CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO NANOTECHNOLOGY

Nanotechnology involves the creation and/or manipulation of materials at the nanometer (nm) scale either by scaling up from single groups of atoms or by refining or reducing bulk materials. A nanometer is $10^{-9}$ m or one millionth of a millimeter. Nano is a Greek word meaning one billionth, and the nanometer defines the length scale that is used to measure systems being studied in nanoscience. For comparison, typical carbon-carbon bond lengths, or the spacing between these atoms in a molecule are in the range 0.12-0.15 nm, and a DNA double-helix has a diameter around 2 nm. Nanomaterials have actually been produced and used by humans for hundreds of years - the beautiful ruby red color of some glass is due to gold nanoparticles trapped in the glass matrix.

Photography is an advanced and mature technology, developed in the middle of eighteenth century, which depends on production of silver nanoparticles sensitive to light. Although widespread interest in nanomaterials is recent, the concept was raised over 40 years ago. Richard Feynman was awarded the Nobel Prize in Physics in 1965 for his contributions to quantum electrodynamics, a subject far removed from Nanotechnology. In 1959 he presented a visionary and prophetic lecture at a meeting of the American Physical Society, entitled “There is plenty of Room
at the Bottom”, where he speculated on the possibility and potential of nanosized materials. To give a sense to this scale, a human hair is of the order of 10,000 to 50,000 nm.

Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale. The use of the term “nanotechnology” can be misleading since it is not a single technology or scientific discipline. Rather it is a multidisciplinary grouping of physical, chemical, biological, engineering, electronic, applications and concepts in which the defining characteristic is one of size. The applications of nanomaterials include titanium dioxide nanoparticles in sunscreen, cosmetics and some food products; silver nanoparticles in food packaging, clothing, disinfectants and household appliances; zinc oxide nanoparticles in sunscreens and cosmetics, surface coatings, paints and outdoor furniture varnishes; and cerium oxide nanoparticles as a fuel catalyst.

Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control. Jortner and Rao (2002) summarizes the main categories of nanoparticle in Table 1.1, according to
their morphologies, material from which they may be composed and the type of application in which they may be used.

**Table 1.1  Nanoparticles-categories and applications**

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>Example material or Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanotubes</td>
<td>Carbon (fullerenes)</td>
</tr>
<tr>
<td>Nanowires</td>
<td>Metals, semiconductors, oxides, sulfides, nitrides</td>
</tr>
<tr>
<td>Nanocrystals</td>
<td>Insulators, semiconductors, metals, magnetic materials</td>
</tr>
<tr>
<td>Other nanoparticles</td>
<td>Ceramic oxides, metals</td>
</tr>
</tbody>
</table>

The fundamental physics and chemistry changes when the dimensions of a solid become comparable to one or more of these characteristic lengths, many of which are in the nanometer range. One of the most important examples of this is what happens when the size of a semiconducting material is in the order of the wavelength of the electrons or holes that carry current. The electronic structure of the system completely changes. This is the basis of the quantum dot, which is a relatively mature application of nanotechnology, resulting in the quantum-dot laser presently used to read compact disks (CDs). If only one length of a three-dimensional nanostructure is of a nanodimension, the structure is known as a quantum well, and the electronic structure is quite different from the arrangement where two sides are of nanometer length, constituting quantum wire. A quantum dot has all three dimensions in the nanorange. These nanoscale phenomena include quantum effect and short range forces such as van der Waals forces. The vastly increased ratio of surface area to volume promotes surface phenomena.
Ordinary materials such as carbon or silicon, when reduced to the nanoscale, often exhibit novel and unpredictable characteristics such as extraordinary strength, chemical reactivity, electrical conductivity, or other characteristics that the same materials do not possess at the micro or macro-scale. A huge range of materials have already been produced including nanotubes, nanowires, fullerene derivatives (bucky balls) and other nanoscale materials. Carbon nanotubes (CNTs) are an example of true nanotechnology: they are less than 100 nanometers in diameter, but are molecules that can be manipulated chemically and physically in very useful ways. They are polymers of pure carbon and can be reacted and manipulated using the well-known and the tremendously rich chemistry of carbon.

1.1.1 History of Carbon family

Solid state carbon has been known to appear in four basic forms: "diamond", "graphite", "non-crystalline" (such as charcoal and activated carbon), and "fullerene molecules" such as \( C_{60} \) (Daenen et al 2003). The activated carbon is widely used as adsorbents. Recently, Crocker et al (2007) used a highly activated carbon for the synthesis of nanocrystalline ceria. The carbon nanotubes thus became the fifth type of solid state carbon.

An important breakthrough in carbon research was realized by the work of Kroto et al (1985) which resulted in the discovery of large family of all carbon molecules, called ‘fullerenes’ (Figure 1.1a). The Royal Swedish Academy of sciences awarded the 1996 Nobel Prize in Chemistry jointly to Professor Robert F. Curl, Harold W. Kroto and Richard E. Smalley for their discovery of fullerenes. They can be crystallized as molecular crystals, which are thus a form of crystalline elemental carbon. The fullerenes are closed cage carbon molecules with the carbon atoms tiling spherical or nearly spherical surfaces, the best known example being \( C_{60} \) with a truncated icosahedral structure. The structure of \( C_{60} \) comprises 12 pentagonal rings, 20 hexagonal
rings, 30 double bonds with a diameter of 7.1 Å. The coordination at every carbon atom in fullerenes is not planar but rather slightly pyramidalized, showing a blend of the \( sp^2 \) and \( sp^3 \) character. \( C_{60} \) (0-dimensional structure) molecular structure shows that every pentagon of \( C_{60} \) is surrounded by five hexagons. The key feature is the presence of five-membered rings, which provide the curvature necessary for forming a closed-cage structure. Kratschmer et al (1990) found that the soot produced by arcing graphite electrodes contained \( C_{60} \) and other fullerenes. It was the ability to generate fullerenes in gram-scale quantities in the laboratory, using a relatively simple apparatus that gave rise to intense research activity on these molecules and caused a renaissance in the study of carbon. There are now thirty or more forms of fullerenes, and also an extended family of linear molecules, carbon nanotubes.

Carbon nanotubes shown in Figure 1.1(b) represent characteristics similar to that of graphite. The molecular structure of graphite resembles stacked, one-atom-thick sheets of chicken wire - a planar network of interconnected hexagonal rings of carbon atoms. When graphene sheets are rolled into a cylinder and their edges joined, they form CNTs. Only the tangents of the graphitic planes come into contact with each other, and hence their properties are more like those of a molecule. CNTs consist primarily of \( sp^2 \), but some \( sp^3 \) character may be induced due to the presence of curvature, especially in the endcaps, or at kinks in the NTs. The characteristics of different carbon isomers are discussed in Table 1.2.
1.1.2 Classification of carbon nanostructures

Carbon nanotubes and nanofibers are graphitic filaments with diameters ranging from 0.4 to 500 nm and lengths in the range of several micrometers to millimeters. Three distinct structural types of filaments have been identified (Figure 1.2) based on the angle of the graphene layers (α) with respect to the filament axis (Rodriguez et al 1995, Bessel et al 2001), namely

- Stacked,
- Herringbone (or cup-stacked) and
- Nanotubular
Table 1.2 Isomers made of carbon

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>0-D</th>
<th>1-D</th>
<th>2-D</th>
<th>3-D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isomers</strong></td>
<td>C₆₀ Fullerenes</td>
<td>Nanotubes carbyne</td>
<td>Graphite Fiber</td>
<td>Diamond Amorphous</td>
</tr>
<tr>
<td><strong>Hybridization</strong></td>
<td>sp²</td>
<td>sp² (sp)</td>
<td>sp²</td>
<td>sp³</td>
</tr>
<tr>
<td><strong>Density (g/cm³)</strong></td>
<td>1.72</td>
<td>1.2-2.0</td>
<td>2.26</td>
<td>~3.515</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.68-3.13</td>
<td>~2</td>
<td>~3</td>
</tr>
<tr>
<td><strong>Bond length (Å)</strong></td>
<td>1.40 (C=C) 1.46 (C-C)</td>
<td>1.44 (C=C)</td>
<td>1.42 (C=C) 1.44 (C=C)</td>
<td>1.54 (C-C)</td>
</tr>
<tr>
<td><strong>Electronic properties</strong></td>
<td>Semiconductor</td>
<td>Metal or semiconductor</td>
<td>Semimetal</td>
<td>Insulating</td>
</tr>
</tbody>
</table>

In the literature today, the common categorization method is to refer to graphitic filaments with the stacked or herringbone form as fibers and those with a nanotubular structure as nanotubes.

Figure 1.2 Types of carbon filaments (a) Stacked, (b) herringbone and (c) tubular structure
1.2 CARBON NANOTUBES

A carbon nanotube has a structure similar to a fullerene, but where a fullerene's carbon atoms form a sphere, a nanotube is cylindrical and each end is typically capped with half a fullerene molecule. As carbon nanotubes have various physical properties and are an important material which can be broadly used for various advanced industries such as electronic and information technology in the 21st century, they are globally in the limelight.

1.2.1 History of fullerene related carbon nanotubes

Endo (1988) grew carbon fibres about 7 nm in diameter using a vapor-growth technique, but these filaments were not recognized as nanotubes and were not studied systematically. Gibson (1992) in a letter to Nature, indicated the formation of nanostructures by disproportionation of CO at 450°C catalyzed by iron oxides (or, rather, Fe after reduction) contained in firebrick. However, these catalytically grown carbon filaments are quite different in their structures from CNTs. They are usually bent or coiled while CNTs exhibit a straight, hollow needle-like appearance (Baker and Harris 1973, Boehm 1973).

It was not until Iijima (1991) used high-resolution transmission electron microscopy to observe carbon nanotubes especially multi walled carbon nanotubes that the field really started to take off. Iijima was fascinated by the Kratschmer et al (1990) Nature paper, and decided to embark on a detailed TEM study of the soot produced by their technique. He had good reasons that it might contain some interesting structures. Ten years earlier he had studied soot formed in a very similar arc-evaporation apparatus to the one used by Kratschmer and Huffman and found a variety of carbon architectures including tightly curved, closed nanoparticles and extended tube-like structures.
Initial high resolution TEM studies were disappointing: the soot collected from the walls of the arc-evaporation vessel appeared almost completely amorphous, with little obvious long-range structure. Eventually, Iijima gave up sifting through the wall soot from an arc-evaporation vessel, and turned his attention to the hard, cylindrical deposit which formed on the graphite cathode after arc-evaporation. Here his efforts were finally rewarded. Instead of an amorphous mass, the cathodic soot contained a whole range of novel graphitic structures, the most striking of which were long hollow fibers, finer and more perfect than any previously seen. Iijima’s beautiful images of CNTs, shown first at a meeting at Richmond, Virginia in October 1991, and published in Nature a month later, prompted fullerene scientist the world over to look again at the used graphite cathodes, previously discarded as junk. Dr. Iijima clarified mechanisms of growth and bending of nanotubes, found metal incorporation into nanotubes, and grew single-wall carbon nanotubes. These studies created a global research boom in the field of carbon nanotechnology.

1.2.2 Structure of carbon nanotubes

An ideal nanotube can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder. Just a nanometer across the cylinder can be tens of microns long, and each end is “capped” with half of a fullerene molecule as shown in Figure 1.3. These carbon nanotubes are concentric graphitic cylinders closed at either end due to the presence of five-membered rings. The arm chair and zigzag type CNTs are discussed in the following sections.
The types of CNTs can be classified as

- **Multi-walled carbon nanotubes (MWNTs)** - consists of a number of concentric tubes a central tube of nanometric diameter surrounded by graphitic layers separated by ~0.34nm (Figure 1.4a). MWNTs have two advantages over SWNTs. Multishell structure is stiffer than the SWNTs, and has improved resistance to chemicals.

- **Double-walled carbon nanotubes (DWNTs)** – consists of two concentric cylindrical graphene layers and their range of diameters is comparable to that of SWNTs (Figure 1.4b). It is the most basic member of the MWNTs family.

- **Single-walled carbon nanotubes (SWNTs)** – can be envisioned as a narrow rectangular strip of nanoscale graphene “chicken wire” with carbon atoms 0.14 nm apart from each apex, rolled up into a seamless cylinder with typical diameters of 1-1.4 nm, and length of 50-100 µm (Figure 1.4c). It contains less topological defects and posses better mechanical and electrophysical properties than MWNTs.
1.2.3 Discovery of single walled carbon nanotubes

Methods to experimentally synthesize single-layer nanotubes were first discovered in 1993, when two groups independently found ways to produce them in macroscopic quantities (Iijima and Ichihashi 1993, Bethune et al 1993). These methods involved co-vaporizing carbon and a transition metal catalyst, and produced single-layer NTs approximately 1 nm in diameter with a length of several microns. In one case, Iijima and Ichihashi (1993) produced single-layer NTs by vaporizing graphite and iron in an Ar/CH$_4$ atmosphere. The tubes were found in the deposited soot. Bethune et al (1993) on the other hand, vaporized Co and graphite under helium buffer gas.
Single-layer NTs were found in both the soot and in web-like material attached to the chamber walls.

1.2.3.1 Types of single-walled carbon nanotubes

There are three different types of SWNTs, called armchair, zigzag and chiral NTs depending on how the graphitic sheets is “rolled up” (Daenen et al 2003). The types of carbon nanotubes are most easily explained in terms of the unit cell of a carbon nanotube - in other words, the smallest group of atoms that defines its structure. The so-called chiral vector of the nanotube, $\mathbf{C}_h$, is defined by $\mathbf{C}_h = n\mathbf{\hat{a}}_1 + m\mathbf{\hat{a}}_2$, where $\mathbf{\hat{a}}_1$ and $\mathbf{\hat{a}}_2$ are unit vectors in the two-dimensional hexagonal lattice, and $n$ and $m$ are integers.

Another important parameter is the chiral angle, which is the angle between $\mathbf{C}_h$ and $\mathbf{\hat{a}}_1$. The nanotubes are generally described as $(n,m)$, where ‘$n$’ indicates the number of carbon atoms around the tube, and ‘$m$’ determines the offset of where the NTs wrap around. When the graphene sheet is rolled up to form the cylindrical part of the nanotube, the ends of the chiral vector meet each other. The chiral vector thus forms the circumference of the nanotube's circular cross-section, and different values of $n$ and $m$ lead to different nanotube structures. It is possible to recognize zigzag, armchair, and chiral CNTs just by following the pattern across the diameter of the tubes, and analyzing their cross-sectional structure which is shown in Figure 1.5, and the rolling of graphene sheet is shown in Figure 1.6.
Figure 1.5  Grid of a graphene sheet with the lattice vector ‘a’ and ‘b’ and the angles $\theta$ and $\phi$ which determine the type of the nanotube.

Figure 1.6  Rolling of graphene sheet for formation of SWNTs

The three types of SWNTs are shown in Figure 1.7,

- **Zigzag** - are formed when either $n$ or $m$ is zero and the chiral angle is $0^\circ$. Zigzag, which is named for the pattern of hexagons as one moves circumferentially around the body of the tubule.
- **Armchair** - are formed when \( n = m \) and the chiral angle is 30°. Arm chair, which describes one of the two conformers of cyclohexane, a hexagon of carbon atoms, and describes the shape of the hexagons as one moves around the body of the tubule.

- **Chiral** - with chiral angles intermediate between 0° and 30°. It is believed to be the most commonly occurring SWNTs. The name chiral means handedness and indicates that the tubes may twist in either direction. The geometry of the chiral SWNT lies between armchair and zigzag SWNTs.

![Some SWNTs with different chiralities](image)

**Figure 1.7** Some SWNTs with different chiralities (a) armchair, (b) zigzag and (c) chiral (Dresselhaus et al 1996)

### 1.2.4 Defects in carbon nanotubes

Topological defects such as pentagons, heptagons, vacancies, or dopant are found to modify drastically the electronic properties of these nanosystems (Charlier 2002). High-quality SWNTs are confirmed to contain one defect per 4 \( \mu \text{m} \) on average, with a distribution weighted towards areas of SWNT curvature. Although this defect density compares favourably to high-quality, silicon single-crystals, the presence of a single defect can have
tremendous electronic effects in one-dimensional conductors such as SWNTs (Fan et al 2005). Introduction of a pentagon into a hexagon network on the cylinder will result in a strain around the pentagon. This strain effect is noticeable as a slight distortion to the cylinder.

C-atoms placed in hexagons and pentagons form the end cap structures. Euler’s theorem leads to a relation \( P = S + 12 \), where \( P \) and \( S \) are the number of pentagons and heptagons incorporated into a closed hexagonal network, respectively. For \( S = 1 \), we have \( P = 13 \), in other words, the number of pentagons should always exceed the numbers of heptagons by 12 in any closed surface of the hexagonal network. Such a surface will contain negative curvature (Iijima et al 1992). It can be easily derived from Euler’s theorem that twelve pentagons are needed in order to obtain a closed cage structure which consists of only pentagons and hexagons. The combination of a pentagon and five surrounding hexagons results in the desired curvature of the surface to enclose a volume. The tube can continue to grow as long as only hexagons are being formed on the open end of the tube. Formation of hexagon requires two carbon atoms to be added at each kink site on the periphery, whereas a single atom is required for the pentagon. In contrast, a higher flux of carbon atoms may increase the rate of formation of heptagons, which need three carbon atoms at each kink site. Once a cap is formed on the tip of a cylinder tube, it can grow no longer. Capping the cylinder tube tips should be completed by clustering six pentagons near the tube tips according to Euler’s theorem.

A second rule is the isolated pentagon rule that states the distance between pentagons on the fullerene shell is maximized in order to obtain a minimal local curvature and surface stress, resulting in a more stable structure. The smallest stable structure that can be made this way is \( C_{60} \) the one just larger is \( C_{70} \) and so on. Another property is that all fullerenes are
composed of an even number of C-atoms because adding one hexagon to an existing structure means adding two C-atoms. Since each unit cell of a nanotube contains a number of hexagons, each of which contains two carbon atoms, the unit cell of a nanotube contains many carbon atoms. If the unit cell of a nanotube is N times larger than that of a hexagon, the unit cell of the nanotube in reciprocal space is 1/N times smaller than that of a single hexagon (Daenen et al 2003).

Elastic stretching elongates the hexagons on the tube surface until at high strain some bonds are broken. This local defect is easily redistributed over the entire surface due to the mobility of these defects in the two-dimensional lattice. Nanotube plasticity manifests itself in other ways too. It has been suggested that a 5-7 ring pair defect, called a Stone-Wales defect (Stone and Wales 1986) in sp² carbon systems, in the nanotube lattice can become mobile under the influence of stress. This leads to a stepwise reduction of the nanotubes diameter.

1.2.5 Properties of carbon nanotubes

There are many useful and unique properties of CNTs. They are

- High Electrical Conductivity
- Highly Flexible- can be bent considerably without damage
- High Thermal Conductivity
- Good Field Emission of Electrons
- High mechanical properties
- High Aspect Ratio (length = ~1000 x diameter)

CNTs can be highly conducting, and hence can be said to be metallic. Their conductivity has been shown to be a function of their chirality,
the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior. Conductivity in MWNTs is quite complex. Furthermore, interwall reactions within multi walled nanotubes have been found to redistribute the current over individual tubes non-uniformly. The properties of SWNTs shown in Table 1.3, describes the comparison with best known materials.

Table 1.3 Properties of single-walled carbon nanotubes

<table>
<thead>
<tr>
<th>Property</th>
<th>Single walled carbon nanotubes</th>
<th>By comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>0.4 to 1.8 nm in diameter</td>
<td>Electron beam lithography can create lines 50 nm wide, a few nm thick</td>
</tr>
<tr>
<td>Density</td>
<td>1.33 to 1.40 g/cm³</td>
<td>Aluminum has a density of 2.7 g/cm³</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>45 billion Pascal</td>
<td>High-strength steel alloys break at about 2 billion Pascal</td>
</tr>
<tr>
<td>Resilience</td>
<td>Can be bent at large angles and restraightened without damage</td>
<td>Metals and carbon fibers fracture at grain boundaries</td>
</tr>
<tr>
<td>Current carrying capacity</td>
<td>Estimated at 1 billion A/cm²²</td>
<td>Copper wires burn out at about 1 million A/cm²²</td>
</tr>
<tr>
<td>Field emission</td>
<td>Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart</td>
<td>Molybdenum tips require fields of 50 to 100 V/µm and have very limited lifetimes</td>
</tr>
<tr>
<td>Heat transmission</td>
<td>Predicted to be as high as 6,000 W/m-K at room temperature</td>
<td>Nearly pure diamond transmits 3,320 W/m-K</td>
</tr>
<tr>
<td>Temperature stability</td>
<td>Stable up to 2,800°C in vacuum, 750°C in air</td>
<td>Metal wires in micro chips melt at 600-1000°C</td>
</tr>
<tr>
<td>Cost</td>
<td>$ 1,500 per gram from Bucky USA in Houston</td>
<td>Gold was selling for about $10/g</td>
</tr>
</tbody>
</table>
NTs are extremely flexible; a SWNT can be bent into an arc with a radius of curvature as small as 20 nm (Dresselhaus et al 1996). Therefore, these materials are expected to possess additional interesting electronic, mechanic and molecular properties. Especially in the beginning, all theoretical studies on carbon nanotubes focused on the influence of the nearly one-dimensional structure on molecular and electronic properties. Both type and diameter are important. The wider the diameter of the nanotube, the more it behaves like graphite. The narrower the diameter of the nanotube, the more its intrinsic properties depends upon its specific type. The Young’s modulus of multi-wall nanotubes is about 1 TPa (Harris 1999). Carbon nanotubes are about 100 times stronger than steel per unit weight.

1.2.6 Applications of carbon nanotubes

The most eye-catching features of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to future applications. Especially, the possibility as an efficient electron source attracts attention because of the thin needle shape. The technology is almost in practical use in the flat panel display industry and in the future, because of its crystal completeness and miniature structure. Carbon nanotube technology is applied to fuel cells, absorbents, sensors, lightweight and high-strength raw material and medicine etc. CNTs can be used as catalyst supports due to their high surface area and the ability of chemical species to attach on their sidewalls. CNTs today are available for industrial applications in bulk quantities up metric ton quantities from Cheap Tubes Incorporation and CAER, University of Kentucky, USA. Several CNT manufacturers have >100 ton per year production capacity for multi-walled nanotubes.

Carbon nanotubes possess many unique properties which make them ideal AFM probes. Their high aspect ratio provides faithful imaging of deep trenches, while good resolution is retained due to their nanometer-scale
diameter. These geometrical factors also lead to reduced tip-sample adhesion, which allows gentler imaging. Nanotubes elastically buckle rather than break when deformed, which results in highly robust probes.

Some commercial products on the market today utilizing CNTs include stain resistant textiles, CNT reinforced tennis rackets and baseball bats. Companies like Kraft foods are heavily funding CNT based plastic packaging. Food will stay fresh longer if the packaging is less permeable to atmosphere. Coors Brewing Company has developed new plastic beer bottles that stay cold for longer periods of time. Samsung already has CNT based flat panel displays on the market. Samsung uses align SWNTs in the transparent conductive layer of their display manufacturing process.

CNTs have the intrinsic characteristics desired in material used as electrodes in batteries and capacitors, two technologies of rapidly increasing importance. CNTs have a tremendously high surface area, good electrical conductivity, and very importantly, their linear geometry makes their surface highly accessible to the electrolyte. Research has shown that CNTs have the highest reversible capacity of any carbon material for use in lithium ion batteries (Gao et al 2000).

The exploration of CNTs in biomedical applications is just underway, but has significant potential. Since a large part of the human body consists of carbon, it is generally thought of as a very biocompatible material. The ability to functionalize the sidewalls of NTs also leads to biomedical applications such as neuron growth and regeneration (Dwyer et al 2002). The oxidized single walled nanohorns (SWNH) and nanofoams, entrap cisplatin, an anticancer agent. Cisplatin-incorporated oxidized SWNHs acts as a potential drug delivery system (Ajima et al 2005).
1.3 SYNTHESIS OF CARBON NANOTUBES

There are a number of methods of synthesizing CNTs. They are arc discharge, laser ablation, chemical vapor deposition (CVD), diffusion flame synthesis, electrolysis, use of solar energy, heat treatment of a polymer, and low-temperature solid pyrolysis. In the case of nanotubes, CVD is very different from the other two common methods used for nanotube production, namely arc discharge (Ebbesen and Ajayan 1992, Journet et al 1997) and laser ablation (Thess et al 1996). Arc discharge and laser ablation can be classified as high temperature (>2700°C) and short time reaction (microseconds-milliseconds), whereas catalytic chemical vapor deposition (CCVD) is a medium temperature (500-1100°C) and long time reaction (typically minutes to hours). Although carbon filaments/nanofiber growth by CCVD was established in the 1960s-1980 (Baker et al 1972, Endo 1988, Baker and Harris 1978), much of the fundamental work on the properties of nanotubes in the early 1990s was performed on nanotubes produced by arc discharge and laser ablation because of their superior straightness and crystallinity due to the high temperature deposition. The main technological drawbacks with arc discharge and laser ablation were that the nanotubes had to be produced separately (i.e., not directly on substrates), purified, and then manipulated onto substrates before use. A major advantage of CVD is that the NTs/nanofibers can be used directly without further purification unless the catalyst particle is required to be removed.

1.3.1 Chemical vapor deposition method

Catalytic CVD is an extremely versatile technique for the production of CNTs and CNFs. From 1998 onward, substantial and rapid progress was made in the development of CVD to establish it as a highly controlled technology for the production of CNTs and nanofibers: today, it is possible to fabricate high quality SWNTs (Kong et al 1998, Hafner et al 1998)
or MWNTs (Hernadi 2002), horizontally (Zhang et al 2001, Ural et al 2002 )
or vertically aligned CNTs (Ren et al 1998, Li et al 1996), as an individual
NTs (Ren et al 1999, Merkulov et al 2000), with controlled diameter (An et al
2002) and length (Dai et al 1999). No vacuum or pumping facilities needed
in most cases, the apparatus becomes relatively simple with fast recycling
time. The advantages of CVD method are as follows:

- Deposition rates are generally higher.
- Deposition of compounds and controlling their stoichiometry is
  relatively easy.
- Doping of the deposit with controlled amounts of impurities is
  fairly easy.
- Deposition of refractory materials is easy at relatively low
  temperature.
- Epitaxial layers are possible.
- Insitu chemical vapor cleaning of the substrate/system is
  possible.

In its simplest form, it is a heated quartz tube in which the
substrates/catalyst is placed. The reactant gases are flowed over the
substrates/catalyst which sits in a removable ceramic boat/holder in the center
of the quartz tube. The horizontal furnace is advantageous because there is no
(or small) temperature gradient within the heated zone (Dai et al 1996). In
most cases the length of the NTs/NFs can be controlled by the length of the
deposition time. When samples are first put into the chamber, the quartz tube
is first flushed with a “carrier” gas. The most popular carrier gases are argon,
hydrogen and nitrogen (Colomer et al 1999, Terrones et al 1997). The furnace
is then heated up to the growth temperature in the inert atmosphere. Hydrogen
is often added to the gas flow to reduce the catalyst particles (e.g., oxides)
during heating. When the growth temperature is reached, the carbon feedstock is introduced. The amorphous carbon is deposited from the thermal decomposition (pyrolysis) of the carbon feedstock gas, whereas CNTs/CNFs are grown from the catalytic decomposition of the carbon feedstock gas. In most cases, “clean” (i.e., amorphous carbon-free) growth of highly crystallized structure is desired and hence the highest deposition temperature without significant self-decomposition of the carbon feedstock is preferred.

1.3.2 Purification of carbon nanotubes

Purification of CNTs generally refers to the separation of CNTs from other entities, such as carbon nanoparticles, amorphous carbon, residual catalyst, and other unwanted species. Three basic methods have been used with varying degrees of success, namely gas-phase, liquid-phase, and intercalation methods.

A new gas-phase method has been developed at the NASA Glenn Research Center to purify gram-scale quantities of single-wall CNTs. This method uses a combination of high-temperature oxidations and repeated extractions with nitric and hydrochloric acid. This improved procedure significantly reduces the amount of impurities such as residual catalyst, and non-nanotube forms of carbon within the CNTs, increasing their stability significantly. One of the efficient methods is oxidation in air at temperatures around 750°C (Tsang et al 1993). Oxidation period is highly important to prevent burning off of the pure nanotubes.

Liquid-phase oxidation using KMnO₄/H₂SO₄ solution is one of the purification methods (Ajayan et al 1993). Extremely pure carbon nanotubes can be obtained by this method, but the final nanotubes may be severely damaged. Graphite intercalation, another purification method showed that the resistance to bromination of carbon nanotubes was better than the carbon
nanoparticles (Chen et al 1996). Hou et al (2002) derived an efficient technique for purification stage. They improved a multi-step purification process including bromination mechanism using bromine water, which could remove undesired impurities with an improved yield. Strong et al (2003) developed an easy and inexpensive method of purifying SWNTs. The method includes oxidative heat treatment and following acid washing. Cheng et al (2000) developed a procedure for purifying SWNTs synthesized by the catalytic decomposition of hydrocarbons. The characterization results revealed that amorphous carbon, catalyst particles, vapor-grown carbon nanofibers and multi-walled carbon nanotubes were removed from the single-walled carbon nanotubes without damaging SWNTs. The yield of SWNTs was 40%, and the purity was about 95% after purification.

Chattopadhyay et al (2002) applied a purification process including a sonication-mediated treatment of obtained SWNT soot in a one-to-one mixture of hydrofluoric and nitric acids. Bougrine et al (1999) reported their purification process for SWNT synthesis as hot water treatment, partial oxidation at 700°C and following oxide dissolving by HCl. To remove surface oxygen from nanotube materials, high temperature annealing was suggested subsequent to oxidative purification (Ebbesen 1997). Andrews et al (2001) also suggested high temperature annealing, so called graphitization, is effective in removing both the catalyst particles as well as microstructural defects within the nanotube.

Biro et al (2002) applied wet and dry chemical purification for the removal of unwanted carbonaceous products and of the catalyst particles. Wet oxidation is found to be effective in achieving both goals and produces a relatively moderate damage of the outer wall of the nanotubes. The catalyst particles encapsulated in the central channel of the carbon nanotubes cannot be removed even if repeated treatments are applied.
1.4 GROWTH MECHANISMS OF CARBON NANOTUBES

Understanding the mechanisms of carbon deposition in CVD from light hydrocarbons has been a challenge from the very beginning. There are several mechanisms proposed for the deposition of carbon (Bokros 1965, Je and Lee 1984, Murphy and Carroll 1992, Shi et al 1997). NT growth on catalyst particles has similarities to traditional gas-solid interaction processes such as thin film deposition on substrate by CVD. The following sequences of steps are involved:

- Diffusion of precursor(s) through a thin boundary layer to the substrate
- Adsorption of reactive species onto the particle surface
- Surface reactions leading to NT formation and gaseous by-products
- Desorption of gaseous product species from the surface
- Diffusion of out gassing species through the boundary layer into the bulk stream.

The most commonly accepted mechanism was postulated by Baker et al (1972) in the early 1970s, who explained the growth of carbon filaments by the catalytic decomposition of carbon feedstock and bulk diffusion of carbon. According to this mechanism, the hydrocarbon gas decomposes on the front-exposed surfaces of the metal particle to release hydrogen and carbon, which dissolve in the particle. The dissolved carbon diffuses through the particle and is precipitated at the trailing end to form the body of the carbon filament. Due to the exothermic decomposition of hydrocarbons, it is believed that a temperature gradient exists across the catalyst particle. Since the solubility of carbon in a metal is temperature dependent, precipitation of
excess carbon will occur at the colder zone behind the particle, thus allowing the solid filament to grow with the same diameter as the width of the catalyst particle. Such a process will continue until the leading tip of the catalyst particle is “poisoned” or deactivated. A common cause of catalyst poisoning is the formation of carbon around it, thus preventing the gas from reaching the catalyst particle. The rate limiting step in the growth is believed to be the diffusion of carbon through the catalyst.

Instead of bulk diffusion, another common growth model is a catalytic process involving the surface diffusion of carbon around the metal particle (Baird et al. 1974, Oberlin et al. 1976). The carbon atoms diffuse over the catalyst surface to form a tubular structure which emanates from the circumference of the catalyst. The tubular structure is favored for carbon filaments with nanometric diameters. A single graphene layer of finite size has many dangling bonds which corresponds to high energy states, and for such a small structure, there would be an enormous percentage of dangling bonds if stacked planar graphite was formed (Dresselhaus and Endo 2001). By the formation of closed tubular carbon shells, the total energy of the system is reduced (Tibbetts 1984).

1.4.1 Tip-growth and base-growth mechanism

There are two growth modes, tip and base-growth modes in CNT synthesis. In the tip-growth mode, the catalytic particles are detached from the substrate and move upward at the top of the growing tubes. On the other hand, in the base-growth mode, the CNTs are stuck on the substrate and remain at the root of the CNTs which are shown in Figure 1.8. The difference in the growth mode observed among the growth methods, however, may be simultaneously explained by the terms of the contact force between the catalyst particle and the substrate (Rodriguez 2000). A weak catalyst-substrate adhesion promotes the tip-growth mode while a strong adhesion promotes the
base-growth mode. Baker et al (1972) arrived this mechanism for carbon filament growth based on temperature dependent growth rates, activation energy for various steps, and electron microscopy observations.

![Visualization of a possible carbon nanotube growth mechanism](image)

**Figure 1.8 Visualization of a possible carbon nanotube growth mechanism**

### 1.4.2 Yarmulke mechanism

An alternative model based on the minimization of surface energy of nanoparticles was suggested by Dai et al (1996). Nanoparticles contain a very high percentage of surface atoms; as a result large amount of surface energy exists. Excess carbon can help solve this problem by assembling a graphene cap on the particle surface, called a “yarmulke”, with its edges strongly chemisorbed to the metal. Since the basal plane of graphite has an extremely low surface energy (10-20 times smaller than most metals), the total surface energy diminishes. A crucial feature of the yarmulke mechanism was its avoidance at all stages of growth of any open graphene edges, which
would expose energetically costly dangling bonds. It also provides an automatic solution to forming caps and resulting structure are tubes which have no seams. Carbon can add to the cylindrical section of a growing layer. Once the smallest yarmulke has formed, insertion of new carbon between the tube edge and the catalytic particle is the best solution, as long as complete over coating of the particle (i.e., encapsulation) is avoided which would deactivate it.

1.5 FACTORS INFLUENCING CARBON NANOTUBE GROWTH

The nature and yield of the carbon deposit obtained in the reaction are controlled by varying different parameters such as nature of the catalytic metals and their supports, hydrocarbon sources, gas flows, reaction temperature, and reaction time, etc. By selecting proper conditions, both the physical (e.g. length, shape, and diameter) and chemical properties (e.g. defects, graphitization) of CNTs can be designed in advance.

1.5.1 Carbon precursor

The choice of the carbon feedstock also affects the growth of CNTs. Baker et al (1972) reported that unsaturated hydrocarbons such as C\textsubscript{2}H\textsubscript{2} had much higher yields and higher deposition rates than saturated gases. They also observed that saturated carbon gases tend to produce highly graphitized filaments with fewer walls compared with unsaturated gases. Thus, hydrocarbons such as C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{4} and CO are commonly used for SWNT growth (Kong et al 1998, Dai et al 1996, Kitiyanan et al 2000, Colomer et al 2000, Alvarez et al 2001), whereas hydrocarbons such as C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{6}H\textsubscript{6}, which are unsaturated and thus have high carbon content, are typically used for MWNT growth (Williems et al 2000, Dai et al 1999). Dai et al (1996) first synthesized SWNTs by CVD on a Mo/Al\textsubscript{2}O\textsubscript{3} catalyst with CO as
the carbon feedstock at 1200°C, but the yield was very low. Mo particles were found to be localized at the tips of the SWNTs (1-5 nm).

Maruyama et al (2002) have developed a method of producing high-quality SWNTs that uses alcohol as a carbon feedstock. This method performs well not only for the mass production of SWNTs, but also for the direct synthesis of SWNTs on non-metallic substrates such as silicon and quartz. Li et al (2002) synthesized carbon nanotubes with nanocrystalline Ni/metallic oxide catalyst from decomposition of methane. When the reaction temperature is higher than 720°C, carbon nanotubes can be obtained. Gulino et al (2005) used ethane as carbon precursor over Fe/Al₂O₃ catalyst in large scale synthesis of carbon nanotubes. They showed that ethane is an effective carbon source to produce high-yield MWNTs. Most widely used carbon precursors are acetylene (Sinha et al 2000, Mukhopadhyay et al 1999), methane (Su et al 2000, Zhu et al 2003a), ethanol (Okazaki and Shinohara 2003, Ortega-Cervantez et al 2005), 2-propanol (Okazaki and Shinohara 2003), ethylene (Jia et al 1999), and toluene (Singh et al 2003). Recently, Qiu et al (2004) showed that coal gas is an effective carbon source to synthesize single-walled carbon nanotubes with ferrocene catalyst by CVD method. Pradhan and Sharon (2002) studied on carbon nanotube synthesis with kerosene, which consist of many small- and long-chain aliphatic and aromatic compounds, as the carbon source.

1.5.2 Synthesis condition

The most common conditions (flow rates, reaction temperature and time) that have been reported for CVD method in the literature for CNT production using acetylene are 10 mL/min, 700°C and 1 hr respectively (Hernadi et al 1996 and Mukhopadhyay et al 1999). Generally continuous inert gas flow is supplied to the reaction chamber. Reaction time and temperature, and gas flow rates of carbon source and inert gas are also
important factors to optimize the carbon nanotube synthesis conditions and product quality (Ortega-Cervantez et al 2005). These parameters are adjusted so that the experimental conditions are optimized. Synthesized carbon nanotube/used catalyst weight ratio, and the weight ratio of the synthesized carbon nanotube to carbon nanotube after purification (e.g., removal of undesired amorphous carbon) are important indications of the quality of the produced carbon nanotubes. Most widely used inert gases are argon and nitrogen with a flow rate of around 100 mL/min. Sometimes inert gas is changed with hydrogen gas to reduce the oxygen content in the reaction environment (Zhu et al 2003a).

It is reported that lower synthesis temperatures than optimum synthesis temperature result in lower carbon nanotube yield in the product (Sinha et al 2000). It is also reported that the reaction temperature plays an important role in the alignment properties and diameter of the synthesized nanotubes (Singh et al 2003). Generally, carbon nanotube growth temperature (or reaction temperature) used is between 550°C and 1000°C, and the reaction temperature may vary according to the catalyst-support material pair. Zhu et al (2003b) synthesized carbon nanotubes on graphite fibers by thermal CVD. They showed that carbon nanotubes could only be grown in a limited temperature range. At low growth temperatures, only a carbon layer is formed on the fiber surface. However, at high temperatures, the diffusion rate of iron particles into carbon fibers was enhanced and the nanotube growth possibility reduced.

The amorphous carbon is deposited due to the decomposition of the hydrocarbon gases used. Some attempts have been made to prevent the formation of amorphous carbon such as the addition of hydrogen (which etches amorphous carbon) into the deposition process together with the hydrocarbon gas or by performing growth at very high gas pressures (> 1atm),
which would inhibit the carbon species from sticking to the substrates as the size of the catalyst tends to become nanoparticle, and therefore prevent the accumulation of carbon.

1.5.3 Support material

It has been found that a single metal and mixture of metals supported on oxides, clays or zeolites have great contribution in terms of catalytic activity to nanotube synthesis (Rakov 2001, Thaib et al 1999, Konya et al 1999, Willems et al 2000). Dispersion and stabilization of the metallic catalyst materials can also be performed by using a number of oxides and mixed oxides (Alvin 1987). It is well known that the catalytic properties of the catalyst-support material combination strongly depend on the interaction between catalyst and the support material (Nagaraju et al 2002). Zhu et al (2003a) used Fe and Co salts as the catalyst on mesoporous silica. They suggested that mesoporous silica might play a templating role in guiding the initial nanotube growth, and also pointed catalyst/support ratio. Instead of single metal catalysts, Co/Mo, Co/V and Co/Fe mixtures supported by either zeolite or alumina have also been used catalysts to decompose C\textsubscript{2}H\textsubscript{2} to produce MWNTs (Williems et al 2000). Su et al (2000) improved the CVD method for SWNT preparation and achieved high-quality SWNTs, greater than 200\% the weight of the catalyst. They attributed their improvement to the strong interactions between the aerogel support and the Fe/Mo catalyst as well as the high surface area of the support. Fonseca et al (1996) produced large amounts of MWNTs by catalytic deposition of C\textsubscript{2}H\textsubscript{2} over Co and Fe catalysts supported on silica or zeolite.

Colomer et al (2000) obtained a product with high yields (70-80\%) of SWNTs by catalytic decomposition of H\textsubscript{2}/CH\textsubscript{4} mixture over well-dispersed metal particles (Co, Ni, Fe) on MgO at 1000\°C. The MgO based support is easily removed by mild acidic treatment that does not damage the CNTs.
Hernadi et al (2002) used several catalyst supports such as silica gel, zeolites and alumina with different pore diameter was tested in acetylene decomposition. Gournis et al (2002) synthesized carbon nanotubes by catalytic decomposition of acetylene over iron-catalyst centers supported on montmorillonite surfaces by ion-exchange. Carbon nanotubes rooted on the clay layers and exhibited various relative orientations and many bridged different clay platelets. The clay in the carbon-modified solid maintains its exchange properties. As a new approach, Higashi et al (2005) synthesized thick carbon nanotubes (80–130 nm) on Pd-loaded diamond catalyst.

Ortega-Cervantes et al (2005) synthesized carbon nanotubes on different substrate materials; quartz, conductive glass, porous alumina and nickel plates, using Fe and Co catalysts and ethanol as the carbon source. Successive nanotube growths were achieved on conducting glass, nickel plates and porous alumina substrates. Nickel plate and porous alumina substrates revealed SWNTs, whereas conducting glass substrate revealed MWNTs. Another approach was synthesizing carbon nanotubes using commercial Al₂O₃ pellets with some nickel concentrations (Makris et al 2005). It is essential to use a proper support material that can be soluble in a solution where carbon nanotubes are not soluble (Sinha et al 2000).

1.5.4 Catalysts

Most of carbon nanotube synthesis techniques require the introduction of catalyst in the form of gas particulates or as a solid support. The selection of a metallic catalyst may affect the growth and morphology of the nanotubes. Seo et al (2004) compared the catalytic activity of Fe, Co, or Ni as the catalyst, and laser treated vanadium plates having high surface area as the catalyst support in the decomposition of acetylene at 720°C under CVD conditions. Best quality carbon nanotubes were obtained over the iron catalyst with high density and small diameter (10–15 nm). Over nickel and cobalt
catalysts, the carbon source was mainly converted to amorphous or fiber-like material. Lee et al (2002) showed that carbon nanotubes can be produced effectively with tungsten-based catalysts. The resulted carbon nanotubes were well-aligned, multi-walled structure and highly pure. Yokomichi et al (2002) studied on the catalytic effects of several coatings with $\text{M(NO}_3\text{)}_{\text{n}}\cdot\text{mH}_2\text{O}$, where $\text{M} = \text{Al, Mg, Mn, Cu, Zn, Fe, Co, and Ni}$, in terms of yield of nanotube formation. The results showed that the yield of nanotube formation significantly depends on M and can be explained in terms of reducing tendency of the catalysts, as well as the size of the catalyst nanoparticles. It has been observed that nickel-catalyzed decomposition of $\text{CH}_4$ and $\text{H}_2$ helps the growth of CNTs at 600°C better than either 500°C or 700°C. In general, admixtures of Li, Cu, Ag, Zn, Cd, B, Al, In, Y, La, Si, Ge, Sn, Ti, Hf, Pb, Bi, S, Se, Cr, W, Mn, Ru, Pd, Pt, mixtures of two metals or of a metal with a nonmetal, and several carbides and oxides have been tested as catalyst (Seraphin and Zhou 1994, Loiseau and Pascard 1996). Qian et al (2003) investigated the activity of such kind of carbon nanotubes for methane decomposition. Their results showed that, with iron and molybdenum containing nanotubes, the conversion of methane increased steadily with temperature. The results were more promising than the experiments with nickel catalyst.

The size of the catalyst is probably the most important parameter for the nucleation of SWNTs. Li et al (2001a) prepared catalyst nanoparticles of uniform diameters (between 3 to 14 nm) by thermal decomposition of metal carbonyl complexes using a mixture of long-chain carboxylic acid and long-chain amine as protective agents. Their results indicate that the upper limit for SWNT growth occurred at catalyst sizes between 4 and 8 nm. Smaller nanoparticles ($\leq$1.8 nm) were more active in producing SWNTs, while nanoparticles with diameters of ~7 nm did not show SWNTs growth. Cheung et al (2002) prepared monodispersed nanoclusters of Fe with diameters of 3, 9
and 13 nm. After growth using C₂H₄, SWNT and DWNT nanotubes were nucleated from the 3 and 9 nm diameter nanoclusters respectively, whereas only MWNTs were observed from the 13 nm nanoclusters. These works clearly suggest that SWNTs are favored when the catalyst particle size is ~5 nm or less.


Large amounts of CNTs can be formed by catalytic CVD of acetylene over cobalt and iron catalysts supported on silica or zeolite (Zhang et al 1999, Ciambelli et al 2005). The carbon deposition activity seems to relate to the cobalt content of the catalyst, whereas the CNTs’ selectivity seems to be a function of the pH in catalyst preparation. Fullerenes and bundles of SWNTs were also found among the MWNTs produced on the carbon/zeolite catalyst. Hernadi et al (1996) reported that CNT could be catalytically synthesized easily using Fe-loading microporous molecular sieve zeolites (NaY, HY and ZSM-5) as catalyst supports. The formation of single-layer nanotubes that could penetrate the nano-pore openings of zeolite Y (which have a diameter of 7.4 Å) was reported to be unfavorable. The carbon nanotubes formed were MWNTs and they were reported to be grown only on the external surface of the catalyst support.

The CNT were proposed to grow over the external surface of the supports and, therefore, the growth directions are still random and the pore sizes are not narrowly distributed. The limited number of applications is related to the lack of mesopores in the zeolite crystals that only contain
intracrystalline micropores (<2 nm diameter). Therefore, only a fraction of the active sites in the zeolites is effectively used for catalytic conversions. Additionally, the desired product has a high probability of undergoing secondary reactions during diffusion in the zeolite micropores, and the result is low selectivity (Schmidt et al 2001). The mesoporous molecular sieves such as M41S materials are a kind of new catalyst supports with many interesting properties. Since zeotypes and other molecular sieves including mesoporous material possess several attractive characteristics such as high surface area and periodic arrays of uniform pores, they can be used as synthesis template for CNTs with regular pore structure. Recently, there are several reports of formation of carbon nanotubes over these mesoporous MCM-41 materials (Amama et al 2005, Yang et al 2005, Katok et al 2006, Yang et al 2003, Ramesh et al 2006 and Somanathan et al 2006).

1.6 M41S FAMILY

M41S materials possess a large uniform pore structure with high surface area and pore volume, resulting worldwide resurgence in this field. One of the most important characteristics of the synthesis of this new family of materials is the liquid crystal templating mechanism. Mobil researchers reported the first family of highly ordered mesoporous molecular sieves by using long chain cationic surfactants as the template or pore forming agent during the hydrothermal sol-gel synthesis. Depending on the synthesis conditions, the materials consist of a hexagonal phase (p6mm) known as MCM-41, a cubic phase (Ia3d) known as MCM-48 and a non-stable lamellar phase known as MCM-50. These three different mesophase of M41S family are shown in Figure 1.9 (Biz and Occelli 1998).
1.6.1 Synthesis Mechanisms of Mesoporous Materials

The synthesis of mesoporous materials is based on the ability of surfactant molecules to form spherical or cylindrical micelles or even higher order phases in aqueous solution. Surfactants are large, organic molecules with a hydrophilic head and a long hydrophobic alkyl tail of variable length. In aqueous solution, these species aggregate their hydrophobic tails together and expose their polar head to the solution in order to reach the minimum energy configuration (Israelachvili 1994, Davis 1994). The micelles thus formed are in dynamic equilibrium with soluble surfactant molecules. The first critical micelle concentration (cmc1) is defined as the lowest concentration at which spherical micelle formation may be observed. The second critical micelle concentration (cmc2) is the concentration at which the transformation is strongly dependent on temperature, anion degree of dissociation and the length of the surfactant alkyl chain (Huo et al 1994a). As the temperature increases, the required concentration for a sphere to rod transformation increases as well.
1.6.1.1 Mobil hypotheses

The researchers at Mobil proposed two synthesis mechanisms to explain the formation of MCM-41 materials (Kresge et al 1992, Beck et al 1992). In the first route, the surfactant hexagonal liquid-crystal phase forms first and directs the growth of the inorganic materials. The $C_nH_{2n+1}(CH_3)_3N^+$ surfactant micelles aggregate into hexagonal arrays of rods. Silicate or aluminate anions present in the reaction mixture interact with the surfactant cationic head groups. Condensation of the silicate species leads to the formation of an inorganic polymer. Upon calcination, the organic template is burned off, leaving inorganic hollow cylinders in a hexagonal arrangement. However, this synthesis pathway did not meet much support in the literature. Cheng et al (1995) pointed out that the hexagonal liquid-crystal phase in the $C_{16}TMACl$- water system at 25°C does not form unless the concentration of $C_{16}TMACl$ exceeds 40%. At lower concentration, only micelles exist in solution. Since MCM-41 may be formed at surfactant concentrations as low as 1 wt% with respect to water content, the model according to which the hexagonal liquid crystal formed first was questioned. Apart from that, in situ $^{14}$N-NMR spectra revealed that the hexagonal liquid-crystalline phase was not present at any time during MCM-41 formation (Chen et al 1993a). Thus, the first synthesis scheme proposed by Beck et al (1992) was abandoned.

In the second approach proposed by Mobil researchers, the presence of silicate species in the reaction mixture initiates the hexagonal ordering (Kresge et al 1992, Beck et al 1992). This second route has encountered more acceptances in the literature. Chen et al (1993b) postulated that randomly distributed rod like surfactant micelles form initially and interact with silicate oligomers to generate randomly oriented surfactant micelles surrounded by two or three monolayers of silica. The isotropic in situ $^{14}$N-NMR resonance was found to be consistent with the resonance of rod like micelles in solution,
as anticipated from the concentration and temperature dependent phase behavior of CTMABr. A base catalysed condensation between silicate species on adjacent rods occurs with further heating. It initiates the long-range hexagonal ordering which corresponds to the minimum energy configuration for the packing of the rods. Figure 1.10 illustrates this synthesis mechanism (Beck et al 1992).

**Figure 1.10  Liquid crystal mechanism via two possible pathways**

1.6.1.2 Layered intermediate

Monnier et al (1993) observed the presence of layered material in addition to amorphous silica after the reaction times of the order of 1 min. Transformation mechanism from lamellar to hexagonal phase proposed by Monnier et al (1993) is shown in Figure 1.11. At longer crystallization times, the lamellar intermediate disappeared and the diffraction pattern of the hexagonal structure was detected in the solid product. This intermediate lamellar complex was imaged by transmission electron microscopy (Alfredson et al 1994). The transition from the lamellar to the hexagonal phase was also confirmed by $^1$H-NMR spectra of the surfactant molecules deuterated at the $\alpha$-carbon (Firouzi et al 1995). In order to account for the presence of a layered intermediate, Stucky’s group proposed another synthesis mechanism (Stucky et al 1994, Koyano and Tatsumi 1996). This synthesis mechanism has been supported by a thermodynamic analysis (Huo et al
1994b, Firouzi et al 1997) and accounts for the morphology of the final mesophase. To them, the synthesis of silica based mesophase may be regarded as the formation of lyotropic liquid crystals from a system in which inorganic species are attached to surfactants. Schematically, the formation of nanostructures proceeds through three steps, which are not necessarily sequential. First small silica oligomers compete for the access to the cationic heads of the surfactant. The type of silica species present in the reaction mixture depends on the pH. At high pH (pH > 9.5), large silicate oligomers are completely ionised and are thus expected to bind preferentially to charged surfactant molecules, which may originate from loosely structured micelles or single-solution species. Charged silica species then coordinate electrostatically with the surfactant molecules. Silicate polymerization within the surfactant-silicate interface occurs next.

![Image](image.png)

**Figure 1.11 Phase transformation mechanism from lamellar to hexagonal phase via charge density matching**
It is favored for two reasons: (i) the concentration of silica near the interface is high and (ii) their negative charges is partially screened by the surfactant. The second step is slow and rate limited. Silica polymerization leads to a strong and extended framework with thermal, mechanical and hydrolytic strengths. As polymerization proceeds, the charge density within the inorganic wall decreases and with it, the number of surfactant cations required for charge compensation. In the early stages of the reaction, the presence of highly charged silica oligomers favors small surfactant head groups and surfactant surface with a minimal curvature.

1.6.1.3 Formation Mechanism of MCM-41 through Ionic Surfactant – Inorganic Species Route

The principle methodology can be extrapolated to prepare mesophases with an electrostatic interaction between charged surfactant ions and charged inorganic species in aqueous solution. A number of mechanistic pathways have been proposed to account for the formation of ordered nanophase structure in the form of hexagonal, cubic or lamellar found in these materials from various starting materials under different reaction conditions. Table 1.4 shows four possible routes for the formation of MCM-41 molecular sieves. In route I, the initially discovered pathway by Beck et al (1992), the negatively charged silica species (I⁻) condense and polymerize on the surface of the positively charged micelles (S⁺) giving rise to the corresponding S⁺I⁻ organic-inorganic complex. In route II, anionic surfactants (S⁻) are employed for structuring cationic inorganic species (I⁺) to form S⁻I⁺ mesostructures (Huo et al 1994a). In the case of route III, the co-operative assembly of S⁺H⁻ I⁺ complexes was suggested through the mediation of the counter ions H⁻ (Huo et al 1994b). The S⁺H⁻ I⁺ pathway involves extremely acidic medium, low temperature, short synthesis time and low surfactant concentration. In route IV, a neutral templating synthesis mechanism was proposed based on
hydrogen bonding between neutral primary amines ($S^0$) and neutral inorganic precursors ($I^0$) (Tanev and Pinnavaia 1995).

Table 1.4 Four possible routes for the synthesis of MCM-41 molecular sieves

<table>
<thead>
<tr>
<th>Route $^a$</th>
<th>Typical example</th>
<th>pH</th>
<th>Resulting phase</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I ($S^+I$)</td>
<td>CTMA + silicate species</td>
<td>$&lt; 7$ or 10-13</td>
<td>Hexagonal, cubic and lamellar</td>
<td>Beck et al (1992) and Huo et al (1994b)</td>
</tr>
<tr>
<td>II ($S^+I^-$)</td>
<td>$C_{16}H_{33}SO_3^-$ + lead oxide $C_{12}H_{25}PO_4^{2-}$ + iron oxide</td>
<td>-1 to 5</td>
<td>Hexagonal Lamellar</td>
<td>Huo et al (1994b)</td>
</tr>
<tr>
<td>III ($S^+H^-$)</td>
<td>CTMABr + silicate species</td>
<td>$&lt; 2$</td>
<td>Hexagonal Lamellar</td>
<td>Huo et al (1994b)</td>
</tr>
<tr>
<td>VI ($S^0I^0$)</td>
<td>$C_{12}H_{25}NH_2 + (C_2H_5O)_4Si$</td>
<td>$&lt; 7$</td>
<td>Hexagonal</td>
<td>Tanev and Pinnavaia (1995)</td>
</tr>
</tbody>
</table>

$^a$ $S^+$ = surfactant ions, $I^-$ = anionic inorganic species and $H^-$ = anionic halides

1.7 HETEROATOM SUBSTITUTED MCM-41

Pure siliceous mesoporous molecular sieves possess a neutral framework, which limits their applications. In order to provide molecular sieves with potential catalytic applications, it is possible, as in the case of zeolites, to modify the nature of the framework by introduction of heteroatoms by hydrothermal methods. Besides, other elements can also be incorporated on the surface of the materials by grafting or impregnation. Several synthesis methods have been proposed and successfully used to synthesize mesoporous MCM-41 molecular sieves (Huo et al 1994a, Stucky et al 1994, Schmidt et al 1994, Zhao and Goldfarb 1995, Koyano and Tatsumi...
Kresge et al (1992) first synthesized mesoporous silicates and aluminosilicates in alkaline condition. Huo et al (1994a) reported the first synthesis of porous silicates in acidic condition while Yanagisawa et al (1990) pillared a layered silica with surfactant cations and after calcination obtained a mesoporous silica with uniform distribution of pores.

In order to impart catalytic activity to the chemically inert mesoporous silicate framework, substitution of Si$^{4+}$ ions by other heteroatoms in the MCM-41 structure has been attempted. When trivalent cations like Al$^{3+}$, B$^{3+}$, Ga$^{3+}$ and Fe$^{3+}$ (Tuel and Gontier 1996, Oberhagemann et al 1995, Sayari et al 1995, Liu et al 1996, Cheng et al 1996, Cheng and Klinowski 1996, Yuan et al 1995) substitute for silicon in the walls of the mesoporous silica, the framework possesses negative charges that can be compensated by protons, providing acid sites. The number of acid sites and strength depend on the amount and nature of the incorporated metal. Such materials are used in acidic reactions and have potential applications in various petroleum refining processes (Casci 1994, Sayari 1996).

When other cations like Ti$^{4+}$ and V$^{4+}$ (Kresge et al 1993, Corma et al 1994, Reddy et al 1994, Luan et al 1996) are incorporated, the corresponding mesoporous materials are used in oxidation reactions. The Ti$^{4+}$ and V$^{4+}$ containing MCM-41 molecular sieves have been used in a variety of oxidation reactions of bulky molecules using either O$_2$ or TBHP as oxidant (Corma et al 1994, Tanev et al 1994, Reddy et al 1994, Sayari 1996). A few reports describe the synthesis and characterisation of mesoporous silica modified by metals like Cr (Zhang and Pinnavaia 1996, Ulagappan and Rao 1996) and Mo (Zhang et al 1996). A few reports describe the synthesis and characterization of mesoporous silica modified by metals like Mo (Zhang et al 1996, Piquemal et al 2003) and Nb (Nowak et al 2003). The incorporation of
iron to MCM-41 materials by various methods as well as the evaluation of iron states in various MCM-41 matrices and its catalytic behaviour are reported (Decyk et al 2003).

Synthesis of bimetallic substituted mesoporous silica materials has attracted much attention. Zhou et al (2001) showed that boron is able to promote aluminium to incorporate into the framework of mesoporous MCM-41 molecular sieves. They reported that the crystal structure of B-Al-MCM-41 is more regular than that of Al-MCM-41. Hartmann et al (1996) reported the synthesis of Ni-Al-MCM-41 and carried out ethylene dimerisation at 70°C. Cu and Zn containing MCM-41 mesoporous molecular sieves were characterized by N\textsubscript{2} and CO adsorption and temperature programmed reduction (Hartmann and Kevan 1999). Velu et al (2002) synthesized Cu-MCM-41 and Cu-Zn-MCM-41 at room temperature and their catalytic activity was tested for the selective oxidation of alcohols to aldehydes. It has been reported that bimetallic Al-Zn-MCM-41 is an active catalyst for industrially important alkylation reactions (Selvaraj et al 2002, 2003 and 2004).

1.8 CARBON NANOTUBES OVER MESOPOROUS MCM-41

Quantum structures obtained via confinement allow probing the relations between size and physical, magnetic and chemical properties (Moller and Bein 1998, Ozin 1992). The porosity of MCM-41 makes it an ideal candidate for the loading and encapsulation of metals, metal oxides and semiconductors as well as molecular liquids, e.g. water (Moller and Bein 1998, Wu and Bein 1994, Llewellyn et al 1994). The fascinating materials formed by the encapsulation of graphite-type (Wu and Bein 1994) or polyaniline (Wu et al 1999) wires in the hexagonal channels of MCM-41 were also reported.
A non-exhaustive list of different metals and semiconductor nanostructures have been successfully synthesized within the pore channels of MCM-41 based mesoporous silica template, such as Ag (Park et al 2004), AgI (Kamalakar et al 2003), Au (Fukuoka et al 2002). In the case of copper and silver, composites were reported with monolithic silica with a good propene–propane selectivity ratio and a high propene adsorption capacity (Kargol et al 2005). More recently, Ni-MCM-41 and Co-MCM-41 produced by the same route are used as catalytic templates to synthesize single-wall or multi-wall nanotubes of uniform diameter (Lim et al 2003, Yang et al 2005a, Ciuparu et al 2004, Yang et al 2003, Yang et al 2005b).

Duxiao et al (2001) reported the catalytic formation of CNTs on Fe-loading hexagonal mesoporous molecular sieves Fe/SiHMS and microporous molecular sieve Fe/NaY. The results confirmed that CNTs were grown inside the channels of Fe/SiHMS and on the external surface of Fe/NaY. Since the microporous Fe/NaY zeolite materials possess windows of 0.5-0.7 nm, the CNTs were grown in different directions on the external surface of the supports with different pore size distribution. The tips of CNTs obtained over Fe/SiHMS were all open, which indicated the strong interaction between catalyst particles and support. SiHMS possesses a mesoporous structure and permits the deposition of iron species on its internal surface. NaY only exhibited a microporous channel structure and some channels are even occluded by the deposited iron species or probably formed coke species. The diameter of SWNTs formed was in the range of 1-3 nm.

Hernadi et al (2002) described the synthesis of MWNTs using Fe or Co supported on zeolite and MCM-41, and acetylene as carbon source. Co and Fe (5 wt %) were introduced to the zeolite NaY and MCM-41 support by ion-exchange and impregnation method. The reactions were carried out at
700°C with a flow rate of 300 mL/min of 10 % C2H2 and 90 % N2 for a period of 1 hr. No nanotubes were observed with isomorphic substitution of Co-MCM-41 and only a tiny CNTs formation was observed with ion-exchanged Co-MCM-41.

Urban et al (2002) have synthesized the MWNTs by a novel method of mesoporous MCM-41 and MCM-48 silicates in the absence of any metal traces. TEM study revealed the diameter distribution of CNT formed was very narrow (5-6 nm in diameter and 200 nm in length). The procedure consists of the preparation of mesoporous silicate structure followed by graphitization of organic template molecules. The graphitization time was found to be optimal between 5 and 30 min at 800°C. The quality of CNTs proved to be high, since their length exceeds 200 nm and had a narrow diameter distribution.

Chen et al (2004a) demonstrated the synthesis of SWNTs with uniform diameter by CO disproportionation over Co-MCM-41. The effect of catalyst prereduction and growth temperature were studied. From the results, it is confirmed that the diameter distribution and quality of SWNTs formed with Co-MCM-41 were controlled by cobalt cluster size. A narrow diameter distribution of SWNT diameter was achieved at an optimized prereduction and reaction temperature of 500-600°C and 750-800°C respectively. The catalysts that were excessively reduced prior to exposure of CO, forms SWNTs with a wider diameter distribution.

Chen et al (2004b) also demonstrated the synthesis of SWNTs by CO disproportionation over Co-MCM-41, and studied the influence of CO pressure and duration of catalyst exposure to CO with respect to carbon yield, selectivity and diameter uniformity of SWNTs. The average diameters of bundled SWNTs were 0.68 to 1.38 nm. The selectivity to SWNTs and their diameter uniformity depend on the reduction of Co, nucleation of the reduced Co atoms into clusters, and initiation and growth of the CNTs. At high CO
pressures, high Co reduction rates occur, leading to SWNT with uniform
diameter. The results confirmed the formation of SWNTs with narrow
diameter at high CO pressures with the exposure duration of 30 min.

Amama et al (2005) reported the synthesis of SWNTs over
Fe-substituted MCM-41 molecular sieves using acetylene as carbon source.
Fe-MCM-41 with 2 wt % Fe showed high selectivity for SWNT production
rather than other loadings. The optimized conditions were found to be 60 min
of growth run using a reactant flow rate of 200 mL/min at 800°C. Reduction
of Fe by the hydrogen produced during C₂H₂ decomposition was responsible
for the formation of metallic Fe, which provided the “seeds” for the SWNT
production.

Chen et al (2006) have studied the formation of SWNTs by varying
the percentage loadings of Co (0.5-4 wt%). The state of the catalyst and size
of the metallic cobalt clusters formed in Co-MCM-41 was studied by X-ray
absorption spectroscopy. Co-MCM-41 with up to 3 wt % cobalt loaded was
used as catalyst for the growth of SWNTs with narrow diameter distribution.
The highest cobalt concentration of 4 wt % produced large cobalt particles,
which lead to the growth of graphite. SWNTs with low defects and uniform
diameter was obtained with 3 wt % loaded Co-MCM-41.

Somanathan et al (2006) have studied the catalytic activity of Co-
MCM-41 which are characterized by XRD, nitrogen adsorption and DRS-UV
spectrum, was tested for the synthesis of carbon nanotubes. The synthesized
CNTs were characterized by SEM, TEM and Raman spectrum. The study
confirmed the formation of SWNTs.
1.9 SCOPE OF THE PRESENT INVESTIGATION

With the revolutionary discovery of so-called fullerenes and CNTs different research fields in the domain of carbon experienced an enormous boom. Until now nanotubes could only be synthesized in small quantities or with complicated methods. The CVD method is believed as the most suitable carbon nanotube synthesis method in terms of product purity and large scale production. When the cost of carbon nanotube production comes into account, the first consideration is the synthesis method. As it is mentioned earlier, CVD is the most suitable low-cost mass production technique of carbon nanotubes. In large-scale production, the cost of carbon source also plays an important role in the final product cost. Graphitization of CNTs offers a low-cost and commercially viable purification process by removing the residual metal catalyst in the nanotubes and reducing the defects in the nanotube structure (Andrews et al 2001).

Intensive research activities to improve the synthesis methods and conditions, quality and productivity of the CNTs reached to rewarding conclusions because of their high strength, stiffness, and electrical conductivity. The invention of mesoporous molecular sieves by Mobil researchers in 1992 has given a new direction to the field of porous materials. MCM-41 has salient features such as hexagonal arrangement with uniform channel structure. However, the tunable pore size (15-100 Å), large surface area (∼1200 m² g⁻¹) and moderate acidity are characteristics of MCM-41 silicates. The pore sizes allow catalytic transformations of large molecules to be carried out, which could not diffuse inside the microporous zeolites. Transition metal catalysts can be incorporated into the pore walls of the mesoporous molecular sieves stabilizing dispersed catalytic sites and also exhibit good structural stability. The catalytic site for CNT synthesis is provided by framework substitution with metals. The mesoporosity and the
well-defined pore structure in combination with high surface area make MCM-41 materials as promising candidates for the synthesis of CNTs. In this thesis, catalyst for the nanotube deposition, carbon precursor, synthesis temperature, and reaction time are discussed as the important parameters affecting the quality of the produced carbon nanotubes. Purification of the nanotubes and the synthesis cost are considered as the important industrial parameters. Also the effects of pretreatment of catalyst, hydrocarbon precursor, and nitrogen as inert gas are underlined.

The scope of the present investigation is envisaged below.

- Hydrothermal synthesis of Fe-MCM-41, Fe,Co-MCM-41, Nb-MCM-41, Mo-MCM-41 and Mn-MCM-41 molecular sieves with different Si/M ratios of 25, 50, 75 and 100, where M = Fe, Fe+Co, Nb, Mo and Mn.
- Physico-chemical characterization of the above materials by low-angle X-ray diffraction (XRD), N$_2$ adsorption isotherms, Fourier Transform Infrared (FT-IR) spectroscopy, thermal analysis, Diffuse reflectance UV (DRS-UV) spectroscopy, Scanning electron microscopy (SEM) techniques and Energy dispersive X-ray (EDX) spectroscopy.
- Study of catalytic activities of the above synthesized catalysts for the formation of carbon nanotubes by CVD technique.
- Catalytic synthesis of SWNTs formed over Fe-MCM-41 molecular sieves using acetylene as carbon precursor.
- Highly selective growth of SWNTs using acetylene and nitrogen gas over mesoporous bimetallic Fe,Co-MCM-41 molecular sieves.
Catalytic growth of SWNTs over mesoporous Mo-MCM-41 molecular sieves by CVD technique with acetylene and nitrogen as sources for carbon and carrier gas, respectively.

Selective growth of SWNTs using Nb-MCM-41 as catalytic template with acetylene gas by CVD technique.

Catalytic growth of multi walled carbon nanotubes over mesoporous Mn-MCM-41 molecular sieves.

Separation and purification of the carbon deposits formed over different metal substituted mesoporous MCM-41 by acid treatment.

Characterizations of CNTs by SEM, TEM, Raman spectroscopy, High angle XRD and TGA.

Effect of temperature, flow rate and reaction time were studied over the better catalysts ratio in order to improve the quality and yield of CNTs.