

## UNIT 4

## CARBON MATERIALS FOR HEALTH, STEALTH AND ENERGY

**CARBON MATERIALS FOR HEALTH, STEALTH AND ENERGY** Introduction to carbon materials – Fullerenes – Production, properties and applications – VanderWaal's solid – Structure of graphene, graphene oxide and reduced graphene oxide – Mechanical and electrical properties of graphene – Graphene based energy storage devices for space applications – Carbon nanotubes – Single-walled and multiwalled CNTs – Synthesis of CNTs by Thermal CVD and laser ablation method – Electrical and mechanical properties of CNTs – Applications of CNTs.

### 4.1 INTRODUCTION TO CARBON AND ITS MATERIALS

Carbon (C) is a nonmetallic element belonging to Group 14 (IV a) of the periodic table. Though it makes only upto 0.025% of the earth's crust, it forms more compounds than all the other elements combined. The cosmic product of the "burning" of three helium nuclei of atomic number 4 is the carbon nucleus of atomic number 12. Elemental carbon is a minor component on the earth's crust. However, carbon compounds form minerals such as dolomite, magnesite, marble and limestone by combining with the carbonates of calcium and magnesium. Carbon occurs widely in the form of coal and as organic compounds in the form of petroleum, natural gas, plant and animal tissue. Carbon gets recycled through carbon cycle where the carbon dioxide present in the atmosphere is converted into carbohydrates by plants during photosynthesis and the reverse reaction of the release of the carbon dioxide back into the atmosphere during metabolism by animals. More than a million carbon compounds are known to exist and several new carbon compounds are getting added to the already existing list on a day to day basis. This diversity and complexity is due to the tendency of carbon atoms for bonding with each other in forming ring, chain and three dimensional conformations and also due to its capacity to bond with other atoms.

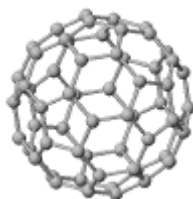
#### 4.1.1 Allotropes of Carbon

Elemental carbon exists in several forms having different physical properties. The well known allotropes are graphite and diamond. They differ in their physical properties due to differential arrangements of carbon atoms in their structure. Diamond and graphite occur naturally on earth and are chemically inert. Diamond (composed of a three-dimensional crystalline array of carbon atoms) is the hardest naturally occurring substance and is a poor conductor of heat and electricity. Graphite (composed of stacked sheets of two-dimensional hexagonal arrays of carbon atoms), on the other hand, is soft and slippery and is a good conductor of heat and electricity. The third allotrope of carbon is fullerene, consisting of a variety of molecules made of only carbon atoms. Spheroidal, closed-cage fullerenes are called buckminsterfullerenes or buckyballs. Cylindrical fullerenes are called carbon nanotubes (CNTs). They were discovered in 1985 while simulating the chemical reactions occurring in the atmosphere of giant stars under laboratory conditions. Fourth form of carbon molecule which is

crystalline and magnetic is the Q-carbon. They are also synthetic and the scientists have speculated its formation within the planetary cores containing hot environmental conditions. Other types of carbon molecules which are amorphous or are less crystalline are carbon black, charcoal, lamp black, coal and coke.

## 4.2 FULLERENES

Fullerene or Buckminsterfullerene denotes a series of hollow carbon molecules forming either a closed cage (“buckyballs”) or a cylinder (carbon “nanotubes”) structure. Fullerene was found to have the structure of a truncated icosahedron and was first discovered by Sir Harold W. Kroto, Richard E. Smalley and Robert F. Curl in the year 1985. During an experiment with laser to vaporize graphite rods in the atmosphere of helium, the chemists obtained a cage like molecules composed of 60 carbon atoms ( $C_{60}$ ) joined by single or double bonds to form a hollow sphere comprising of 12 pentagonal faces and 20 hexagonal faces, a structure resembling a soccer ball. The  $C_{60}$  molecule was named buckminsterfullerene (or buckyball) after the American architect R. Buckminster Fuller constructed a geodesic dome on the same structural principles. The most stable form of a carbon aggregate containing several thousands of atoms is found to be the closed bucky ball. Discovery of fullerenes have led to an entirely new understanding of the behavior of sheet materials and their properties.



**Fig 1: Buckminsterfullerene ( $C_{60}$ )**

Studies on fullerenes indicated that  $C_{60}$  and  $C_{70}$  are exceptionally stable and provided convincing evidence for the cage structure proposal. There were developments in the discovery of other metastable species, such as  $C_{28}$ ,  $C_{36}$ , and  $C_{50}$  and also confirmed the presence of “endohedral” complexes, in which an atom is trapped inside the cage and the size of the entrapped atom determining the size of the smallest surrounding possible cage.

Fullerenes are the only pure, finite form of carbon which due to its high symmetry, need no atoms to satisfy their surface chemical bonding requirements as in the case of other allotropes of carbon such as the diamond and graphite.

Related to this are the carbon “onions” consisting of carbon cages one inside the other. They have millions of carbon particles in dozens of concentric shells.

### 4.2.1 Preparation

The first method of production of fullerenes was by laser vapourization of carbon in an inert atmosphere. This method resulted in the synthesis of microscopic amounts of fullerenes. In the year 1990, a new apparatus was developed by Wolfgang Krätschmer and Donald R. Huffman where an arc was used to vaporize graphite to produce fullerenes in substantial yield. Macroscopic quantities of fullerenes can be synthesized by this method. Metals like alkali, alkaline earth metals and lanthanoids can be trapped in a fullerene cage by vaporizing graphite rods impregnated with the selected metal.

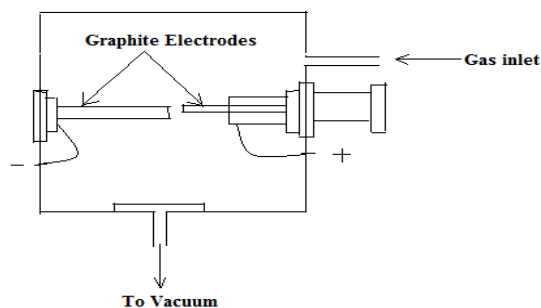
#### Method of Synthesis

Fullerenes are produced by Kratschmer–Huffman method. It is a straightforward and low cost method for generating large quantities of fullerene containing carbon soot. It consists of a chamber which is filled with helium gas at a pressure of 100 torr. An electric arc is produced by a power supply for 10-15 seconds. This results in the vapourization of graphite to form soot inside the chamber. The chamber is then cooled for 5-10 minutes and the pressure inside is brought down to atmospheric pressure. By scraping the deposited soot, around 10% yield of  $C_{60}$  can be obtained. The fullerenes in the soot can be extracted by dissolving it in a small amount of toluene. After extraction, toluene is removed by rotary evaporator which leave behind a solid mixture of mostly  $C_{60}$  along with small amounts of larger fullerenes. Pure  $C_{60}$  can be obtained by liquid chromatography where the mixture is dissolved in toluene and by passing through a column of activated charcoal mixture of silica gel, the magenta colored  $C_{60}$  comes out first followed by the red colored  $C_{70}$ . The colored solutions are collected separately and the toluene is removed using rotary evaporator.

In the Krätschmer-Huffman (KH) experiment, carbon radicals are produced by slow evaporation of a resistively heated graphite rod where the density of the carbon vapour is far lower than that obtained with the pulsed laser vaporization. Also, the rate of cooling of the condensing carbon vapour is much slower in the KH method that greatly assists the clustering in the critical size range to form  $C_{60}$ . By adjusting the helium buffer gas pressure, the rate of migration of the carbon vapours from the hot graphite rod can be controlled for the  $C_{60}$  formation. The experimental factors that can be modified to maximize the yield of the fullerene clusters in the soot are the vaporization current density and the helium partial pressure.

Another method of synthesis involves the use of AC (alternating current) or DC (direct current) to produce  $C_{60}$  and the other fullerenes in good yield and is followed in the commercial synthesis of fullerenes.

Other techniques for the synthesis of fullerenes include hydrocarbon combustion, low-pressure helium sputtering, electron beam evaporation and inductively coupled RF evaporation for the vaporization of the graphite targets.



**Fig 2: Synthesis of fullerenes**

### 4.2.2 Properties

In fullerene, each carbon is bonded to three other carbon atoms and are  $sp^2$  hybridised. The  $C_{60}$  molecule has two bond lengths – the 6:6 ring bonds are the double bonds and are shorter than 6:5 bonds.  $C_{60}$  molecule is not superaromatic as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalization. Hence it behaves as an electron deficient alkene and therefore reacts readily with electron rich species. The molecule can readily accept and donate electrons. The molecule can readily add atoms of hydrogen and halogens. The halogen groups can be replaced by other functional groups, such as phenyl, thus opening new routes to the synthesis of wide range of novel fullerene derivatives exhibiting advanced materials behaviour.

Important crystalline compounds of  $C_{60}$  with alkali and alkaline earth metals have shown to exhibit superconductivity at relatively high temperatures above 19 K. Superconductivity is observed in the range of 19-40 K, equivalent to -254 to -233°C or -425 to -387°F.

Metals can be physically trapped in a fullerene cage ( $M@C_{60}$ ) and the resulting compounds have been extensively studied. Alkali, alkaline earth metals and early lanthanoids may be trapped by fullerenes cages by using graphite rods containing the metal.

Fullerenes are soluble in common solvents such as benzene, toluene and chloroform.

### 4.2.3 Applications

Fullerene applications are wide ranging from additives to polymers, photoconductors, photoresists and from bio-active agents to cosmetics. Buckminsterfullerenes have a wide range of electrical properties. It may alternately exist in insulating, conducting, semiconducting, or superconducting forms.

- Fullerenes are active molecules and are used as antioxidants as they can readily react with radicals due to its high affinity for electrons. This property is due to the presence of large number of conjugated double bonds. Fullerenes have low energy unoccupied molecular orbital and can react with a number of

radicals. A single C<sub>60</sub> molecule can interact with upto 34 methyl radicals and therefore is called “radical sponge”. Radical sponge is added to cosmetics for preventing skin damage and premature aging without any side effects.

- Fullerenes are used as antiviral agents. This application is due to its unique molecular structure, antioxidant effect and biological compatibility. The important and the most exciting aspect of fullerene is its ability to suppress the replication of human immunodeficiency virus (HIV) so as to delay the onset of the acquired immunodeficiency syndrome (AIDS).
- Fullerenes form conjugates with proteins and DNA which has a potential application in developing anticancer therapy. Fullerenes get excited upon light irradiation and while returning to the ground state they release energy which splits up oxygen to generate singlet oxygen that is cytotoxic in nature.
- Fullerenes are a class of inorganic carriers showing good biocompatibility, greater selectivity, retain biological activity and can undergo easy diffusion. Fullerenes are used in the delivery of hydrophobic drugs for their slow release with safety and great efficacy at the site of action. The surface of fullerene is covered with a chemotherapeutic agent which gets transported and target the cancer cell.
- Fullerene reagent forms a protective layer on DNA and helps in extending the life of DNA of the endosomes.
- Fullerenes are excellent electron acceptors and are used in organic photovoltaic cells in complexed and polymer forms to produce bulk heterojunctions.
- Fullerenes have optical limiting properties and are used in protective eye wear and sensors for protecting the eyes or the sensor.
- A Fullerene molecule can hold upto 36 hydrogen atoms during the breaking and the formation of the C=C bonds. The color of the hydrogenated fullerenes changes from black to brown, red, orange and finally to yellow depending on the increase in the hydrogen content. These materials are highly promising in the development of a better, safer and more efficient hydrogen storage devices.
- Fullerenes can form lightweight metals with greater tensile strength without compromising on the ductility of the metal. This is due to the small size and high reactivity of the sp<sup>2</sup> hybridized carbon atom. This enables dispersion strengthening metal matrix by the interaction of fullerenes with the metals.
- Closed fullerene structures containing sulfides of tungsten and molybdenum are found to exhibit excellent solid-lubricant properties. They act as dry lubricants in coating application.

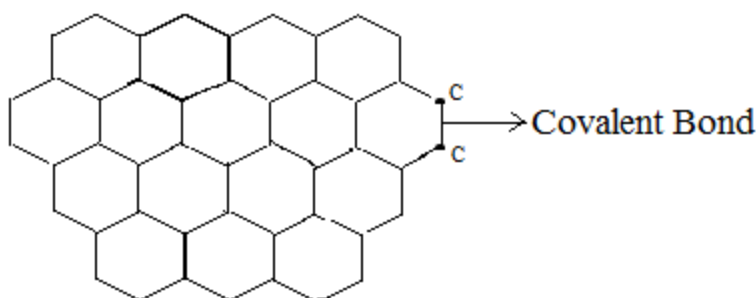
### **4.3 VANDER WAALS SOLID - GRAPHENE**

Graphene is the thinnest compound known to man at one atom thick. It is the lightest material known (with 1 square meter weighing around 0.77 mg), the strongest compound discovered (100-300 times stronger than steel with a tensile strength of 130 GPa and Young's modulus of 1 TPa), the best conductor of heat at room

temperature and also the best conductor of electricity. Graphene has uniform light absorbing ability across the visible and near-infrared parts of the spectrum.

### 4.3.1 Structure of Graphene

Graphene is a monolayer of carbon atoms, tightly bound in a honeycomb lattice. It is an allotrope of carbon in the form of a plane of  $sp^2$  hybridized carbon atoms with a molecular bond length of 0.142 nm. Layers of graphene stacked on top of each other form graphite with an interplanar spacing of 0.335 nm. The layers of graphene are held together by van der Waals forces, which can overcome during exfoliation of graphene from graphite.



**Fig 3: Structure of Graphene**

#### 4.3.1.1 Preparation

Graphene was synthesized first by chemical vapour deposition (CVD) method. CVD method is an expensive and complex process which involves the use of toxic chemicals to grow graphene as a monolayer by exposing platinum, nickel or titanium carbide to ethylene or benzene at high temperatures. This method had many drawbacks that made graphene unavailable for developmental research and commercial uses. However, studies on the graphene's interfacial adhesive energy has proved the possible separation of graphene effectively even from metallic surfaces thereby reducing the toxic waste that gets generated during the synthesis. Consistent research is being carried out to produce graphene on custom substrates with control over impurities such as ripples, doping levels, domain size and relative crystallographic orientation of the graphene layers.

### 4.3.2 GRAPHENE OXIDE

Graphene oxide is a material consisting of a monomolecular layer of graphite with various oxygen functionalities such as epoxide, carbonyl, carboxyl and hydroxyl groups. Graphene oxide is an exfoliated form of graphite oxide in water using sonification, ultimately producing single or few layer of graphene called graphene oxide (GO). Graphene oxide is a dispersion consisting of a few layers of flakes or monolayer flakes. The most common method of producing graphite oxide is the Hummers or the Offeman method in which

graphite is treated with a mixture of sulphuric acid, sodium nitrate and potassium permanganate. Most common method of preparation of graphite oxide is by the oxidation of graphite using oxidising agents like potassium permanganate in sulfuric acid. Sodium nitrate is now replaced with a combination of phosphoric acid and sulphuric acid and has been found to be more efficient with an increase in the oxidation level upto 70%. Graphene oxide is a by-product of this oxidation where the interplanar spacing between the layers of graphite gets increased. The main difference between graphite oxide and graphene oxide is the interplanar spacing between the individual atomic layers of the compounds, caused by water intercalation which disrupts the  $sp^2$  bonding network and thereby making it an electrical insulator. During oxidation, oxygenated functionalities are introduced in the graphite structure which not only expand the layer separation but also makes the material hydrophilic. The main difference between graphite oxide and graphene oxide is, thus, the number of layers. Chemical reduction of graphene oxide is currently viewed as the most suitable method of mass production of graphene.

#### **4.3.2.1 Properties**

The important advantage of graphene oxide is its easy dispersibility in water and other organic solvents. Its dispersibility in different matrices, due to the presence of the oxygen functionalities, is a very important property while mixing the material with ceramic or polymer matrices for the improved mechanical and electrical properties. Graphene oxide's properties can be altered by introducing functional groups which results in a chemically modified graphenes with more adaptable properties and makes it useful for various applications.

For example, substituted amines are introduced for the organic covalent functionalization in order to increase the dispersibility of the chemically modified graphenes in organic solvents for its utilization in optoelectronics.

#### **4.3.3 REDUCED GRAPHENE OXIDE**

Reduced graphene oxide (rGO) is prepared by reduction of graphene oxide by thermal, chemical or electrical treatment methods. It can also be prepared by reducing the electrically insulating graphene oxide using hydrazine. Due to the toxic nature of hydrazine, alternatives to hydrazine including  $NaBH_4$ , ascorbic acid and HI have been used. Different reducing agents results in various carbon to oxygen ratio and chemical compositions in rGO. Electrochemical reduction of graphene oxide is a method that has been shown to form very high quality reduced graphene oxide, having identical structure similar to pristine graphene. The reduced graphene oxide resembles graphene and there is always some oxygen functional groups inside or on the surface of the reduced graphene oxide causing structural defects.

##### **4.3.3.1 Properties**

rGO can be made as a thin film from an aqueous dispersion of GO in water and has moderate conductivity. Hence it is attractive for use in electronic devices. Graphene oxide act as an electrical insulator due to the disruption of the  $sp^2$  bonding networks. For increasing the conductivity, graphene oxide has to be reduced during which the honeycomb hexagonal lattice would be recovered. This reduced graphene oxide is difficult to disperse due to its tendency to form aggregates.

#### **4.3.3.2 Applications**

Carbon forms the basis for all known life on earth, making graphene potentially an eco-friendly, sustainable solution for an almost limitless number of applications. Applications within different scientific disciplines have exploded since discovery of graphene with huge impact being made in high-frequency electronics, bio, chemical and magnetic sensors, ultra-wide bandwidth photodetectors and energy storage and generation. Other promising areas of application are composites, energy, telecommunications, electronics, sensors and imaging and biomedical technologies.

Nanocomposites of rGO have been used for high capacity energy storage in lithium ion batteries. Electrically insulating metal oxide nanoparticles adsorbed onto rGO has been found to increase the performance of these materials in batteries. Increased energy storage capacity and cycle stability are shown to be present for  $Fe_3O_4$  on rGO compared to pure  $Fe_3O_4$  or  $Fe_2O_3$ . Large surface area rGO has been synthesised using microwaves for exfoliation and reduction of GO and is useful as an energy storage material in supercapacitors.

Chemically modified graphene oxides carrying porphyrin-functionalized primary amines and fullerene-functionalized secondary amines show increasing performances in nonlinear optics.

#### **4.3.4 Graphene - Mechanical properties**

Graphene, a new two dimensional material containing a monolayer of covalently bonded carbon atoms has unique mechanical and transport properties. Graphene has high in-plane stiffness-Young modulus and superior strength. The exceptional mechanical properties of graphene makes it a superstrong structural and functional material.

A graphene membrane which was mechanically deposited onto a substrate was found to show both non-linear elastic behaviour and brittle fracture. Graphene has Youngs modulus (E) of 1 TPa, a third order elastic stiffness (D = -2.0 TPa) and an internal strength (int) of 130 GPa. Extremely high values of E and int makes graphene an attractive material for structural and other applications. Also, graphene can be bent easily that can be exploited in practice.

The presence of defects influence the plastic deformation and fracture. Usually observed defects in graphene are vacancies, Stone-Wales defects, dislocations and grain boundaries. Dislocations and grain boundaries cause the



most significant effects on its mechanical properties. Dislocations serve as carriers of plastic flow in graphene whereas, grain boundaries decreases its strength characteristics.

According to nanoindentation measurements of graphene membranes, the upper bound for the in-plane breaking stress is found to be 35 GPa and this value is much lower than the intrinsic strength (130 GPa) of pristine graphene.

Bending of graphene sheet during compression has been exploited in the design of polycrystalline graphene specimens and those with tuned folded structures are found to affect both the transport and mechanical characteristics. This feature is also found to be interesting for the design of nanodevices based on folded graphene specimens.

Due to ultrahigh strength of graphene, its inclusions are effectively used in the enhancement of both strength and fracture toughness in composite materials. Nanocomposites were fabricated using ceramic matrixes and inclusions in the form of graphene platelets (GPLs) for the improved fracture toughness of the ceramic materials. For example, silicon nitride with 1 wt% GPL nanocomposites with homogeneously dispersed GPLs have been fabricated in which each GPL consisted of several graphene layers of thickness in the range of 1-10 nm. The mechanism behind the dominant toughening are crack branching, crack deflection and crack bridging. Inclusions in the form of graphene sheets are also found to enhance the mechanical characteristics in polymer-based nanocomposites. Young's modulus of the nanocomposite with 0.125% weight fraction of graphene inclusions is found to be 65% greater than that of the graphene free counterpart.

Role of graphene inclusions in the form of sheets and platelets as strengthening and toughening structural elements in nanocomposites is a promising breakthrough compared to nanoparticles and carbon nanotubes.

In spite of commendable achievements, studies on the mechanical properties exhibited by graphene are in their infancy with many important problems yet to be explored and remain unsolved in the new and intriguing research area related to graphene.

#### **4.3.5 Graphene - Electrical properties**

Graphene is used to make supercapacitors with high capacities, high power densities, longevity and also the development of electronic components has been progressing at a high rate. Batteries and capacitors have been limiting due to size, power capacity and efficiency. Laser-scribed graphene (LSG) supercapacitors demonstrated power density comparable to that of high-power lithium-ion batteries. LSG supercapacitors are highly flexible, light, quick in charge, thin and very inexpensive to produce. Graphene is used to boost capacity, charging rate and longevity. Graphene tin oxide as an anode in lithium ion batteries has higher potential capacity and almost no reduction in storage capacity between charges which effectively makes technology such as electronically powered vehicles a much more viable mode of transport.

Graphene can be used to improve energy generation, including the improvement of perovskite solar cells (PSCs) which are highly promising next-generation solar power sources with very high efficiency. Addition of reduced graphene oxide spacer layer to a PSC, resulted in a low-cost production of PSCs with 20% efficiency.

Graphene is used in energy storage in advanced electrodes. Graphene combined with silicon nanoparticles form anode that maintain 92% of their energy capacity over 300 charging-discharging cycles, with a high maximum capacity of 1500 mAh per gram of silicon. The energy density values achieved are well above 400 Wh/kg. Thin film of graphene was produced using spray-coating deposition technique which enabled its large-scale production for the development of supercapacitors with very high power densities. Graphene-metal oxide hybrid electrodes exhibit up to 1100 mAh g<sup>-1</sup> for the first 10 cycles and the specific energy density is maintained at 1000 mAh g<sup>-1</sup>, even after 130 cycles. By hybridizing the metal oxide matrix with graphene, the interaction between the interstitial ions and the hybrid matrix is vastly improved for enhanced conductivity. Due to the large surface area of graphene, the metal ions can be stored via surface adsorption and induced bonding.

Graphene is an ideal candidate for radio frequency (RF) flexible electronics. The flexible nature of graphene allows for various electronic devices on flexible substrates such as the graphene-based supercapacitors, wearable touch panels, strain sensors, self-powered triboelectric sensors, flexible and robust touchscreen devices etc.

Graphene based photonic devices are becoming highly promising because of the ability of graphene to absorb light over a large bandwidth. Graphene is an excellent heat conductor which is highly useful in the reduction of heat consumption in graphene based photonic devices.

Graphene Hall sensors with carrier mobility in excess of 200,000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> with current-related sensitivity up to 5700 V/AT and voltage-related sensitivity up to 3 V/VT has been demonstrated in graphene encapsulated boron nitride. Flexible graphene Hall sensors has been found to have sensitivity similar to that of the rigid silicon Hall sensors.

#### **4.3.6 Graphene based Energy Storage Devices in Space Application**

Modern energy storage device for electric automobiles, small and large electronic appliances and modern aircraft is the lithium-ion battery. The lithium-ion battery has energy densities of the order of 100 Wh/kg and require long charging times. Ultracapacitors, on the other hand, can be recharged in seconds. However, their energy densities are lower than that of lithium-ion batteries. Increase in the performance of both types of devices have been made with the addition of nanostructured electrodes to lithium-ion batteries and by the use of activated carbon in ultracapacitor electrodes. Incorporation of the nanostructured electrodes have reduced the ion diffusion distances and introduction of the dopants have increased the ion transport efficiency in lithium-ion batteries. Activated carbon used in the ultracapacitors have resulted in the increase in the energy densities which

is still lower than those of the lithium-ion batteries. Development of the thin film ultracapacitors with graphene electrodes have made possible to attain energy densities comparable to those of thin-film lithium ion batteries and power densities comparable to those of activated carbon ultracapacitors. The surface area of graphene is larger than that of the activated carbon, allowing for ultracapacitors with very large capacitances. An energy storage device with these characteristics could be used for robotic and Martian exploration missions and crewed habitats.

Graphene's usefulness has already been established on earth and now the recent area of research is to extend its applications in space.

One of the important possible uses of graphene in space applications is its testing in space-like applications. Graphene was tested for its ability to enhance the performance of satellites' cooling systems by employing the material's unique thermal qualities. Graphene is being used in what are called as loop-heat pipes, which are pumps that move fluid without the need for any mechanical parts. This mechanism is very important for space operations as there will be no wear and tear.

For space application, the metallic wick, the main element of the loop-heat pipe, would be coated with graphene. Graphene's thermal properties enable improved heat transfer and the porous structure of the material increases the surface area by which the liquid comes into contact and allows it flow through the wick. The results of this micro-gravity test revealed a high performance of the graphene-coated wicks compared to untreated ones and the coated wicks are tested in a low-gravity parabolic flight. With its success, researchers are working on the development of a prototype that uses graphene on a satellite or space station for testing in space. Related to this is a research initiative dedicated to developing new technologies based on graphene called the "Graphene Flagship" to test graphene for light sails which could lead to a new way of propelling satellites in space using light from lasers or the sun. "Graphene flagship" is a collaboration between the European Space Agency and academic consortium to carry out zero gravity test during a parabolic flight using graphene.

## **4.4 CARBON NANOTUBES**

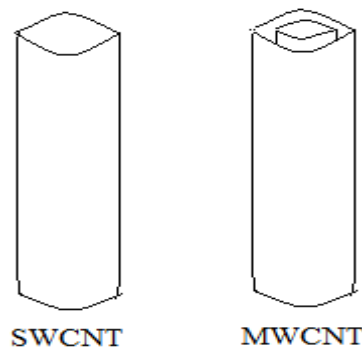
Carbon nanotubes (CNTs) are molecules consisting of rolled-up two dimensional sheets of graphene, containing hexagons and pentagons, forming cylinder.

CNTs have carbon atoms which are  $sp^2$  hybridized and are bonded with each other forming strong covalent bonds. This feature along with the nanotubes' tendency to rope together through van der Waals forces, provide the opportunity to develop ultra-high strength, low-weight materials with highly conducting electrical and thermal properties which makes them attractive for various applications. Carbon nanotubes are first discovered by S. Ijima in the year 1991.

#### 4.4.1 Single-walled and Multiwalled Carbon Nanotubes

CNTs are of two types. They are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Single-walled carbon nanotubes (SWCNTs) are cylinders containing only one cylinder made of single graphene sheet. Several graphene sheets when folded to form cylinders one inside the other are called multi-walled carbon nanotubes.

SWCNTs have diameter in the range of 1-2 nm and length in the range of 1-100  $\mu\text{m}$ . MWCNTs have outer diameter in the range of 2-20 nm and inner diameter 1-3 nm. They have length in the range of 1-100  $\mu\text{m}$  with inter tubular distance of 0.34 nm. The two types of CNTs have length reaching even millimeters starting from micrometers.



**Fig 4: Types of CNTs**

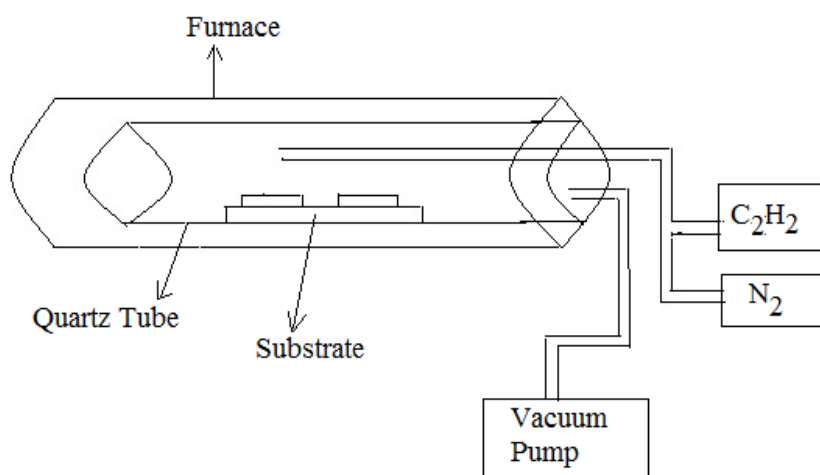
#### 4.4.2 Synthesis of CNTs

##### 4.4.2.1 Chemical Vapour Deposition (CVD) method

CVD method, also called as thermal CVD, consists of forming carbon nanotubes by decomposing an organic gas over a substrate coated with metal catalyst nanoparticles.

Thermal CVD method consists of a quartz tube enclosed in a furnace. The substrate made of silica, mica, quartz or alumina on which the CNTs has to be formed is placed inside the furnace. The substrate is coated with metal catalyst nanoparticles like Fe, Co or Ni. Carbon precursors such as acetylene ( $\text{C}_2\text{H}_2$ ), ethylene ( $\text{C}_2\text{H}_4$ ) or methane ( $\text{CH}_4$ ) gas is passed into the furnace and the temperature inside is fixed in the range of 500-900°C. At

these temperatures, the carbon precursor starts to dissolve in the metal catalyst till the point of supersaturation. The saturated carbon starts to precipitate in the form of cylinders which are called the carbon nanotubes. The diameter of the tube is determined by the size of the nanoparticles used as the catalyst. Thermal CVD can be used to produce both SWCNTs and MWCNTs.

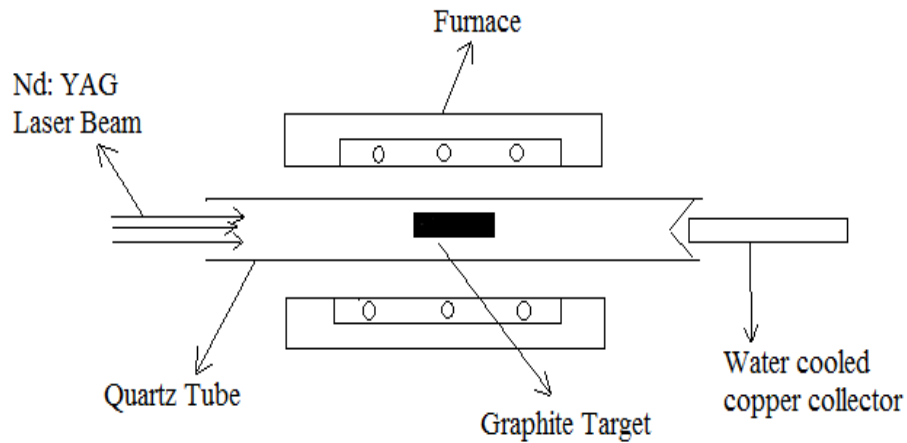


**Fig 5: Thermal CVD**

#### **4.4.2.2 Laser Ablation method**

Laser ablation method consists of a furnace, a quartz tube with a window on one side, a graphite target doped with metal catalyst such as cobalt or nickel at the center of the tube. An argon flow system is maintained at a constant pressure and flow rate. A water-cooled copper collector is present outside the furnace.

A continuous or pulsed laser beam from Nd:YAG (Neodymium-doped-yttrium aluminium garnet) is made to fall on the graphite target through the window and the furnace temperature is maintained at 1200°C. When the laser beam falls on the graphite target, the target gets vaporised to form carbon particles containing atoms and molecules. The formed carbon atoms and molecules are swept by the flowing argon gas having a flow rate of 1 cm s<sup>-1</sup> and a pressure of 500 torr. When the carbon particles reach the water cooled copper collector, they undergo condensation and grow in the form of carbon nanotubes.



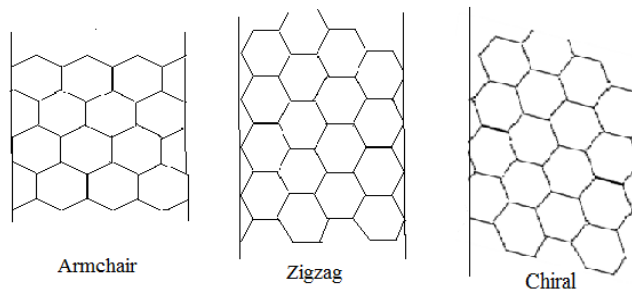
**Fig 6: Laser Ablation Method**

Laser ablation method has several advantages such as high quality single walled carbon nanotubes can be produced, diameter of the nanotubes can be controlled and growth dynamics can be followed.

### 4.4.3 Properties of Carbon Nanotubes

#### 4.4.3.1 Electrical Properties

The electrical property of carbon nanotubes depends on the direction of rolling-up of the graphene sheets, called helicity (chirality) and the diameter of the nanotube. Helicity is the rolling of the hexagonal chains with respect to the tube axis. There are three different types of CNTs based on helicity. They are armchair, zigzag and chiral carbon nanotubes.

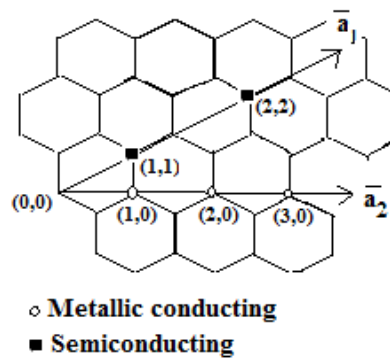


**Fig 7: Types of carbon nanotubes**

Turning a graphene sheet by 30 degrees will convert the configuration from armchair to zigzag or vice versa. SWCNTs' conductivity depends on the chiral vector. They behave like a metal and have high electrical conductivity or can show semiconducting property or can be non-conducting. A slight change in helicity can transform its metal conductivity to semiconducting type.

Armchair tubes (n, m) are metallic as they are highly symmetrical and the conditions for the metallic property to dominate are  $n - m = 0$  or  $(n - m)/3 = \text{integer}$ , where n and m are the chiral vectors. Examples: (8, 2), (6, 3) and (7,7) tubes are metallic.

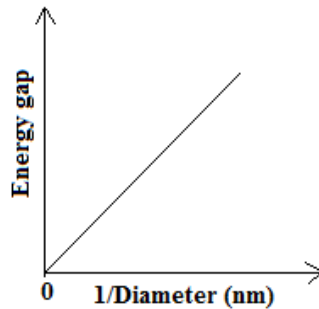
Zigzag and chiral tubes are either metallic or semiconducting. Semiconducting property dominates when  $(n - m)/3 \neq \text{integer}$ . Examples: (9,1), (5,3) tubes are semiconducting.



**Fig 8: Vector representation of metallic and semiconducting carbon nanotubes**

Metallic CNTs have high conductivity and can carry billion amperes of current per square centimeter whereas a copper wire can carry only million amperes of current per square centimeter due to resistive heating which melts the copper wire at high currents. The high conductivity for CNTs is due to minimum defects and hence imparts low resistance to the flow of current. Due to high thermal conductivity, there is no resistive heating during the flow of high currents in CNTs.

The low conductivity in the case of chiral and zigzag forms is due to the replacement of hexagonal rings with pentagonal or heptagonal rings. This type of defect can affect the electrical conductivity severely in CNTs. For SWCNTs, the band gap is in the range of 0.4 – 1 eV and is found to decrease with the increase in the inverse diameter of the nanotube.



**Fig 9: Plot of Energy gap versus Diameter of carbon nanotubes**

#### **4.4.3.2 Mechanical Properties**

CNTs also have unique thermal and mechanical properties that render them with highly beneficial properties for the development of new materials.

**Tensile strength:** It is the amount of stress required to pull a material. CNTs are very strong and have tensile strength which is 100 times more than that of steel having the same diameter. The tensile strength of CNTs is around 45 billion pascals whereas for steel it is only 2 billion pascals. This high tensile strength for CNTs is due to the following reasons:

- i) Strong interlocking of the carbon atoms through covalent bond.
- ii) CNTs does not have weak points like grain boundaries, dislocations etc and is considered to be a single molecule.

**Youngs modulus:** It is the measure of elasticity or flexibility of the material. The elasticity is inversely proportional to the Youngs modulus value. CNTs have high Youngs modulus value (1.28 – 1.8 TPa) compared to that of steel (0.21 TPa) which shows that CNTs are 5 to 10 times harder than steel.

#### **Thermal Conductivity:**

CNTs have high thermal conductivity as they don't get heated or get cooled very well. Thermal conductivity of CNTs is 10 times that of silver, 15-20 times that of copper and 2 times that of diamond. CNTs conduct heat through the material by the vibration of the covalent bonds present between the carbon atoms. The strong covalent bonds are helpful in transmitting the heat throughout the nanotube thereby providing good thermal conductivity.



**Density:** Density of CNTs is one fourth that of steel and half that of aluminium. Hence CNTs are light weight materials having density in the range of 1.33 – 1.44 g/cm<sup>3</sup>.

#### 4.4.4 Applications of Carbon Nanotubes

Carbon Nanotubes have wide variety of applications in different fields. Carbon nanotubes are ideal candidates for use in electronic devices, chemical/electrochemical and biosensors, transistors, electron field emitters, lithium-ion batteries, white light sources, hydrogen storage cells, cathode ray tubes (CRTs), electrostatic discharge (ESD) and electrical-shielding applications.

Important applications of CNTs are:

Carbon nanotubes (CNTs) have large surface area, high chemical stability and controlled surface chemistry. Hence they are used as catalyst support.

CNTs are used as additives to synthetics by removing the agglomeration in order to spread evenly on the substrate. They can be chemically bonded with the substrate, like a plastic material, by functionalizing it on the surface.

CNTs can store high weight percentage of hydrogen without any leakage. Therefore used in hydrogen-oxygen fuel cells to store hydrogen.

CNTs are used in various biomedical applications. The physical properties of CNTs, such as mechanical strength, electrical conductivity, and optical properties, are of great value for creating advanced biomaterials with increased solubility and biocompatibility, enhanced material compatibility and cellular responsiveness. CNTs are used in targeted drug delivery due to its adaptability under different conditions.

CNTs are used as actuators where there is conversion of electrical energy to mechanical energy for inducing movements.

CNTs act as sensing materials in sensors for the detection of pressure, temperature, mass, light, stress, strain etc. Though studies have shown that CNTs are robust and inert structures, their electrical properties are found to be extremely sensitive to the effects of charge transfer and chemical doping by various molecules. Sensors based on CNTs are field effect transistors (FET). CNTs-FETs have been widely used to detect gases such as greenhouse gases in environmental applications. Functionalization of CNTs have made them even more selective to the target analyte. For example, flexible hydrogen sensors have been made using single-walled carbon nanotubes decorated with palladium nanoparticles.

Semiconducting SWCNTs are now considered as strong candidates for the next generation of high-performance, ultra-scaled and thin-film transistors as well as for opto-electronic devices to replace silicon electronics. CNTs act as ideal field emitters due to high current density, low turn-on and operating voltage. Thin film CNTs are used in making thin film solar cells, organic LEDs and touch screens as they are transparent to visible light to produce electricity.

CNTs are stiff, tough and strong having superior mechanical properties and are useful in the production of very strong, light weight materials that find applications in building, structural engineering and aerospace.

“Nano inks” which is an ink formulation based on CNT dispersions are found to be highly useful in Printed electronics and in making transparent electrodes, thin-film transistors, light-emitting devices and solar cells.

CNTs are used in making aircraft components due to its high fatigue strength.

Efficient water transport through carbon nanotubes with openings of less than one nanometer have been used as high flow membranes in energy-efficient water purification. They are found to provide protection against biological agents due to their very small pore size which is less than 5 nanometers wide.

### **Part A Questions**

1. What are allotropes of carbon? Name them.
2. What are fullerenes?
3. Define graphene.
4. Differentiate graphene oxide and reduced graphene oxide.
5. Why graphene called as van der Waals solid?
6. Mention any two applications of fullerenes.
7. List out any two important properties of graphene oxide.
8. Mention two applications of rGO.
9. What are carbon nanotubes?
10. Name the two types of CNTs.

11. How are SWCNTs classified based on chirality?
12. Differentiate SWCNT and MWCNT.
13. Give the advantages of Laser ablation method of synthesis of CNTs over thermal CVD method.

### **Part B Questions**

1. Explain in detail about the various allotropes of carbon.
2. What are fullerenes? Explain the Krätschmer and Huffman method of synthesis of fullerenes with a neat diagram.
3. Comment on the important properties of fullerenes.
4. Discuss the applications of fullerenes.
5. Write short note on graphene, graphene oxide and reduced graphene oxide.
6. Explain the structure of graphene with a neat diagram.
7. Write short note on the mechanical properties of graphene.
8. Explain the electrical properties of graphene.
9. Elaborate on the use of graphene in space applications.
10. Differentiate SWCNT and MWCNT with appropriate diagrams.
11. Explain in detail the thermal method of synthesis of CNTs with a neat diagram.
12. Explain laser ablation method of synthesis of CNTs with a diagram.
13. Discuss on the mechanical properties of CNTs.
14. Elaborate the electrical properties of CNTs with respect to chirality.
15. Write in detail the various applications of CNTs.