTs, which were produced by the pulsed laser vaporization method. SWNTs were thoroughly oxidized in air, and then treated with a concentrated HCl or NaOH solution. Subsequently, the SWNT samples were dispersed in N,N-dimethyformamide (DMF) at different concentrations in the range of 0.1-0.2 mg/mL in a sonication bath. Finally, the dispersed solution was filtered using the magnetic filtration. According to the use of both chemical and magnetic purification steps, the metal catalyst content was reduced to 0.3 wt.%, but the carbon yield was decreased to 50% of the initial value. The magnetic filtration was concluded to be very effective in the removal metal catalyst..

Hu et al. (2005) studied the effect of zeta potential on the dispersability which employed chemical oxidation including with physical and mechanical separations. Initially, as-SWNTs were refluxed with the concentrated HNO_3, and resultant mixture were centrifuged and decanted. Then, water was added into the purified SWNTs in order to re-suspend them by varying solution pH. Consequently, from this phenomenon provide the net charge on the surface and carbonaceous impurities (CIMP), leading to formation of double layer which prevents the particles form aggregates. The products can be divided in two sections: .supernatant part composed of carbonaceous impurities whereas sediment part consisted of SWNTs. Therefore, at pH = 2 obtains high stabilities of aqueous dispersion of SWNTs around, 83% relative purities as well as 38% yields. Disadvantage is time consumption in purification, and also defects on side wall of SWNTs.

Igarashi et al. (2004) studied the effects of strong acid treatment (HF) and gas oxidation to purify SWNTs. The SWNTs were prepared via catalytic chemical vapor deposition (CCVD) using ethanol as carbon source over the Co/Mo on zeolite catalyst. The results showed that the catalyst removals were 70% and 94% for the HF treatment and the combined oxidation and HF treatment, respectively. It is

considerable that use of oxidation and HF treatment was insufficient to completely eliminate impurities of SWNTs. In this view point, they have modified method 2 by adding oxidation step after HF treatment again in order to reduce the amorphous carbon which protected chemical solution permeation through the metal oxide. Finally, the purities of SWNTs were increased up to 95-97% without any defect on SWNTs exhibited on Raman spectra; however various investigators make an attempt to reduce the use of this chemical because of their toxicity, cruel acid and harmful human being.

Chattopadhyay et al. (2002) conducted a study on removal of the entrapped such as HNO_3, H_2SO_4, HF and HCl. They found the best ratio of 1:1 of HF/HNO_3 for the maximum catalyst removal. Sodium dodecyl lauryl sulfate (SDS) surfactant was found to be effective to disperse the treated SWNTs. In addition, Raman spectroscopy indicated that the structure of the purified SWNTs was not changed by the use of HF/ HNO_3.

Bandow et al. (1997) employed microfiltration to purify SWNTs produced by laser ablation. This technique was found to separate the as-prepared SWNTs into three fractions (CNS, CS_2 soluble, and SWNTs). First of all, polyaromatic carbon and fullerene were extracted by soaking the as-prepared SWNTs. Then, the CS_2 insoluble fraction, CNS, metal nanoparticles and SWNTs, was re-suspended in aqueous solution using a cationic surfactant (benzalkonium chloride). Subsequently, SWNTs were trapped on membrane filter without serving of acid, heat or oxidative treatment. Finally, the purity of the SWNTs increased 90 wt.% The advantage of this method is that most SWNTs in the as-prepared samples were retained and captured in the final product.

Harutyunyan et al. (2002) used microwave to purify SWNTs which were synthesized by using arc-discharge. SWNTs were first treated at 500°C for 20 min, leading to both the oxidation and rupture of the carbon passivation layer over the catalyst particle. Subsequently, the samples were treated by using acids. Either concentrated HNO_3 or HCl was used to dissolve most of the catalyst in the sample. The combined microwave and mild acid treatment were possible to remove residual metal lower than 0.2 %wt as well as the recovery yield for this step was 35%. The microwave method was effective without large loss of SWNTs. Nevertheless this

process utilizes highly energy consumption as compared to the other processes, and is not applicable to scale up with a relatively low production cost.

As mentioned above, all purification methods described in the literature provide high treatment cost and may damage the SWNTs structure. Therefore, in this study, froth flotation was investigated as an alternative way for the purification of SWNTs.

2.6 Surfactant

A surfactant, which is a contraction of the term of Surface Active Agent, is characterized by possessing in the same molecule to have two distinct groups which differ greatly in their solubility relationships (Winsor., 1948). Surfactants are an organic compound that composes of one lyophilic (solvent-loving) which is usually an ionic or highly polar group and one lyophobic (solvent-fearing) which is generally a long-chain hydrocarbon or non polar group. However, these two parts can be namely hydrophilic and hydrophobic, respectively, as schematically depicted in Figure 2.6. Surfactants are among the most versatile products of the chemical industry for example pharmaceuticals, detergents, drilling muds used in prospecting for petroleum and the flotation agents.
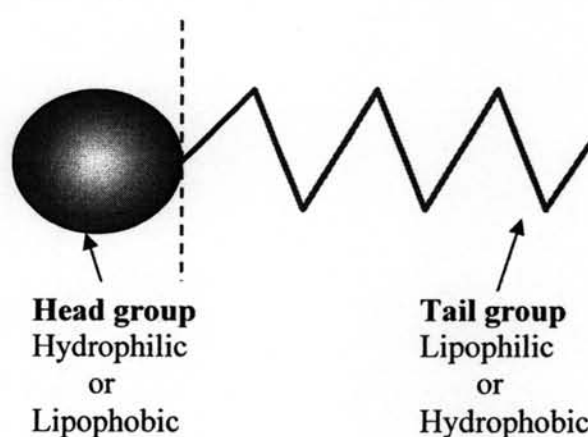

Head group
Hydrophilic
or
Lipophobic

Tail group
Lipophilic
or
Hydrophobic

Figure 2.6 Schematic of surfactant molecule monomer (Rosen, 1989).

One of the unique properties of surfactant is to spontaneously orient between the surface and interface of the system, resulting in decreasing the surface or interfacial tension of the medium in which it is dissolved. Therefore, the hydrophilic portion of the molecules extends into an aqueous phase whereas the hydrophobic tails extend into the gaseous phase or oil phase. This process is named as "adsorption" that can significantly alter the physical properties of the solution.

In addition, surfactants can be classified in four categories depending on the nature of the hydrophilic group [Rosen, 1989]

a) Anionic surfactants can adsorb onto positively hydrophilic surface, because the surface-active portion of anionic surfactant has a negative charge.

b) Cationic surfactants can adsorb onto negatively hydrophilic surface because the surface-active portion of cationic surfactant has a positive charge.

c) Zwitterionic surfactants, since they carry both positive and negative charges that might adsorb into both negatively and positively charged surfaces without changing the charge of the surface.

d) Nonionic surfactants can adsorb onto the surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface depending upon the nature of surface.

Another substantial phenomenon of minimizing the contact between the lyophobic group of the surfactant and water molecules is to form micelles; a lowest concentration to form a few aggregate, known as micelle is called the critical micelle concentration (CMC). This process is called "micellization" as presented in Figure 2.7.
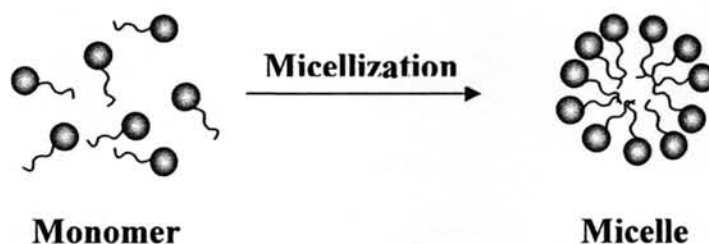

Monomer   Micelle

Figure 2.7 The formation of micelle at critical micelle concentration.

In general, there are two natures of the micelles consisting of normal micelles and inverse micelle. In water or aqueous solutions, normal micelles form with hydrophobic and hydrophilic groups exposing to the interior and the external aqueous solvent, respectively. The configuration might be spherical, rod-like, dis-like or lamella, depended on the structure and concentration of surfactant. The interior of the micelle acts as a tiny oil like-environment. The size of micelles is generally not larger than a few nm in diameter. On the other hand, inverse micelles are formed in a non-polar solvent with the hydrophilic part in the interior and hydrophobic part in the external, as illustrated in Figure 2.8.
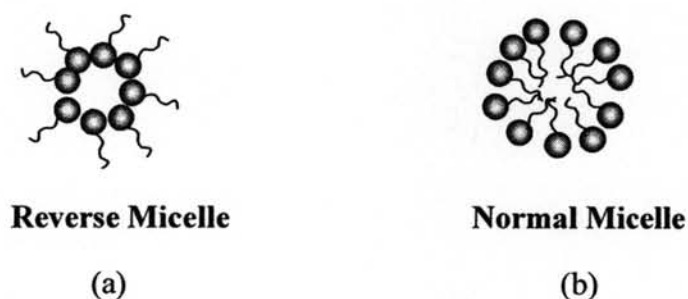

Reverse Micelle   **Normal Micelle**

(a)   (b)

Figure 2.8 Schematic the structure of surfactant aggregated forming normal or reverse micelle.

Surfactants play an important role in several separation processes such as flotation. Flotation is one of interesting processes since it can provide several advantages especially, low treatment cost. The role of surfactant in froth flotation is to promote the foam formation and to stabilize foam generated. In addition, because of their amphipathic mature, they tend to adsorb at interfaces. Thus, they can themselves act as collectors in flotation. (Sebba *et al.*, 1989)

2.7 Separation of Single-Walled Carbon Nanotubes (SWNTs)

Several techniques for the purification of SWNTs are summarized as follows:

a) Micro filtration: This technique is based on the difference in the size of the solid particles separation and the pore size of a filter. Any solid particles having SWNTs smaller diameters than the filter size can pass through the filter. However, this technique not only requires high energy consumption for the separation the SWNTs because of high pressure drop, but also has a significant loss of SWNTs.

b) Cutting: SWNTs are chemically wound by partially functionalizing the tubes; for example with fluor. Then, the fluorated carbon will be driven off the sidewall with pyrolisation in the form of CF_4 or COF_2. This method will leave behind the chemically cut nanotubes. Mechanical cutting of the nanotubes can be accomplished by ball-milling. Consequently, the bonds will break due to the high friction between the nanoparticles and the nanotubes will be disordered.

c) Chromatography: This technique allows smaller molecules to take a longer time through the end of the column while large molecule will come out first. However, this technique is mainly used to separate small quantities of SWNT. In addition, in this technique, the SWNTs have to be either dispersed or solvated in which consumes time.

d) Centrifugal: This method consumes a lot of energy for the separation the SWNTs, also requires a much longer time to obtain high qualities of SWNTs.

2.8 The Froth Flotation Technique

Froth flotation is a physicochemical (Kroschwitz *et al.,* 1992) using surfactants to generate foams which can carry selectively and desired material from water. Froth flotation has been first used in minerals processing industry since the mid-1800's. Many of its broad-based applications to mineral recovery was extensively developed in the period of 1900 to 1925. Today, at least 100 different minerals are processed using froth flotation. Another major usage of froth flotation is the coal industry for desulferization and the recovery of fine coal, once discarded as waste. Since the 1950's, flotation has been applied in many non-mineral industries including sewage treatment; water purification; paper de-inking; and chemical, plastics, and food processing (Kroschwitz and Howe-Grant, 1992). Particularly, the advantages of froth flotation-based separation process are

biodegradable and environmental innocuousness, low energy requirement as well as re-useable surfactant.

The flotation process utilizes the differences in the surface properties of the particulates, normally with the addition of the reagents to achieve the separation (Wasan., 1991). Surfactant plays a critical role in flotation process due to the interactions with the solid particles. Flotation involves the removal of particulate by frothing, whereas foam fractionation involves the separation of soluble species by foams (Scamehorn and Harwell, 1989).

In froth flotation, separation of a binary solids mixture may be accomplished by surfactant adsorbed at the solid-liquid interface between a dispersed phase (bubbles) and a continuous phase. The accumulation of surfactants at the air/water interface results in lowering of the excess Gibbs free energy of the interface. Hence, removed materials adhere to the rising bubbles while air is introduced into the slurry. The difference in the density between the air bubbles and water provides buoyancy that preferentially raises the hydrophobic solid particles to the top of the column. The skimmed foam contains the removed solid particles with a high concentration (after the foam is broken). The basic schematic of a froth flotation column is depicted in Figure 2.9. There are two distinct zones in the froth flotation column that consists of a bubbly zone and a froth zone. A surfactant is used to not only facilitate adhesion of target materials to the bubble surface but also act as a froth prompter/stabilizer (Feng and Aldrich, 2000).

The froth flotation process is based on the wettability differences of particles to be separated. Differences of wettability among solid particles can be natural, or can be induced by the use of chemical adsorbates. Froth flotation is often used to separate solids of similar densities and sizes, which prevent other types of separations based upon gravity that might be employed. It may be difficult to take advantage of surface-property differences to induce selective hydrophobicity for the small particle sizes. On the other hand, particles greater than 65 mesh tend to be readily sheared from the bubble surfaces by collision with other particles or vessel walls. However, relatively low-density materials, such as coal, may be successfully separated up to 10 mesh in some systems (Kroschwitz and Howe-Grant, 1992).
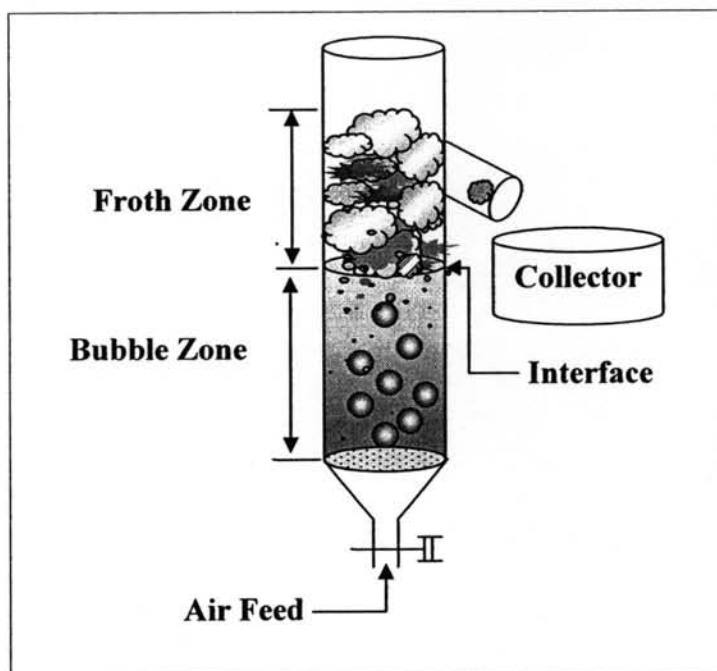
Figure 2.9 Schematic of the froth flotation process.

Froth flotation involves three phases of solid, liquid, and gas and the corresponding potential phase interfaces: solid-liquid, solid-gas, and solid-liquid-gas. The hydrophobic (aerophilic) or hydrophilic nature of the solids at the solid-liquid-gas interfacial region is determined by the wettability of the solid. An interfacial phenomenon of flotation is a surface chemical-based process, where numerous phenomena that simultaneously occur at the solid-liquid-air interfacial region. In this context, the variable known as contact angle (θ) illustrated in Figure 2.10, is an important correlative parameter. At $\theta = 0^\circ$, the liquid spreads on the solid; in aqueous media in contact with air such a solid is said to be hydrophilic substance and is wetted by water. Air bubbles do not adhere to hydrophilic solids in water. Conversely, hydrophobic solids are not wetted by water; air bubbles do adhere to them and the value of the contact angle is larger than zero degrees, i.e., $\theta > 0^\circ$ (Kroschwitz and Howe-Grant, 1992).

The three interfacial tensions at equilibrium (Figure 2.10) conform to Young's equation (eq.2.1): where γ represents solid-gas, solid-liquid, and liquid-gas interfacial tension as indicated by subscripts.

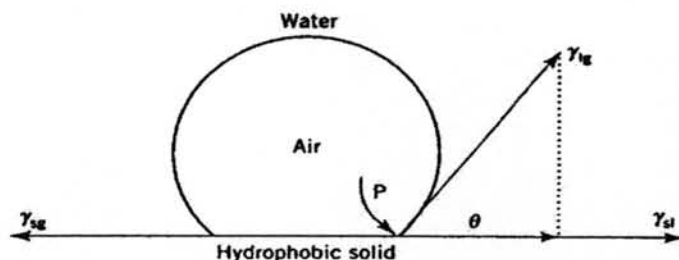$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos \theta \qquad (2.1)$$

Figure 2.10 The concept of contact angle with a captive bubble in an aqueous. medium, adhering to a hydrophobic solid: P is the three-phase contact point. Here, the vector γ_{lg} passes through P and forms a tangent to the curved surface of the air bubble. The contact angle θ is drawn into the liquid.

Strictly speaking, Equation 2.1 represents a special case that does not take into consideration the effects of gravity or external forces such as electric and magnetic field. It also needs to be modified for rough (nonflat) and heterogeneous (impure) surfaces as well as corner and edge effects. However, it has a thermodynamic that occurs between the three phases when they are in contact. Soldering, welding, joining, and detergency (qv), are but a few examples of systems besides flotation where wetting and spreading phenomena play significant roles.

Thus, in order to obtain a successful separation using froth flotation, it is usually necessary to selectively enhance the hydrophobicity of one of the solid components that is hydrophilic or not strongly hydrophobic. This selective modification of the wettability of solids in froth flotation is obtained using additional reagents termed collectors.