# SYNTHESIS OF CARBON NANOTUBES USING PALM OIL BY THERMAL CVD METHOD

A Dissertation submitted in partial fulfillment
of the requirements for the award of the Degree of

**MASTER OF TECHNOLOGY**

**IN**

**NANOSCIENCE AND TECHNOLOGY**

Submitted by


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**SESSION 2013-2014**

# CERTIFICATE

This is to certify that the dissertation title "**Synthesis of Carbon Nanotubes using Palm Oil by thermal CVD Method"** is the authentic work of **Mr. Amresh Kumar Vishwakarma** under my guidance and supervision in the partial fulfillment of requirement towards the degree of Master of Technology in run by the Department of Applied Physics in **Delhi Technological University.**

| | |
|---|---|
| **Dr. Pawan Kr. Tyagi** | **Prof. S.C. Sharma** |
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| Delhi technological university | Delhi technological university |

# CANDIDATE DECLARATION

I hereby declare that the work presented in this dissertation entitled "**Synthesis of Carbon Nanotubes using Palm Oil by thermal CVD Method**" has been carried out by me under the guidance of **Dr. Pawan Kr. Tyagi**, Assistant Professor, Department of Applied Physics, Delhi Technological University, Delhi and hereby submitted for the partial fulfillment for the award of degree of Master of Technology in Nanoscience and Technology at Applied Physics Department, Delhi Technological University, Delhi.

I further undertake that the work embodied in this major project has not been submitted for the award of any other degree elsewhere.

**Amresh Kr. Vishwakarma**

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M.Tech

*Dedicated to*

*My Family*

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Finally I would like to thank almighty God for his blessings without which nothing is possible in this world.

**Amresh Kr. Vishwakarma**

**Date: -**

**Place:-**

# ABSTRACT

Carbon nanotubes (CNTs) are a new class of materials that have wonderful novel and useful properties. The estimated increase in manufacture makes carbon nanotube more exposing to human being. CNT has a very wide application in electronics due to increasing resistivity of copper with scaling of transistor. Due to the rising demands of current density requirements are needed to identify new wiring solutions for nanometer scale VLSI technologies. Metallic carbon nanotubes have the property that can potentially used the challenges faced by copper and hence extend the lifetime of electrical interconnects. CNTs are also useful in many biomedical applications, and hence their biocompatibility, biodistribution needs to be carefully assessed. Different types of CNTs can be produced in different ways. Most common technique used are arc discharge, laser ablation, CVD and flame synthesis. CNT produced by this method have impurity hence we need to purify it. Purification techniques are oxidation, acid treatment, annealing, sonication, filtering and funcationalisation technique. Economically large scale production and purification techniques still have to be developed.

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# Introduction

## 1.1 INTRODUCTION

Carbon is a IV group element, it has two crystalline forms: diamond and graphite. Carbon nanotubes (CNTs) are allotropes of carbon. It has novel properties that make them useful in many applications in nanotechnology, optics, electronics and materials science. They show surprising strength and unique electrical and thermal properties. Carbon nanotubes (CNTs) are the basic building blocks of nanotechnology. Thermal conductivity of CNTs is much higher than purest form diamond [1]. Its electrical conductivity is also very high greater than conductivity of copper. Its tensile strength is hundred times of steel [2]. It has very huge application but its production in grams seems to be very difficult. Carbon nanotubes are long thin cylinders of carbon and were discovered by lijima`s in 1991. Carbon nanotubes (CNTs) belong to members of fullerene structural family, which have spherical bucky balls like structure. The nature of bonding in carbon nanotubes is described by applied quantum chemistry, i.e. orbital hybridization. The nature of chemical bonding in carbon nanotubes is of $sp^2$ bonds, similar to graphite. This $sp^2$ bonds structure is stronger than the $sp^3$ bonds and hence provides the molecules a unique high strength [3]. Nanotubes will align themselves into “ropes” which is held together by Van der Waals forces. Under high pressure carbon nanotubes can merge together to produce strong, unlimited-length wires through high-pressure nanotubes linking. Carbon nanotubes are the most successful materials and attracting a broad range of scientists and industries due to their attractive physical and chemical properties. This session will explain electronic, mechanical, optical and structural properties of a carbon nanotube for the solution of engineering problems.

## 1.2 Carbon Nanotubes

Name of CNT is derived from their size, since it has diameter in the range of a few nanometers, while its length can be up to several millimeters. CNT can be categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWC  NTs) depending upon the number of walls. Carbon nanotubes consist of hundreds of concentric shells of carbons having separation of 0.34 nm. The network of the shells is closely resembles to the honeycomb arrangement of the carbon atoms in the graphite sheets. The wonderful mechanical and electronic properties of the carbon nanotubes stem in their quasi-one dimensional (1D) structure and the graphite-like arrangement of the carbon atoms in the shells. Hence, the carbon nanotubes have very high Young's modulus and very high tensile strength, which makes CNT suitable for composite materials with improved mechanical and electrical properties. The carbon nanotubes can be of metallic or semi conducting depending on their structural parameters.

Nanotube has received a enormous attention from researchers over the last few years and promises a host of interesting applications. There are many other types of carbon nanotubes, such as inorganic kinds which are made from boron nitride, to organic ones, which are made from self assembling of cyclic peptides (protein components) or from naturally-occurring heat shock proteins (extracted from bacteria that flourish in extreme environments). However, carbon nanotubes promise the greatest variety of applications, and currently appear to have highest commercial potential. Only carbon nanotubes can cover this white paper.

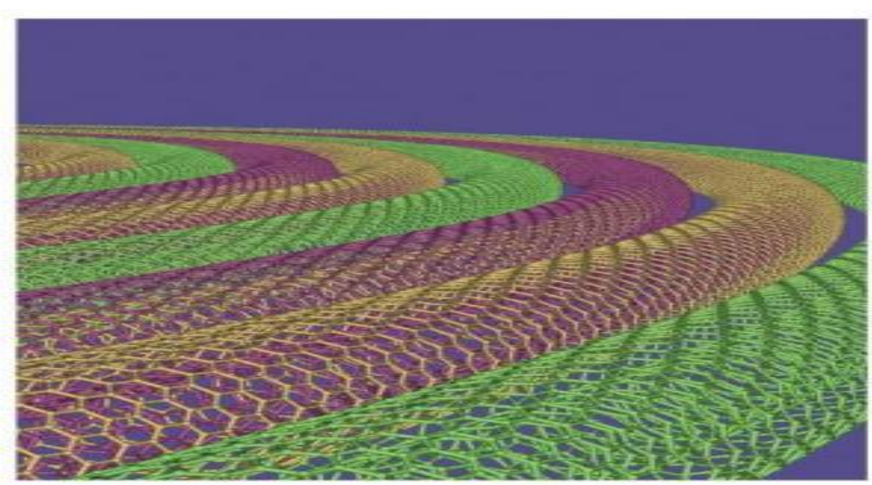


Figure1.1 Carbon nanotubes can cover this white paper [4]

## 1.3 TYPES OF CARBON NANOTUBES

### 1.3.1 Single walled CNTs

Single-wall carbon nanotubes (SWCNTs) are tubes of graphite that are normally capped at the ends.. The structure of a SWNTs can be visualized as a layer of graphite, a single layer of atom thick, called graphene, which is rolled into a cylinder like structure. They have a single cylindrical wall.The minimum diameter of a carbon nanotube is around 0.4 nanometres. An average diameter is around the 1.2 nanometre, depending on the process used to synthesise them.

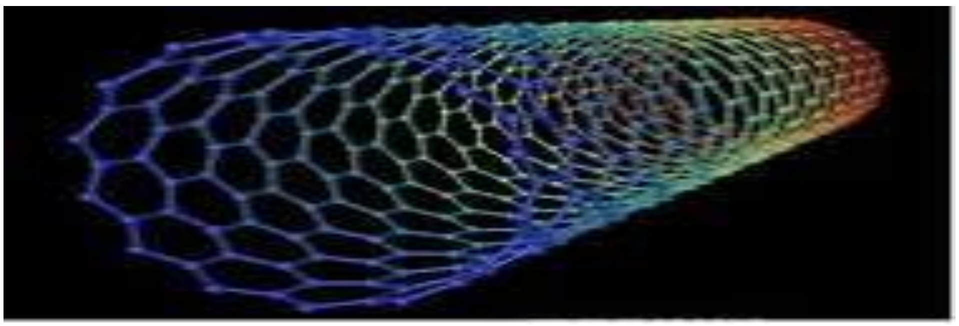


Figure 1.2 Diagram of single wall carbon nanotube [5]

Most SWCNTs typically have a diameter closely equal to 1 nm. However, the tube length can be many thousands of times longer. SWCNTs are more liable yet harder to make than MWCNTs. They can be twisted, flattened, and can be bent into small circles without breaking. SWCNTs have unique electronic, optical and mechanical properties which can be used in many applications, such as field-emission displays, nanosensors, nanocomposite materials and logic elements. These materials are expected to play a major role in the next generation of miniaturized electronics. SWCNTs can be used to make excellent conductors and the most building block of SWCNTs system is the electric wires. One most useful application of SWCNTs is in the development of the first intramolecular field effect transistors (FETs).

### 1.3.2 Structure

The bonding in carbon nanotubes is $sp^2$ hybridized bond, in with each atom joined to other three neighbours. The nanotubes can be considered as rolled-up of graphene sheets (graphene is an individual graphite layer). There are three different ways in which a graphene sheet can be rolled into a cylindrical tube.

The "armchair" and "zig-zag" refer to the collection of hexagons around the circumference. The third class of tube and it is the most common, is known as chiral, which means that it can exist in two mirror-related forms. Example of a chiral nanotube is as shown in figure below.

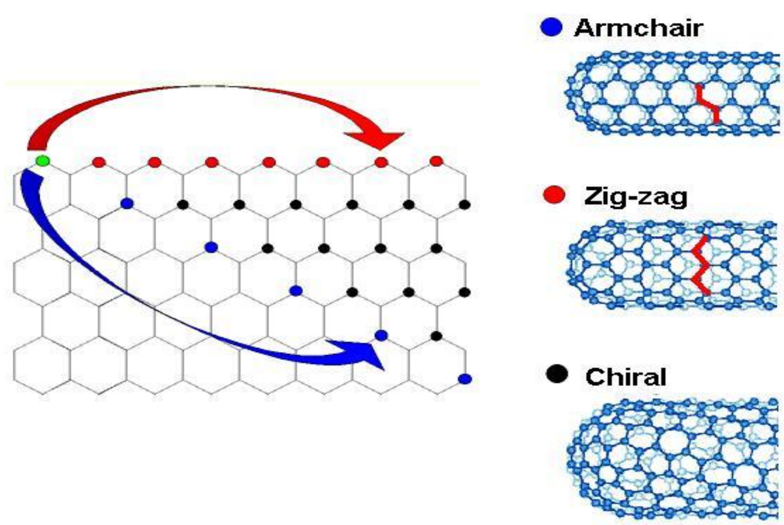



Figure 1.3 Different types of CNT [6]

A carbon nanotube consists of either single cylindrical graphene sheet (single-wall carbon nanotube, SWCNT) or of several concentric cylinders with an interlayer spacing of 0.34 – 0.36 nm which is close to the spacing of turbostratic graphite [7]. There are many other possibilities to form a cylinder with a graphene sheet: one of the simplest way of visualizing this is "**de Heer abacus**". A "de Heer abacus" is used to realize a (n,m) tube, in which move n times $a_1$ and m times $a_2$ from the origin to get to point (n,m) and roll-up these points into the sheet so that the two points coincide [8].

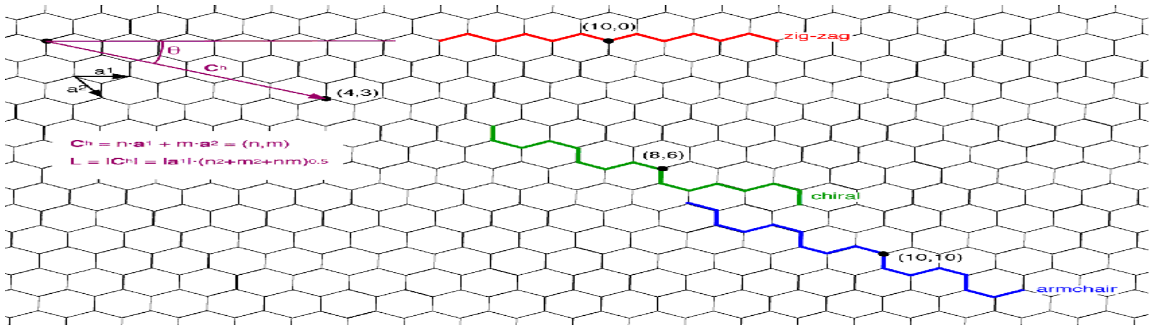



Figure 1.4 Symmetry of different CNT [9]

One can roll up the sheet along one of the symmetry axis which gives either a zig-zag tube or an armchair tube. It is also possible to roll these sinle layer of sheet in such a direction that differs from symmetry axis to obtains a chiral nanotube, in which each unit cell are aligned on a spiral way. Besides the chiral angle, we can also varied the circumference of the cylinder. The CNT can be classified as armchair, zigzag and chiral nanotubes of different diameters [10].

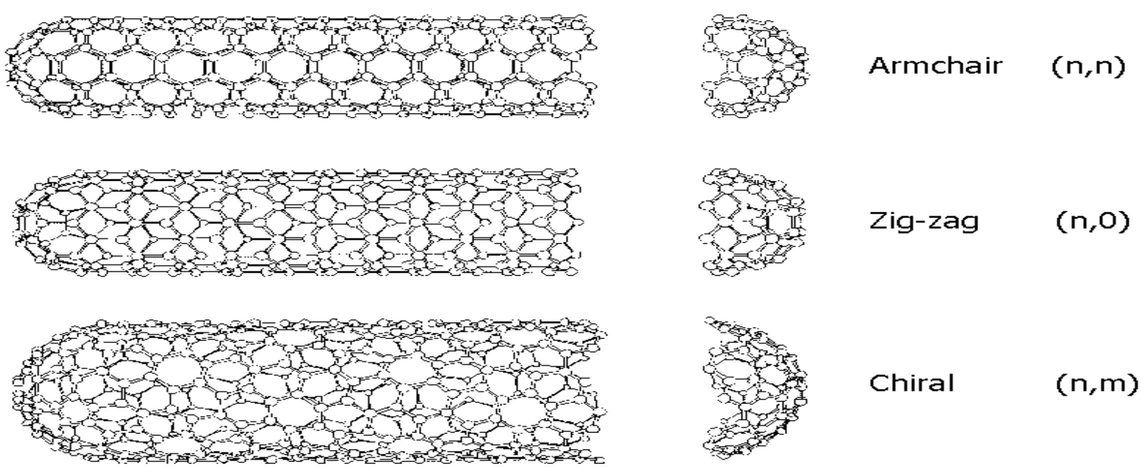



Figure 1.5 Models of different single wall nanotubes [11]

The lengths of SWCNTs and MWCNTs are usually over 1 µm and diameters range from ~1 nm (for SWCNTs) to ~50 nm (for MWCNTs). Perfect SWCNTs are usually closed at both ends by fullerene-like half spheres that contain both pentagons and hexagons. As shown in electron microscopy images below, a SWCNTs has a well-defined spherical tip, whereas the shape of a MWCNTs cap is more polyhedral than spherical. An open

MWCNT doesn't have a cap and the ends of the graphene layers and the internal cavity of the tube are exposed.

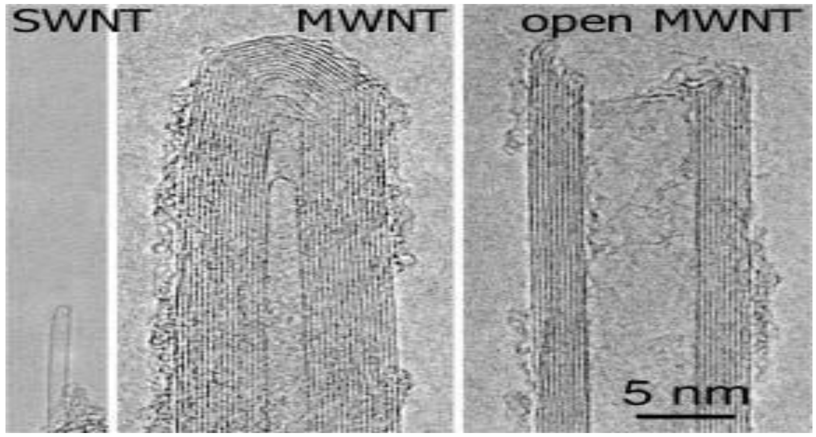



Figure 1.6 Transmission electron microscopy (TEM) images of the ends of different nanotubes. Where black line corresponds to one graphene sheet viewed over edge [12]

Defects are usually present in the form of pentagons and heptagons in the hexagonal lattice. Pentagons are mostly found at the cap and produce a positive curvature of the graphene layer. Heptagons will give raise to a negative curvature at the tube wall. Defects consisting of various pentagons and/or heptagons have also been observed.

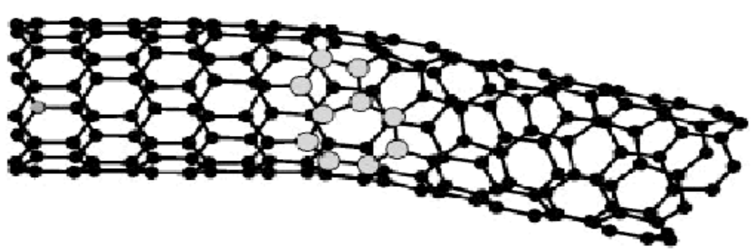


Figure 1.7 Diagram to show defect in CNTs [13]

A simple model shows that the diameter and chirality of the tube are changed from one side of the defect to the other side. Such an arrangement forms a link between two different tubes and is called a junction.

### 1.3.3 Multi-walled CNTs

Multi-walled carbon nanotubes (MWCNTs) consist of multiple rolled of graphene sheets in on themselves to form a tube shape. There are two common models that can be used to explain the structures of multi-walled carbon nanotubes. the Russian Doll model explain that the  sheets of graphite are arranged in concentric cylinders whereas  the Parchment model explain that  a single sheet of graphite is rolled in around itself to resembling a scroll of parchment or a rolled up newspaper. The interlayer distance in MWCNTs is about 0.33 nm.

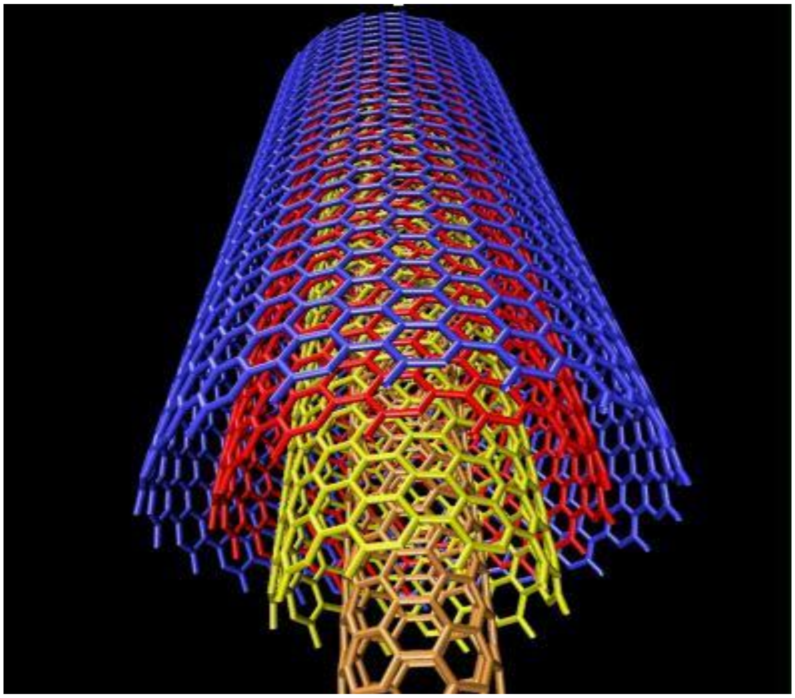


Figure 1.8 Diagram of multiwall carbon nanotube [14]

Although it is easier to synthesis significant quantities of MWCNTs than SWCNTs, but the structure of MWCNTs are less well understood than single-wall carbon nanotubes because they have very high complexity and variety. MWCNTs always have more defects than SWCNTs and these reduce their desirable properties.

Many of the applications now being considered multi-walled carbon nanotubes, because MWCNTs are easier to produce in large quantities at a cheaper price and have been available in a very huge amount for much longer than SWCNTs. One of the major manufacturers of MWCNTs at the now is Hyperion Catalysis. They does not sell the nanotubes directly but they nanotubes pre-mixed with polymers for composites applications. The tubes have 8 to 15 walls and are about 10 nanometers wide and 10 micrometers long. Nowadays many Companies plans to produce similar types of MWCNTs in hundreds of tons a year, this quantity is greater but not so huge. This indicate that even these less extraordinary properties CNTs can make a sizable market in the near future.

### 1.4 SYNTHESIS OF CNTs

There are various number of methods for making CNTs. The first method for producing CNTs in reasonable quantities was by applying an electric current between two carbonaceous electrodes in an inert gas atmosphere. This method is called plasma arcing. This method involves the evaporation of one electrode called as cation followed by deposition at the other electrode.

Another method of synthesis of carbon nanotubes involves plasma arcing in the presence of cobalt with a concentration of 3% or greater. The carbon nanotube gets deposited on cathode and have rod like morphology. When cobalt is added as a catalyst then the nature of the product changes to web like structure, having strands of 1mm. The mechanism by which cobalt changes this process is indistinct, however we assume that metals affect the local electric fields and hence they formed the five-membered rings.

## Carbon nanotubes can be synthesized by different methods

1) Arc discharge method

2) Laser ablation method

3) Chemical vapour deposition method

   a) Plasma enhanced chemical vapour deposition (PECVD)

   b) Thermal chemical vapour deposition (TCVD)

   c) Vapour phase growth

## 1.4.1 Arc discharge method

Carbon nanotubes were firstly observed in 1991 in the carbon soot of graphite electrodes during an arc discharge by using a current of 100 amperes that was intended to produce nanotubes.

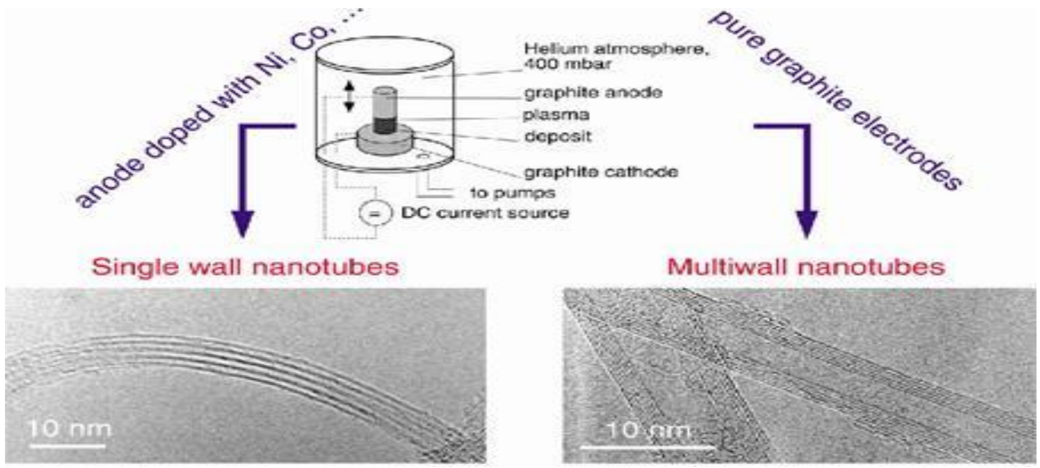



Figure 1.9 Type of CNT produced by Arc discharge method [15]

The arc discharge method was initially used for producing carbon nanotubes as it is the most common and easiest method to produce CNTs. However this technique produces a complex mixture of components, and requires purification. This method synthesize CNTs through arc-vaporization of two carbon rods placed end to end and are separated by approximately 1mm in an vacuum chamber that is usually filled with inert gas at low pressure. Recent investigations shows that it is also possible to synthesis CNTs with the arc discharge method in liquid nitrogen. A direct current of 50 to 100 A, potential difference of 20 V, creates a high temperature discharge between the two electrodes.

The arc discharge vaporizes the surface of one of the carbon electrodes, and forms small rod-like structures which get deposited on the other electrode. This method produces CNTs in high yield which depends on the uniformity of the plasma arc, and the temperature of carbon electrode. The carbons present in the negative electrode get sublimates because of the high temperatures produced by the discharge. This technique has been the most widely used method of nanotube synthesis. The yield percentage for this method is approximate 30 percent by weight and it produces both single- walled and multi-walled carbon nanotubes with lengths of up to 50 micrometers.

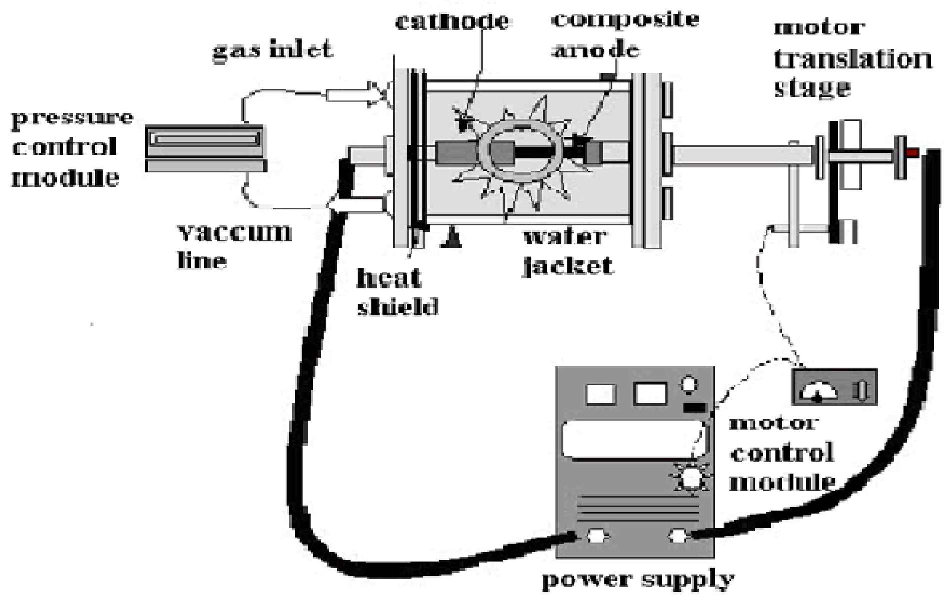



Figure 1.10 Schematic diagram of Arc discharge method [16]

### 1.4.2 Laser ablation process

In laser ablation process a pulse of laser vaporizes the graphite target in a high temperature reactor chamber which contains inert gas. The carbon nanotubes get developed on the cooler surfaces of the reactor, due to condensation of vaporized carbon. A water-cooled surface is present in the system to collect the carbon nanotubes. In 1996 by using dual pulsed laser CNTs were synthesized and obtain yields of >70wt% purity. Samples were prepared by laser vaporization of graphite rods with a catalyst mixture of Cobalt and Nickel in 50:50 at 1200 °C in argon flow, then the sample is heated in a vacuum at 1000 °C to remove the $C_{60}$ and other fullerenes. The first laser pulse was followed by a second pulse, which is used to vaporize the target more uniformly. The second laser pulse breaks up the larger particles ablated by the first one. Hence the use of two successive laser pulses minimizes the amount of carbon deposited as soot

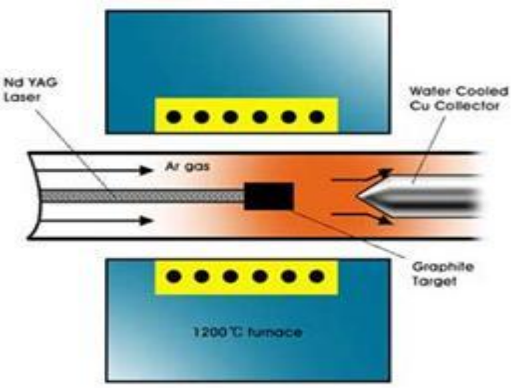



Figure 1.11 Diagram of high temperature reactor chamber [17]

The particles obtains by this method appears as a mat of “ropes”, which is 10-20nm in diameter and 100μm or more in length. Each rope consists of a bundle of single walled nanotubes that are aligned along a common axis. By varying the catalyst composition, the growth temperature and other process parameters, the average diameter and size of nanotubes can be varied. Both Arc-discharge and laser vaporization are currently the primary methods for obtaining small quantities of high quality CNTs. However, both methods have many drawbacks. The first is that both methods involve evaporating of carbon source, so it is difficult to increase the production for the industrial level using these approaches. The second issue relates that laser vaporization methods grow CNTs in highly twisted forms, which is mixed with unwanted forms of carbon and metal species. Thus The CNTs produced by these methods are difficult to purify for practical applications.

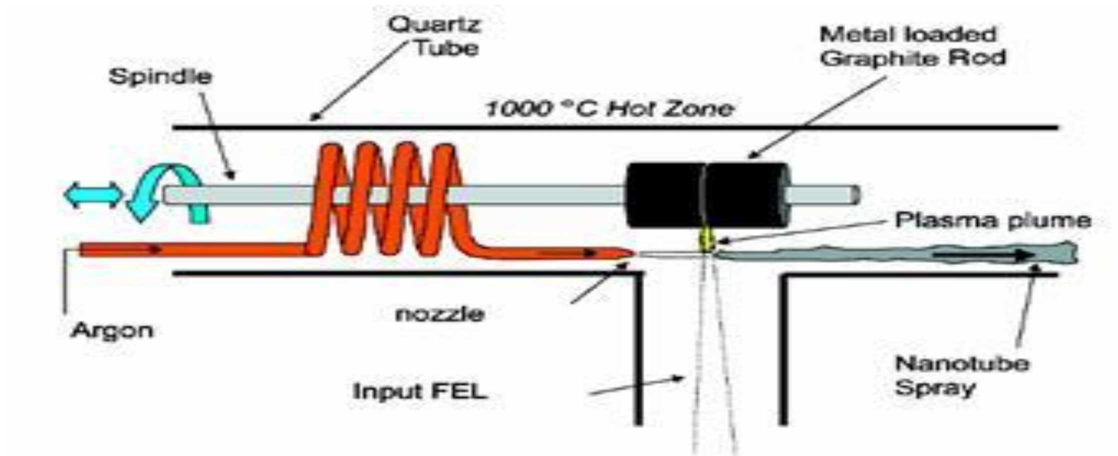



Figure 1.12 schematic diagram of Laser ablation method [18]

This method has higher yield of around 70% and produces mainly single-walled carbon nanotubes with a controllable diameter which is determined by the reaction temperature.

### 1.4.3 Chemical vapour deposition

Chemical vapor deposition of hydrocarbons over a metal catalyst is a conventional method that has been used to produce a variety of carbon materials such as carbon fibers and filaments. For last many years, large amounts of CNTs were formed by catalytic CVD of acetylene over cobalt and iron catalysts supported on silica or zeolite.

Bundles of single walled nanotubes were also found among the multi walled nanotubes produced on the carbon or zeolite catalyst. Synthesis of CNTs form ethylene is in under research. Catalysts such as iron, cobalt, and nickel, containing single metal or a mixture of metals will induce the growth of isolated single walled carbon nanotubes. We can synthesize CNTs which are open ended i.e having no caps by using Ethylene in the reaction temperatures of 545 °C for Nickel-catalyzed CVD, and 900 °C for an unanalyzed process.CVD process can also be used to obtain 'nanotube chips' which contain single walled nanotubes at particular locations. We can increase the yield of single walled nanotubes by using catalytic decomposition of an $H_2/CH_4$ mixture over well-dispersed metal particles such as cobalt, nickel, and iron on magnesium oxide at 1000 °C. We can also synthesize the composite powders containing well-dispersed CNTs by selective reduction in an $H_2/CH_4$ atmosphere of oxide solid solutions between a nonreducible oxide of $Al_2O_3$ or $MgAl_2O_4$ and one or more transition metal oxides. This reduction process produces very small transition metal particles at a temperature >800 °C. The decomposition of methane over the freshly formed nanoparticles prevents their further growth, and this give a very high proportion of single walled nanotubes and fewer multi walled nanotubes.

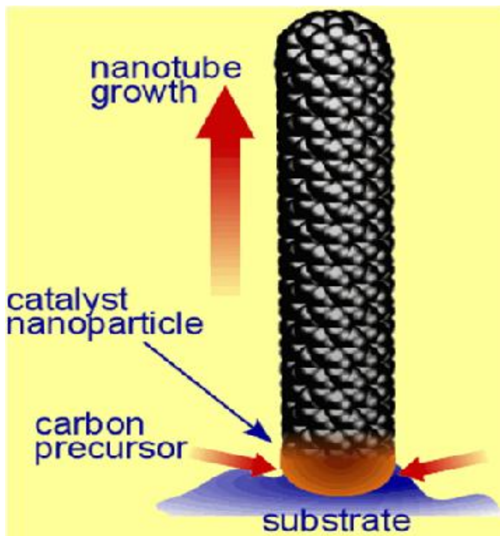



Figure 1.13 Growth diagram of CNT [19]

By using CVD process we can synthesis a substrate with a layer of metal catalyst particles commonly nickel, cobalt, iron, or a combination. The diameters of the nanotubes will depend upon the size of the metal particles. This can also be controlled by patterned deposition of metal or by plasma etching of a metal layer. The substrate temperature is about 700 °C. To start the growth of nanotubes, we introduce two gases into the reactor. First is a process gas (such as ammonia, nitrogen, hydrogen, etc.) and second is a carbon-containing gas (such as ethanol, methane, ethylene, acetylene etc.).

CVD is a most general method for the commercial production of carbon nanotubes. For the growth of CNTs, the metal nanoparticles is mixed with a catalyst support (e.g., MgO, $Al_2O_3$, etc) to increase the surface area for catalytic reaction of the carbon feedstock with the metal particles for the higher yield. There is a drawback in this synthesis route, that the removal of the catalyst supports by an acid treatment, which can damage the original structure of the carbon nanotubes.

### 1.4.4 Plasma enhanced chemical vapour deposition

Plasma-enhanced chemical vapor deposition (PECVD) is a process which is used to deposit thin films from a gas state (vapor) to a solid state on a substrate. After creation of plasma, chemical reaction between the two gases will take place. The plasma is generally created in between the electrode (the space which is filled with the reacting gases) by RF frequency or DC discharge. The PECVD method generates a glow discharge in a reaction chamber by a high frequency voltage applied between both electrodes.

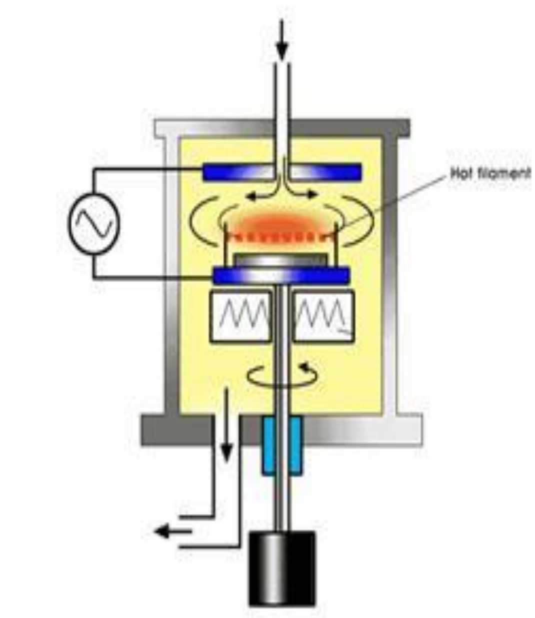



Figure: 1.14 Schematic diagram of plasma CVD apparatus [20]

The substrate is placed on the grounded electrode to obtain a uniform film. And the reaction gas is supplied from the opposite plate. We use catalyst such as Fe, Ni and Co. when the nanoscopic metal particles are formed then carbon nanotubes will be grown on these metal particles of the substrate by glow discharge, which is generated from high frequency power. A reaction gas that contains carbon such as $CH_4$, $C_2H_6$, $C_2H_2$, $C_2H_4$, CO is supplied in to the chamber during the discharge. The catalyst plays a very important role on the diameter, growth rate, wall thickness and morphology of carbon nanotubes. Nickel (Ni) is the most appropriate catalyst for the growth of aligned (MWCNTs). The diameter of the MWCNTs is about 15 nm. The highest yield of carbon nanotubes is about 50% and is obtained at relatively low temperatures (below 330 °C).

### 1.4.5 Thermal chemical vapour deposition

In this method Fe, Ni, Co or an alloy of the three catalytic metals is firstly deposited on a substrate. When the substrate is etched in a diluted HF solution with distilled water then the specimen is placed in a quartz boat [21]. The boat is placed in a CVD furnace and nanometer-sized catalytic metal particles are formed after an additional etching of the catalytic metal film using $NH_3$ gas at a temperature of 750 to 1000 $^{o}$C.

Figure: 1.15 Schematic diagram of thermal CVD apparatus.

### 1.4.6 Vapour phase growth

In vapour phase growth we directly supply the reaction gas and catalytic metal in the chamber without a substrate. Vapour phase growth apparatus consists of two furnaces which are placed in the reaction chamber. We use ferrocene as catalyst. In the first furnace the vaporization of carbon is maintained at low temperature where fine particles are formed. When they reach to second furnace, decomposed carbons are absorbed and diffused on the metal particles. Here, synthesized the carbon nanotubes. The diameter of the carbon nanotubes lies in the range of 2 - 4 nm for SWCNTs and between 70 and 100 nm for MWCNTs.

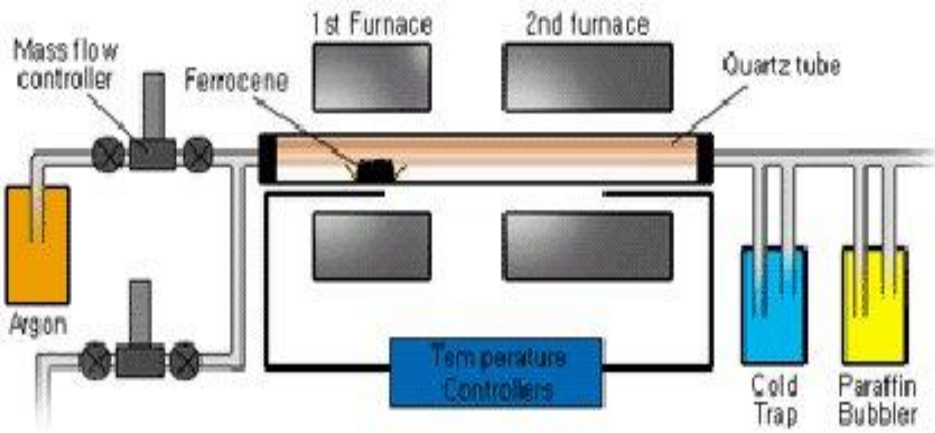



Figure 1.16 Schematic diagram of a vapour phase growth apparatus[22]

## Comparison between various synthesize methods

| Arc Discharge Method | | Chemical Vapour Deposition | Laser Ablation (vaporization) |
|---|---|---|---|
| Who | Ebbesen and Ajayan, NEC, Japan 1992 [23] | Endo, Shinshu University, Nagano, Japan [24] | Smalley, Rice, 1995 [25] |
| How | Connect two graphite rods to a power supply, place them a few millimeters apart, and throw the switch. At 100 amps, carbon vaporizes and forms hot plasma. | Place substrate in oven, heat to 600 $^{o}$C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of CNTs | Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the CNTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs |
| Typical yield | 30 to 90% | 20 to 100 % | Up to 70% |
| SWNT | Short tubes with diameters of 0.6 - 1.4 nm | Long tubes with diameters ranging from 0.6-4 nm | Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm. |
| M-WNT | Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm | Long tubes with diameter ranging from 10-240 nm | Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible. |

## 1.5 PROPERTIES OF CNTs

The most important properties of CNTs are:-

### 1.5.1 Strength and elasticity

CNTs are the strongest and stiffest materials on earth. It has very high tensile strength and elastic modulus. This strength is due to the covalent $sp^2$ bonds formed between individual carbon atoms.

The single sheet of graphite forms a planar honeycomb like lattice. Each atom is connected through a strong chemical bond to three neighboring atoms [26]. For this reason, CNTs have ultimate high-strength. SWCNTs are stiffer than steel and are very resistant to damage from physical forces. Pressing on the tip of a nanotubes will cause it to bend, but it will not get damage. When the force is removed the nanotubes returns to its original state. This property makes CNTs very useful as probe tips for very high-resolution scanning probe microscopy.

The current Young's modulus value of single walled nanotubes is about 1 Tera Pascal. But a value of Young's modulus as high as 1.8 Tpa has been reported. Other values which are higher than that have also been reported. The differences may arise through different experimental measurement techniques. Others have shown theoretically that the Young's modulus depends on the size and chirality of the single walled nanotubes, ranging from 1.22 Tpa to 1.26 Tpa. They have calculated a value of 1.09 Tpa for a generic nanotube. However, when working with different multi walled nanotubes, others have noted that the modulus measurements of multi walled nanotubes using AFM techniques do not strongly depend on the diameter. CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, tensional or bending stress.

### 1.5.2 Thermal conductivity and expansion

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as ballistic conduction, but good insulators laterally to the tube axis. The temperature stability of carbon nanotubes is established to be up to 2800 °C in vacuum and about 750 °C in air.

CNTs have been shown to exhibit superconductivity below 20 K (aprox. 253 °C).Many applications of CNTs, such as in nanoscale molecular electronics, sensing and actuating devices, or as reinforcing additive fibers in functional composite materials, have been proposed. Reports of several recent experiments on the preparation and mechanical characterization of CNT-polymer composites have also appeared. These measurements suggest modest enhancements in strength characteristics of CNT-embedded matrixes as compared to bare polymer matrixes. Preliminary experiments and simulation studies on the thermal properties of CNTs show very high thermal conductivity. It is expected, therefore, that nanotubes reinforcements in polymeric materials may also significantly improve the thermal and thermo mechanical properties of the composites.

### 1.5.3 High aspect ratio

CNTs represent a very small, high aspect ratio conductive additive for plastics of all types. High aspect ratio means that a lower loading of CNTs is needed compared to other conductive additives to obtain the same electrical conductivity. This low loading preserves more of the polymer resins' toughness, especially at low temperatures, as well as maintaining other key performance properties of the matrix resin. CNTs have proven to be an excellent electrical conductivity in plastics. Their high aspect ratio, about 1000:1 imparts electrical conductivity at lower loadings, compared to conventional materials such as carbon black, chopped carbon fiber, or stainless steel fiber.

### 1.5.4 Electrical Conductivity

Metallic CNTs has very high electrical conducting, and hence can be said to be metallic. Their conductivity depends on their chirality, the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical properties. Conductivity in MWCNTs is quite complex. "armchair"-structure of CNTs have better electrical conductivity than other metallic CNTs. Interwall reactions within multi walled nanotubes have been found to redistribute the current over individual tubes non-uniformly. Hence due to this there is no change in current across different parts of metallic single-walled nanotubes. The behavior of the ropes of semi-conducting single walled nanotubes is different, in that the transport current changes abruptly at various positions on the CNTs.

The conductivity and resistivity of single walled nanotubes can be measured by placing electrodes at different parts of the CNTs. The resistivity of SWCNTs is of the order of $10^{-4}$ ohm-cm at 27 °C. The current density achieved was $10^7$ A/cm$^2$. Theoretical single walled carbon nanotube is able to sustain much higher stable current densities, as high as $10^{13}$ A/cm$^2$. It is found that single walled carbon nanotubes may contain defects. These defects allow the single walled carbon nanotubes to act as transistors. Likewise, joining CNTs together may form transistor-like devices. A nanotube with a natural junction behaves as a rectifying diode. It is also found that single walled nanotubes can pass electrical signals at speeds up to 10 GHz when used as interconnects on semi-conducting devices.

### 1.4.5 Electronic properties

The electronic properties of SWCNTs have been studied in a large number of theoretical works. All models show that the electronic properties changes from metallic to semi conducting with diameter and chirality. This is due to the very peculiar band structure of graphene.

Electron motion in graphene is equivalent to that of a neutrino or a relativistic Dirac electron with vanishing rest mass. This causes the appearance of a nontrivial Berry's phase under $2\pi$ rotation in wave-vector space. The energy bands in carbon nanotubes are determined by periodic boundary conditions. Aharonov-Bohm flux determined uniquely by the circumferential chiral vector. A nanotube becomes metallic when the flux vanishes and semiconducting when the flux is nonzero. The conductivity of graphene is essentially independent of the Fermi energy. Various schemes are now being proposed and tested for the purpose of opening the band gap in graphene.

All armchair tubes are metallic. Zig-zag and chiral tubes show a small very small band gap due to the curvature of the graphene sheet, while all other tubes are semi-conducting with a band gap that scales approximately with the inverse of the tube radius. Bandgaps of 0.4 – 1 eV can be expected for SWCNTs.

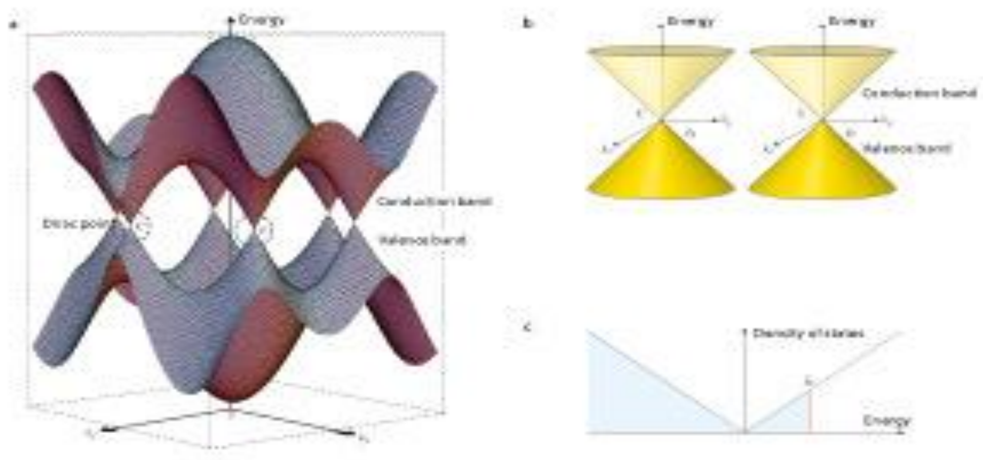


Figure 1.17 Band gap diagram of SWCNT [27]

### 1.5.6 Mechanical properties

Carbon nanotube is the one of the strongest materials in nature. Carbon nanotubes (CNTs) are basically long hollow cylinders of graphite sheets. A graphite sheet has a 2D symmetry; hence carbon nanotubes by geometry have different properties in axial and radial directions. It is found that CNTs are very strong in the axial direction. It`s Young's modulus on the order of 270 - 950 GPa and tensile strength of 11 - 63 GPa.

On the other hand, CNTs are soft in the radial direction. The first transmission electron microscope observation suggested that the van der waals forces can deform two adjacent nanotubes. Later, nanoindentations with AFM were performed by several groups to measure radial elasticity of MWCNTs. Tapping or contact mode of AFM was recently performed on single-walled carbon nanotubes. Radial direction elastic property of CNTs is very important for carbon nanotube composites where the embedded tubes are subjected to large deformation in the transverse direction under the applied load on the composite structure. One of the main problems in characterizing the radial elasticity of

CNTs is the knowledge about the internal radius of the CNT; carbon nanotubes with identical outer diameter may have different internal diameter. AFM is used to find the exact number of layers and hence the internal diameter of the CNT. In this way, we can characterize the mechanical property more accurate.

**Comparison of mechanical properties**

| Material | Young's modulus (TPa) | Tensile strength (GPa) | Elongation at break (%) |
|---|---|---|---|
| SWNT | ~1 (from 1 to 5) | 13–53 | 16 |
| Armchair SWNT | 0.94 | 126.2 | 23.1 |
| Zigzag SWNT | 0.94 | 94.5 | 15.6–17.5 |
| Chiral SWNT | 0.92 | NA | NA |
| MWNT[E] | 0.2–0.8–0.95 | 11–63–150 | NA |
| Stainless steel | 0.186–0.214 | 0.38–1.55 | 15–50 |
| Kevlar–29&149 | 0.06–0.18 | 3.6–3.8[l] | ~2 |

## 1.6 Applications

Carbon nanotubes have amazing electrical conductivity, heat conductivity and mechanical properties. They are also the best electron field-emitter. These extraordinary characteristics give CNTs potential in numerous applications.

### 1.6.1 Structural

- **Clothes**: waterproof tear-resistant cloth fibers
- **Concrete**: In concrete, they increase the tensile strength, and halt crack propagation.
- **Sports equipment**: Stronger and lighter tennis rackets, bike parts, golf balls, golf clubs and baseball bats.
- **Polyethylene**: Adding them to polyethylene increases the polymer's elastic modulus by 30%.
- **Space elevator**: This will be possible only if tensile strengths of more than about 70 GPa. We can make a space elevator.
- **Ultrahigh-speed flywheels**: Very high strength to weight ratio enables very high speeds to be achieved.

### 1.6.2 Electromagnetic

- **Buckypaper**: It is a thin sheet of nanotubes that are 250 times stronger than steel and 10 times lighter .It is used as a heat sink for chipboards and a backlight for LCD screens.
- **Computer circuits**: A nanotube formed by joining nanotubes of two different diameters end to end can act as a diode. CNTs can also be used to dissipate heat from tiny computer chips because of their very high thermal conductivity.
- **Conductive films**: CNTs are also introduced in developing transparent, electrically conductive films to replace indium tin oxide (ITO). Printable water based inks of carbon nanotubes are desired to enable the production of these films to replace the ITO. Nanotubes films can be used in displays for cell phones, computers, PDAs, and ATMs.

- **Electric motor brushes:** Nanotubes composite motor brushes are better-lubricated, cooler-running, less brittle, stronger and more accurately moldable. Since brushes are a critical failure point in electric motors, and also don't need much material, they became economical before almost any other application.
- **Light bulb filament**: Alternative to tungsten filaments in incandescent lamps.
- **Solar cells**: Organic photovoltaic devices (OPVs) are fabricated from thin films of organic semiconductors, such as polymers and small-molecule compounds that are on the order of 100 nm thick.

Figure 1.18 organic photovoltaic cell [28]

- **Superconductor**: Nanotubes show superconducting property at low temperatures.
- **Ultra capacitors**: Nanotubes, when bound to plates of capacitors increase the surface area and thus increase energy storage ability.
- **Others**: Artificial muscles, magnets, optical ignition etc.

### 1.6.3 Chemical

- **Air pollution filter**: Future applications of carbon nanotube membranes which is used for filtering carbon dioxide from power plant .
- **Biotech container**: Nanotubes can be opened and filled with materials such as biological molecules, raising the possibility of applications in biotechnology.
- **Water filter**: Nanotube membranes can be used in filtration of water. This technique can purportedly reduce desalination costs by 75%.

### 1.6.4 Mechanical

- **Oscillator**: CNTs are fastest known oscillators (> 50 GHz).
- **Liquid flow array**: Liquid flows up to five times faster than predicted through array.

### 1.6.5 Carbon nanotube interconnects

Metallic CNTs can be used in Very-large-scale integration (VLSI) interconnects because of their high thermal stability, high thermal conductivity and large current carrying capacity. An isolated CNT can carry current densities of 1000 MA/sq-cm without any damage even at an elevated temperature of 250 $^{0}$C, thereby eliminating electro-migration dependability concerns that plague Cu interconnects.

### 1.6.6 Transistors

Carbon nanotubes can be used to make single molecular transistors.Successful implementation of molecular transistors in large must show signal amplification. Signal amplification makes it possible to separate signals along a sequence of logical operations. CNTs produce very less noise caused by thermal fluctuations and environmental disturbances.

### 1.6.7 Electrical circuits

Carbon nanotubes have very high electrical conductivity at their unique dimension that makes them ideal components of electrical circuits. However, there is no consistent way to arrange carbon nanotubes into a circuit. The productions of electrical circuits from CNTs are very different from the traditional IC fabrication process. Researchers try to manipulate nanotubes one-by-one with the tip of an AFM in a pains taking and time consuming process. However CNTs can be grown through a CVD process on a wafer from patterned catalyst material, which serve as growth sites and allow designers to position one end of the nanotube. Even if nanotubes could be specifically positioned, but there is a problem amongst the engineers. They are unable to control the types of nanotubes-metallic, semiconducting, single-walled, multi-walled-produced.

### 1.6.8 Other applications

- CNTs can also be used in nano electromechanical systems.
- CNTs can also be used in gene delivery vehicle to destroy cancer cells.
- Because of the versatile structure of the CNT, it can be used for a variety of tasks in and around body.
- CNTs can be used as light emitting semiconductors.

# Chapter-2

# Literature Review

## 2.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is the most popular method of producing multi walled carbon nanotubes. In this method Fe, Ni, Co or an alloy of the three catalytic metals is firstly deposited on a substrate [29]. The substrate is etched in a diluted HF solution then the sample is placed in a quartz boat. Then the quartz boat is placed in furnace where temperature of furnace is maintained between 750 to 1050 $^{o}$C In this process, thermal decomposition of a hydrocarbon vapor is achieved in the presence of a metal catalyst [30]. Hence, it is also known as thermal CVD or catalytic CVD

### 2.1.1 History of CVD

In 1890, A French scientists observed the formation of carbon tubes during the experiments. Which involves the passage of cyanogens over red-hot porcelain [31]. In middle of twentieth century, CVD was an conventional method for producing carbon nanofibers which uses thermal decomposition of hydrocarbons in the presence of metal catalysts [32].

### 2.1.2 Advantages of CVD

As compared to laser-ablation and arc-discharge methods, CVD is a simple and cost-effective method for synthesizing CNTs at low temperature. CNT grown by arc-discharge and laser ablation methods are superior to the CVD-grown ones [33] .However, in yield and purity, CVD is superior than the arc and laser methods. When we are talking about the structure control, CVD is the only answer. CVD is flexible in the sense that it offers harnessing plenty of hydrocarbons in any state, enables the use of various substrates, and allows CNT growth in a variety of forms, such as powder, thin or thick films, aligned, straight or coiled, or a desired architecture of nanotubes on predefined sites of a patterned substrate[34]. It also provide better control on the growth parameters

## 2.2 CNT Synthesis

Figure 2.1 show the experimental set-up used for CNT growth by CVD method. The process involves passing a hydrocarbon vapour through a quartz tubular reactor in which a catalyst material is present at sufficiently high temperature (750–1200 °C) to decompose the hydrocarbon. CNTs grow on the catalyst in the quartz tube, which are collected upon cooling the system to room temperature [35]. In the case of a liquid hydrocarbon (alcohol,benzene,palm oil etc.), the liquid is heated in a flask and an inert gas is ppassed through it, which in turn carries the hydrocarbon vapor into the reaction zone. We can directly kept the solid hydrocarbon in the low-temperature zone of the reaction tube. Volatile materials (camphor, naphthalene, ferrocence etc.) directly turn from solid to vapor, and perform CVD while passing over the catalyst kept in the high-temperature zone [36].

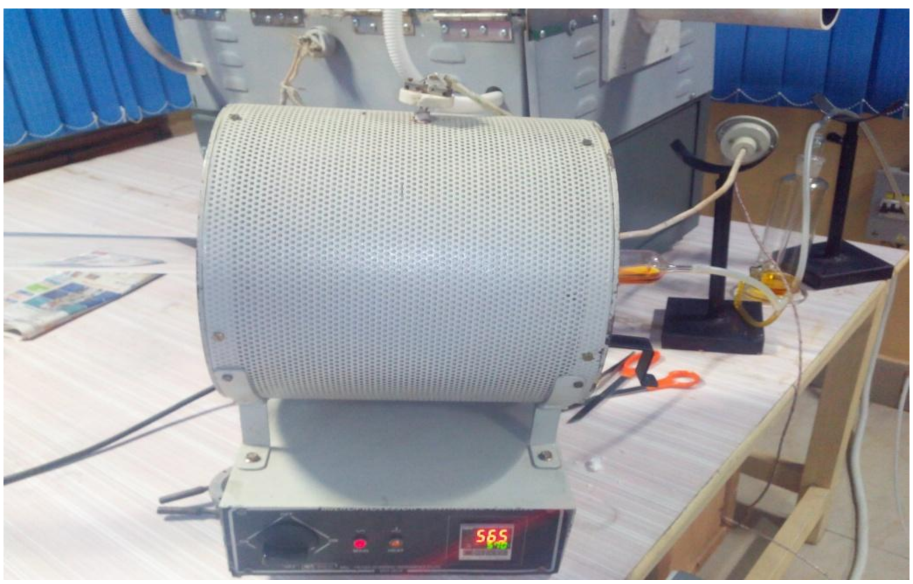


Figure 2.1 Schematic diagram of a CVD setup [DTU lab]

### 2.2.1 CNT Precursors

Most commonly used CNT precursors are methane, ethylene, acetylene, benzene, xylene, palm oil and carbon monoxide. The molecular structure of the precursor has a negative effect on the morphology of the CNTs grown. Linear hydrocarbons such as methane, ethylene, acetylene, thermally decompose into atomic carbons generally produce straight hollow CNTs. On the other hand, cyclic hydrocarbons such as benzene, xylene, cyclohexane, fullerene, produce relatively curved CNTs with the tube walls often bridged inside [37]. Experimental result shows that low-temperature CVD (600–900 ˚C) yields MWCNTs, whereas high-temperature (900-1200 ˚C) reaction produces SWCNT growth. This indicates that SWCNTs have a higher energy of formation. That is why MWCNTs are easier to grow from most of the hydrocarbons, while SWCNTs grow from selected hydrocarbons like carbon monoxide, methane, etc. which have a higher stability in the temperature range of 900–1200 ˚C. Commonly efficient precursors of MWCNTs (like. acetylene, benzene, etc.) are unstable at higher temperature and lead to the deposition of large amounts of carbonaceous compounds other than the nanotubes.

### 2.2.2 CNT Catalysts

For synthesizing CNTs, most commonly-used catalyst are Fe, Co, Ni, because of two main reasons: (i) high solubility of carbon in these metals at high temperatures; and (ii) high carbon diffusion rate in these metals. Besides that, high melting point and low equilibrium-vapor pressure of these metals offer a wide temperature window of CVD for a wide range of carbon precursors. Recent considerations are that Fe, Co, and Ni have stronger adhesion with the growing CNTs and hence they are more efficient in forming SWCNTs [38]. The catalyst-particle size dictates the tube diameter. The key factor to get pure CNTs is achieving hydrocarbon decomposition on the catalyst surface alone. Apart from the popular transition metals (Fe, Co, Ni), other metals of this group, such as Cu, Au, Ag, Pt, Pd were also found to catalyze various hydrocarbons for CNT growth.. On the role of CNT catalysts, it is worth mentioning that transition metals are proven to be efficient catalysts not only in CVD but also in arc-discharge and laser-vaporization methods. Therefore, it is likely that these apparently different methods might come into a common growth mechanism of CNT, which is not yet clear

### 2.3 CNT Growth Control

It is well known that hydrocarbons are easily broken at high temperatures. Such a thermal decomposition which is called Pyrolysis. However, in the presence of suitable metal catalysts, a hydrocarbon can be decomposed at lower temperatures (catalytic pyrolysis).The key of CNTs growth by CVD is to achieve the hydrocarbon decomposition on the metal surface alone and do not allow the hydrocarbon to break uncatalyzed, Beyond the catalyst surface. Restriction of pyrolysis to the catalyst surface is controlled through proper selection of hydrocarbon and catalyst materials, concentration of the catalyst, and the CVD reaction temperature [39].

### 2.3.1 Effect of Catalyst Material and Concentration

CNTs growths were carried out with different metal catalysts (Fe, Co, Ni) separately. Iron was found to have high catalytic effect in hydrocarbon decomposition leading to higher CNT deposits, but those CNTs were poorly graphitized. On the other hand, cobalt catalyst resulted in better-graphitized CNTs but the yield went down. Hence a mixture of the two metals were tried to combine their individual advantages, and it was successful. Large volumes of well-graphitized MWCNTs were obtained [40]. Additional advantage of using the bimetallic catalyst was that CNTs could be grown at much lower temperature i.e. 550 ˚C. It is because the melting point of the mixture of Fe and Co is lower than their individual melting points. Moreover, alloys are known to be better catalysts than pure metals. These trends suggest that tri-metallic catalysts should also give interesting results, though the interpretation of result would be more complicated. No much effort is known in this direction. Besides the catalyst material, the catalyst concentration also plays an important role in the CNT growth. If we decrease the catalyst concentration below 2.4 wt% no CNT is formed. Lower catalyst concentrations (2.4–5%) exhibited SWCNT growth (at 850 ˚C and above), whereas higher concentrations favored MWCNT growth [24]. A combined Fe + Co concentration of 40% accounted for the highest yield of MWCNTs. This concludes that SWCNTs or MWCNTs can be selectively grown by proper selection of catalyst materials and their concentration.

### 2.3.2 Effect of Temperature

All the growth conditions other than temperature for the samples studied here were kept constant to study only the temperature effect. We observe that no CNT growth at temperatures at and lower than 825 °C. We observed uniform formation of catalyst nanoparticles with average diameter of about 25 nm. Although no CNT growth was observed, uniform formation of catalyst nanoparticles are so important in the growth of carbon nanotubes as they controls the diameter of nanotubes. For the growth at 850 °C, CNT formation was rather bulky and short, with average diameter of 20.4 nm. For the CNTs grown at 875 °C, we obtained CNTs with average diameter of 15.4 nm and they were longer than the previous CNTs grown at 850 °C [41]. The CNTs grown at 900 °C had an average diameter of about 14.2 nm. When we increased the growth temperature to 925°C, we observed very thin and longer nanotubes, whose average diameter were about 10.5 nm. Hence the temperature affect CNTs diameter inversely.

### 2.3.3 Effect of Vapor Pressure

The effect of gas pressure on the structure of carbon nanotubes has been experimentally investigated in the CVD process. The yield of CNTs increases significantly with the gas pressure, reaches 600% at 600 Torr, then start decreasing with further increase of gas pressure. At low reacting gas pressure we obtain completely hollow cores of CNTs, whereas at high pressure the CNTs are bamboo like structure. The density of bamboo-structured CNTs increases considerably with the increase of gas pressure [42]. This shows that the structure and yield of CNTs are strongly affected by the growth gas pressure

# Chapter-3

## EXPERIMENTAL DETAILS

## 3.1 The Experimental Setup

The experimental setup consists of

- A horizontal reaction furnace
- Quartz tube
- PID controller
- Command module
- Control valves
- Gas sources
- Thermocouple

**Horizontal Reaction Furnace: -** CVD apparatus consists of horizontal reaction furnace with a heating capacity of up to 900°C. The length of the furnace is 40cm and has an inner diameter of 10cm.

**Quartz Tube: -** The quartz tube used to carry out the deposition has a length of 1.2m with outer diameter of 3.6cm and inner diameter of 3.2cm. The quartz tube is placed inside the horizontal reaction furnace.

**PID Controller:-** A proportional integral differential (PID) controller is provided in the furnace to control the temperature, time and heating rate of the reaction.

**Command Module: -** The command module shows the rate of carbon source and hydrogen, which enters the reaction tube.

**Control Valves: -** Control valves are used to control the flow rate of gases passed in to the furnace.

**Gas Sources: -** Control valves are used to control the flow rate of gases passed in to the furnace.

**Thermocouple: -** Thermocouple is a temperature-measuring device consisting of two dissimilar conductors that contact each other at one or more spots.

## 3.2 Experimental Procedure

- 2.5 mg of ferrocene is mixed with 50 ml palm oil
- About 4 ml of mixer is placed on quartz boat
- The boat was placed in middle of the furnace.
- Flow the argon gas through tube at 250 sccm and hydrogen gas at 100 sccm.
- Reaction furnace was heated at deposition temperature of 500 to 875 °C for 1 hour and allowed to cool down
- Black substance was then collected form the wall of Quartz tube and quartz boat.
- The collected powder like samples is characterized by scanning electron microscope (SEM) operated at 15.0 KV and transmission electron microscope(TEM) operated at 200 KV to know the structure, diameter and identification of sample

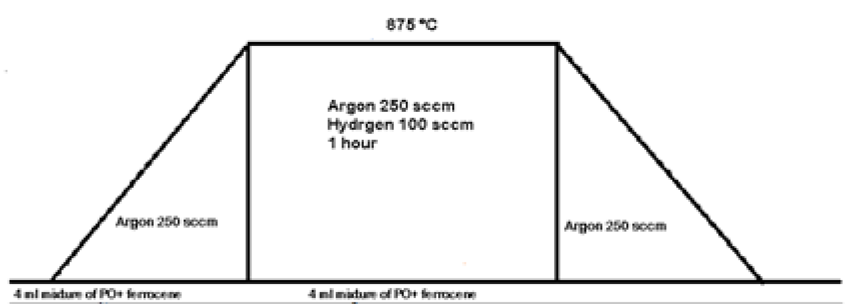


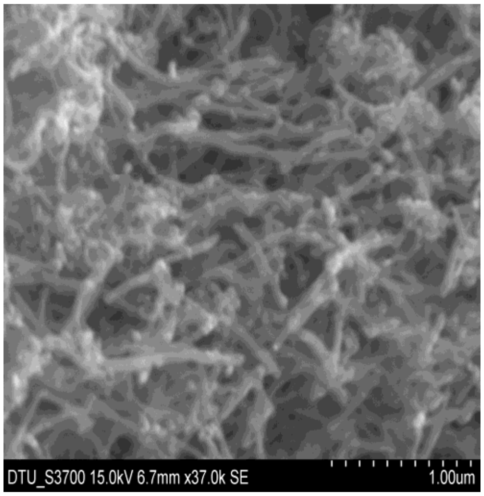

Figure- 3.1 Growth procedure of CNT

# Chapter-4

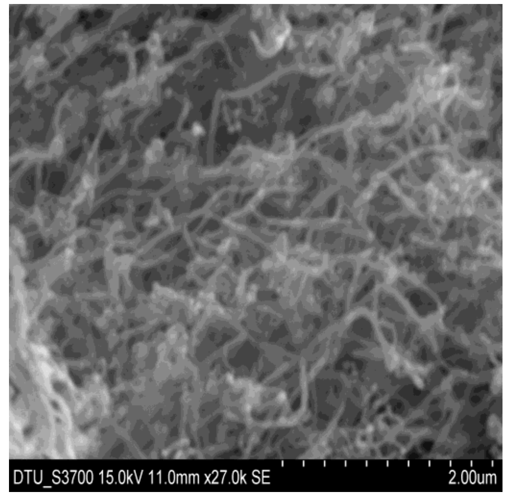
# Results and Discussion

# RESULT AND DISCUSSION

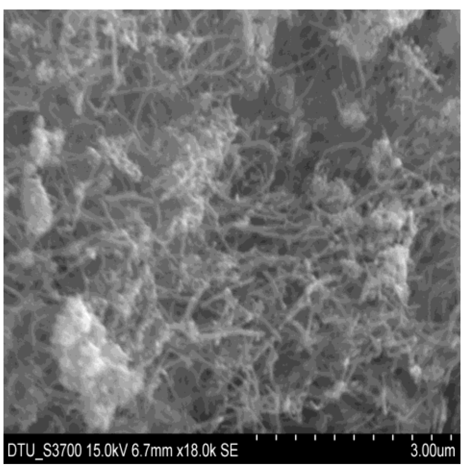
## 4.1 SEM IMAGES OF CNTs



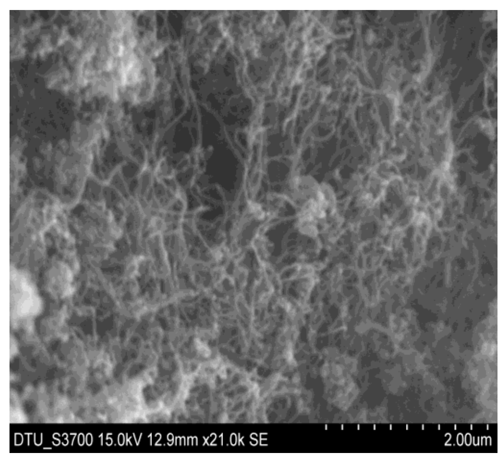

(a)




(b)



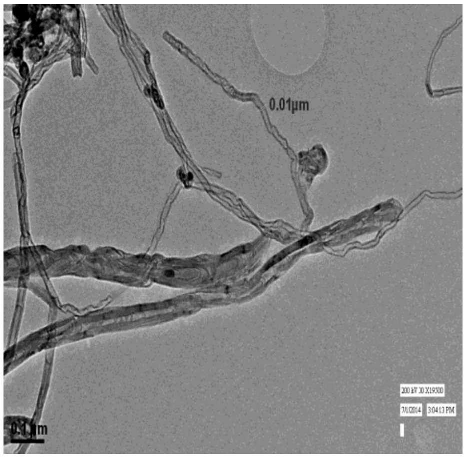

(c)



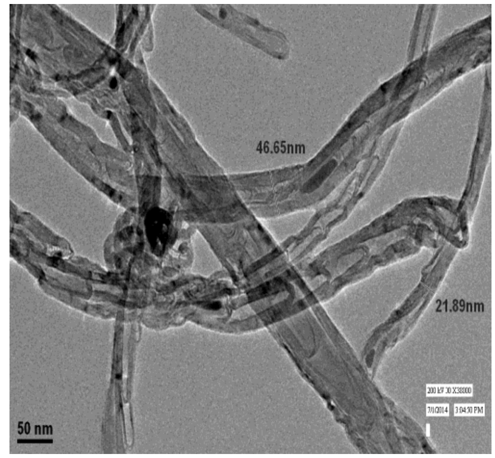

(d)

**FIGURE 4.1** (a) SEM image of CNTs obtain from quartz boat, (b) SEM image of CNTs obtain from quartz boat, (c) SEM image of CNTs obtain from quartz boat, (d) SEM images of CNTs obtain from quartz boat

## 4.2 TEM IMAGES OF CNTs




(a)

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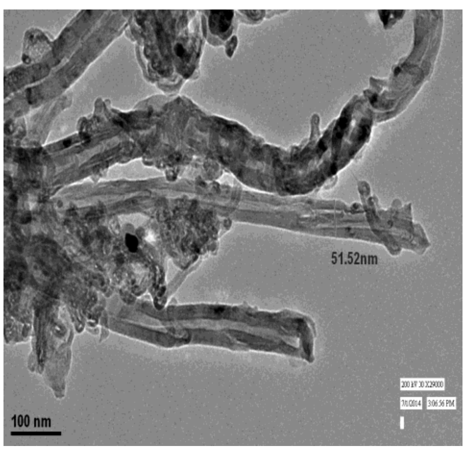
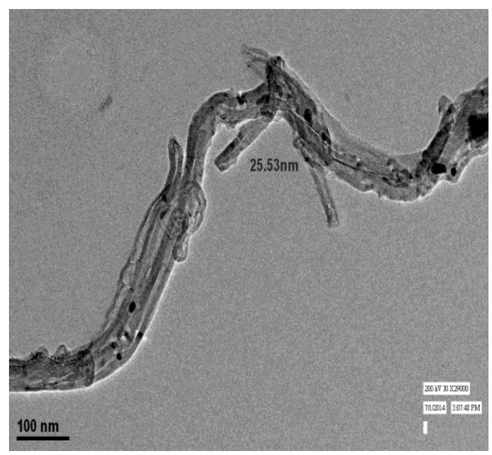



(b)




(d)

**FIGURE 4.2** (a) TEM image of CNTs obtain from quartz boat, (b) TEM image of CNTs obtain from quartz boat, (c) TEM image of CNTs obtain from quartz boat, (d) TEM images of CNTs obtain from quartz boat

Figure 4.1 shows the SEM image of CNTs obtained from thermal catalytic decomposition of palm oil. Figure 4.1(b), (c) & (d) show a dense CNT forest of tubes. A higher magnification view of CNT (figure 4.1(a)) shows that they are multi-walled carbon nanotubes (MWCNTs). Individual tubes were found to be twisted in bundles.

Figure 4.2 shows TEM images of individual multi-walled carbon nanotubes. The tube was $\approx$ 40nm consisting of many layers. CNTs tubes are filled by iron carbide particle at some position. Most of the part of CNT is hollow.

We have concluded that waste cooking palm oil can be utilized as an efficient, economical and environmental friendly carbon source for CNT synthesis. SEM and TEM results shows that CNT obtained were multi walled CNTs. They have average diameter of approx 40 nanometer. Significantly this implies that other cooking from other vegetables or animals are also can be used for the synthesis of carbon nanotubes possibly for scaled up industrial production of bulk CNTs.

# Chapter-5

## Conclusion and Future Scope

# CONCLUSION AND FUTURE WORK

Rise in demand and production, and simplicity of carbon nanotubes would lead to the extensive use in a wide variety of applications. The use of nanotechnology for human will become common need in 21st century. As world is suffering from serious problem of pollution, therefore hydrogen will becoming need of 21st century & carbon nanotubes also provide better solution for hydrogen storage.

Carbon naotubes have the ability to change architecture, the automobile industry, material science, the space program and a variety of activities and products associated with daily living. These nanotubes are able to be produced on industrial mass scales and the commercial production of carbon nanotubes through synthesis make them incredibly affordable costing as little as 95 dollar per gram at present-with the price going down every year-making them a uniquely affordable in the creation of carbon nanotubes biofuels.

Carbon nanotubes biofuels are growing in popularity amongst and researches because these biofuels are much stronger than any of these previously studied or created. They may have implications for all present uses of biofuels including, alternative fuel source vehicles, pacemakers, portable energy supplies and even glucose sensors

Carbon nanotubes market was growing at a very fast rate till 2006-2007. We can conclude that most of the demands of human, in this and fore coming generation will be fulfilled by carbon nanotubes

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