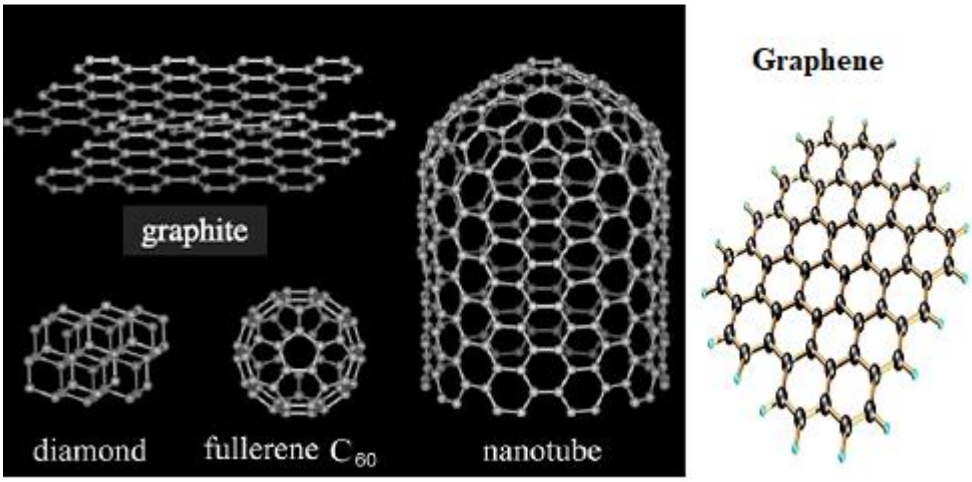
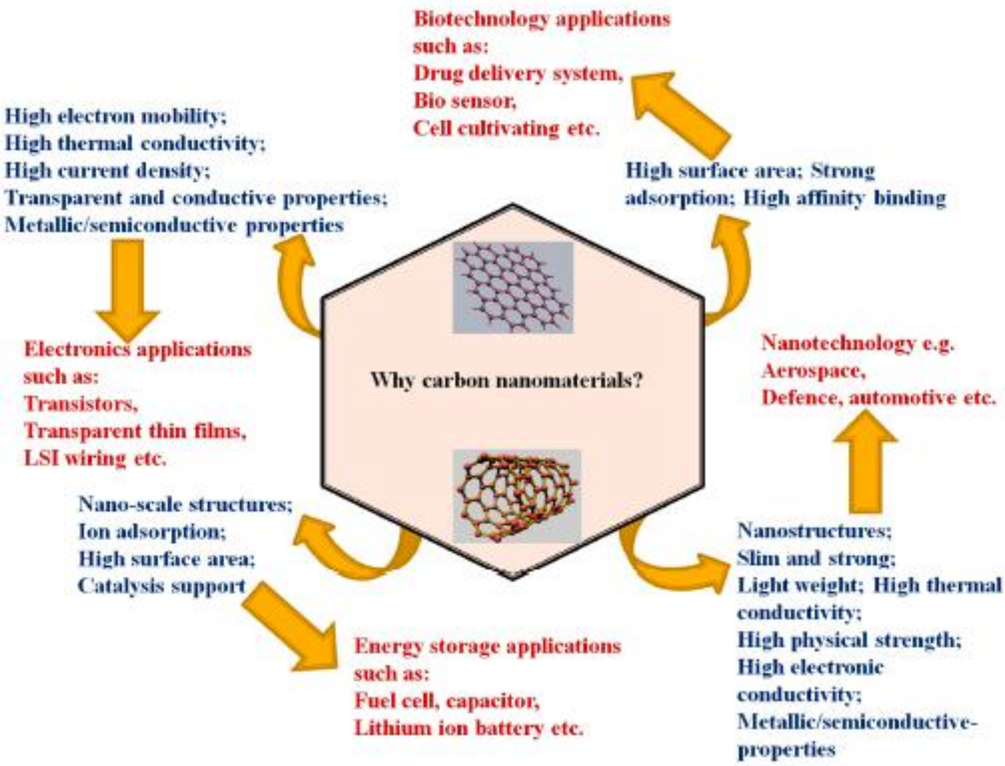
FORMS OF CARBON



APPLICATIONS OF CARBON NANOMATERIALS

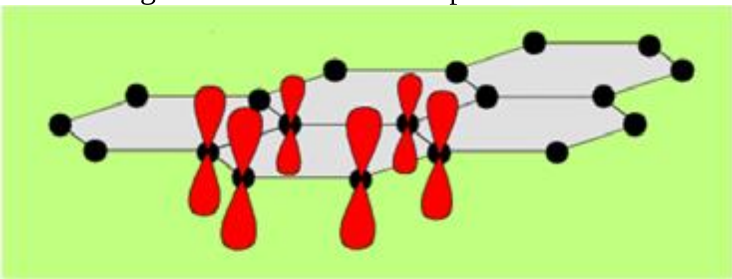


GRAPHENE

STRUCTURE:

Graphene is a crystalline material and is basically a single atomic layer of graphite. Its thickness is about 0.345nm.

In graphene, each carbon atom is sp2 hybridized and is bonded to three other carbon atom on a two dimensional plane, while the remaining 2p orbital exists perpendicular to the plane, contributing 1 conduction electron per C atom.



Properties:

1. High electrical and thermal conductivity. Thermal conductivity much higher than silver.
2. High thermal stability .
3. High tensile strength, about 100 times higher when compared to steel in bulk.
4. High intrinsic carrier mobility > 10^5 cm^2/Vs which is nearly 100 times larger than that in the present silicon devices.
5. Optical transparency.
6. Resistant to strong acids and alkali.

SYNTHESIS (Modified Hummer's method):

Hummer's method is widely used for preparation of graphene as the yield of graphene is high in this method. The method is based on separating the layers of graphite.

The method involves the following steps:

Graphite flakes (naturally occurring)

↓ Oxidised with $KMnO_4$ and H_2SO_4

Graphite oxide

↓
1. Excess $KMnO_4$ is removed by adding H_2O_2
2. Washed with HCl and dried

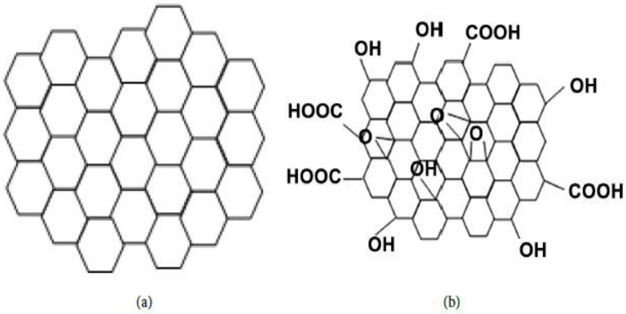
Dry graphite oxide powder

↓ Sonication in distilled water (subjected to ultrasound vibrations) To separate the layers of graphite oxide.

Graphene oxide

↓ Reduced with hydrazine hydrate $N_2H_4.H_2O$

Reduced graphene oxide.



Graphene monolayer Graphene oxide

Graphite oxide and graphene oxide contain various functional groups like –COOH, >C=O, epoxide, -OH.

The reduced graphene oxide contains a C/O atomic ratio of about ≈10 and has a conductivity $\approx 10^4$ S m^{-1}.

Applications:

(A) Electronic applications

- **Super-Small Transistors :** 1-nanometer graphene transistor is possible (one atom thick and 10 atoms across. Graphene has the potential of replacing silicon as a semiconductor and becomes the base material for integrated circuits, ultra capacitors, and future electronic devices.

- **High frequency electronic devices:** The charge carrier mobilities of graphene are very high.

- **Graphene based quantum computation:** Graphene may be an ideal q-bit.

(B) Material applications

- New composite materials: Composite materials based on graphene will have great strength and low weight, which can be used for gasoline tanks, plastic containers, sports' equipment, aircraft and automobile parts, wind turbines, and medical implants.

- Screens and coatings: Graphene is a transparent conductor, it can be used as transparent conducting electrodes for touch screens, light panels, solar cells, and organic light emitting devices.

- Energy storage: Graphene is capable of absorbing a large amount of hydrogen due to the large surface area, and it is possible to make energy storage devices based on graphene. Graphene powder can also be used in electric batteries, replacing graphite. The large surface-to-volume ratio and high conductivity can lead to improvements in the efficiency of batteries.

(C) Sensing applications

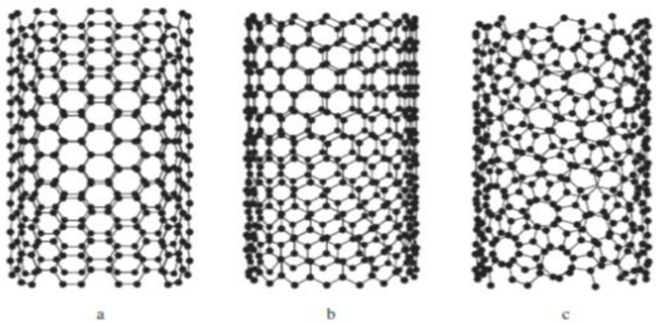
- **Gas sensors:** Graphene can be an excellent material for solid-state gas detection. Its 2D structure, ability to store high amounts of hydrogen, and change in local electrical resistance makes molecule detection much easier.

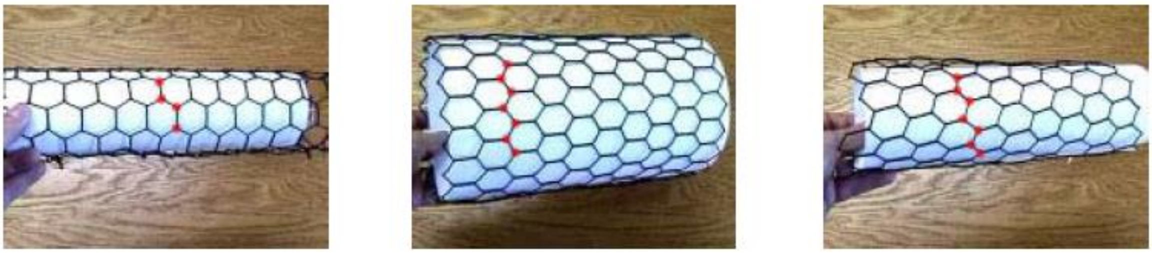
CARBON NANOTUBES

CNTs are cylindrical molecules with a diameter ranging from 1 nm to 10 nanometers and length up to a few micrometers.

Crystal Structure of Nanotubes

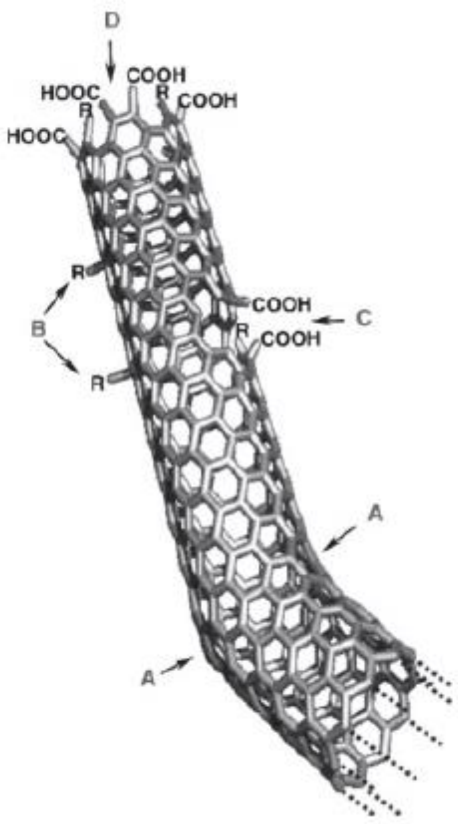
- Carbon nanotubes can be considered to consist of a graphene sheet wrapped into a cylinder.
- All carbon atoms are involved in aromatic rings, the C=C bond angles are no longer planar as they should ideally be. This means that the hybridization of carbon atoms are no longer pure sp^2 as in graphene but get some percentage of the sp3(pyramidalised) character. The percentage of sp^3 character increases as the tube radius of curvature decreases.
- The cylinder is open at the ends. The tubes may have closed ends also. Closing the tubes requires the introduction of curvature which is achieved by introducing 6 pentagons into the hexagonal lattice. Thus at each nanotube tip $6\times5 = 30$ carbon atoms are involved in pentagonal rings.
- Single walled nanotubes (SWNTs) consist of a single sheet of graphene rolled to form a cylinder with diameter of order of 1 nm and length of up to centimeters. Multi-walled nanotubes (MWNTs) consist of an array of such cylinders formed concentrically and separated by 0.35 nm, similar to the basal plane separation in graphite. MWNTs can have diameters from 2 to 100 nm and lengths of tens of microns.
- Depending on the direction in which the graphene sheet is rolled, or the configurations, three types of CNTs are possible, namely, the armchair(a), zigzag(b) and chiral configurations(c).
- The chirality of the nanotube affects the optical, mechanical and electronic properties.





- All armchair SWNTs are metallic, the rest are semiconducting.
- Semi-conducting nanotubes have band gaps that scale inversely with diameter, ranging from approximately 1.8 eV for very small diameter nanotubes to 0.18 eV for the widest possible stable SWNT.

Defects in a SWNT:



a) five-or seven-membered rings in the carbon framework, instead of the normal six-membered ring, leads to a bend in the tube.
b) *sp3*-hybrideized defects (R=H and OH).
c) carbon framework damaged by oxidative conditions, which leaves a hole lined with –COOH groups.
d) open end of the SWNT, terminated with COOH groups. Besides carboxyl groups, other terminal groups such as -NO2, -OH, -H, and >C=O are possible.

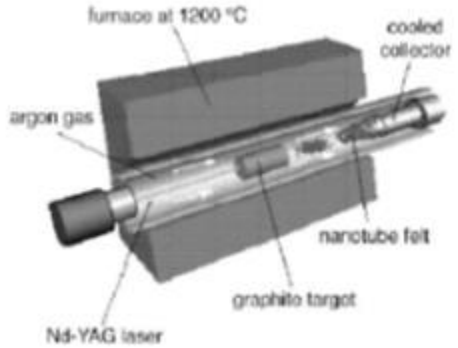
SYNTHESIS (CNTs and fullerenes)
PLASMA BASED SYNTHESIS METHODS:
In these methods, graphite target is vapourised at high temperatures (2500-3000℃) by passing an electric arc or by laser ablation in an inert atmosphere. When pure graphite is used as the target, MWNT and fullerenes are formed and when a metal-impregnated graphite target is used SWNTs are produced.

Arc discharge method:
In the arc discharge method, the experimental setup comprises two graphite rods connected to copper electrodes and the whole electrode system is enclosed in a glass bell jar equipped with a pump to evacuate the air and a helium inlet. When an electric arc is passed through the graphite rods in helium atmosphere, the temperature at the rods reaches 2500‑3000˚C and the graphite is vaporised as a plasma, which subsequently cools on contact with the helium atmosphere to form a soot. The sooty deposit on the cathode contains more amount of carbon nanotubes.

Single-walled nanotubes are produced when Co and Ni or some other metal is used as catalyst, embedded in the graphite that is used as the anode.

Laser Ablation Method:

In this method a pulsed or continuous laser is used to vaporize a graphite composite target (containing 1.2 % of cobalt/nickel with 98.8 % of graphite) that is placed in a quartz tube furnace with an inert atmosphere of of Ar or He at about~500 Torr pressure and 1200°C. Nanometer-size metal catalyst particles are formed. The metal particles catalyze the growth of SWNTs in the plasma, but many by-products are formed at the same time.



The soot actually comprises a mixture of soluble fullerenes C*n* (*n* <100), giant fullerenes C*n* (*n* >100), nanotubes and amorphous carbon. Using suitable extraction techniques, the soluble fullerenes can be isolated from the soot. Chromatographic methods are then used to separate the various fullerenes.

Subsequently the amorphous carbon and metal particles (used as catalyst) are removed to purify the CNTs.

Chemical vapor deposition (CVD)

Chemical vapour deposition is the catalytic decomposition of hydrocarbon like methane or carbon monoxide feedstock with the aid of supported transition metal catalysts.

It is carried out in two step process:-

• Catalyst like Ni, Fe or Co is deposited on a substrate.

• Carbon source (CH_4, CO or acetylene) is then placed in gas phase in the reaction chamber. The gas is converted to atomic level by using energy source like plasma or heated coil. The carbon atoms then diffuse towards substrate coated with catalyst and grow as nanotubes over the metal catalyst. Temperature used for synthesis of nanotube is 650 – 900℃ range. The typical yield is 30%.

PROPERTIES OF CNTs

Mechanical Properties

Carbon nanotubes are the strongest and stiffest materials Their strength is due to the strong C-C bonds. They are extremely strong along their axes and have a very large Young‘s modulus as high as 1Tpa to 1.8 Tpa in SWNTs. The modulus of a SWNT depends on the diameter and chirality.

A single perfect nanotube is about 10 to 100 times stronger than steel per unit weight.

Electrical properties:

Carbon nanotubes can be metallic or semiconducting depending on their structure. Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon.

Thermal Properties:

Better thermal conductivity compared to copper.

The temperature stability of carbon nanotubes is estimated to be up to 2800 °C in vacuum and about 750 °C in air.

Chemical Properties:

The chemical reactivity of a CNT is higher when compared with a graphene sheet because of the curvature of the CNT surface and end caps. The end caps of nanotubes tend to be composed of highly curved fullerene-like hemispheres, which are therefore highly reactive, as compared with the side walls. The sidewalls themselves contain defect sites.

Hence chemical functionalization is possible by introducing functional groups onto carbon form of CNTs. It can be performed at the end caps of nanotubes or at their sidewalls which have many defects.

Treatment of CNTs with strong acid such as HNO_3, $H2SO_4$ or a mixture of them or with strong oxidants such as KMnO4 and ozone tends to open the tubes and to subsequently generate oxygenated functional groups such as carboxylic acid, ketone, alcohol and ester groups. To these functional groups many different types of chemical moieties can be attached and these can be used in drug delivery, genetic engineering, tissue engineering and in biosensors.

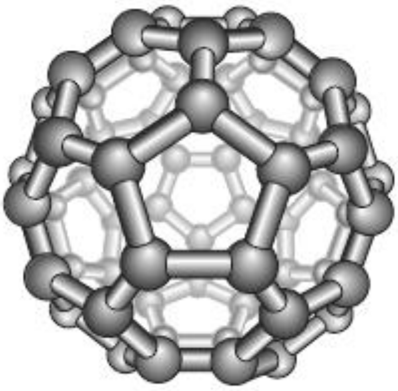
APPLICATIONS

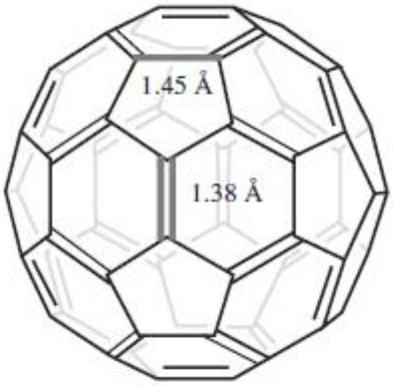
- The high tensile strength and low weight makes it applicable in aerospace applications, sports goods like tennis racket and bullet proof jackets.
- There is great interest in the possibility of constructing nanoscale electronic devices from nanotubes, and some progress is being made in this area. There are several areas of technology where carbon nanotubes are already being used. These include flat-panel displays, scanning probe microscopes and sensing devices.
- The chemical functionalization of CNTs make them applicable in targeted drug delivery, tissue engineering, genetic engineering.
- They are capable of storing H_2 gas upto about 65% of their weight and hence are potential H2 storage materials.

FULLERENES

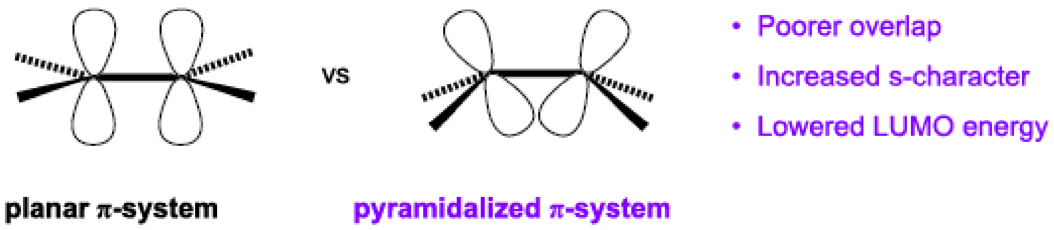
STRUCTURE OF FULLERENES

- Fullerenes are molecules with a cage structure containing $2(10 + n)$ carbon atoms which form 12 pentagons and n hexagons.
- Buckminster fullerene C60 is the smallest stable fullerene. This molecule has the shape of a truncated icosahedron. It is in fact the exact replica of a football formed from 12 pentagons and 20 hexagons, with each pentagon surrounded by 5 hexagons. C60 is a highly symmetrical molecule in which all the carbon atoms are equivalent.
- There are two types of carbon–carbon bond in this molecule.Bonds at joining two hexagons are 6–6 bonds, while those joining ahexagon and a pentagon are 5–6 bonds. Now the 6–6 bonds are shorter thanthe 5–6 bonds. Hence, the 6–6 bonds have the character of a double bond,whereas the 5–6 bonds have the character of a singlebond.



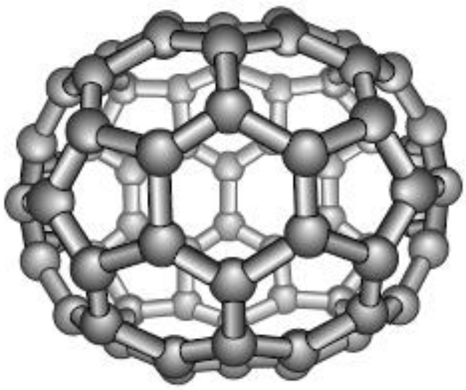


- Each carbon atom is sp2 hybridised and the unhybridised p-orbital is involved in π-bonding. π-systems are curved and are composed of pyramidalized carbon atoms (small amount of sp3 hybrid character). .



Pyramidalization not only imposes curvature, but it also imparts significant electronic perturbations. Less parallel the alignment of p-orbitals the poorer will be their overlap, and that will lead to weaker π-bonds.

Buckminsterfullerene is the only isomer of C60, and it is also the smallest fullerene obeying the isolated pentagon rule(Only those molecules having all the pentagons separated from each other by hexagonal rings are stable) . The second stable fullerene is C70. Its structure also respects the isolated pentagon rule and it has an oval profile, rather like a rugby ball.



- Since only the fullerenes C*x* respecting the isolated pentagon rule are stable, the magic numbers *x* are 60, 70, 72, 76, 78, 84, and soon. All these fullerenes, with the exception of C72, are in fact obtained when graphite is evaporated in a helium atmosphere.

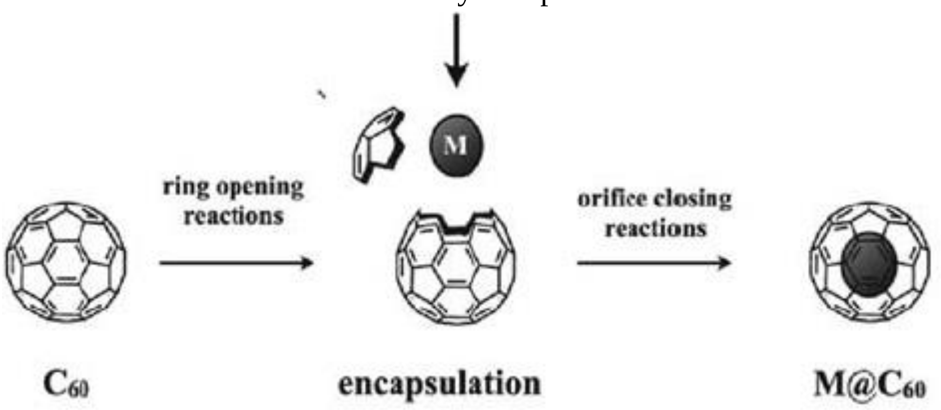
PROPERTIES OF BUCKMINSTERFULLERENE

- C60 is the most abundant of the fullerenes .
- **Soluble in** the aromatic solvents, such as benzene, toluene, or 1-chloronaphthalene. Solutions of C60 have a characteristic purple-magentacolour.

- **Chemical Properties**
- Aromaticity of C60 is less than benzene; it behaves like a polyene and is a good electron acceptor. C60 can accept up to 6 electrons by six successive single-electron reductions and these reductions are reversible processes, and also that the anions thus obtained(C_{60}^{n-} where n = 1,2,…,6) remain stable for several days at low temperatures.
- Fullerene reacts with alkali metal ions to form alkali metal fullerides. In these compounds, the alkali metal ions are present in the interstices of the crystal lattice of fullerenes. M3C60 (where Mis Na, K, Rb, Cs) exhibit metallic behaviour. The K,Rb and Cs fullerides become superconducting at low temperatures (≈30K)

  Functionalisation of fullerenes:
- There are several approaches available to functionalize the fullerene. For example C_{60} has an electrophilic tendency, and can undergo addition reactions in the presence of nucleophilic reagents. These reactions can be utilised to functionalise fullerene with many molecular groups with specific functions to yield molecules with novel properties.
- **Formation of Endohedral Fullerenes:**

  Atoms, molecules, or ions can be trapped inside the cavity of a fullerene cage to form endohedral fullerenes. H_2, N_2, and a wide variety of noble gases and transition metal atoms have been successfully encapsulated inside the fullerene.



APPLICATIONS OF FULLERENES:

- **Functionalized Fullerenes for Photovoltaics/Solar Cells**:

Many polymer-fullerenes are used in organic photovoltaics since they exhibit ultrafast photo-induced charge transfer.

- **Antioxidants and Biopharmaceuticals:**

Since fullerenes react readily with free radicals, which are dangerous to the body, they could potentially act as antioxidants . Much research is being carried out in the control of nervous damage caused due to diseases such as Alzheimer's and Lou Gehrig's disease (ALS) by the applications of fullerenes. The sponge-like effect of fullerenes towards radicals,results in destruction of 20 free radicals per C60 radical. The bioactivity of the fullerene-based antioxidants is 100 times more effective than the current leading drugs in the market.

- **Hydrogen Storage**:

Fullerenes are able to retain a maximum of 6.1% of hydrogen due to their cage-like molecular structure.When hydrogenated, they form a C–H bond, whose strength is lower than the strength of the C–C bond. Therefore, when heated, the C–H bond breaks, preserving the distinctive structure of the fullerene.

Endohedral Fullerenes:

Insertion of a metal ion in the cages of the C60 molecule produces an endohedral fullerene. Rare earth ions such as Gd inserted in the fullerene could potentially be used as diagnostic MRI contrast agents for several diseases. These materials are highly stable even at higher temperatures and more effective than fullerenes.

N @ fullerenes (Nitrogen encapsulated) is explored for quantum computing, photonics.

Fullerenes for Drug Delivery:

Attachment of hydrophilic moieties to the hydrophobic C60 fullerene makes it soluble in water. Consequently, they become capable of transporting drugs to the cells. Hence they are used in drug delivery.