Synthesis, Properties and Applications of Carbon Nanotubes: Review Article

[1]Neera Sharma, [2]Preeti Sharma
[1,2]Department of Physics
[1,2]Agra College, Agra, U.P., India

Abstract: In this review article introduction about Carbon nanotubes is given. Authors study the synthesis process, purification methods, properties and applications of SWCNTs, DWCNTs and MWCNTs. It is found that CNTs can be used in wide number of applications because of their unique mechanical and electrical properties. Research is going on the properties of CNTs by experimental methods, theoretical methods and MD simulation method.

***Index Terms* – Carbon nanotubes, Properties, Applications**

I. Introduction:

Carbon nanotubes are allotropes of carbon having very large length-to-diameter ratio. They have very unique properties like very high elasticity, high tensile strength etc. Their electrical and thermal properties are also discussed in this article. Depending on these properties they have wide range of applications.

Carbon nanotubes (CNTs) were discovered by Iijima in 1991 [1]. Their diameter is in nanometer and their length can be up to several mms. Therefore, their length-to-diameter ratio is very high. As their name suggest, carbon nanotubes are cylindrical having tube like appearance. CNTs are graphite sheets rolled in the form of seamless cylinder. CNTs are synthesized by bottom up chemical synthesis process. CNTs are of two types – single walled carbon nanotube (SWCNT) and multi walled carbon nanotube (MWCNT).

Single walled carbon nanotubes are graphene sheets rolled in the form of seamless cylinder of radius on nanometer scale having a hexagonal lattice of carbon. SWCNT diameter differs 0.4 to 2 to 3 nm, and their length is typically of the micrometer range. SWCNTs usually can come together and form bundles (ropes) [2]. Fig.1 shows a single-wall carbon nanotube.

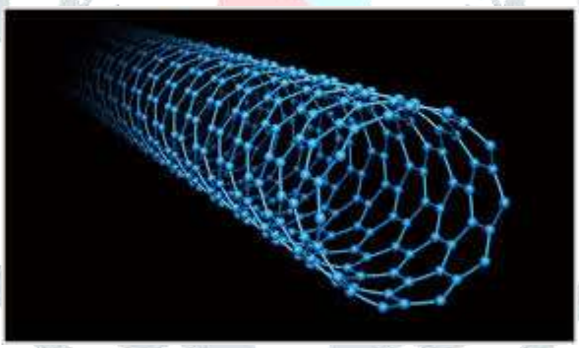

Fig.1Single walled carbon nanotubes [3]

Multi walled carbon nanotubes are multiple concentric nanotubes cylinder as shown in fig.2. Depending on the number of layers, the inner diameter of MWCNTs diverges from 0.4 nm up to a few nm and outer diameter varies from 2 nm up to 20 to 30 nm. Their axial size differs from 1μm up to a few cm [2]. The structure of multi walled carbon nanotubes can be described by using two models Russian doll model and the parchment model [4].

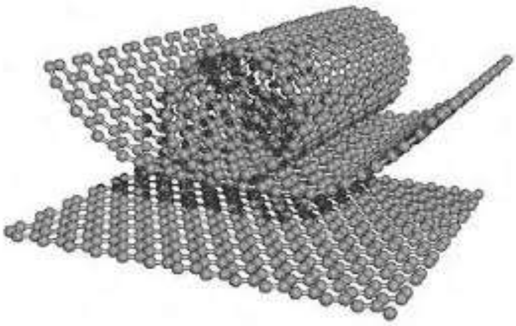

Fig.2 Multi walled carbon nanotubes [5]

In Russian Doll model, one carbon nanotube lies within another nanotube of larger diameter. On the other hand, in Parchment model, a single graphene sheet wrapped around itself manifold times [4].

Comparison between SWCNT and MWCNT [6]:

SWCNT	MWCNT
Single layer of graphene	Multiple layer of grapheme
Catalyst is required for synthesis	Can be produced without catalyst
Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition	Bulk synthesis is easy
Purity is poor	Purity is high
A chance of defect is more during functionalization	A chance of defect is less but once occurred it is difficult to improve
Less accumulation in the body	More accumulation in the body
Characterization and evaluation is easy	It has very complex structure
It can be easily twisted and is more pliable	It cannot be easily twisted

Depending on the rolling of graphene sheet, carbon nanotubes have three configurations –

- Armchair
- Zigzag
- Chiral

The three types of CNTs are shown in fig.3

The configuration of SWCNT is defined by two indices (n,m) that describe chiral vector. These are key parameters of a nanotube. n being in axial direction and m being in radial direction. When m=0, the nanotubes are named as zigzag nanotubes; when n=m, the nanotubes are named as armchair nanotubes, and other state are called chiral[3].

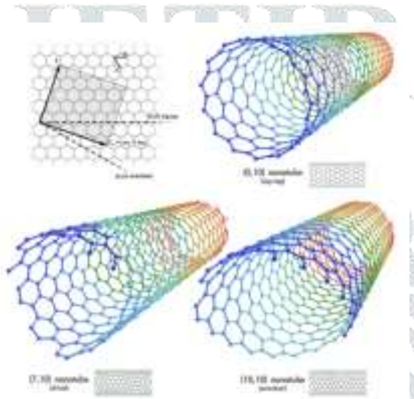

Fig.3: Different configuration of carbon nanotubes [7]

Fig.4 shows a graphene sheet indicating chiral vector and chiral angle.

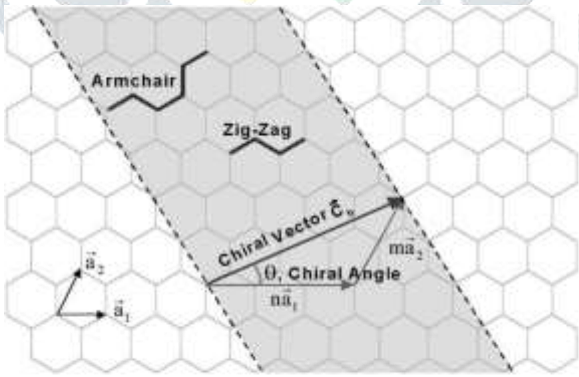

Fig.4 Graphene sheet [8]

The chiral vector $C = na_1+ma_2$ (a_1 and a_2 are base vectors of graphite) [6,9] also determines the tube diameter d, which can be given by

$$d = \frac{a\sqrt{m^2 + n^2 + mn}}{\pi}$$

Where a = $1.42\times\sqrt{3}$ corresponds to the lattice constant in the graphite sheet.

II. Synthesis of CNTs:

Arc-discharge, laser ablation and chemical vapor deposition have been the three main methods used for carbon nanotube synthesis [10]. For SWCNTs, none of the three synthesis methods has yielded bulk materials with homogeneous diameters and chirality thus far [11].

2.1 Electric Arc Discharge method:

In this method, structural defects are least. In this method, arc discharge between high-purity water-cooled graphite electrodes with diameters between 6 to 12 mm and separated by 1 to 2 mm in a chamber filled with helium at pressure 500 torr is used [12]. The chamber also contains evaporated carbon molecules and some amount of metal catalyst particles such as cobalt, nickel, iron. Fig.5 shows an arrangement for arc discharge method.

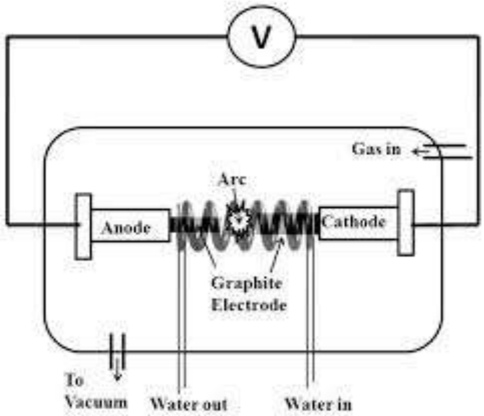

Fig.5 Electric arc discharge method [13]

Direct current is passed through the chamber and the chamber is pressurized and heated to 4000 K. CNTs are obtained in the cathode soot and chamber soot [4]. Studies have shown Ni-Y-graphite mixtures can produce high yields of SWCNTs [14]. The main advantage of this technique is ability and potential for production of large quantity of nanotubes [4]. On the other hand, the disadvantage is relatively little control over the alignment (chirality) of the created nanotubes [4].

2.2 Laser ablation method:

The principles and mechanisms of laser ablation method are similar to the arc-discharge method, but in this method, but the needed energy is provided by a laser which hit a pure graphite pellet holding catalyst materials [4].

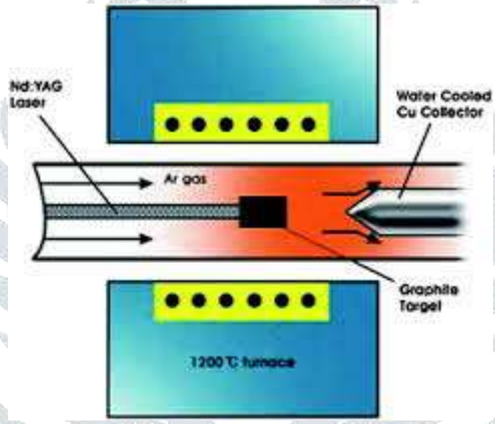

Fig.6: Laser ablation method [15]

In this method, a pure graphite block is placed in a quartz tube in Ar atmosphere inside a furnace [16]. The furnace is heated to 1200˚C. The laser beam is used to vaporize graphite within the quartz. Metal particles are added for the synthesis of CNTs [3]. Fig.6 shows an arrangement for laser ablation method.

Laser pulse power is increased to decrease the diameter of CNTs [17]. To increase the quantity of CNTs, ultrafast laser pulses are used [18].

The main advantage of this method is that it consists high yield and relatively low metallic impurities [4]. On the other hand, the main disadvantage is that the nanotubes obtained by this technique are not necessarily uniformly straight but instead do contain some branching [4].

This method is not economically advantageous because

- High-purity graphite rods are required [4].
- The laser power required are great [4].
- The quantity of nanotubes synthesized per day is low [4].

2.3 Chemical Vapor Deposition (CVD):

There are different types of CVDs –

- Catalytic chemical vapor deposition (CCVD) - Either thermal [19] or plasma enhanced (PE) oxygen assisted [1] CVD
- Water assisted CVD [20,21,22]
- Microwave plasma enhanced CVD (MPECVD) [23]
- Radio-frequency CVD (RF-CVD) [24]
- Hot filament CVD (HFCVD) [25,26]

The standard technique for the synthesis of CNTs is CCVD [4].

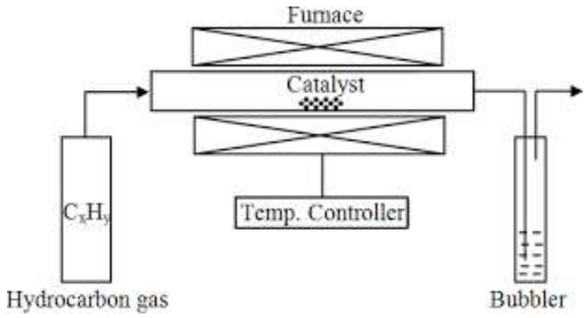

Fig.7 Chemical vapor deposition method [27]

In this method, a layer of metal catalyst prepares and processes a substrate at approximately 700˚C. Metal catalyst [28] or a combination [29] is used for growth of CNTs. The 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 [30]. Most commonly used gaseous carbon sources are methane, carbon monoxide and acetylene. The carbon diffuses towards the substrate, where it will bind. The synthesis of CNTs by CVD is a two-step process – 1) catalyst preparation step and 2) actual synthesis of the nanotube [30]. Fig.6 shows an arrangement for the synthesis of CNTs using chemical vapor deposition method.
The advantages of CCVD method are –

- Economically practical method for large scale CNT production [31].
- High purity if CNTs is obtained [31].
- Reaction can be easily controlled [31].
- By this method, excellent alignment, as well as positional control on nanometer scale, can be achieved [30].

2.4 Large Scale Production of CNTs:
Due to properties of CNTs, they can be used in various applications. So, large scale production of CNTs is essential. Production of MWCNTs is larger than SWCNTs. Most of the production of CNTs is derived from chemical vapor deposition (CVD). There is need of increasing production of CNTs due to need of them.

Here is a table that gives a comparison between the different methods of synthesis [4]

Method	Arc Discharge	Laser ablation	CVD
Yield rate	>75%	>75%	>75%
SWCNT or MWCNT	Both	Both	Both
Advantage	Simple, inexpensive and high quality nanotubes	Relatively high purity, room temperature synthesis	Simple, low temperature, high purity, large scale production, aligned growth possible
Disadvantage	High temperature, purification required, tangled nanotubes	Method limited to the lab scale, crude product purification require	Synthesized CNTs are usually MWCNTs, defects

III. Purification of CNTs:

The nanotubes synthesized by above methods are impure and there is need of purification of these CNTs. All purification procedures have the following main steps[24] –

- Deletion of large graphite particles and aggregations with filtration.
- Dissolution in appropriate solvents to eliminate catalyst particles (concentrated acids as solvents) and fullerenes (use of organic solvents).
- Chromatography to size separation and remove the amorphous carbon clusters.

The techniques [32,33] used for purification of CNTs are –

1. Oxidation
2. Acid treatment
3. Annealing
4. Ultra sonication
5. Micro filtration
6. Ferromagnetic separation
7. Cutting
8. Functionalization
9. Chromatography

Any one of the above technique for purification can be used depending on the method of synthesis.

IV. Properties of CNTs:

MWCNTs and SWCNTs have similar properties. Because of multilayer nature of MWCNTs, the outer walls can not only shield the inner carbon nanotubes from chemical interactions with outside substances but also present high tensile strength properties, which do not exist in SWCNTs (or exist partially) [19].

4.1 Electrical Properties:

CNTs have very interesting electrical properties. Electrical properties of CNTs depend upon chiral vector. Graphene is a zero gap semiconductor but CNTs can be metals or semiconductor with different sized energy gap depending on the indices (n,m). It is observed that when n=m, i.e, armchair nanotubes are metallic in nature. When n-m=3j, where j is a non-zero integer, i.e. zig-zag nanotubes are semiconductor with very small energy band gap. Rest all CNTs are semiconductors with very large energy band gap [34,35,36]. As the radius of tube R increases, the energy band gap in the large and small energy band gap nanotubes decreases with 1/R and $1/R^2$ respectively. For practical purposes zig-zag nanotubes are considered as metallic at room temperature [34,35,36].

The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length. In theory metallic nanotubes can carry an electrical current density of 4×10^9 A/cm^2 which is 1000 times greater than metals such as copper [37]. Unique dimensions and unusual current conduction make them ideal component of electrical circuits. Nanotube based transistors have been made that operate at room temperature and that are capable of digital switching using a single electron [38].

4.2 Thermal Properties:

The thermal properties of carbon nanotubes are directly related to their unique structure and small size [39]. 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. They can withstand up to 750˚C at normal and 2800˚C in vacuum atmospheric pressures [40,41]. The thermal conductivity of nanotubes is large, even in bulk samples: aligned bundles of SWNTs show a thermal conductivity of > 200W/m *K* at room temperature [39]. The temperature of the tubes and the outside environment can affect the thermal conductivity of CNT. Nanotube based composites may be useful for their potentially high thermal conductivity [39].

The specific heat of CNTs is linearly dependent on temperature [42].

As diamond and graphite shows the highest known thermal conductivity at room temperature, it is likely that the thermal conductivity of nanotubes should also be high. At room temperature, the thermal conductivity of CNTs is as high as 6600 W/m-K, which is comparable to a good metal and within an order of magnitude of that of highly crystalline graphite or diamond [43]. Carbon nanotubes possess high thermal conductivity in the axial direction. The thermal conductivity of unaligned samples is about one order of magnitude smaller [44].

Composite materials have high thermal conductivity have a number of potential applications, particularly in heat sinking for electronics and motors [39].

Here is a table [45] showing transport properties of different conductive materials:

Materials	Electrical Conductivity	Thermal Conductivity W/m-K
CNTs	10^6-10^7	>3000
Copper	6×10^7	400
Carbon fiber-pitch	$2 – 8.5\times10^6$	1000
Carbon fiber-PAN	$6.5 – 14\times10^6$	8 - 105

4.3 Mechanical Properties:

The mechanical properties of CNTs are strongly dependent on the structure of nanotubes. CNTs are the strongest and the stiffest material ever known. Carbon nanotubes have high strength plus extraordinary flexibility and resilience. The small diameter of a carbon nanotube (CNT) also has an important effect on the mechanical properties [46]. They have higher tensile strength than steel and Kevlar. SWCNTs have a tensile strength hundreds of times stronger than steel. Another amazing property of CNTs is also elasticity. Under high force and pressure sitting and when exposed to great axial compressive forces, it can bend, twist, kink and finally buckle without damaging the nanotube. The elasticity of CNTs does have a limit, and it is possible to temporarily deform the shape of a nanotube. Some of the defects in the structure of CNTs can weaken its strength. Elasticity in both SWCNTs and MWCNTs is determined by modulus of elasticity. The modulus of elasticity of MWCNTs can be determined by transmission electron microscopy (TEM). TEM measures and examine the thermal vibrations at both ends of tubes [4].

Here is a table [37] giving comparison between Young's modulus, tensile strength and density of different materials –

Material	Young's modulus (GPa)	Tensile strength (GPa)	Density (gm/cm^3)
SWCNT	1054	150	N/A
MWCNT	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

V. Applications of CNTs:

Due to small size, high elasticity, high tensile strength, high thermal and electrical conductivity and many more properties, CNTs can be used in a large number of applications, which are as follows –

- Carbon nanotubes can be used as carrier for drug delivery [51].
- The gelatin CNT mixture (hydro-gel) can be used as potential carrier system for bio medicals [52].

- Antibiotic, Doxorubicin given with nanotubes is reported for enhanced intracellular penetration [52].
- CNTs can be used as drug carrier for treatment, detection and diagnosis of cancer cells. Anticancer drug Poly phosphazene platinum given with nanotubes had enhanced permeability, distribution and retention in the brain due to controlled lipophilicity of Nanotubes [52].
- They can be used as lubricants or glidants in tablet manufacturing due to Nano size and sliding nature of graphite layers bound with Van der Waal forces [52].
- Because of high tensile strength, CNTs can act as bone substitutes and implants if filled with calcium and shaped/arranged in the bone structure [52].
- Both SWCNT and MWCNT can be employed as implants in the form of artificial joints and other implants without host rejection response [52].
- CNTs can be used for miniaturization of electronic circuits because of their small size.
- In genetic engineering, CNTs and carbon Nano horns (CNHs) are used to manipulate genomes and atoms [52]
- Their tubular nature has proved them as a vector in gene therapy.
- CNTs and CNHs are antioxidants in nature. Hence they are used to preserve drugs formulations prone to oxidation [52].
- They can be used in anti-aging cosmetics and with zinc oxide as sunscreen to prevent oxidation of important skin components [52].
- CNHs offer large surface area and hence, the catalyst at molecular level can be incorporated in nanotubes in large amount and simultaneously can be released in required rate at particular time [52].
- Metallic CNTs are highly conductive material. SWCNTs can be used to make metallic ropes which offer resistance of $10^{-4}\Omega$-cm at 27˚C.
- Due to very high modulus of elasticity of SWCNTs, they can be used to make an ultimate high strength fiber.
- Due to high elasticity, CNTs are extremely useful as probe tips for high resolution scanning probe microscopy.
- CNTs can produce waterproof and tear-resistant fabric [53].
- CNTs can be used to make bullet proof jackets [53].
- Due to extraordinary mechanical properties, CNTs can be used to make sport equipment such as golf balls, golf clubs, stronger and lighter tennis rackets etc [53].
- CNTs can be used as alternative to tungsten filament in incandescent lamps [54].
- CNTs can be used in solar cells. They replace indium tin oxide to allow the light to active layers and generate photocurrent [55].
- CNTs can act as antenna for radio and other electromagnetic devices due to its durability, light weight and conductive properties [56].
- CNTs are best materials for air filters because they possess high absorption capacity and large surface area [57].
- CNT membranes can be used as water filters. It can reduce distillation cost by 75% [53].
- CNT based sensors can detect temperature, air pressure, chemical gases (CO, NH_3 etc.), molecular pressure, strain etc [58].
- CNTs can be used for energy storage [59].
- CNTs have great potential to be tumor nano-theranostic tool. These can be used for cancer diagnosis and therapy in future [60].
- CNTs can be used in photodetectors that works in near IR and IR regions [61].

VI. Limitations of CNTs [52]:

- Lack of solubility in most solvents compatible with the biological milieu (aqueous based).
- The production of structurally and chemically reproducible batches of CNTs with identical characteristics.
- Difficulty in maintaining high quality and minimal impurities.

VII. Conclusion:

A large number of theoretical and experimental studies have been done on mechanical properties of CNTs, but there is very small number of applications where CNTs can be used. Now-a-days, atomistic and molecular dynamics simulation is used to study mechanical properties of CNTs. So that CNTs can be used in large number of potential applications for the welfare of mankind. Thus, studies are needed on the above mentioned lines.

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