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The wondrous world of carbon nanotubes: Structure, synthesis, properties and applications

Kumkum Sarangdevot^{*1} and B. S. Sonigara²

¹*Pacific College of Pharmacy, Udaipur (Rajasthan), India* ²*B. N. College of Pharmacy, Udaipur (Rajasthan), India*

ABSTRACT

In this paper we review history, types, structure and different synthesis methods for carbon nanotubes (CNTs) including arc discharge, laser ablation & chemical vapor deposition. CNTs are hollow carbon structures with one or more walls, a small diameter on the nanometer scale and a large length in comparison. Because of their remarkable electronic and mechanical properties, they are unique and exciting and offer tremendous opportunities for the development of fundamentally new material systems. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology. Their unique surface area, stiffness, strength and resilience have led to much excitement in the field of pharmacy.

Key words: Carbon nanotubes, Single walled CNTs, Multiwalled CNTs, Application of CNTs

INTRODUCTION

The word nanotube is derived from their size, because the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair) and can be up to several micrometers in length. A nanotube (also known as a buckytube) is a member of the fullerene structural family.

Carbon nanotubes (CNTs) are hollow carbon structures with one or more walls, a small diameter on the nanometer scale and a large length in comparison. They exhibit a well-ordered arrangement of carbon atoms linked via sp^2 bonds which renders them among the stiffest and strongest fibres known¹⁻². Carbon nanotubes possess many novel properties (outstanding mechanical, electrical, thermal, and chemical properties: 100 times stronger than steel, best field emission emitters, can maintain current density of more than 10-9 A/cm², thermal conductivity comparable to that of diamond) which make them potentially useful in a wide variety of applications³ (*e.g* optics, nanoelectronics, composite materials, conductive polymers, sensors, etc).

ORIGINS OF FULLERENES

Carbon has been thoroughly studied and its properties known and documented for many years. Readily combining with many different elements, carbon is found in innumerable simple and complex molecular compounds. Previous to 1985, however, pure carbon was thought to exist in only two naturally occurring, solid forms: diamond and graphite. This all changed in 1985 and scientists were forced to alter their perception of the natural world with the discovery of a third allotropic form of solid carbon, the buckminsterfullerene. Buckminsterfullerenes, or the more affectionately named, "buckyball," are symmetrical, ball- shaped molecules consisting of sixty carbon atoms

arranged in an icosahedral geometric structure resembling a soccer ball. Buckminster fullerenes are so named because of their resemblance to the geodesic dome structures created by famed architect R. Buckminster Fuller⁴.



Figure 1: 3D Visualization of the Buckminster Fullerene Molecule⁵

Buckyballs were discovered by accident in August of 1985 at Rice University in Houston Texas by Richard Smalley and Harry Kroto⁶. They vaporized a sample of graphite with an intense pulse of laser light and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer. The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of 60 carbon atoms, C_{60} . After this discovery, other related molecules (C_{36} , C_{70} , C_{76} and C_{84}) composed of only carbon atoms were also discovered and the buckyball were recognized as a new allotrope of carbon. This new class of carbon molecules is called the fullerenes.

Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before⁷. Fullerenes consist of hexagons and pentagons that form a spherical shape. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started.

DISCOVERY OF CARBON NANOTUBES:

Carbon nanotubes, originally discovered by Iijima in 1991, are structures made up of thin sheets of benzene ring carbons rolled up into the shape of a seamless cylinder and are often capped on at least one end by a spherical buckyball structure. These light, chemically stable cylinders conduct heat better than diamond and are one of the strongest materials in existence⁸. CNTs amazing physical properties have astounded researchers from nearly every field of science, providing them with a promising new tool full of potential.

Carbon nanotubes (CNTs) are hollow carbon structures with one or more walls, a small diameter on the nanometer scale and a large length in comparison. The bonding in carbon nanotubes is sp^2 , with each atom joined to three neighbours, as in graphite. The tubes can therefore be considered as rolled-up graphene sheets (graphene is an individual graphite layer). This bonding structure, which is stronger than the sp^3 bonds found in diamond, provides the molecules with their unique strength. Under high pressure, nanotubes can merge together, trading some sp^2 bonds for sp^3 bonds, giving the possibility of producing strong, unlimited length wires through high-pressure nanotube linking⁹⁻¹⁰.



Figure 2: Structure of carbon nanotube

NANOTUBE GEOMETRY:

Carbon nanotubes (CNTs) are rolled up seamless cylinders of graphene sheets, exhibiting many unique physical, mechanical and chemical properties which have gleaned tremendous interest in the past decade. Depending on the number of graphene layers from which a single nanotube is composed, CNTs are classified as single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs)^{11,12}.

Single -walled carbon nanotubes (SWNTs):

SWNTs were discovered¹³ in 1993. These are the stars of the nanotube world, and somewhat reclusive ones at that, being much harder to make than the multi-walled variety. SWNTs consisting of a single sheet of carbon benzene rings wrapped into the shape of a cylinder of 1–2 nm diameter and lengths ranging from as short as 50 nm up to 1 cm. They are almost always closed at each end by a fullerene cage. The caps closing a SWNT, overwhelmingly, are one half of a buckyball molecule at each end. At present, most SWNT's are found in curled and curved strands rather than straight lines. Variations in the angle of the graphite planes that make up the bulk of a single-walled nanotube form the basis of how they are classified. The way the graphene sheet wraps can be represented by a pair of indices (*n*, *m*) called the chiral vector. The relationship between *n* and *m* defines three categories of CNTs. "Zigzag" nanotubes are so named because the angle at which the garphene sheet is rolled up makes it parallel to the row of zigzag bonds in the hexagonal structure(*n* = 0 or *m* = 0 and chiral angle equal to 0⁰). "Armchair" nanotubes are so named because the graphene sheet rolls up at an angle that is perpendicular to the bonds in the hexagonal lattice arm chair (*n* = *m* and chiral angle equal to 30⁰). The last classification, chiral nanotubes, has sheets aligned along the cylinder at some chiral angle other than armchair or zigzag (other values of *n* and *m* and chiral angles lie between 0 and 30⁰).



Figure 4: Molecular modals of (a) armchair configuration, (b) zig-zag arrangement, and (c) chiral conformation

SWNTs with different chiral vectors have dissimilar properties such as optical activity, mechanical strength and electrical conductivity. SWNTs exhibit important electric properties that are not shown by MWNTs. The most basic building block of these systems is the electric wire and these are excellent conductors¹⁴.

SWNTs were used in the development of the first intramolecular field-effect transistors (FETs) and intramolecular logic gate using SWNT FETs.¹⁵ To create a logic gate, a p-FET and an n-FET are required. Because SWNTs are p-FETs when exposed to air and n-FETs when unexposed to oxygen, they were able to protect half of a SWNT from oxygen exposure, while exposing the rest to oxygen. This results in a single SWNT that act as a NOT logic gate with both p- and n-type FETs within the same molecule.

Multi Walled carbon nanotubes (MWNTs):

MWNTs consist of multiple layers of graphite rolled in on themselves to form a tube shape with an interlayer spacing of 3.4 Å. The outer diameter of MWNTs may range from 1 to 50 nm while the inner diameter is usually of several nanometers. Two models are used to describe the structures of MWNTs such as the *Russian Doll* model where the sheets of graphite are arranged in concentric cylinders, *e.g.*, a (0, 8) SWNT within a larger (0, 10) SWNT and in the parchment model, a single sheet of graphite is rolled in around itself. The interlayer distance in MWNTs is close to the distance between graphene layers in graphite, approximately 3.4 (330 pm)¹⁶.

Table 1- Comparison between SWNT and MWNT

Sr. No.	SWNT	MWNT		
1.	Single layer of graphene.	Multiple layer of graphene.		
2.	Catalyst is required for synthesis.	Can be produced without catalyst.		
3.	Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition.	Bulk synthesis is easy.		
4.	Purity is poor.	Purity is high.		
5.	A chance of defect is more during functionalization.	A chance of defect is less but once occurred it's difficult to improve.		
6.	Less accumulation in body.	More accumulation in body.		
7.	Characterization and evaluation is easy.	It has very complex structure.		
8.	It can be easily twisted and are more pliable.	It cannot be easily twisted.		



Figure 5: MWNT with multiple concentric tubes of graphene

PROPERTIES

Interest in CNTs has grown at a very rapid rate because of their many exceptional properties, which span the spectrum from mechanical robustness to novel electronic transport properties.

Mechanical properties

The small diameter of a carbon nanotube has an important effect on the mechanical properties, compared with traditional micron-size graphitic fibers¹⁷. Perhaps the most striking effect is the opportunity to associate high flexibility and high strength with high stiffness, a property that is absent in graphite fibers.

Tensile strength:

CNTs are the strongest and stiffest materials on earth, in terms of tensile strength and elastic modulus respectively.

The SWCNT is about 100 times stronger than steel, yet one-sixth of its weight. Its hollow center and chicken-wirelike structure makes it very light, being 1/6th the weight of copper, and about half the weight of aluminum¹⁸. It is extremely challenging to measure the tensile strength of CNTs. Tensile load testing was performed by Yu *et al*¹⁹ on SWCNT bundles and tensile strength values ranging from 13 to 52 GPa were reported. Yu *et al*²⁰ have also conducted tensile testing of MWCNTs. It was found that only the outermost layer breaks during the loading process .The tensile strength corresponding to this layer of CNT ranges from 11 to 63 GPa. Nanotubes get their strength from the strong carbon-to-carbon bonds that hold together its fullerene lattice. Each carbon is covalently bonded to three other carbons. This strong bonding mechanism, coupled with the stability of the geometric structure of nanotubes, makes them remarkably strong²¹.

Elasticity:

Knowledge of the Young's modulus (E) of a material is the first step towards its use as a structural element for various applications. The Young's modulus is directly related to the cohesion of the solid and therefore to the chemical bonding of the constituent atoms. The Young's modulus of a CNT is related to the sp² bond strength and should equal that of a graphene sheet when the diameter is not too small to distort the C–C bonds significantly²². Lourie and Wagner²³ reported Young's modulus of 2.8–3.6 TPa, for SWNT and 1.7–2.4 TPa for MWNT. Direct tensile loading tests of SWNT¹⁹ and MWNT²⁰ have been performed by Yu *et al.* The Young's modulus obtained ranges from 320 to 1470 GPa (mean: 1002 GPa) for SWNT and from 270 to 950 GPa for MWNT. When exposed to great axial compressive forces, nanotubes have been shown to bend, twist, kink, and finally buckle. The tubes, however, do not break under the compressive loads.

This distinctive behavior is illustrated in Figure 6. When tested under great axial compression, it has been found that nanotubes appear to behave consistent with the Euler Limit. The Euler Limit specifies the point at which a straight tube will buckle. Since the deformation in a nanotube is elastic, the tube returns to its original shape when the load is removed⁶.



Figure 6: Elastic buckling mechanisms of SWNT

Table 2- The Physical Properties of Carbon Nanotubes

Equilibrium Structure

Average Diameter of SWNT's		1.2 -1.4 nm	
Distance from opposite Carbon Atoms (Line	2.83 Å		
Analogous Carbon Atom Separation (Line 2)	2.456 Å	
Parallel Carbon Bond Separation (Line 3)		2.45 Å	
Carbon Bond Length (Line 4)		1.42 Å	
C - C Tight Bonding Overlap Energy		~ 2.5 eV	
Group Symmetry		(10, 10) C5V	
Lattice: Bundles of Ropes of Nanotubes		Triangular Lattice	(2D)
Lattice Constant		17 Å	
Lattice Parameter:			
(10, 10) Armchair	16.78 Å		
(17, 0) Zigzag	16.52 Å		
(12, 6) Chiral	16.52 Å		
Density:			
(10, 10) Armchair	1.33 g/cm3		
(17, 0) Zigzag	1.34 g/cm3		
(12, 6) Chiral	1.40 g/cm3		
Interlayer Spacing:			
(n, n) Armchair	3.38 Å		
(n, 0) Zigzag	3.41 Å		
(2n, n) Chiral	3.39 Å		
Optical Properties			
Fundamental Gap:			
For $(n \ m)$: n-m is divisible by 3 [M		0 eV	
			0.5-11
For (n, m); n-m is not divisible by 3	Semi-conducti	ngj	~0.5eV
Electrical Transport			
Conductance Ouantization			(12.9 k O
			(

)-1

Resistivity Maximum Current Density	10-4 O -cm 1013 A/m2
Thermal Transport	
Thermal Conductivity	~ 2000 W/m/K
Phonon Mean Free Path	~ 100 nm
Relaxation Time	~ 10-11 s
Elastic Behavior	
Young's Modulus (SWNT)	~ 1 TPa
Young's Modulus (MWNT)	~ 1.28 TPa
Maximum Tensile Strength	~ 100 GPa

Electrical Properties:

Rolling up a graphene sheet on a nano-meter scale has dramatic consequences on the electrical properties²⁴. CNTs are regarded as molecular wires whose electronic properties are largely determined by extended molecular orbits. The chirality and diameter of a CNT is extremely important, because it influences its properties. In electrical terms, chirality and diameter determine whether a CNT will behave as a metal or a semiconductor. Depending on the specific realization, the nanotube may be a true one-dimensional metal or a semiconductor with a gap³. For metallic behaviour, CNTs can have conductivity up to eight times higher than that of copper. If a nanotube is rolled up evenly, like a sheet of paper with the top and bottom edges lined up, then it acts like a metallic conductor, efficiently carrying electricity. If a nanotube is rolled up askew, like a misbuttoned shirt, then its electrical properties change to those of silicon-like semiconductor where current can be switched on and off²⁵. Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if n = m, the nanotube is metallic; if n - m is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair (n = m) nanotubes are metallic, and nanotubes (6,4), (9,1), etc. are semiconducting. However, this rule has exceptions, because curvature effects in small diameter carbon nanotubes can strongly influence electrical properties. Thus, a (5,0) SWNT that should be semiconducting in fact is metallic according to the calculations. Likewise, vice versa- zigzag and chiral SWCNTs with small diameters that should be metallic have finite gap (armchair nanotubes remain metallic).

A flat sheet of graphite is considered to be a semi- metal. It possesses properties of both metals and semiconductors like copper wire and silicon chips, respectively. In its metallic form, electrons freely move in the sheet, while in its silicon state, electron movement is retarded. Since a nanotube is in essence a rolled up sheet of graphite, it possesses many of these same characteristics. When the seams of the sheet are mated together at an angle that allows each side to match evenly, the quantum mechanical wave functions will similarly match. This evenly matched configuration limits the types of wave functions the electrons are allowed to exhibit and thus affects the motion of the electrons. In certain cases, if a particular defect is present in the honeycomb structure of the tube lattice, it will cause a part of the tube to conduct electricity while a different section of the tube will act as a semiconductor. This phenomenon is referred to in electronics as a Shottky Barrier, and is a common, necessary component in many electronic devices²⁶.

When the structure of an SWNT is perfectly aligned, in other words the ends of the graphite sheet match up in a straight line, the tube takes on the characteristics of a ballistic conductor. A ballistic conductor ensures that each electron that enters one end exits the conductor at the opposite end. This highly efficient system possesses very little resistance. Only superconducting materials have resistance values lower than ballistic conductors²⁷.

Thermal properties:

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. Nanotubes are extremely stable at high temperatures. Because of their small size, quantum effects are important, and the low-temperature specific heat and thermal conductivity show direct evidence of 1-D quantization of the phonon band structure. Modeling of the low-temperature specific heat allows for determination of the on-tube phonon velocity, the splitting of phonon subbands on a single tube, and the interaction between neighboring tubes in a bundle. Theoretical work pre-dicts a room-temperature thermal conductivity over 200 W/m K for bulk samples of single-walled nanotubes (SWNTs), and over 3000 W/m

K for individual multiwalled nanotubes (MWNTs). Addition of nanotubes to epoxy resin cans double the thermal conductivity for a loading of only 1%, showing that nanotube composite materials may be useful for thermal management applications²⁸.CNTs can withstand 2800° C in a vacuum and up to 750° C at normal atmospheric pressures. It is these thermal characteristics as well as other factors that make nanotubes so well suited to serve as electrical conductors. Typical metallic conductors melt at temperatures between 600° C and 1000° C²⁹. In graphite, phonons dominate the specific heat above 20° K³⁰, whereas in SWNTs and MWNTs, the phonon contribution dominates at all temperatures³¹.

PRODUCTION OF MULTI-WALLED AND SINGLE-WALLED NANOTUBES

Producing nanotubes for research purposes, and in the future for industrial applications, is performed in numerous ways; most of which rely on the heating of graphite to a sufficient temperature that a plasma state is reached. The vaporized carbon atoms produced in the plasma condense in the form of soot, which is then collected and processed to extract the desired fullerene products. The three methods most commonly used are Arc Discharge, chemical vapor deposition (CVD), and laser vaporization.

A. Arc Discharge Method¹⁰⁻¹³

In 1991, Iijima reported the preparation of a new type of finite carbon structures consisting of needle-like tubes. The tubes were produced using an arc-discharge evaporation method similar to that used for the fullerene synthesis.

In this method, nanotubes are produced through arc vaporization of two carbon rods placed end to end with a distance of 1mm in an environment of inert gas such as helium, argon at pressure between 50 to 700 mbar. Carbon rods are evaporated by a direct current of 50 to 100 amps driven by 20V which will create high temperature discharge between two electrodes. Due to this, anode will get evaporated and rod shaped tubes will be deposited on cathode. Bulk production of CNTs depends on uniformity of plasma arc and temperature of deposition.



Figure 7: Experimental set-up of an arc discharge apparatus

1. Production of SWNTs:

In the production of SWNTs anode is dipped with a metal catalyst such as Fe, Co, Ni, Y, or Mo. It produces SWNTs with a diameter of 1.2 to 1.4nm. Efficiency of SWNT production by arc discharge method is improved with, a) Inert Gas

Argon with a lower diffusion coefficient and thermal conductivity has given nanotube with smaller diameter (1.2nm) and 0.2nm diameter decrease with 10% increase in argon: helium ratio, when Nickel and Yttrium is used as a catalyst (4.2: 1).

b) Optical Plasma Control

As the distance between anode and cathode increases, anode vaporization increases, due to which strong visible vortices around cathode is occurred. With a nickel and yttrium catalyst (C/Ni/Y is 94.8:4.2:1) the optimum

nanotubes were produced at a pressure of 660 mbar for pure helium and 100 mbar for pure argon. The nanotubes diameter ranges from 1.27 to1.37 nanometer.

c) Catalyst

By changing metal catalyst, nanotubes with a diameter of 0.6 to 1.2nm are produced. Catalysts used are Co and Mo.

d) Open Air Synthesis with Welding Arc Torch

This method is specifically used for SWNTs with graphite rod containing metal catalyst. Ni and Y (3.6: 0.8 at %) are fixed at side wall of water cooled, steel based electrode, torch arc aimed at the edge of target and soot is deposited on substrate behind the target. The arch is operated at 100 amps current and shielding Ar gas flowed through torch to enhance arc jet formation. This method is very convenient and inexpensive with Ni:Y(3.6: 0.8). Nanotubes produced by this method are of diameter of 1.32nm.

2. Production of MWNTs

MWNTs are produced with the use of pure graphite arc with an inner diameter 1-3nm and outer diameter10nm (approx.). Since catalyst is not used in this process there is no need for a heavy acidic purification. So, MWNTs can be formed with a less number of defects. Different methods used to synthesize are,

a) Synthesis in Liquid Nitrogen¹¹

MWNTs are formed by generating arc-discharge in liquid nitrogen. For which low pressure and expensive inert gas are not needed. Yield is about 70% of reaction product.

b) Magnetic Field Synthesis¹²

MWNTs formed by this method are defect free and having high purity. In this arc- discharge is controlled by a magnetic field around the arc plasma. Extremely pure graphite rods (purity > 99.999 %) are used as electrodes. Highly pure MWNTs (purity > 95 %) are obtained without further purification, which disorders walls of MWNTs.

c) Plasma Rotating Arc Discharge¹³

The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapor perpendicular to the anode and the rotation distributes the micro discharges uniformly and generates stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature. At the rotation speed of 5000 rpm, a yield of 60 % was found at a temperature 1025° c without the use of a catalyst. The yield can be increased up to 90% after purification if the rotation speed is increased and the temperature is enlarged.

B. Laser Ablation Method¹³:

In 1996, Smalley and co-workers produced high yields (>70%) of SWNTs by laser-ablation (vaporization) of graphite rods with small amounts of Ni and Co at $1200^{9}C^{32}$. A pulsed or continuous laser is used which will vaporize a graphite target in an oven at $1200^{9}c$. The oven is filled with helium or argon gas in order to keep the pressure at 500 torr. Since the optimum background gas and catalyst mixture is the same as in the arc discharge process, this method is almost similar to arc discharge. This method is very expensive so it is mainly used for SWNTs. Laser vaporization results in higher yield of SWNTs with narrower size distribution than those produced in arc discharge process. Catalyst used for SWNTs is Ni: Y (4.2: 1 at %).



Figure 8: Laser ablation method

Different methods used to synthesize are,

a) Ultra Fast Pulses from a Free Electron Laser (FEL) Method:

In this method the pulse width is ~ 400 fs. The repetition rate of the pulse is increased from 10 Hz to 75 MHz. The intensity of the laser bundle is ~5 x 1011 w/cm². A jet of preheated argon gas is located near the rotating graphite target. In that argon gas deflects the ablation 90⁰ away from incident beam direction, clearing carbon soot from front of target. If this system is upgraded with full power a yield of 45gm/ hr can be achieved. Catalyst used is Ni, Co or Ni, Y.

b) Continuous Wave Laser-Powder Method:

This method, CO2 laser is used in an argon stream. Laser ablation of mixture of graphite and catalyst powder is carried out, due to which thermal conductivity losses are significantly reduced. The catalyst used is Ni: Co (1:1) and yield is 5 gm/hr. MWNTs can be also produced with pure graphite.

C. Chemical Vapors Deposition Method¹⁴⁻¹⁵:

Carbon filaments and fibers have been produced by thermal decomposition (or chemical vapor decomposition) of hydrocarbons in the presence of a catalyst since the 1960s. A similar approach was used for the first time by Yacaman³³ et al. in 1993 and in 1994 Ivanov³⁴ and co-workers to grow MWNTs.

Chemical vapour deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to "crack" the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. Excellent alignment, as well as positional control on nanometer scale, can be achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes.

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant. The temperatures for the synthesis of nanotubes by CVD are generally within the 650–900^oC range. Typical yields for CVD are approximately 30%. These are the basic principles of the CVD process. In the last decennia, different techniques for the carbon nanotubes synthesis with CVD have been developed, such as plasma enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, vapour phase growth, aero gel-supported CVD and laser assisted CVD.

a) Plasma enhanced chemical vapour deposition:

The plasma enhanced CVD method generates a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. Figure 9 shows a schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure.

A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metal, such as Fe, Ni and Co are used on for example a Si, SiO₂, or glass substrate using thermal CVD or sputtering. After nanoscopic fine metal particles are formed, carbon nanotubes will be grown on the metal particles on the substrate by glow discharge generated from high frequency power. A carbon containing reaction gas, such as C_2H_2 , CH_4 , C_2H_6 , CO is supplied to the chamber during the discharge.

The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni seems to be the most suitable pure-metal catalyst for the growth of aligned multiwalled carbon nanotubes (MWNTs). The diameter of the MWNTs is approximately 15 nm. The highest yield of carbon nanotubes achieved was about 50% and was obtained at relatively low temperatures (below 330^oC).

b)Thermal chemical vapour deposition:

In this method Fe, Ni, Co or an alloy of the three catalytic metals is initially deposited on a substrate. After the substrate is etched in a diluted HF solution with distilled water, the specimen is placed in a quartz boat. The boat is

positioned in a CVD reaction furnace, and nanometre-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 $1050^{\circ}C$. As carbon nanotubes are grown on these fine catalytic metal particles in CVD synthesis, forming these fine catalytic metal particles is the most important process. Figure 10 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.

When growing carbon nanotubes on a Fe catalytic film by thermal CVD, the diameter range of the carbon nanotubes depends on the thickness of the catalytic film. By using a thickness of 13nm, the diameter distribution lies between 30 and 40 nm. When a thickness of 27 nm is used, the diameter range is between 100 and 200 nm. The carbon nanotubes formed are multiwalled.



Figure 9: Schematic diagram of plasma CVD apparatus



Figure 10: Schematic diagram of thermal CVD apparatus

c) Alcohol catalytic chemical vapour deposition:

Alcohol catalytic CVD (ACCVD) is a technique that is being intensively developed for the possibility of large-scale production of high quality single wall nanotubes SWNTs at low cost. In this technique, evaporated alcohols, methanol and ethanol, are being utilised over iron and cobalt catalytic metal particles supported with zeolite. Generation is possible is possible at a relatively low minimum temperature of about 550°C. It seems that hydroxyl radicals, who come from reacting alcohol on catalytic metal particles, remove carbon atoms with dangling bonds, which are obstacles in creating high-purity SWNTs. The diameter of the SWNTs is about 1 nm. Figure 11 shows the ACCVD experimental apparatus.

The lower reaction temperature and the high-purity features of this ACCVD technique guarantee an easy possibility to scale production up at low cost. Furthermore, the reaction temperature, which is lower than 600° C, ensures that this technique is easily applicable for the direct growth of SWNTs on semiconductor devices already patterned with aluminum.



Figure 11: ACCVD experimental apparatus

d)Vapour phase growth:

Vapour phase growth is a synthesis method of carbon nanotubes, directly supplying reaction gas and catalytic metal in the chamber without a substrate. Figure 12 shows a schematic diagram of a vapour phase growth apparatus. Two furnaces are placed in the reaction chamber. Ferrocene is used as catalyst. In the first furnace, vaporisation of catalytic carbon is maintained at a relatively low temperature. Fine catalytic particles are formed and when they reach the second furnace, decomposed carbons are absorbed and diffused to the catalytic metal particles. Here, they are synthesised as carbon nanotubes. The diameter of the carbon nanotubes by using vapour phase growth are in the range of 2–4 nm for SWNTs and between 70 and 100 nm for MWNTs.



Figure 12: Schematic diagram of a vapour phase growth apparatus

e) Aero gel-supported chemical vapour deposition:

In this method SWNTs are synthesised by disintegration of carbon monoxide on an aero gel-supported Fe/Mo catalyst. There are many important factors that affect the yield and quality of SWNTs, including the surface area of the supporting material, reaction temperature and feeding gas. Because of the high surface area, the porosity and ultra-light density of the aero gels, the productivity of the catalyst is much higher than in other methods. After a simple acidic treatment and a oxidation process high purity (>99%) SWNTs can be obtained. When using CO as feeding gas the yield of the nanotubes is lower but the overall purity of the materials is very good. The optimal reaction temperature is approximately 860^oC.

f) Laser-assisted thermal chemical vapour deposition:

In laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO_2 laser, which was perpendicularly directed onto a substrate, pyrolyses sensitised mixtures of $Fe(CO)_5$ vapour and acetylene in a flow reactor. The carbon nanotubes are formed by the catalysing action of the very small iron particles. Figure 13 shows the experimental set-up for laser-assisted CVD.

By using a reactant gas mixture of iron pentacarbonyl vapour, ethylene and acetylene both single- andmulti-walled carbon nanotubes are produced. Silica is used as substrate. The diameters of the SWNTs range from 0.7 to 2.5 nm. The diameter range of the MWNTs is 30 to 80 nm.



Figure 13: Experimental set-ups for laser-assisted CVD

g)CoMoCat process:

In this method, SWNTs are grown by CO disproportionation at $700 - 950^{\circ}$ C. The technique is based on a unique Co-Mo catalyst formulation that inhibits the sintering of Co particles and therefore inhibits the formation of undesired forms of carbon that lower the selectivity. During the SWNT reaction, cobalt is progressively reduced from the oxidic state to the metallic form. Simultaneously Molybdenum is converted to the carbidic form. Co acts as the active species in the activation of CO, while the role of the Mo is possibly dual. It would stabilise Co as a well-dispersed Co²⁺ avoiding its reduction and would act as a carbon sink to moderate the growth of carbon inhibiting the formation of undesirable forms of carbon.

It is found that one of the critical conditions for an effective reactor operation is that the space velocity has to be high enough to keep the CO conversion as low as possible. Figure 14 shows a fluidised bed reactor for a CoMoCat process. The most important advantage of fluidised bed reactors is that they permit continuous addition and removal of solid particles from the reactor, without stopping the operation.

This method can be scaled-up without losses in SWNT quality. By varying the operation conditions, SWNTs can be produced with different diameter ranges. The CoMoCat catalyst has a high selectivity towards SWNTs, namely 80 - 90%.

In Table 3 several diameter ranges at different temperatures are given.



Table 3- Diameter range versus temperature

Figure 14: Schematic diagram of a CoMoCat apparatus

h)High pressure CO disproportionation process:

The High pressure CO disproportionation process (HiPCO) is a technique for catalytic production of SWNTs in a continuous-flow gas phase using CO as the carbon feedstock and $Fe(CO)_5$ as the ironcontaining catalyst precursor. SWNTs are produced by flowing CO, mixed with a small amount of $Fe(CO)_5$ through a heated reactor. Figure 15 shows the layout of CO flow-tube reactor. Size and diameter distribution of the nanotubes can be roughly selected by controlling the pressure of CO. This process is promising for bulk production of carbon nanotubes.

Nanotubes as small as 0.7 nm in diameter, which are expected to be the smallest achievable chemically stable SWNTs 48, have been produced by this method. The average diameter of HiPco SWNTs is approximately 1.1 nm. The yield that could be achieved is approximately 70%. The highest yields and narrowest tubes can be produced at the highest accessible temperature and pressure. SWNT material with 97% purity can be produced at rates of up to 450 mg/h with this process.

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization
Who	Ebbesen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Nagano, Japan	Smalley, Rice, 1995
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms 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 NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 Microns), with individual diameter from 1-2 nm.
MWNT	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.
Production	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis Possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Conclusion	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

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Application of CNTs:

CNTs have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area. The combinations of these characteristics make CNTs unique materials with the potential for diverse applications.

1. CNTs in medical application: In a recent report, business opportunities for nanostructured materials in biotechnology and medicine were estimated to be of the order of 180 billion US\$ in 2015.

CNTs in Drug Delivery:

Drug delivery has been a major area of focus for researchers aiming to improve the efficacy of therapeutic molecules. Researchers are trying to overcome some obstacles these include poor drug distribution among cells, unwanted damage to healthy tissue, toxicity, and lack of the ability to select a particular cell type for treatment³⁵. However, researchers have found that CNTs possess the characteristics to serve as a model drug delivery system, avoiding common barriers typical of traditional drug delivery methods. CNTs have the potential to carry drugs in the organism as they are hollow and much smaller than the blood cells.

Wu W *et al*³⁶ postulated that delivery of antibiotic amphotericin B by means of CNTs would reduce the amount of antibiotic necessary resulting in improved potency reduced toxicity. One major obstacle in traditional delivery of this drug is that it has a low solubility and causes membrane leakage in eukaryotic cell.

Barroug A *et al*³⁷ studied that cisplatin incorporated oxidized SWNTs have showed slow release of cisplatin in aqueous environment. The released cisplatin had been effective in terminating the growth of human lung cancer cells, while the SWNTs alone did not show anticancer activity.

Cristina R *et al*³⁸ have created an alginate polymeric film embedded with SWNT, and have studied the release of bovine serum albumin from this SWNT-incorporated polymer. Their results indicate that the proteins released from the MWNT polymer construct maintained their biological function, and that it shows potential for drug delivery applications.

CNTs in cancer therapy:

CNTs are tubular materials with nanometer-sized diameters and axial symmetry, giving them unique properties that can be exploited in the diagnosis and treatment of cancer. They can be functionalized (i.e., surface engineered) with certain functional groups in order to manipulate their physical or biological properties. In addition to the ability of CNTs to act as carriers for a wide range of therapeutic molecules, their large surface area and possibility to manipulate their surfaces and physical dimensions have been exploited for use in the photothermal destruction of cancer cells.

Yinghuai Z *et al*³⁹ have recently developed a new approach to Boron Neutron Capture Therapy in the treatment of cancer using substituted Carborane-Appended Water-Soluble single-wall carbon nanotubes. Substituted C2B10 carborane cages were successfully attached to the side walls of SWNTs via nitrene cycloaddition. The decapitations of these C2B10 carborane cages, with the appended SWNTs intact, were accomplished by the reaction with sodium hydroxide in refluxing ethanol. During base reflux, the three-membered ring formed by the nitrene and SWNT was opened to produce water-soluble SWNTs in which the side walls were functionalized by both substituted nido-C2B9 carborane units and ethoxide moieties.

Zhuang L *et al*⁴⁰ have been conducted on in vivo biodistribution and highly efficient tumor targeting of carbon nanotubes in mice for cancer therapy. Investigations are being done on the biodistribution of radio-labelled SWNTs in mice by in vivo positron emission tomography (PET), ex vivo biodistribution and Raman spectroscopy. It was found that SWNTs that are functionalized with phospholipids bearing polyethylene glycol (PEG) are surprisingly stable *in vivo*. The effect of PEG chain length on the biodistribution and circulation of the SWNTs was studied. Effectively PEGylated SWNTs exhibited relatively long blood circulation times and low uptake by the reticuloendothelial system (RES). Efficient targeting of integrin positive tumor in mice was achieved with SWNTs coated with PEG chains linked to an arginine–glycine–aspartic acid (RGD) peptide. A high tumor accumulation was attributed to the multivalent effect of the SWNTs.

Panchapakesan B^{41} conducted an experiment to kill the malignant cells by putting the carbon nanotubes in water to make them absorb it. Then, an 800 nanometer laser is shot at the SWNTs which cause them to actually explode because of the water that they absorb. These water molecules heat up to about 100° c when they are hit with the laser that has an intensity of approximately 50 to 100 mW/cm². At this temperature, the water evaporates and develops an extreme pressure which in turn causes the SWNTs to explode. These "micro explosion" kill all of the malignant cells that surround the explosion.

Dhar S *et al*⁴² have developed "longboat" anticancer system in which the chemotherapeutic agent cisplatin is attached from one end to the folic acid derivative and from the opposite end to a SWNT via an amide link.

CNTs in Gene Delivery:

CNTs solubility & biocompatibility can be improved by attaching various functional groups to the sidewalls of nanotubes. These attachments of functional groups make functionalized CNTs (f-CNTs) which can be used for the delivery of proteins & genes. The basic premise of gene delivery is to insert a gene into a cell and activate it through transcription and translation, thereby producing a protein as the end result. Functionalized CNTs are being intensively explored in advanced biotechnological applications ranging from molecular biosensors to cellular growth substrates.

Singh R *et al*⁴³ studied the capability of ammonium-functionalized single-walled CNTs to penetrate human and murine cells and facilitate the delivery of plasmid DNA leading to expression of marker genes. They studied about the interactions of three types of f-CNTs, ammonium-functionalized single-walled and multiwalled carbon

nanotubes (SWNT-NH₃⁺; MWNT-NH₃⁺), and lysine-functionalized single-walled carbon nanotubes (SWNT-Lys-NH₃⁺), with plasmid DNA. Nanotube–DNA complexes were analyzed by scanning electron microscopy, surface plasmon resonance, PicoGreen dye exclusion, and agarose gel shift assay. The results indicate that all three types of cationic carbon nanotubes are able to condense DNA to varying degrees, indicating that both nanotube surface area and charge density are critical parameters that determine the interaction and electrostatic complex formation between f-CNTs with DNA.

Pan B *et al*⁴⁴ were fabricated polyamidoamine dendrimer modified multi-walled carbon nanotubes (dMNTs), and it characterized by high-resolution transmission electron microscopy, atomic force microscopy, x-ray photoelectron spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy and thermogravimetric analysis, revealing the presence of dendrimer capped on the surface of carbon nanotubes. Compared with the composites of CNT–NH₂–asODN and dendrimer–asODN, no. 5 generation of dendrimer-modified MNT–asODN composites exhibit maximal transfection efficiencies and inhibition effects on tumor cells. The intracellular gene transport and uptake via dMNTs should be generic for the mammalian cell lines.

Nunes A *et al*⁴⁵ have studied capability of different cationic polymer-grafted multiwalled carbon nanotubes (MWNTs) (polymer-g-MWNTs) to efficiently complex and transfer plasmid DNA (pCMV- β Gal) in vitro without promoting cytotoxicity. In this study Carboxylated MWNT is chemically conjugated to the cationic polymers polyethylenimine (PEI), polyallylamine (PAA), or a mixture of the two polymers. Gel migration studies confirm pDNA binding to polymer-g-MWNT with different affinities, highest for PEI-g-MWNT and PEI/PAA-g-CNT constructs. They concluded that polymer-g-MWNTs might be considered in the future as a versatile tool for efficient gene transfer in cancer cells in vitro.

2. CNTs in biological imaging: In addition to applications for drug delivery and treatment, the intrinsic optical properties of SWNTs make them useful as optical probes. Owing to their quasi 1-D nature, SWNTs exhibit strong resonance Raman scattering, high optical absorption and photoluminescence in the near-infrared (NIR) range, all of which have been utilized for imaging in biological systems in vitro and in vivo.

Weisman R *et al*⁴⁶ have utilized near infrared (NIR) fluorescence microscopy to image SWNTs in phagocytic cells. They used SWNTs at varying concentrations to track their ex vivo uptake in mouse peritoneal macrophage cells. NIR fluorescence imaging revealed that there was no difference in population growth, adhesion, morphology and confluence between the control and the cultures containing SWNTs. Detectable emission was seen only in cells incubated with SWCNTs.

Cherukuri P *et al*⁴⁷ have used in vivo NIR imaging to assess the biocompatibility of SWNTs in an intact organism, Drosophila melanogaster. This study suggests the effectiveness of SWNTs as NIR probes for studying individual nanotubes in tissue specimens or inside living organisms during the course of tissue regeneration.

Zavaleta C *et al*⁴⁸ indicates the use of Raman imaging for real-time monitoring of SWNTs for disease (tumor) targeting and localization. Specifically disease targeting SWNTs (RGD–SWNT, arginine–glycine–aspartic acid) were examined for localization in diseased (tumor) mice as against plain SWNT. The images showed a higher accumulation of RGD–SWNTs in the tumor compared to the non-functionalized SWNT mouse group, and there was significantly less accumulation in the liver and spleen.

De La Zerda A *et al*⁴⁹ used RGD–SWNTs to target tumors in mice, and demonstrated that an eight fold greater PA signal was seen in these compared to non-targeted SWNTs. The results suggest that SWNT-enhanced noninvasive deep tissue PA imaging at high spatial resolution can be obtained for imaging nanotherapeutics in the body. The PA techniques can also help understand several intrinsic factors of tissues and cells, for example vascularization and oxygen saturation in diseased tissues and tissue engineering constructs.

CNTs in lithium–ion batteries: For the fabrication of light-weight and efficient batteries, lithium is one of the best elements due to its unique properties (it has the lowest electronegativity and electrons are easily donated from Li^+). However, due to the high reactivity of Li, the negative Li electrode reacts easily and thus the metal is no longer efficient. However, it is possible to intercalate Li ions within graphite-like structures so that Li^+ can migrate from a graphitic anode to the cathode (usually LiCoO₂, LiNiO₂, and LiMn₂O₄). The electrodes are normally separated by

polyolefin. The theoretical Li storage capacity in graphite is 372 mAh/g (LiC₆), and the charge and discharge phenomena in these batteries are based on the Li⁺ intercalation and de-intercalation.

$$\begin{array}{c} Charge\\ LiCoO_2 + y \ C < \longrightarrow \\ Discharge \end{array} > Li_{(1-x)} + CoO_2 + Li_xC_y \end{array}$$

Charge $y C + xLi + xe^- < ----> Li_xC_y$ Discharge

Like graphite, nanotubes can store ions of lithium – a commonly used material in certain batteries. Unlike graphite, however, nanotubes may be able to hold the lithium ions both inside and outside due to its tubular structure⁶. It has been speculated that a higher Li capacity may be obtained in carbon nanotubes if all the interstitial sites (inter-shell van der Waals spaces, inter-tube channels, and inner cores) are accessible for Li intercalation.

Che GL *et al*⁵⁰ also demonstrated that aligned CNT arrays can be used in the anode fabrication within LiC batteries and that the intercalation capacity (490 mAh/g) doubles that of standard carbon. In 1990, Sony was the first company to commercialize such batteries, and at present this technology is used in portable computers, mobile phones, digital cameras, etc.

4. Hydrogen Storage: The area of hydrogen storage in carbon nanotubes remains active and controversial. Materials with high hydrogen storage capacities are desirable for energy storage applications. Metal hydrides and cryo-adsorption are the two commonly used means to store hydrogen, typically at high pressure and/or low temperature. Extraordinarily high and reversible hydrogen adsorption in SWNT containing materials and graphite nanofibers (GNFs) has been reported. Because of their cylindrical and hollow geometry, and nanometer-scale diameters, it has been predicted that the carbon nanotubes can store liquid and gas in the inner cores through a capillary effect. An even higher hydrogen uptake, up to 14-20wt%, at $20-400^{\circ}$ C under ambient pressure was reported in alkali-metal intercalated carbon nanotubes⁵¹. H₂ storage in CNTs may be advantageous in the fabrication of fuel cells mainly for powering electric vehicles.

5. **CNTs as Biosensors:** Carbon nanotubes have been used as biosensors in a variety of ways. There has been much interest in using 'bulk' quantities of nanotubes in macroscopic electrodes to replace, or complement, existing electrode materials such as glassy carbon or precious metals.

Muguruma H *et al*⁵²Carbon nanotube–plasma polymer-based amperometric biosensors for ultrasensitive glucose detection have been fabricated. Two amperometric enzyme biosensors were fabricated. A mixture of the enzyme glucose oxidase (GOD) and a CNT film was sandwiched with 10-nm-thick acetonitrile plasma-polymerized thin films (PPFs). In order to facilitate the electrochemical communication between the CNT layer and GOD, CNTs were treated with oxygen plasma. The device with single-walled CNTs showed a sensitivity higher than that of multi walled CNTs. The glucose biosensor showed ultrasensitivity (a sensitivity of 40 μ A mM-1 cm-2, a correlation coefficient of 0.992, a linear response range of 0.025 –1.9 mM, a detection limit of 6.2 μ M at S/N = 3, +0.8V vs Ag/AgCl), and a rapid response (<4 seconds in reaching 95% of maximum response).

Timur S *et al*⁵³A microbial biosensor based on carbon nanotube (CNT) modified electrodes was developed. Pseudomonas putida DSM 50026 cells were used as the biological component and the measurement was based on the respiratory activity of the cells estimated from electrochemical measurements. The effects of pH and temperature were also examined. The study found that whole cell P. putida biosensors using Os-redox polymers could be good alternatives for the analysis of different substrates such as glucose as well as xenobiotics in the absence of oxygen with high sensitivity because of the fast electron collection efficiency between the Os-redox polymer and the bacterial cells.

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