# CHAPTER II

LITERATURE REVIEW

2.1 Introduction to Carbon Nanotubes

Two crystalline structures of carbon that have been certainly known and found in nature are diamond and graphite. However, fullerenes and carbon nanotubes have emerged as new forms of carbon materials. Fullerenes are large, closed-cage, and have spherical structure formed from hexagonal and pentagonal carbon rings. Regularly, fullerene contains sixty or seventy carbon atoms in its molecule. Carbon nanotubes can be viewed as seamless graphene cylinders (graphene is an individual graphite layer) closed at each end with half of fullerene as shown in Figure 2.1

(a)   (b)
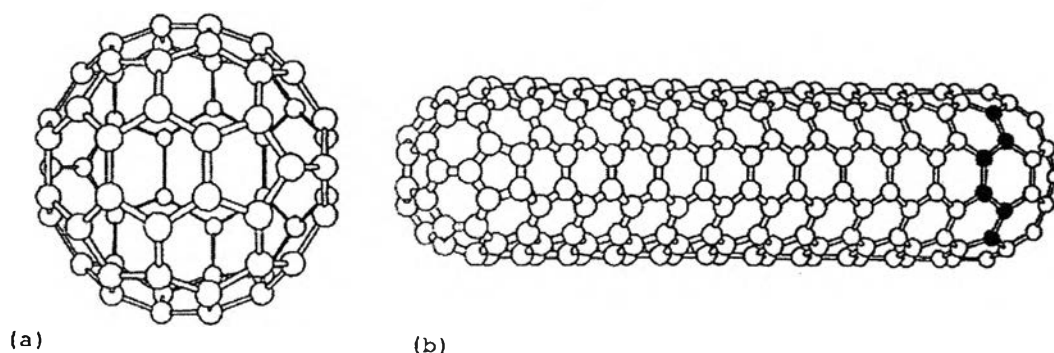
Figure 2.1 Carbon nanostructures (a) a fullerene (b) a carbon nanotube (Tang *et al.*, 2001).

Based on their structure, the carbon nanotubes can be generally categorized into two types, multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs). MWNTs were first discovered in 1991 in cathode deposit from carbon arc discharge experiment (Iijima, 1991). The electron microscope revealed that these carbon nanotubes consist of at least two concentric cylinders of graphitic layer with the spacing between the nanotubes walls close to the spacing in between the graphitic layers in graphite. Subsequently, in 1993, two research groups independently reported the synthesis of SWNTs in carbon arc discharge experiments that used metals as catalysts (Ijima *et al.*, 1993, and Bethune *et al.*, 1993). SWNTs can be considered as individual tubes made of single cylinders of graphic layer.

Since their discovery, carbon nanotubes have been investigated by many researchers all over the world. Typically, the outer diameter of MWNTs is ranging from 2.5 nm to 30 nm and the length is ranging from a few tens of nanometers to several microns, while the diameter of individual SWNTs is about 1 to 2 nm and the length can be up to several microns. The SWNTs are curled and looped rather than straight, and can be alone or in groups as bundles or ropes. The long in length but small in diameter of carbon nanotubes lead to a high aspect ratio (length to diameter), therefore they can be considered as nearly one-dimensional structures. Due to its nanosize and high aspect ratio, these materials are expected to possess additional interesting electronic, mechanic and molecular properties in the area of nanoscience and nanotechnology.

2.2 Structures of Carbon Nanotubes

The bonding in carbon nanotubes is sp^2, with each atom joined to three neighbors, as in graphite. The tubes can therefore be considered as rolled-up graphene sheets. In ideal case, a carbon nanotube consists of either one cylindrical graphene sheet (SWNT) or of several nested cylinders with an interlayer spacing of 0.34–0.36 nm that is close to the typical spacing of turbostratic graphite (MWNT). In general, the whole family of nanotubes is classified as zigzag, armchair, and chiral tubes of different diameters, as shown in Figure 2.2. The first two of these, armchair and zig-zag, have a high degree of symmetry. The terms "armchair" and "zig-zag" refer to the arrangement of hexagons around the circumference. The third class of tube, which in practice is the most common, is known as "chiral", meaning that it can exist in two mirror-related forms, so the equivalent atoms of each unit cell are aligned on a spiral.

The structure of a nanotube can be specified by a vector, (n,m), which defines how the graphene sheet is rolled up. This can be understood with reference to the Figure 2.3. To produce a nanotube, one can move n times in a_1 direction and m times in a_2 direction from the atom labelled (0,0) to get to the point (n,m) and roll-up the sheet so that the two points coincide. It can be seen from the Figure 2.3 that n = m for all armchair tubes, while m = 0 for all zig-zag tubes.
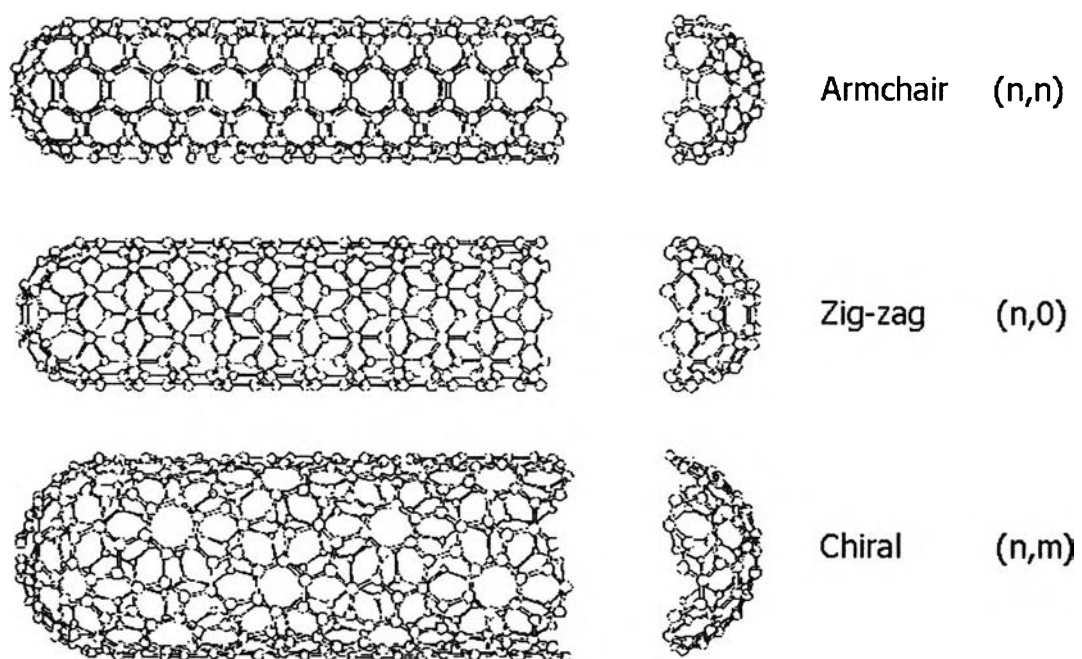
Figure 2.2 Models of different single-walled carbon nanotubes (Saito *et al.*, 1992).
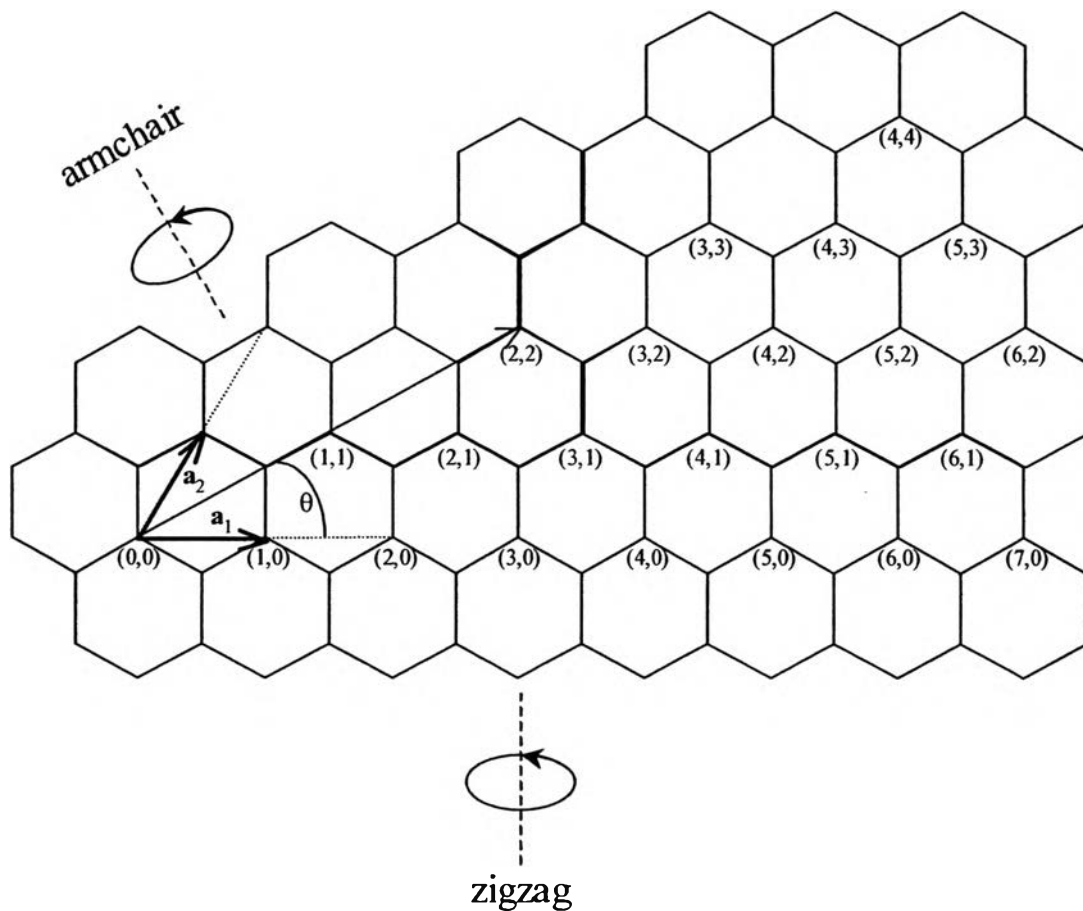
Figure 2.3 Unit vector a_1 and a_2 of the two dimensional lattice graphene sheet.

2.3 Properties and Applications of Carbon Nanotubes

Intense research over the past few years has revealed that this carbon nanotubes simultaneously possesses superb properties for many applications. With diameters in a few nanometers, carbon nanotubes have shown their exceptional properties in a broad range of electronic, molecular, and structural properties because of their size where quantum effects become important. These remarkable properties have been theoretically predicted, and gradually some of these predicted properties have been experimentally confirmed as these materials become available; especially the single-wall type. However, certain properties still cannot be tested due to limitation of technology that can manipulate nanoscale objects.

In electronic properties, several research groups around the world showed theoretically in late 1991 that carbon nanotubes can be either metallic or semi-

conducting type depending on their structure and diameter. The differences in conducting properties are caused by the molecular structure, which can be related to the chiral vector of a nanotube, and that results in a different band structure and thus a different band gap. The differences in conductivity can easily be derived from the graphene sheet properties. Based on theoretical calculations, SWNTs is anticipated to be metallic if the value of n = m or the value n - m can be divided by three. If not, the nanotube is predicted to be semi-conducting. Thus, it is expected that one-third of nanotubes would be metallic, while two-thirds would be semi-conducting. The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length. In theory, metallic nanotubes can contain an electrical current density more than 1,000 times of the metals such as silver and copper (Collins *et al.*, 2000).

In mechanical properties, carbon nanotubes can be a very strong material because they have a very high Young modulus in their axial direction (Treacy *et al.*,1996), which can be greater than 1 TPa, and a maximum tensile strength close to 63 GPa (Yu *et al.*, 2000), about 50 times higher than steel.. The carbon nanotubes as a whole is very flexible because of the great length. Moreover, they have shown a combination of lightweight (density = $1.3 - 1.4$ g/cm^3 (Collins *et al.*, 2000) with high elastic modulus. Therefore, these compounds can be used as reinforcers in composite materials that need anisotropic properties.

In chemical reactivity (Niyogi *et al.*, 2002), the carbon nanotubes reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of carbon nanotubes in different solvents can be controlled.

From the outstanding physical and chemical properties with unique characteristics that have been demonstrated, carbon nanotubes are potentially useful for several applications (Ajayan *et al.*, 2001) as following: micro-electronics/semiconductors, conducting composites, controlled drug delivery/release, artificial muscles, biosensor, supercapacitors, batteries, field emission flat panel

displays, field effect transistors and single electron transistors, probes for scanning probe microscope, nano lithography, nano electronics, doping, nano balance, nano tweezers, data storage, magnetic nanotube, nanogear, nanotube actuator, molecular quantum wires, hydrogen storage, noble radioactive gas storage, solar storage, waste recycling, electromagnetic shielding, dialysis filters, thermal protection, nanotube reinforced composites, reinforcement of armour and other materials, reinforcement of polymer, avionics, collision-protection materials, and fly wheels.

2.4 Production of Carbon Nanotubes

Several techniques have been developed to produce nanotubes, but currently there are three major ways to produce the carbon nanotubes in sizeable quantities, including arc discharge, laser ablation, and chemical vapor deposition (CVD). Most of these processes take place in vacuum or with process gases. In arc discharge, a vapour is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapour. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon–containing feedstock gas (methane or carbon monoxide). CVD growth of carbon nanotubes is able to take place in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by CVD methods; advances in catalysis and continuous growth processes are making carbon nanotubes more commercially viable.

In order to yield SWNT, it is necessary to have transition metals present in the system of carbon arc discharge and laser vaporization technique. However, depending upon the catalysts and reaction condition, transition metals can possibly generate multi-wall or single-wall carbon nanotubes in gas phase catalytic method. This section will briefly introduce the growth mechanisms and the production of carbon nanotubes (both multi-wall and single-wall type) from the arc discharge, the laser vaporization techniques as well as the chemical vapor deposition of carbon containing gas.

2.4.1 Growth Mechanisms

There are several theories on the exact growth mechanism for carbon nanotubes. However, the growth mechanism is still a subject of controversy. One theory (Sinnot *et al.*, 1999) postulates that metal catalyst particles are floating or are supported on graphite or another substrate. It presumes that the catalyst particles are spherical or pear-shaped, in which the deposition will take place on only one half of the surface or on lower curvature side for the pear shaped particles. The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter. However, it does not precipitate from the apex of the hemisphere, which accounts for the hollow core that is characteristic of these filaments. For supported metals, filaments can form either by extrusion which is also known as base growth in which the nanotube grows upwards from the metal particles that remain attached to the substrate, or the particles detach and move at the head of the growing nanotube which is known as tip-growth, as demonstrated in Figure 2.4. Depending on the size of the catalyst particles, SWNTs or MWNTs are grown. In arc discharge, if no catalyst is present in the graphite, MWNTs will be grown on the C_2-particles that are formed in the plasma.
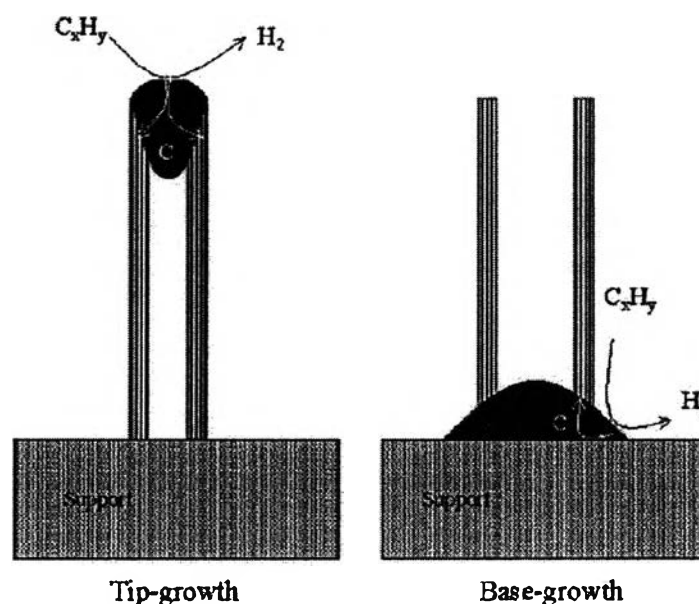

Figure 2.4 Visualisation of a possible carbon nanotubes growth mechanism (Dupuis, 2005).

2.4.2 Arc Discharge

Carbon nanotubes were initially discovered using this technique, it has been the most widely used method for nanotube synthesis of both MWNTs and SWNTs with few structural defects. It is worth noting that this technique has been in use for a long time for the production of carbon fibers and that it is very probable that nanotubes were observed before 1991 but not recognized.

MWNTs can be produced in a carbon arc apparatus similar to the one depicted in Figure 2.5 using the method described by Ebbesen and Ajayan (1992). An arc discharge can be operated by connect two graphite rods to a power supply, place them millimeters apart, and throw switch. At 100 amps, carbon vaporizes in a hot plasma because of the high temperatures caused by the discharge.. MWNTs by arc discharge are long and straight tubes closed at both ends with graphitic walls running parallel to the tube axis. Iijima *et al.* and Bethune *et al.* reported in 1993 that an arc discharge with a cathode containing metal catalysts (such as cobalt, iron or nickel) mixed to graphite powder results in a deposit containing SWNTs. SWNTs are usually assembled in ropes but some single tubes can also be found in the deposits. The yield for this method is up to 30 percent by weight, however they tend to be short (50 microns) with random sizes and directions.
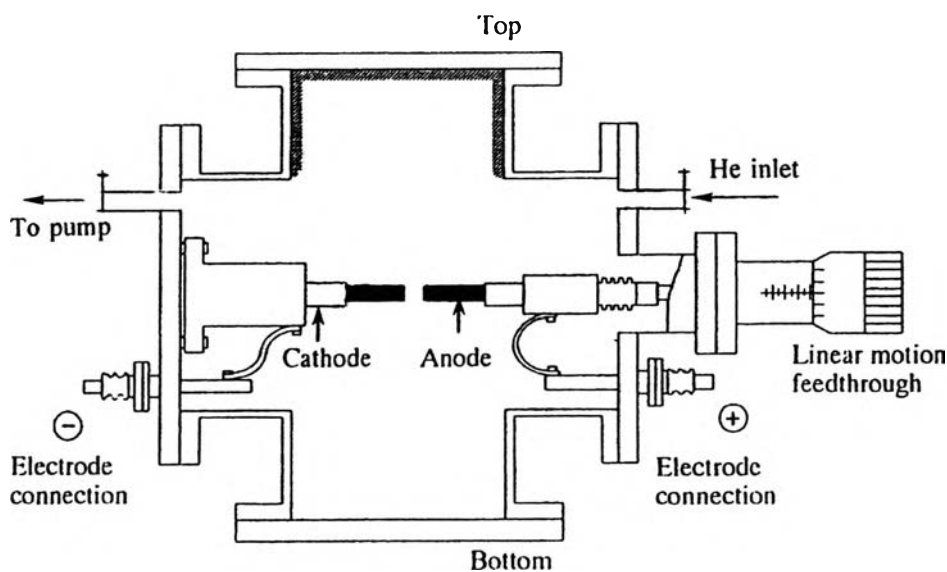
Figure 2.5 A carbon arc discharge apparatus (Harris, 1999).

2.4.3 Laser Ablation

Another method to grow SWNTs using laser ablation was demonstrated in 1996 by Smalley's group and has prompted a lot of interest. Thess *et al.* (1996) showed that the synthesis could be carried out in a horizontal flow tube under a flow of inert gas at controlled pressure. In this set-up, as shown in Figure 2.6, the flow tube is heated to ~1200°C by a tube furnace. Laser pulses enter the tube and strike a target consisting of a graphite target to create multi-walled carbon nanotubes (Guo *et al.*, *1995a*) or a mixture of graphite and a metal catalyst such as Co or Ni to produce SWNTs (Guo *et al.*, 1995b). The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses from the laser vaporization plume and are deposited on a collector outside the furnace zone.

This method has a yield of around 70% and produces primarily SWNTs with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition because it requires expensive lasers (Collins *et al.*, 2000).
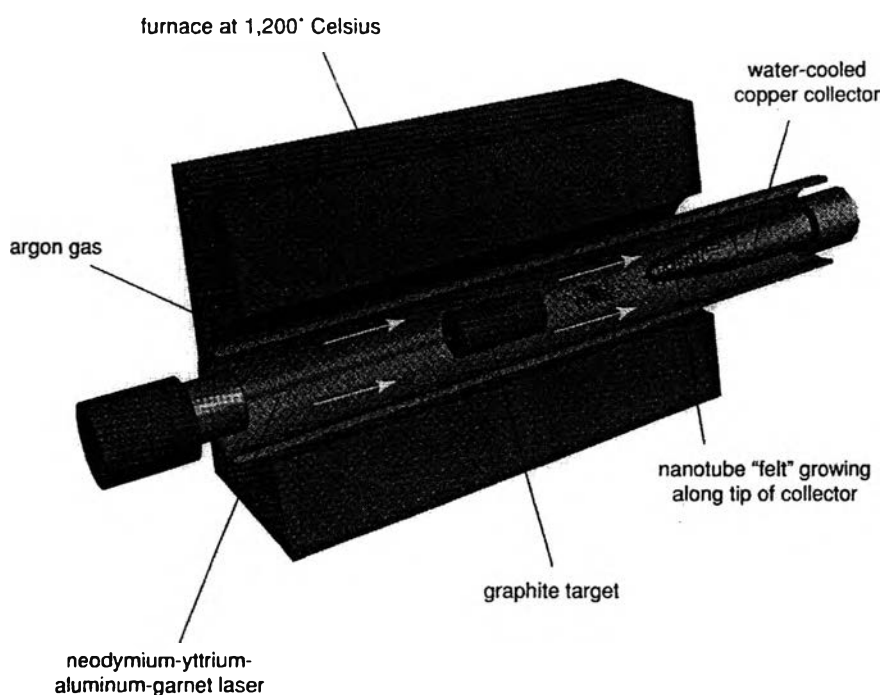
Figure 2.6 Laser vaporization apparatus (Yakobson *et al.*, 1997).

2.4.4 <u>Chemical Vapor Deposition (CVD)</u>

The catalytic vapor phase deposition of carbon was first reported by Walker Jr. *et al.* in 1959. Usually, a catalyst is necessary to promote the growth. A similar approach was used for the first time in 1993 by Yacaman *et al.* to grow MWNTs from the decomposition of acetylene over iron particles.

Generally, chemical vapor deposition (CVD) for carbon nanotubes 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. The energy source is used to crack the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a layer of metal catalyst particles, usually a first row transition metal such as Ni, Fe, Co, or a combination. Carbon nanotubes will be formed at the sited of the metal catalyst if the proper parameters are maintained. The growth mechanism of carbon nanotubes is depending on the size of catalytic metal particle and adhesion between the catalyst particle and the substrate. The CVD process can be easily set-up as shown in Figure 2.7.

Commonly used gaseous carbon sources for carbon nanotubes synthesis include acetylene, methane (Colomer *et al.*, 2000), carbon monoxide (Nikolaev *et al.*, 1999; Kitiyanan *et al.*, 2000), alcohols (Maruyama *et al.*, 2002) and other hydrocarbon gases (Cheng *et al.*, 1998). The catalyst that contains metal nanoparticles can also be produced by other ways, including reduction of oxides or oxides solid solutions. The diameters of the nanotubes that are to be grown are related to the size of the metal particles. This can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer. The temperatures for the synthesis of nanotubes by CVD are generally within the 650–950°C range (Yudasaka *et al.*, 1995; Yudasaka *et al.*, 1997; Alvarez *et al.*, 2002) where the growth of SWNTs requires higher temperature than that of MWNTs due to the fact that they have a higher energy of formation. Typical yields for CVD are approximately 30%.

Of the various means for nanotube synthesis, CVD shows the most promise for industrial scale deposition in terms of its price/unit ratio (Resasco *et al.*, 2002).

There are additional advantages to the CVD synthesis of nanotubes. Unlike the above methods, CVD is capable of growing nanotubes directly on a desired substrate, whereas the nanotubes must be collected in the other growth techniques. The growth sites are controllable by careful deposition of the catalyst. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow SWNTs rather than MWNTs (Sinnot *et al.*, 1999). Additionally, no other growth methods have been developed to produce vertically aligned nanotubes (Ren *et al.*, 1998; Collins *et al.*, 2000) as well as positional control on nanometer scale (Ren *et al.*, 1999).

Recently, this area of synthesis has been advanced by a team of researchers at Rice University. The team, until recently led by the late Dr. Richard Smalley, has concentrated upon finding methods to produce large, pure amounts of particular types of nanotubes. Their approach grows long fibers from many small seeds cut from a single nanotube; all of the resulting fibers were found to be of the same diameter as the original nanotubes and are expected to be of the same type as the original nanotubes. Further characterization of the resulting nanotubes and improvements in yield and length of grown tubes are needed (Boyd, 2006).
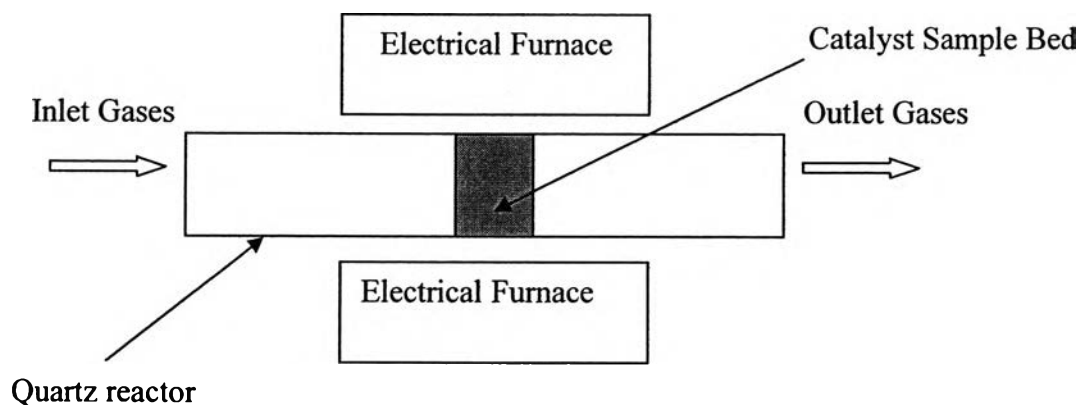
Figure 2.7 A typical reactor set up for catalytic vapor phase deposition of carbon nanotubes.

Currently, there are two catalytic chemical vapor processes that appeared to be the most promising for an industrial scale: the high-pressure carbon monoxide disproportionation reaction over iron catalytic particle clusters (HiPCO process), and the catalytic disproportionation of carbon monoxide or hydrocarbon over a silica supported cobalt–molybdenum catalyst (CoMoCAT process).

The high-pressure carbon monoxide (HiPCO) process has catalytic particles formed in-situ by thermal decomposition of iron penta-carbonyl. The process can be operated continuously by using continuous filtration to separate the carbon nanotubes containing the iron catalyst from the unreacted carbon monoxide. Carbon nanotubes contain iron particles (~5–6 at.%) that are formed from the decomposition of the iron carbonyl which act as the growth nucleation sites. The iron nanoparticles are not enclosed in heavy graphitic shells as in the arc or laser vaporization processes and are relatively easier to remove. A major drawback of the HiPCO process is the low rate of carbon monoxide conversion (~15–20% per cycle) even at high pressure. The unconverted carbon monoxide feedstock can be recycled to the reactor (Bronikowski et al., 2001). A commercial process using the HiPCO reactor is being developed by Carbon Nanotechnologies Incorporation, Houston, TX, a start-up company from Rice University.

The cobalt-molybdenum catalytic (CoMoCAT) process employs the synergistic effect between the cobalt and molybdenum to give high selectivity (better than 80%) to carbon nanotubes from CO disproportionation at 700-950°C and a total pressure ranging from 1 to 10 atm. Carbon monoxide disproportionation reaction is exothermic and can be limited by equilibrium at the high temperatures required to activate CO on the catalyst. High carbon monoxide pressures are used in order to mitigate the temperature effect and enhance the formation of carbon nanotubes. Resasco et al. (2002), reported that the extent of Co-Mo interaction is a function of the Co:Mo ratio in the catalyst. At low Co:Mo ratios, Co interacts with Mo in a superficial cobalt molybdate-like structure, whereas at high ratios, it forms a non-interacting Co_3O_4 state. The formation of carbon nanotubes is enhanced at low Co:Mo ratios because the Co:Mo interaction inhibits the cobalt sintering that usually results at the high temperatures.

Recently, The CoMoCAT process has been developed by using fluidized bed reactor to replace fixed bed reactor. The latest type of reactor would give intimate contact between CO and the silica supported Co-Mo catalyst powder with high specific surface area. The residence times of the carbon nanotube could be controlled, and the activity of the catalyst utilized to ensure high conversion. There would be efficient heat and mass transfer between the carbon nanotube agglomerates and the bulk gas phase to have temperature control as needed to more-closely approach equilibrium. The carbon nanotubes formed in the CoMoCAT reactor are attached to the silica-supported catalyst particles, and an effective sequence of purification processes is required to remove these impurities. A commercial process using the CoMoCAT reactor is being developed by SouthWest Nanotechnologies, Inc., Norman, OK, a start-up company from the University of Oklahoma.

2.5 Purification of Carbon Nanotubes

One of the problems, that is next to large-scale synthesis, is the purification of the as-prepared carbon nanotubes. Although the carbon nanotubes were produced by the best conditions in various synthesis techniques, the as-prepared carbon nanotubes still contain a number of impurities such as graphite nanoparticles, amorphous carbon, smaller fullerenes, and metal catalyst particles. The amount and type of impurities are also dependent on the production techniques. In addition, for gas phase catalytic chemical vapor deposition, catalysts supporting material (i.e. silica, zeolite, alumina, and magnesium oxide) is often presented in the final product in addition to all impurities as in other production techniques. These impurities will interfere with most of the desired properties of the SWNTs. In the fundamental research, it is preferred to obtain SWNTs as pure as possible. However, in carbon nanotubes application, the necessary level of purity may be varied, depends on the field of application. For examples, in the application as reinforcing filler, carbon nanotubes may not required high purity, while the high purity is very significant in electronic application. In this section, the physical and chemical purification techniques that will be summarized include oxidation, acid treatment, annealing,

ultrasonication, micro filtration, ferromagnetic separation, cutting, functionalization and chromatography.

2.5.1 Oxidation

The oxidative treatment of carbon nanotubes in air/oxygen removes carbonaceous impurities such as amorphous carbon and helps expose the catalytic metal surface enclosed in the carbon nanotube for further purification techniques (Chiang *et al.*, 2001a; Harutyunyan *et al.*, 2002). It can be performed either in gas or liquid phase. The key of oxidative treatment is based on that the carbon with different structures shows different rate of oxidation in air or pure oxygen. The less stable carbon structure is easier to be oxidized than the more stable structure. For example, amorphous carbon is oxidized more readily than carbon nanotubes. However, the carbon nanotubes can also be oxidized if the temperature and time is not in a good control. In addition, the presence of catalytic metal particles is also acts as oxidizing catalyst (Hou *et al.*, 2001), so the metal content should certainly be taken into consideration, when looking at the oxidizing time.

There are a couple of examples for clearing the metal surface, to prepare the sample for a metal removal step. The first one is mild oxidizing in a wet environment with soluble oxidizing agents, such as H_2O_2 and H_2SO_4 (Farkas *et al.*, 2002). These will only oxidize the defects and will clear the surface of the metal. Most commonly, the metal catalyst stays intact during these processes, but when oxygen is used in a wet atmosphere, the outer layer of the metal will be oxidized (Chiang *et al.*, 2001b). Then, the density of this surface increases and the surface covering carbon layer ruptures. Not only the carbon impurities are oxidized now, but also the metal is partially oxidized and exposed. Quite different from the oxidative techniques above is microwave heating. The microwaves will heat up the metal and will catalytically oxidize the carbon attached to the metal.

2.5.2 Acid Treatment

In general the acid treatment will remove the metal catalyst. Before this treatment, however, the surface of the metal must be exposed by oxidative treatment or ultrasonication. The metal catalyst is then exposed to acid and solvated. The

carbon nanotubes remain in suspended form. When using a treatment in HNO_3, the acid only has an effect on the metal catalyst. It has no effect on the carbon nanotubes and other carbon particles (Kajiura *et al.*,2002). If a treatment in HCl is used, the acid also has a little effect on the carbon nanotubes and other carbon particles (Moon *et al.*, 2001). Bandow *et al.* (1997) also showed that the mild acid treatment (4 M HCl reflux) is basically the same as the HNO_3 reflux, but here the metal has to be totally exposed to the acid to solvate it.

2.5.3 Annealing

Due to high temperatures in the range of 873 to 1873 K, the nanotubes will be rearranged and defects will be consumed (Georgakilas *et al.*, 2002). The high temperature also causes the graphitic carbon and the short fullerenes to pyrolyse. When using high temperature vacuum treatment at 1873 K (Kajiura *et al.*,2002), the metal will be melted and can also be removed.

2.5.4 Ultrasonication

Particles are separated due to ultrasonic vibrations. By this purification technique, agglomerates of different nanoparticles will be forced to vibrate and become more dispersed. The separation efficiency of the particles is dependent on the surfactant, solvent and reagent used.

The solvent influences the stability of the dispersed tubes in the system. In poor solvents the carbon nanotubes are more stable if they are still attached to the metal. But in some solvents, such as alcohols, monodispersed particles are relatively stable (Shelimov *et al.*, 1998). When an acid is used, the purity of the carbon nanotubes depends on the exposure time. When the tubes are exposed to the acid for a short time, only the metal solvates, but for a longer exposure time, the tubes will also be chemically cut (Chiang *et al.*, 2001b).

2.5.5 Magnetic Purification

In this technique, ferromagnetic catalyst particles are mechanically removed from their graphitic shells (Thien-Nga *et al.*, 2002). The carbon nanotubes suspension is mixed with inorganic nanoparticles, such as ZrO_2 or $CaCO_3$, in an

ultrasonic bath to remove the ferromagnetic particles. Then, the particles are trapped with permanent magnetic poles. After a subsequent chemical treatment, a high purity nanotubes material will be obtained. This process does not require large equipment and enables the production of laboratory-sized quantities of carbon nanotubes containing no magnetic impurities.

2.5.6 Micro Filtration

Micro filtration is based on size or particle separation. carbon nanotubes and a small amount of carbon nanoparticles are trapped in a filter. The other nanoparticles, such as catalyst metal, fullerenes, and carbon nanoparticles, are passing through the filter. One way of separating fullerenes from the carbon nanotubes by micro filtration is to soak the as-prepared carbon nanotubes first in a CS_2 solution. The CS_2 insolubles are then trapped in a filter. The fullerenes which are solvated in the CS_2, pass through the filter (Bandow *et al.*, 1997).

An alternate filtration technique is cross flow filtration. In cross flow filtration the membrane is a hollow fiber. The membrane is permeable to the solution. The filtrate is pumped down the bore of the fiber at some head pressure from a reservoir and the major fraction of the fast flowing solution which does not permeate out the sides of the fiber is fed back into the same reservoir to be cycled through the fiber repeatedly. A fast hydrodynamic flow down the fiber bore (cross flow) sweeps the membrane surface preventing the build-up of a filter cake (Borowiak-Palen *et al.*, 2002).

2.5.7 Cutting

Cutting of the can either be induced chemically, mechanically, or a combination of these. Carbon nanotubes can be chemically cut by partially functionalizing the tubes, for example with fluorine (Gu *et al.*, 2002). Then, the fluorated carbon will be driven off the sidewall with pyrolization in the form of CF_4 or COF_2. This will leave behind the chemically cut nanotubes.

Mechanical cutting of the nanotubes can be induced by ball-milling. Here, the bonds will break due to the high friction between the nanoparticles and the nanotubes will be disordered (Gao *et al.*, 2000). A combination of mechanical and

chemical cutting of the nanotubes (Farkas *et al.*, 2002) is ultrasonical induced cutting in an acid solution. In this way the ultrasonic vibration will give the nanotubes sufficient energy to leave the catalyst surface. Then, in combination with acid the nanotubes will rupture at the defect sites.

2.5.8 Functionalization

Functionalization is based on making carbon nanotubes more soluble than the impurities by attaching other groups to the tubes. Now it is easy to separate them from insoluble impurities, such as metal, with filtration (Nayogi *et al.*, 2001; Zhao *et al.*, 2001). Another functionalization technique also leaves the carbon nanotubes structure intact and makes them soluble for chromatographic size separation (Georgakilas *et al.*, 2002). For recovery of the purified carbon nanotubes, the functional groups can be simply removed by thermal treatment, such as annealing.

2.5.9 Chromatography

This technique is mainly used to separate small quantities of SWNTs into fractions with small length and diameter distribution. The SWNTs are run over a column with a porous material, through which the SWNTs will flow. The columns used are GPC (Gel Permeation Chromatography) and HPLC-SEC (High Performance Liquid Chromatography - Size Exclusion Chromatography) columns. The number of pores the SWNTs will flow through, depends on their size. This means that, the smaller the molecule, the longer the pathway to the end of the column will be and that the larger molecules will come off first. The pore size will control what size distribution can be separated. However, a problem is that the SWNTs have to be either dispersed or solvated. This can be done by ultrasonication (Farkas *et al.*, 2002) or functionalization with soluble groups (Nayogi *et al.*, 2001; Zhao *et al.*, 2001).

2.6 Characterization of Carbon Nanotubes

Several techniques have been broadly studied for carbon nanotubes characterization such as electron microscopy, Raman spectroscopy, Infrared

spectroscopy, temperature-programmed analysis, scanning tunneling microscopy (STM), electron energy loss spectroscopy, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), etc. This section will briefly discuss certain techniques that have been widely employed to characterize carbon nanotubes from various production processes. Definitely electron microscopy and Raman spectroscopy are two main methods that are widely utilized to study the carbon nanotubes. But, these two techniques are still considered to be relatively elaborated and only suitable for qualitative characterization. It is necessary establish a rapid and economical method for monitoring and studying the production of carbon nanotubes. Temperature program analysis technique, which looks promising for carbon nanotubes quantitative analysis, therefore will be subsequently reviewed.

2.6.1 Electron Microscopy

Electron microscopy has been a major technique in characterization of carbon nanotubes. In fact, both MWNTs and SWNTs were first observed through electron microscopy (Iijima, 1991; Iijima and Ichihashi, 1993; Bethune *et al.*, 1993). Electrons having characteristic wavelengths of less than an angstrom render a high resolution of carbon nanotubes images. In transmission electron microscopy (TEM), the two dimensional images of carbon nanotubes are obtained from transmitted electron. TEM are able to give sub-nanometer resolution, therefore it is highly suitable for studying structure of carbon nanotubes such as diameter of individual SWNT and MWNT tube, diameter of SWNTs bundle, graphitic layer of MWNTs as well as crystallinity of carbon sample.

For scanning electron microscopy (SEM), the electron beam scans over the sample surface causing backscattered electron. The three dimensional information are achieved from the contrast of images with the resolution in the scale of nanometer scale, thus, SEM is proper for obtaining overall structure of carbon nanotubes, but not for detailed structure.

2.6.2 Raman Spectroscopy

Raman spectroscopy is one of the most powerful tools for characterization of carbon nanotubes. Without sample preparation, a fast and non-destructive analysis

is possible. All allotropic forms of carbon are active in Raman spectroscopy (Arepalli *et al.*, 2004): fullerenes, carbon nanotubes, amorphous carbon, polycrystalline carbon, etc. The position, width, and relative intensity of bands are modified according to the carbon forms (Ferrari *et al.*, 2000). The most characteristic features are summarized in Figure 2.8, as following: (i) a low-frequency peak < 200 cm^{-1} (or bunch of peaks for polydisperse samples when resonating conditions are met) characteristic of the SWNT assigned to a A_1g "breathing" mode of the tubes, whose frequency depends essentially on the diameter of the tube (RBM: radial breathing mode); (ii) a large structure (1340 cm^{-1}) assigned to residual ill-organized graphite, the so-called D-line (D: disorder); (iii) a high-frequency bunch (between 1500 and 1600 cm^{-1}) called G band also characteristic of nanotubes, corresponding to a splitting of the E_2g stretching mode of graphite (Mamedov *et al.*, 2002). This bunch could be superimposed with the G-line of residual graphite (Hiura *et al.*, 1993); (iv) a second order observed mode between 2450 and 2650 cm^{-1} assigned to the first overtone of the D mode and often called G mode; (v) a combination mode of the D and G modes between 2775 and 2950 cm^{-1}.
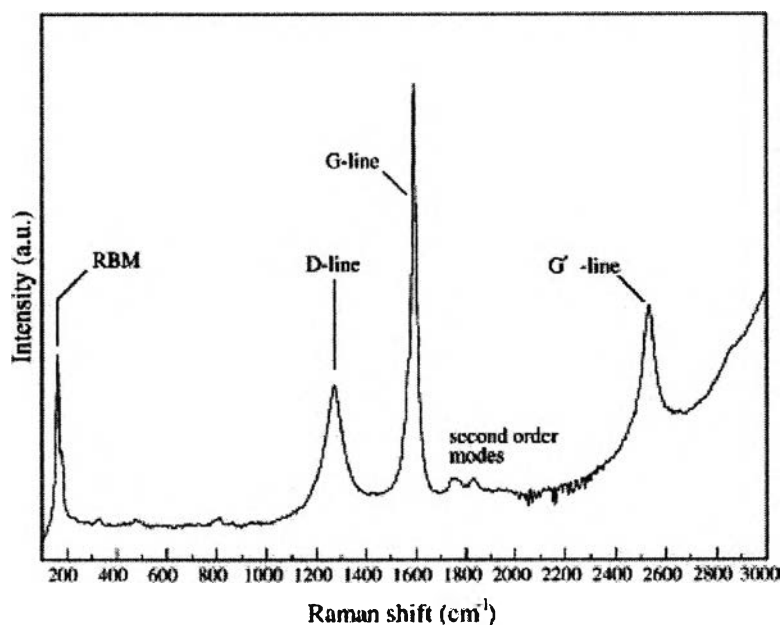
Figure 2.8 Raman spectrum showing the most characteristic features of carbon nanotubes: radial breathing mode (RBM), the D band, G band and G band. Second order modes are also observed. Spectrum obtained from SWNTs sample (diameter of about 1.07 nm) mixed with KBr using a Elaser = 1.16 eV (λ = 1064.5 nm) excitation.

2.6.3 Temperature-Programmed Analysis

Temperature-programmed analysis is a technique which monitors the change in sample, e.g. weight or chemical reaction, while the temperature increases linearly in time. If the sample's weight is the monitored parameter, this technique is often called thermal gravitation analysis (TGA). For instance, carbon with different morphology is burnt at different temperature; therefore temperature program analysis is a technique that is suitable to study carbon structures. In addition TGA is a simple technique that provides a reliable result. However, it is necessary to keep in mind that the oxidation of carbon is sensitive to the presence of other materials, e.g. metals that can act as a catalyst to facilitate carbon burning.

In order to opening MWNTs' cap, Ajayan and co-workers compared the oxidation of fullerenes and MWNTs in air for 15 minutes and they found that the weight of fullerene started dropping dramatically when the temperature was at around 470°C and completely disappeared at temperature around 630°C (Ajayan *et al.*, 1993). The nanotubes samples started to show substantial loss of weight once they were heated above 700°C, and at about 850°C the entire sample was burnt off. Despite the wide distribution in shapes and sizes of MWNTs, the oxidation curves are smooth over the temperature range. The authors proposed that the oxidation of carbon nanotubes first occurs at the caps of nanotubes and carbon are consumed layer by layer resulting in opening the tube's caps and thinning the nanotubes. Thermal gravitation analysis of laser produced SWNT is also reported by Rinzler and colleagues (1998). With air as an oxidizing agent, they found that the unpurified SWNTs start burning at temperature around 400°C with the maximum rate of burning at around 480°C. However, the purified SWNTs show the major weight loss at temperature almost 600°C with the high rate at about 650°C. Furthermore, the TGA of purified SWNTs with 0.1 % oxygen in argon does not show a major fraction loss until the temperature after 600°C. According from the authors, the major weight reduction of unpurified SWNT at lower temperature is due to the present of other forms of carbon that can be burnt at lower temperature. The oxidizing reaction at low temperature provides the heat for prematurely burning of more stable carbon. In general, it is accepted that SWNTs will be oxidized at temperature higher than amorphous carbon and C_{60}, but lower than MWNT and graphitic carbon fiber.

In the case of a minute amount of carbon, e.g. deposited carbon on catalysts, TGA is not sufficiently effective due to its low sensitivity. Instead of sample weight monitoring, the carbon dioxide gas evolution is followed. This technique is well known in catalysis field as temperature-programmed oxidation (TPO).

2.7 Froth Flotation Technique

Froth flotation is a surface-chemistry based process for separation of fine solids that takes advantage of the differences in wettability at solid particle-surfaces. Solid surfaces are often naturally wettable by water and termed hydrophilic. A surface that is non-wettable is water repelling and termed hydrophobic. If a surface is hydrophobic, it is also typically air attracting, termed aerophilic, and is strongly attracted to an air interface, which readily displaces water at the solid's surface. In froth flotation, separation of a binary solids mixture may be accomplished by the selective attachment of hydrophobic solid particles to gas bubbles (typically air). The other hydrophilic solid particles remain in the liquid (typically water). The difference in the density between the air bubbles and water provides buoyancy that preferentially lifts the hydrophobic solid particles to the surface where they remain entrained in a froth which can be drained off or mechanically skimmed away, thus, effecting the separation.

Froth flotation is often used to separate solids of similar densities and sizes, which prevent other types of separations based upon gravity that might otherwise be employed. It is especially useful for particle sizes below 150 mesh, which are typically too small for gravity separation using jigging and tabling. However, it may be difficult to take advantage of surface-property differences to induce selective hydrophobicity for particles smaller than 400 mesh. 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).

Froth flotation has been used in the minerals processing industry since the mid-1800's with many of its broad-based applications to mineral recovery

extensively developed between 1900 and 1925. Today, at least 100 different minerals, including almost all of the world's copper, lead, zinc, nickel, silver, molybdenum, manganese, chromium, cobalt, tungsten, and titanium, are processed using froth flotation. In 1997, the estimated worldwide mineral production, using froth flotation, was two billion tons. Another major usage of froth flotation is by the coal industry for desulferization and the recovery of fine coal, once discarded as waste. Since the 1950's, flotation has also been applied in many non-mineral industries including sewage treatment; water purification; paper de-inking; and chemical, plastics, and food processing. The development of froth flotation continues today with the need to recover minerals from increasingly poorer grades of ore, as well as its non-traditional application to other types of materials.

There are several different types of froth flotation systems in use today including the mechanical type and the flotation column. The type of froth flotation apparatus in Figure 2.9 is the batch, sub-aerated mechanical type. The flotation step is accomplished by the preparation of a pulp, consisting of solid-liquid slurry that may contain up to 40% solids, to which chemical reagents known as collectors are added in a conditioning tank. The reagents are added to render some material hydrophobic that they selectively adhere to air bubbles introduced into the pulp in a flotation cell. On the other hand, some reagents enhance selectivity through activation and depression phenomena. Frothers are also used to generate a mineral-laden froth layer and enhance particle-bubble adhesion. The products from the flotation cell are a concentrate and a tailings stream. The concentrate proceeds to the next step for further cleaning or treatment by hydro- or pyrometallurgical methods for the extraction of metals and other valuable compounds, while the tailings, which are ore components stripped of their valuable material content, are collected in lagoons known as tailings ponds.
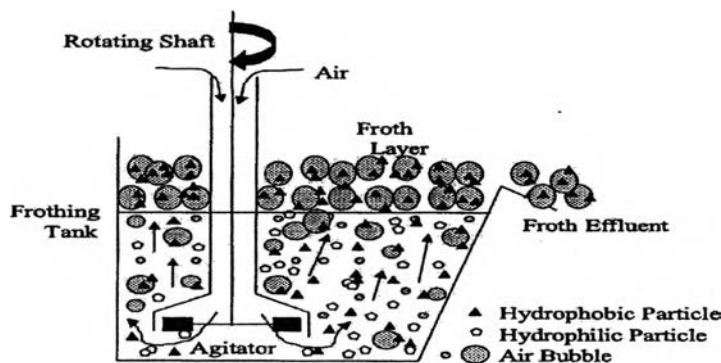
Figure 2.9 Sub-aerated mechanical froth flotation apparatus.

2.7.1 Wettability

Froth flotation involves three phases (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-base process, where numerous phenomena that simultaneously occur at the solid-liquid-air interfacial region determine it's out come. In this context, the variable known as contact angle θ illustrated in Figure 2.10, is an important correlative parameter. At $\theta = 0°$, the liquid spreads on the solid; in aqueous media in contact with air such a solid is said to e hydrophilic 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., $\theta > 0°$ (Kroschwitz and Howe-Grant, 1992).

The three interfacial tensions at equilibrium (Figure 2.10) conform to Young's equation (Equation 1): where γ represents solid-gas, solid-liquid, and liquid-gas interfacial tension as indicated by subscripts.

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos \theta \qquad (1)$$

Strictly speaking, equation 1 represents a special case that does not take into consideration the effects of gravity or external forces such as electric and magnetic filed. 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 otherwise hydrophilic or not strongly hydrophobic. This selective modification of the wettability of solids in froth flotation is obtained using additional reagents termed collectors.
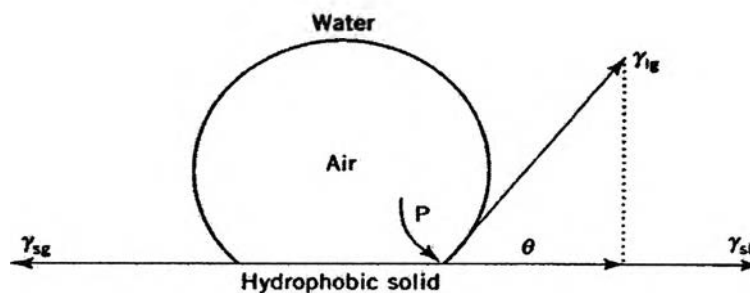
Figure 2.10 The concept of contact angle with a captive bubble in an aqueous. medium, adhering to a hydrophobic solid: P is the three-phase contact point. Here, the vector γ_{lg} passes through P and forms a tangent to the curved surface of the air bubble. The contact angle θ is drawn into the liquid.

2.7.2 Collectors

To invoke selective hydrophobicity, substances know as collectors are used. Collectors are typically hetropolar organic substances – they contain both nonpolar and polar chemical groups. The nonpolar end is almost always a long-chain or cyclic hydrocarbon group that is hydrophobic. The collector must be able to attach to the solid, and it does so through its polar end, which is typically an ionic group termed the solidophil group.

While the solidophil group of a suitable collector contacts a substance at a surface site that can chemically interact with the solidophil group, the collector bonds to the surface of the substance via chemisorption or ionic bonding. The nonpolar end of the collector then orients outward from the solid surface forming a nonpolar

chemical envelop surrounding the solid particle, including hydrophobic behavior on an otherwise hydrophilic solid surface. The solid particle can then more readily attach to an air bubble via the hydrophobic end of the collector.

Consequently, a key to successful froth flotation is to selectively induce, using a suitable collector, hydrophobicity on the desired material to be recovered while retaining hydrophilicity of the nondesirable material. It should also be noted that the strength of the induced hydrophobicity of the substance via the collector is directly relatable to the length of the hydrocarbon group while the strength and selectivity of the collector's ionic bonding is controlled by the type of solidophil group.

There are many different types of the collectors, and they are classified as to the type of ion (anionic or cationic) that is formed upon their dissociation in aqueous solutions.

Table 2.1 Contact angles for various solids and collectors
(adapted from Encyclopedia of Chemical Technology 4th Edition, Vol. 11 (1997))

Solid	Collectors and Conditions	θ(degs)
colemanite	5×10^{-3} M sodium oleate	43
copper metal	1.5×10^{-4} M sodium oleate	93
Fluorite	1×10^{-5} M sodium oleate, pH = 8.1	91
Galena	1×10^{-3} M potassium ethyl xanthate	60
ilmenite	1.3×10^{-3} M sodium oleate solution, T = 75°C, pH = 8	80
Silica	1.1×10^{-5} M dodecylammonium chloride, pH = 10	81
graphite	Water	86-96
Coal	Water	20-60
Stibnite	Water	84
Sulfur	Water	85
molybdenite	Water	75
Talc	Water	88
Iodyrite	Water	20

As previously discussed, the effect of the collectors on the hydrophobicity of the solids can be related to the contact angle, θ. Examples of the contact angles modified by various collectors for various minerals are indicated in Table 2.1, as well as those for naturally hydrophobic materials for comparison.

2.7.3 Frothers

In addition to collectors, another important component in successful flotation is the presence of frothers. Once its surface is rendered hydrophobic, a solid particle must be able to attach to an air bubble. While it may be possible to initially obtain solid particle attachment to air bubbles in an agitated liquid under aeration alone, these air bubbles are unstable and quickly break down due to collision with other bubbles, solid particles, and the vessel walls. In addition, the bubble size may not be sufficient to effectively carry a solid particle to the surface of the liquid. Consequently, additional materials, termed frothers, are added to promote the formation of stable air bubbles under aeration. Frothers, like collectors, are typically comprised of both a polar and nonpolar end. The nonpolar hydrophobic ends orient themselves into the air phase. Bubble wall strength is enhanced by simultaneous strong polar-group and water-dipole reaction (hydration) at the air-liquid interface resulting in greater bubble stability due to a localized increase in surface tension.

Frothers are generally classified by their polar groups with the most common being the hydroxyl (-OH), carboxyl (-COOH), carbonyl (=C=O), amino ($-NH_3$), and sulfo ($-OSO_2OH$ and $-SO_2OH$) groups. Table 2.2 lists some common frothers according to their chemical grouping. Effective frothers typically contain at least five or six carbon atoms in their straight-chain, nonpolar group to obtain sufficient and stable interaction with the air phase. For branched-chain hydrocarbons, the number of carbon atoms in the nonpolar group may range up to sixteen. However, a frother must be at least slightly soluble in the liquid medium and increasing the straight-chain-hydrocarbon length (perhaps up to a maximum of eight, e.g., octyl alcohol) will eventually lead to too low of solubility for effective frothing. Thus, a suitable frother must provide a balance between sufficient nonpolar interaction with air and solubility in water. With respect to the polar groups, one or

two are usually sufficient to interact at the liquid-air interface to provide sufficient frothing properties, and additional polar groups provide little benefit.

Table 2.2 Examples of frothers

Frother	Formula

Aliphatic Alcohols
 	
   MIBC (4-methyl-2-pentanol)
 	
   di-acetone alcohol
 	
   2-ethyl 3-hexanol
	$CH_3(CH_2)_nCH_2OH$, n = 3-5
	
	$CH_3CH(CH_3)CH_2CH(OH)CH_3$
	
	$(CH_3)_2(OH)CH_2COCH_3$
	
	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$

Cyclic Alcohols
 	
   Pine oil (terpineol)
 	
   Eucalyptus oil (cineole)
	
	$C_{10}H_{17}OH$
	
	$C_{10}H_{16}O$

Phenols
 	
   Cresol
 	
   Xylenol (e.g., xylitol)
	
	$CH_3C_6H_4OH$
	
	$HOCH(CHOH)_3CH_2OH$

Alkoxyparaffins 1,1,3-triethoxybutane	 $CH_3CH_2CH(OC_2H_5)CH(OC_2H_5)_2$

Polyglycols
 	
   Poly (propylene glycol) monoalkyl
   ethers
 	
   Poly (ethylene glycol) s
	
	$R(OC_3H_6)_nOH$, n = 2-5, R = CH_3,
	C_4H_9
	
	$R(OC_2H_4)_nOC_2H_4OH$, n = 2-5

Other Sulfo-cetyl alcohol	 $CH_3(CH_2)_{14}CH_2OSO_2OH$

Most of the frothers in Table 2.2 are hydroxyl-group-type frothers, and, thus, have little collector properties. However, because of the inherent heteropolarity of collectors, a collector can also serve as a frother in some systems. This is true of the carboxyl-type frother, sodium oleate, and the sulfo-solidophil fatty acids. Certain collector/frother combinations may also exhibit a synergistic separation effect. However, one designs a flotation system based upon a collector specific to the modification of the surface properties of the solid required for separation. The type

of frothing agent is a secondary consideration that is chosen after the collector to provide suitable frothing conditions and noninterference with the collector or separation system.

2.7.4 Modifiers

Additional modifiers such as activators, depressants, dispersants, and pH regulators are also commonly used in froth flotation. Activators may be added to chemically "resurface" the slid to increase the interaction with collectors that are otherwise ineffective alone. Depressants form a polar chemical envelope around the solid particle that enhances hydrophilicity or selectively prevents interaction with collectors that may induce unwanted hydrophobicity. Dispersants act to break agglomerated particles apart so that single particles interact with the collectors and air bubbles. Regulators are commonly used to control the pH since the hydrophobicity of systems is often optimal within a certain pH range. Frothers also often need a certain pH range in order to form stable bubbles. The presence of reducing agents may also serve to prevent the presence of soluble ions due to oxidation that may undesirably activate certain minerals.

The froth flotation is widely utilized in the area of mineral processing. In addition to the mining and metallurgical industries, flotation also finds applications in sewage treatment, water purification, bitumen recovery from tar sands, and coal desulfurization. The development of froth flotation continues today with the need to recover minerals from increasingly poorer grades of ore, as well as its non-traditional application to other types of materials.

Musa Sarikaya and Gulhan Ozbayoglu (1994) reported that the floatability of oxidized coal was investigated by means of electrokinetic studies, contact angle measurements and flotation tests. Electrokinetic measurements showed that the zeta potential of unoxidized and oxidized coal samples depends on pH. Hydroxonium and hydroxyl ions are potentially significant ions, both for oxidized and unoxidized coal. Increasing oxidation times decreased the measured iso-electric points and increased the negative zeta potential. In the presence of cationic collectors the negative value of the zeta potential for oxidized coal was changed to a positive value below pH 9.3-10.9 depending on the type and concentration of collector used. Contact angle

measurements indicated that the natural floatability of unoxidized coal was found to deteriorate an oxidation. Addition of cationic collectors increased the value of the contact angle of oxidized coal. Flotation tests showed that as the degree of oxidation increases, the floatability of coal decreases. Cationic collectors were found to be effective in the flotation of oxidized coal.

2.8 Nature of Surfactants

A surfactant or surface-active agent has a characteristic molecular structure consisting of hydrophilic (water-loving) which is usually polar group and hydrophobic (water-hating) which is usually hydrocarbon or nonpolar group. One of important properties of surfactant was to adsorb onto the surface or interface of the system resulting to decreasing the surface or interfacial tension of the medium in which it is dissolved. The interface indicates a boundary between any two immiscible phases and the surface indicates an interface where one phase in a gas, usually air.

Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, nonionic and zwitterionic (Rosen, 1992). Anionic surfactant is a surfactant molecule whose polar group is negatively charged such as sodium dodecyl sulphate, $(CH_3(CH_2)_{11}SO_4^-Na^+)$. Nonionic surfactant is a surfactant molecule whose polar group is not electrically charged such as polyoxyethylene alcohol, $(C_nH_{2n+1}(OCH_2CH_2)_mOH)$. Zwitterionic surfactant is a surfactant molecule whose polar group contains both negatively and positively charged groups such as lauramidopropylbetaine, $(C_{11}H_{23}CONH(CH_2)_3N+(CH_3)_2CH_2COO^-)$ at neutral and alkaline solution pH.

A single molecule of surfactant is called monomer and at sufficiently concentration in solution, monomers or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization that is illustrated in Figure 2.11 and the lowest total surfactant concentration at which micelles re present is critical micelle concentration (CMC).

Surfactant solutions with concentrations above the CMC can dissolve considerably large quantities of organic materials than surfactant solutions with concentrations below the CMC. Since at the CMC, surfactant molecules form

spherical micelles with the hydrophobic or hydrocarbon group on the interior and the hydrophilic group on the exterior. Therefore, oil or organic contaminants that are also hydrocarbon can solubilize at the center core of micelles. Furthermore, the solubilization increases as the number of micelles in the solution increases (Clarence and Neogi, 1985).
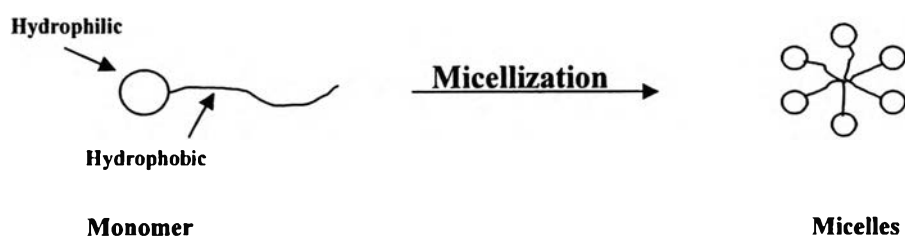
Figure 2.11 Schematic diagram of monomer, micelles and micellization.

Normal micelles which have hydrophobic part in the interior and hydrophilic part in the external solvent are formed in aqueous solutions or water. Inverse micelles which have hydrophilic part in the interior and hydrophobic part on the outside are formed in nonpolar solvents. Figure 2.12 illustrates the picture of normal and reverse micelles (Rosen, 1992).

Figure 2.12 Schematic diagram of normal micelles and reverse micelles.

Surfactants are widely used for many applications such as detergents, flotation, paints, cosmetics and enhanced oil recovery. Mixtures of different surfactants are used more than individual surfactants due to economical as well as beneficial effects. Mixtures of ionic and nonionic surfactants are commonly used in practical surfactant applications because the solution behaviors of these surfactants

can be complimentary. For instance, in laundry detergent formulations, anionic surfactants are used to maximize solubilization while nonionic surfactants are used to maximize water hardness tolerance. An addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsion between the charged surfactant geads and greatly electrostatic repulsion between the charged surfactant geads and greatly facilitate mixed micelle formation (Shiloach and Blankschtein, 1998).

Surfactants play an important role in separation procedures such as flotation. Flotation is one of interesting processes since it can serve as energy barrier, thus enabling fluid media to be stabilized in the form of very small globules thereby exposing an enormously increased interfacial area, where transfer from one phase to another can occur very rapidly. In addition, because of their amphipathic mature, they tend to adsorb at interfaces. Thus, they can themselves act as collectors in flotation procedures (Sebba, 1989).