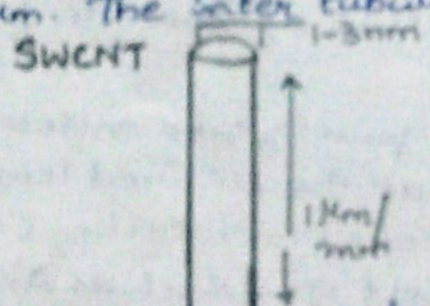
UNIT-4
CARBON MATERIALS FOR HEALTH, STEALTH AND ENERGY.

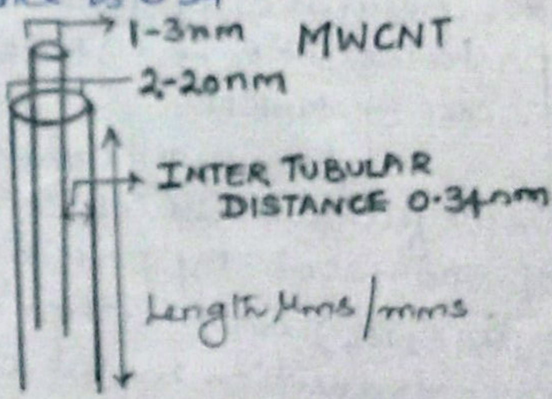
1. What are carbon nanotubes? How are they Synthesized?

Carbon nanotubes are cylindrical carbon molecules with atleast one dimension in nanometer Scale. when a graphene sheet is rolled into a cylinder it forms a Carbon nanotube.

Types of carbon nanotube:

1. Single walled carbon nanotube [SWCNT]: Nanotubes with single sheet of graphene with diameter 1-2 nm and length 1-100 μm
2. Multi walled carbon nanotube [MWCNT]: Nanotubes with more number of concentric rings of graphene sheets with outer diameter 2-20 nm, inner diameter 1-3 nm, length 1-100 μm. The inter tubular distance is 0.34 nm.



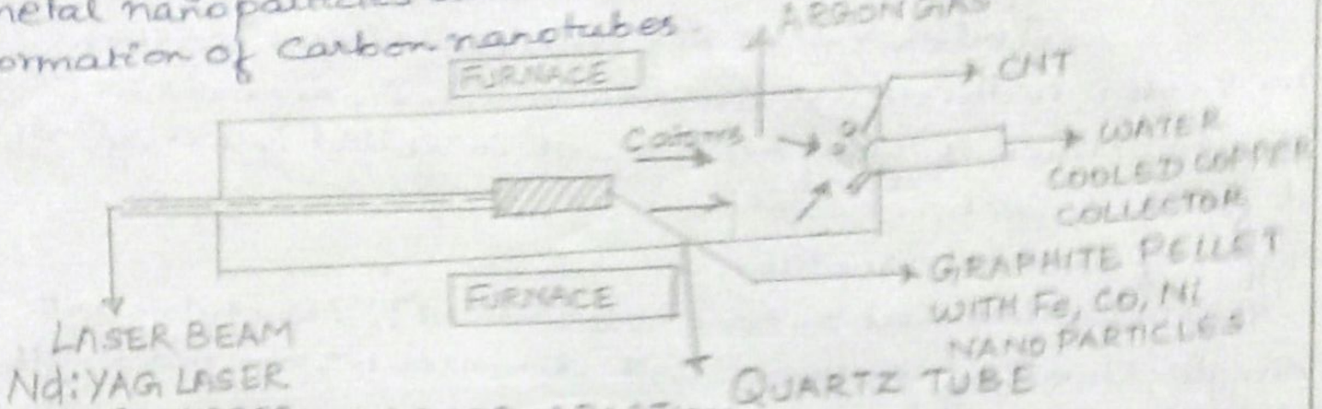


Synthesis of Carbon nanotubes

(a) Laser Ablation Method:-

The laser ablation apparatus consists of a furnace, a quartz tube with a window and a graphite pellet (target) doped with small amounts of Co, Ni, Fe Nano particles. The furnace is filled with an inert gas of argon with a flow rate of 1cm/sec and a pressure of 500 Torr. A water cooled copper condenser is present outside the furnace. A laser beam from Nd:YAG laser [Neodymium doped Yttrium Aluminum garnet Nd:$Y_3Al_5O_{10}$] or CO_2 is introduced and focussed onto the graphite pellet placed in the centre of the furnace, which is

maintained at 1200°c. At this temperature, the target is
vapourized to form small carbon atoms or molecules which
are sweeped by argon gas to colder copper collector
where they condense to form carbon nanotubes. The
metal nanoparticles acts as nucleation sites for the
formation of carbon nanotubes.



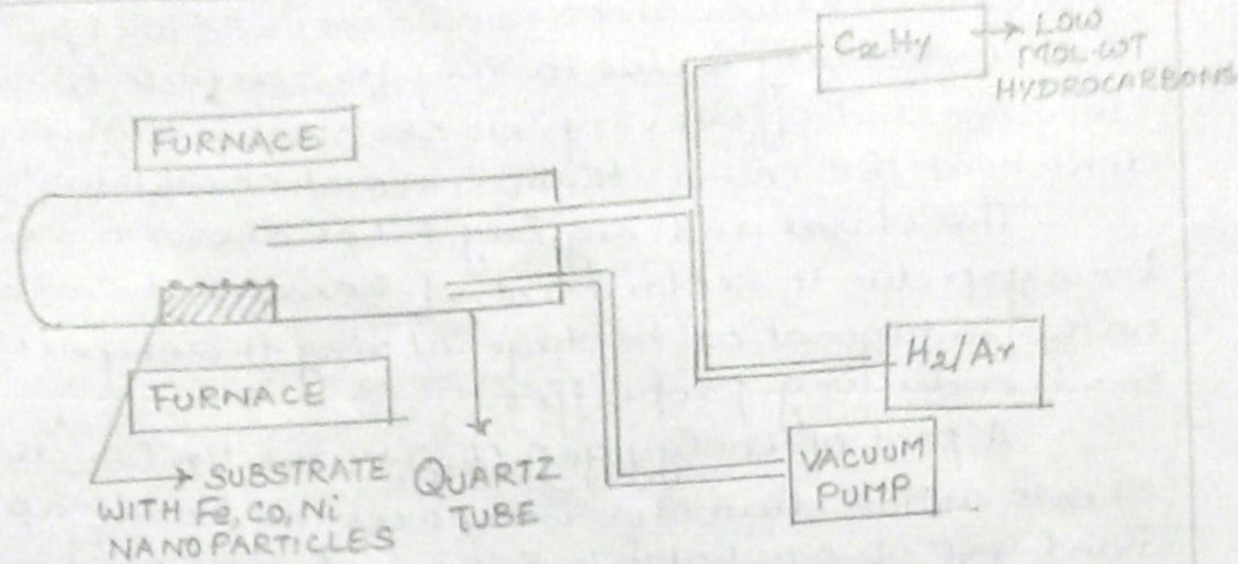
•LASER ABLATION

(b) Chemical Vapour Deposition [CVD].

CVD involves decomposing a hydrocarbon gas
such as methane, acetylene, ethylene etc, at high
temperatures of 1100°c in the presence of metal nano
particles like Fe, CO, Ni or a mixture of these to form
SWCNT or MWCNT.

The CVD, consists of a quartz tube enclosed
in a furnace which is heated at the desired temperature
of 500-1200°c by passing a gaseous hydrocarbon (CH_4,
C_2H_2, C_2H_4) with either H_2 or inert gas such as Ar
over transition metal catalyst (Fe, Co, Ni) on inert
support such as alumina, SiO_2, Zeolites. At these
temperatures, the hydrocarbon undergoes decomposition
as $C_xH_y \longrightarrow xC + y/2\, H_2$.

The carbon atoms formed dissolves in the metal nano
particle catalysts and becomes saturated. The
saturated carbon then precipitates to form CNTs
on the surface of the catalyst coated on the substrate.
The diameter of the tube is determined by the size of
the nano particle catalyst. The method produces
carbon nanotubes with open ends commercially.



CHEMICAL VAPOUR DEPOSITION

2. Explain the electrical and Mechanical properties of CNT.

Carbon nanotubes can be both metallic or semi conducting depending on the helicity and the diameter of the nanotubes. Helicity refers to rolling of hexagonal chains with respect to tube axis. Three types of CNTS arises due to rolling:

1. Arm-chair : The Hexagonal carbon atoms lie parallel to tube axis with $n=m \neq 0$, The chiral angle, $\theta = 30°$.
2. Zig-Zag :- The hexagonal carbon atoms lie perpendicular to tube axis with $n \neq m$, $m=0$. The chiral angle $\theta = 0°$.
3. Chiral : The hexagonal carbon atoms lie in the angle of $0°-30°$ and the tube exhibit a twist or swirl around the hexagons.

Tubes with arm-chair configuration are metallic due to its symmetry. while tubes with Zig-Zag or chiral can be either metallic or semiconducting depending on the chiral vector.

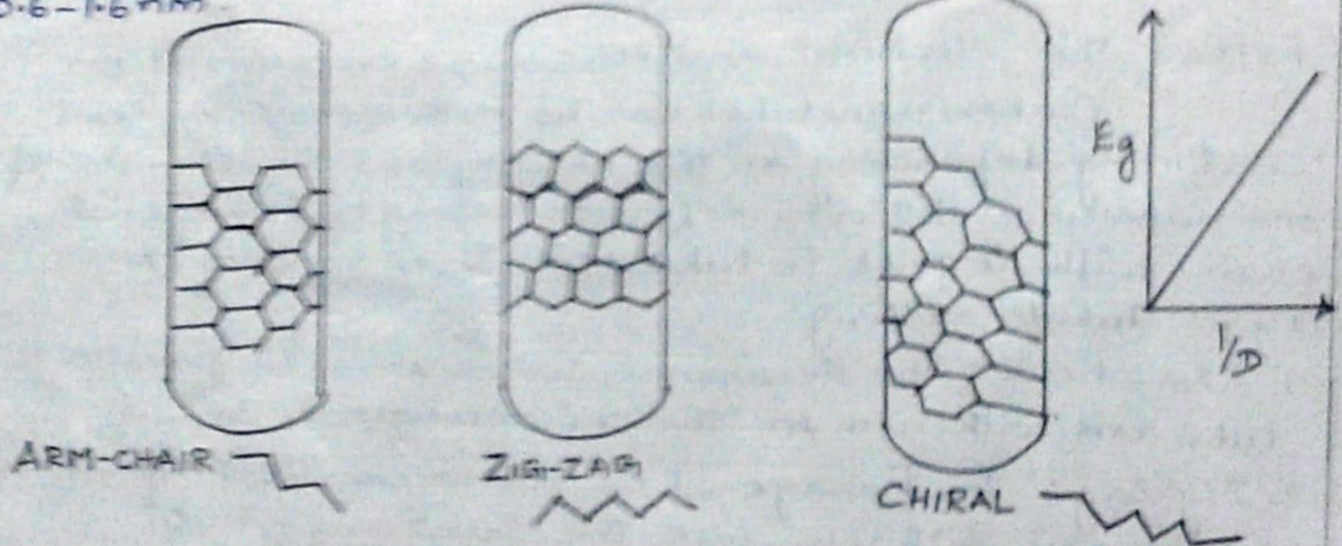
Metallic properties dominate when $\frac{n-m}{3}$ is an integer (includes zero).

Semi conducting properties dominate when
$$\frac{n-m}{3} \neq \text{integer}.$$

In metallic state, the conductivity of CNT is very high and carries billion amperes current/cm² ($10^9 A/cm^2$). The high conductivity is due to very few defects to scatter electrons and offers very low resistance. High currents don't heat the CNT as their thermal conductivity is high.

The chiral and Zig-Zag tubes shows a very small band gap due to replacement of hexagonal carbon ring with pentagonal or heptagonal ring thereby exhibiting semiconducting properties.

A plot of energy gap (E_g) versus 1/D (D-diameter) shows as the diameter increases the band gap decreases. Band gap of 0.4-1.0eV is seen in SWCNT of diameter 0.6-1.6nm.



b. Mechanical properties :-

Tensile strength :- It is the amount of stress applied to pull the material. The tensile strength of CNTS is 30 times more than that of steel. High tensile strength in CNTs is due to interlocking of carbon-carbon bonds through covalent bond and few structural defects like grain dislocation at the walls. The tensile strength of CNT is 60GPa while steel is <2GPa.

Young's Modulus :- The young's modulus of CNT is 1.28-1.80 TPa which is about 10 times more than that of steel (0.21TPa), indicates that CNTS are stiff to bend. In

Reality, the CNT bend with relatively ease since the diameters of the tube are extremely small compare to its length. CNTS are straightened back without any damage due to few structural defects.

c. Thermal conductivity:

The thermal conductivity of CNT is 6000 w/m.k while that of diamond is 3000 w/m.k. The thermal conductivity of CNT is 10 times that of silver. The CNT conduct heat by vibration of covalent bonds holding the carbon atoms. The stiffness of carbon bonds transmits heat throughout CNT exhibiting high thermal conductivity.

d. Density: The density of CNT is 1.33-1.43 g/cm^3 while that of Al is 2.7 g/cm^3. They are light weight materials.

3. Discuss the applications of Carbon Nanotubes.

1. As a catalyst or a support for various chemical reactions.

a) SWCNTs acts as a catalysts for the reduction of NiO and $AlCl_3$ to base metal.

b) MWCNTs acts as catalyst for the partial reduction of MoO_3 to MoO_2 at 475°c.

c) CNTS are used for the formation of CdS crystals by reducing CdO with H_2S gas at 400°c.

2. As Electrodes in Fuel cells and in Lithium-ion battery.

CNTS can hold 6.5% hydrogen by weight thereby used as anodic material in H_2-O_2 fuel cell. It can also stores lithium ions in which one lithium atom can be stored for every 6 carbon atoms of CNTS, thereby used as anode as a replacement for graphite in lithium-ion battery.

3. Chemical Sensors:

CNTS can be used as sensor to detect gases like NO_2, N_2O_5, NO_x on the basis of increase in its electrical conductivity.

4. Flat panels for TVs and Computers:

Millions of MWCNTS are arranged below the screen to provide pixel which are exploited in flat panel display.

5. Interconnects for Microdevices:

CNTS have been developed to replace copper as interconnects in integrated circuits.

6. Drug Delivery:

CNTS can be used as drug carriers to deliver at targeted cells as they easily adapt themselves and enter the nuclei of the targeted cells.

7. Aerospace components:

CNTS are light weight materials, good fatigue strength over a long time used in aircraft.

PART-A QUESTIONS

1. What are carbon nanotubes?

Carbon nanotubes are cylindrical carbon molecules with hexagonal and pentagonal structure possessing unique electrical and mechanical properties.

Define graphene.

A single layer of graphite with hexagonal display of carbon atoms in sp^2 hybridisation.

Define Helicity:

The rolling of hexagonal carbon chains with respect to tube axis is known as helicity. It results in

3 types of configurations
1. Arm-chair 2. Zig-Zag 3. Chiral.

4. Give the classification of SWCNT based on chirality.
They are classified as.
1. Arm-chair :- The hexagonal carbon atoms lie parallel to tube axis with $n=m, m\neq0. \theta=30^\circ$.
2. Zig Zag : The hexagonal carbon atoms lie perpendicular to tube axis with $n\neq m, m=0, \theta=0^\circ$.
3. Chiral :- The hexagonal carbon atoms lie in the angle of $0^\circ-30^\circ$ and the tubes exhibit a twist or swirl

5. Distinguish between SWCNT and MWCNT.

SWCNT	MWCNT.
Nanotube with a single layer of graphene sheet.	Nanotubes with a concentric rings of graphene sheet.
Its diameter is 1-2nm, and the length is 1-100 μm.	Outer diameter 2-20nm Inner diameter 1-3nm. Length 1-100μm. Inter tubular distance = 0.34nm
Catalyst is required for synthesis	No catalyst.
Purity is Poor, easily twisted and flexible.	Purity is high, can't be twisted.

6. what are advantages of laser ablation over CVD?
1. High Quality CNTs can be produced.
2. The diameter of the nanotubes can be controlled.

UNIT-IV - PART-A

7. Define Graphene oxide.

Graphene Oxide is a material consisting of a monomoleculal layer of graphite with various Oxygen functionalities like epoxide, OH groups exhibiting hydrophilic character.

8. Differentiate graphene Oxide and reduced graphene Oxide.

Graphene Oxide	Reduced graphene Oxide
Formed by oxidation of graphite	Formed by reduction of graphene Oxide
It is an electrical insulator and hydrophilic in nature	It is moderately electrical conducting and hydrophobic in nature.

9. why graphene is called Vanderwaal's Solid?

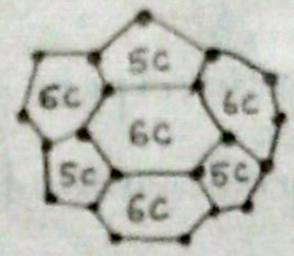
Graphene, a single layer of graphite have bond distance similar to graphite, which is a Vanderwaal's solid. Hence graphene is also termed as a Vanderwaal's solid.

10. Mention any two applications of reduced graphene Oxide.

1. Reduced graphene Oxide with iron oxide particles are used as electrode materials in Lithium-ion batteries
2. Nanocomposites of reduced graphene Oxide are used as Supercapacitors
3. Chemically modified graphene Oxide with amino functional groups are used in non-linear optics.

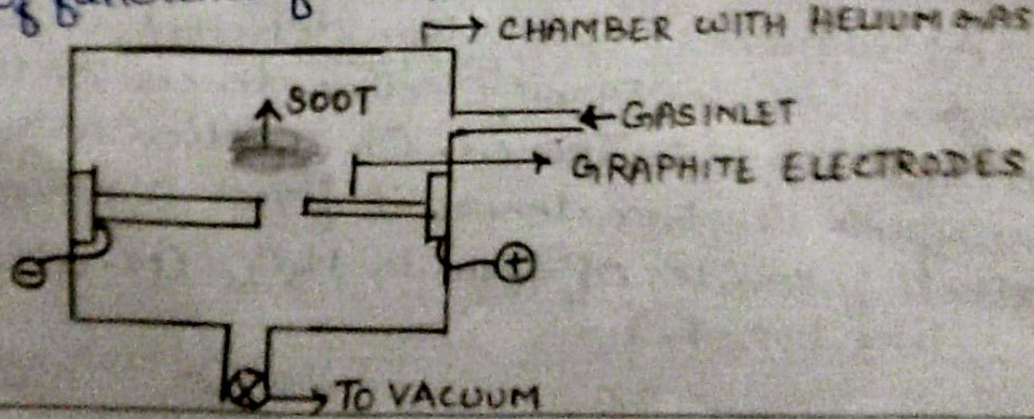
(4) what are Fullerenes? Explain Huffmann method for the Synthesis of fullerenes with their properties.

Fullerenes are a group of polymorphic forms of Carbon atoms, with discrete molecules consisting of hollow cluster of large number of carbon atoms. Each molecule is composed of carbon atoms that are bonded to one another to form both hexagonal carbon and pentagonal geometrical configurations. In C_{60} fullerene, there are 20 hexagons and 12 Pentagons. which are arranged in such a way that no two pentagons share a common side. The molecular surface exhibits symmetry of a soccer ball. These fullerenes molecules resembles geodesic domes built by Buckminister Fuller, hence known as Fullerene.

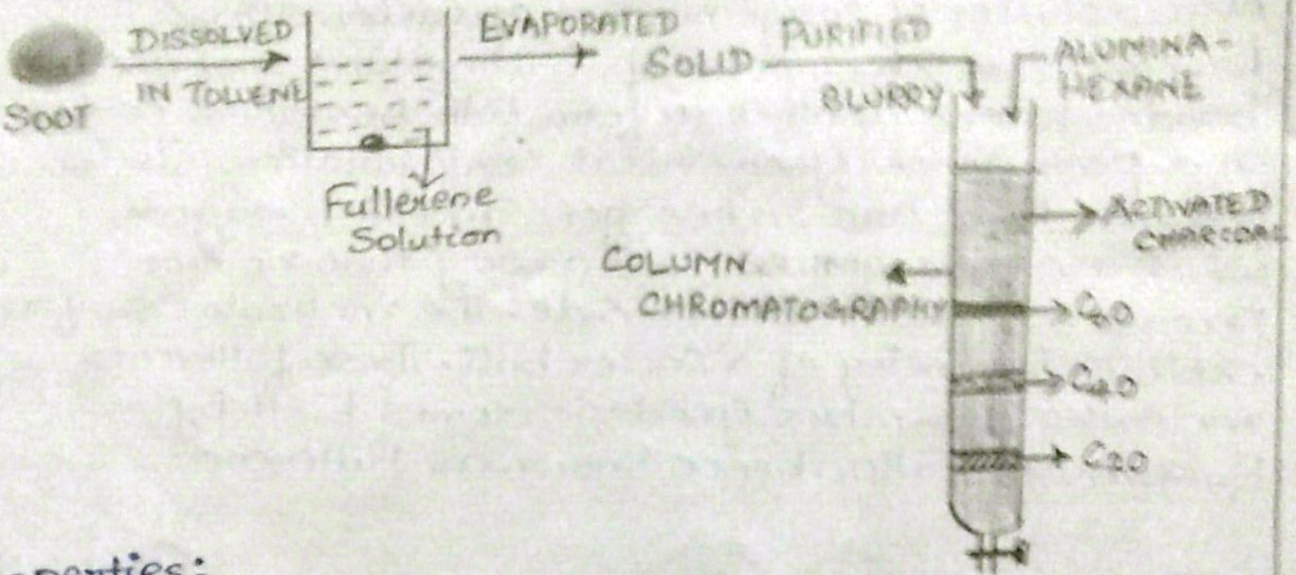


Huffmann Method:-

It is a low cost method for preparing fullerenes. It consists of a chamber containing two graphite electrodes. The chamber is filled with an helium gas of 100 torr pressure. when an voltage is applied, an electric arc produced results in vapourization of graphite to form soot inside the chamber. The soot contains 10% fullerenes which is extracted by dissolving in toluene. After extraction, toluene is removed and a solid mixture of fullerenes from $C_{20}-C_{100}$ is obtained.



It is then separated and purified by a column chromatography containing activated charcoal and silica gel. The individual fullerenes are separated using alumina - hexane as an eluent.



Properties:

It is a mustard coloured solid, appears brown to black on increasing the thickness.

It is soluble in aromatic hydrocarbons forming coloured soluble.

On sublimation, it forms a translucent magneta coloured face-centred cubic crystals.

Fullerenes are electrical semiconducting material.

In fullerenes, each carbon is bonded to three other carbon atoms in sp^2 hybridisation. It has two types of carbon bond length, one hexagonal carbon bond length (6:6) and the hexagonal - pentagonal bond length (6:5). The 6:5 bonds are shorter than double bonds (6:6) resulting in poor electron delocalisation. Hence, fullerenes are - semiconductors (Vanderwaal's insulator)

As Fullerenes are electron deficient, it can react readily with inorganic or organic electron donors so that its conductivity is increased. On reaction with inorganic electron donors it forms superconducting alkali fullerides of formula M_3C_{60} (M - alkali metal like K, Cs, Fr).

On reaction with organic electron donor TDAE (tetrakis (dimethylamino)ethylene it forms a ferromagnetic material.

Applications of Fullerene.

1. Fullerenes are used as antioxidants in cosmetics for preventing skin damage. As fullerenes react readily with radical, it can trap methyl radical there by used as 'radical sponge' in cosmetics.

2. Fullerenes are used as antiviral agents as they conjugate with proteins of viruses. They can suppress the replication of HIV viruses and prevents AIDS.

3. They are used in delivery of hydrophobic drugs due to its biocompatibility, easy diffusion in the treatment of cancer.

4. They are excellent electron acceptors and are used in solarcells by forming heterojunctions.

5. Fullerenes containing sulphides of tungsten & Mo exhibit excellent solid-lubricant properties.

(5) Discuss the synthesis of Graphene by Hummer's method.

The Hummer's method for synthesis of Graphene involves 1) Oxidation of graphite to graphene oxide followed by its (2) Reduction. The reduced graphene oxide have structure resembles that of graphene. The direct synthesis of graphene by mechanical process or by CVD method is expensive and it is difficult to isolate graphene. Hence, Hummer's method is preferred in synthesizing graphene which involves two steps.

1) Oxidation of graphite to graphene oxide.
2) Reduction of graphene oxide.

1) Graphene oxide:

Graphite is treated with a mixture of oxidising agents like $KMnO_4$ in H_2SO_4, $NaNO_3$, H_3PO_4 etc, where by graphite oxide and graphene oxide is obtained.

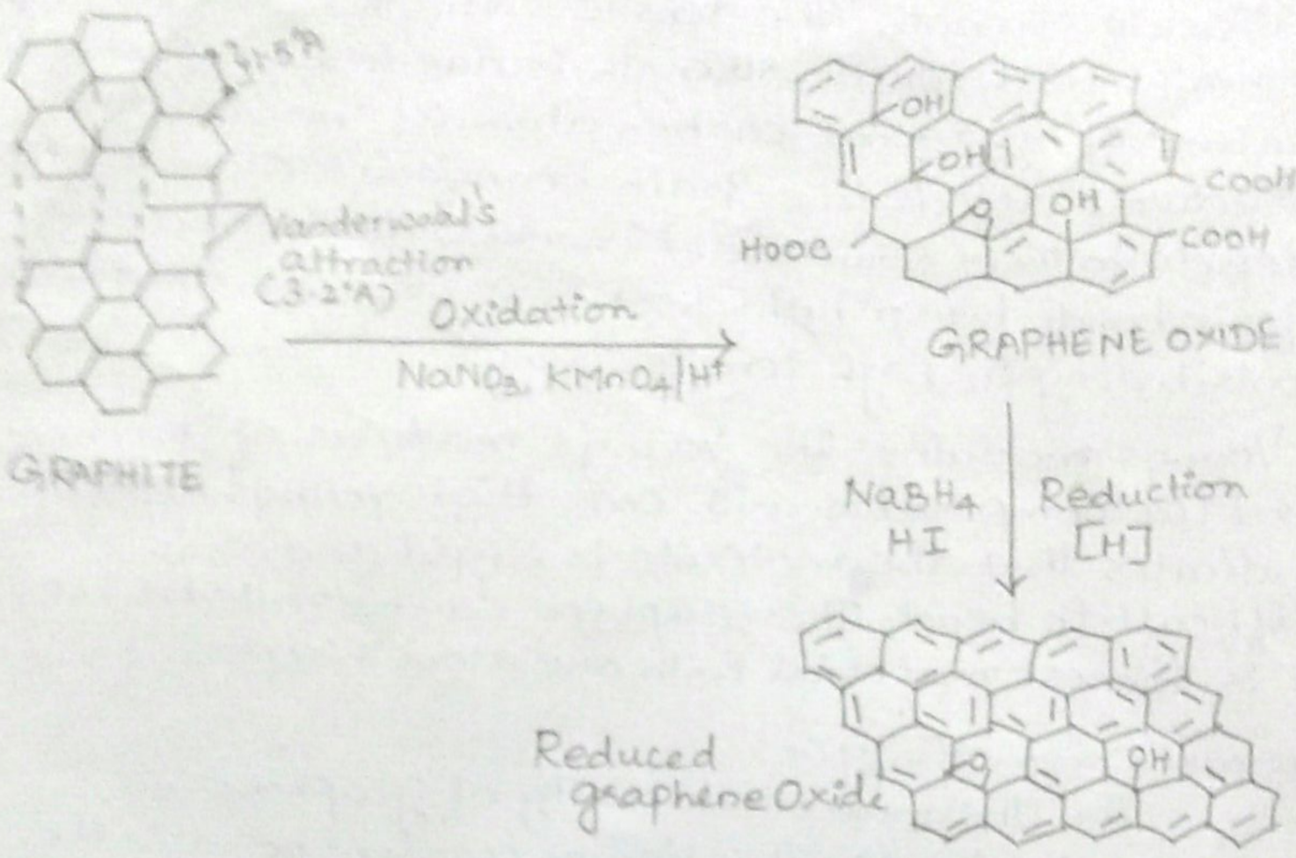
$$\text{Graphite} \xrightarrow[\substack{NaNO_3 \\ [O]}]{KMnO_4/H^+} \text{Graphite Oxide} + \text{Graphene Oxide.}$$

During oxidation, the oxygen functionalities like epoxide, carbonyl, carboxylic, ether, hydroxyl groups are introduced in graphite structure to form products. The main difference between graphite oxide and graphene oxide is the interplanar spacing between the individual atomic layers. In graphene oxide, the water is intercalated (during oxidn. reaction of graphite) between the layers causing disruption of sp^2 hybridisation thereby acting as insulator and hydrophilic nature.

2) Reduction of graphene Oxide:-

The graphene Oxide is treated with reducing agents like $NaBH_4$, N_2H_4, Ascorbic acid, HI to form reduced graphene oxide. It resembles graphene, since there are some oxygen functional group present on the surface or inside the structure causing defects. During reduction, the oxygen functionalities are replaced by 'H' atoms during which the honeycomb hexagonal lattice is recovered and exhibits moderate conductivity.

$$\text{Graphene Oxide} \xrightarrow[\text{Reduction}]{[H]} \text{reduced graphene oxide (rGO)}$$



⑥ Discuss the electrical and Mechanical properties of graphene.

Electrical properties:-

Graphene is a Zero-bandgap energy semimetal with high electrical conductivity. of $10^9\ A/cm^2$. In graphene, both holes and electrons act as charge carriers.
In graphene, each carbon atom is connected to 3 other Carbon atoms on two dimensional honey-comb lattice leaving $1e^-$ freely available for electrical conduction. These highly mobile pi electrons are located above and below the graphene sheet. The graphene electrons act as photons due to lack of mass and can travel upto Submicrometer distance without Scattering known as ballistic transport. The e's like photons are responsible for high electrical conductivity.

Mechanical Property

(1) Tensile strength: The tensile strength of graphene is 130GPa. High tensile strength is due to high symmetrical nature of hexagonal carbon atom as there are no structural defects like grain boundaries, Stone-walls defects in their structure. Moreover, the interlocking of C-C bonds by sp^2 hybridisation is strong in graphene contributing to high tensile strength.

(2) Young's modulus: The Young's modulus of graphene is 1TPa comparable with CNT. High Young's modulus indicates that the molecule is rigid and it is difficult to bend. The graphene can be rolled since it is thinnest material with one atom thickness.

Thermal Conductivity:-

The thermal conductivity of graphene is 4000W/mK is due to vibration of covalent bond in the hexagonal structure (Honey comb lattice). The stiffness of carbon bond contributes to high thermal conductivity in transmitting heat.

(4) Discuss the applications of graphene.

1. Graphene is used as anode materials in advanced batteries.
2. Graphene is used as anode material as graphite-tin Oxide in Lithium-ion batteries.
3. Laser-Scribed graphene are used as flexible, light weight Supercapacitors (able to store charges).
4. Graphene is used as electrode materials in Perovskite solar cells.
5. It is used as Radiofrequency flexible electronic devices in wearable touch panels, touchscreen devices.
6. Graphene is used as 'loop-heat pipes' in Satellites which are pumps that move fluids without any mechanical parts thereby reduce the wear and tear.