UNIT-III

Modern Engineering materials

Nano materials: Introduction, classification, preparation (arc discharge, laser ablation and chemical vapor deposition methods), properties and applications of carbon nano tubes and fullerenes. Preparation of nanomaterials-sol-gel method, characterization by scanning electron microscopy (SEM)

Semiconductors, band diagram in solids, Semiconductor devices (p-n junction diode as rectifier and transistors)- preparation of single crystal semiconductors- Czochralski process, purification of semiconductors-Zone refining,

Super conductors - Introduction basic concept, applications

Supercapacitors: Introduction, Basic Concept-Classification – Applications

Introduction: Nano means one billionth or 10^{-9} and therefore a Nano meter is just one billionth of a meter. **Nano materials** are those which possess at least one dimension in the nano scale i.e. 1 to 100 nm. Nanotechnology is a field of applied science focused on the design, synthesis and application of materials and devices on the nanoscale.

When a bulk material is changed into Nano sized particle, the properties also change. The properties that are changed at nano scale are:

Properties of Nano Materials

1. **The physical properties** like melting point, adsorption and catalytic activity are dependent onthe surface area or more precisely the surface to volume ratio. As the size of the particle decreases, the surface to volume ratio increases tremendously. More atoms are on the surface rather than in the bulk (inside of a particle). Therefore, the melting point decreases, the catalytic activity, adsorption increases as the particle size decreases.
2. **The optical properties and electric properties** depend on the band structure or density of states. As the particle size decreases, the band gap increases in semiconducting materials and therefore shows different colours with different sizes. (Ex. CdTe particles in solution show colours from blue, green, yellow red as the size increases from 1 to 50 nm.
3. **The magnetic properties** of magnetic (Ferro, anti-Ferro, Para and dia) materials change with size of the particles i.e. as the size approaches individual domain size, they can be magnetizedto a great extent and multi domain structure disappears and we get single domain structure. Ex. Fe particles of size below 16 nm can be magnetized to more than the bulk iron.

   The mechanical properties of ceramics which are usually brittle can be enhanced to a large extent if the crystallite sizes are small in the nano-range rather than highly crystalline nature.

   Because of the small crystallites embedded in amorphous matrix, they get more malleability (less brittle) and still have high tensile strength. Carbon nanotubes have high mechanicalstrength because of rigid structure of hexagonal carbon atoms.
4. **Chemical Properties:** Based on the surface area to volume effect, nanoscale materials have

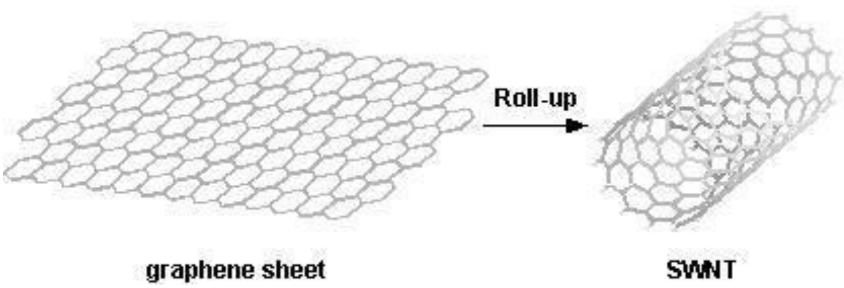
a) Increased total surface area.
b) Increased number of atoms accessible on the surface.
c) Increased catalytic activity of those large number surface atoms.
d) Different/tunable surface catalytic properties by the change in shape, size and

composition.

Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemicalreactions.

Types of Carbon Nano materialsCarbon Nano Tubes (CNTs)

- Carbon Nano Tubes (CNTs) were discovered by S. Iijima in the year 1991.
- They are long, thin tube like cylinders made of hexagonal rings of carbon atoms, Bondedovalently by sp^2 hybridization



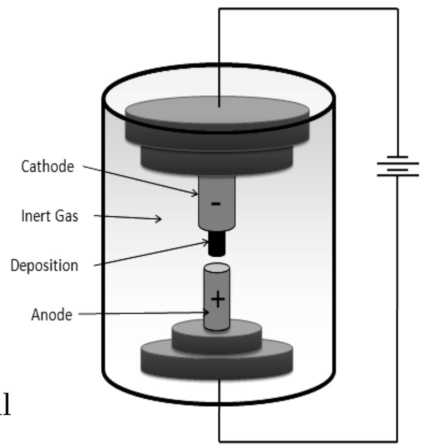
- A sheet of graphite is rolled into a cylinder or twisted to make a tube of few nm in diameterand up to hundreds of micrometers long (length to diameter ratio 28,000,000 :1)
- These Nano tubes have a hemispherical "cap" at each end of the cylinder (closed CNTs) Andthey can be open also (open CNTs)
- CNT diameter = ~1.2 nm

CNTs are two types depending upon the way in which they are arranged.

(a) A single walled nanotubes (SWNT) (b) A multi walled nanotubes (MWNT)

Preparation of Carbon Nano Tubes:

Arc discharge method (Krotschmer and Huffman method, 1990)



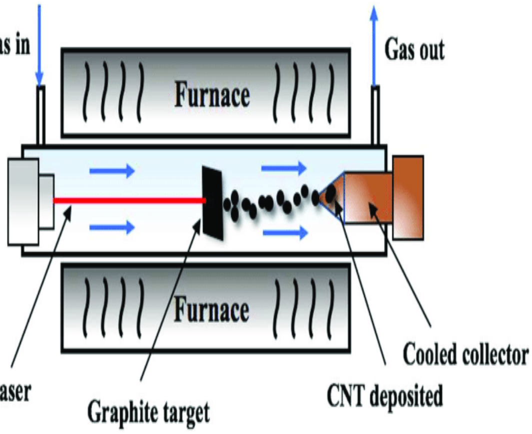
- Electrical discharge between graphite electrodes (mixed with metal catalyst like (Fe, Co, Ni etc.) in an atmosphere of Helium, argon at low pressure 50 -700 mbar produces carbon Nano tubes along with other carbon mass.
- A direct current of 50-100 A and voltage of 20V creates High temperature arc between the electrodes.
- The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod. The resulting soot (on the graphite cathode, inner walls of evaporation chamber) is scraped and dissolved in polar organic solvents. The metal catalysts are separated by treating with mild acid/base and then dissolved in aromatic organic solvent (colored solution).
- The colored solution is separated from the black insoluble soot (settling at the bottom)

and then CNTs are isolated by column chromatography.

- Depending on the exact technique, it is possible to selectively grow SWNTs, or MWNTs.

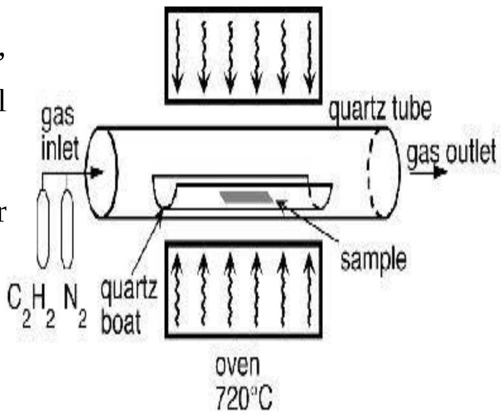
Control factors: Pressure of Helium & Argon, their ratio, the current & voltage, the catalyst type, size and content, the distance between electrodes etc. determine the type of CNTs their quality, quantity and diameter.

Laser ablation method



- In this method, a high energy pulsed laser vaporizes a graphite target in a high temperature reactor, while an inert gas like He or Ar is fed into the chamber (500 Torr)
- A pulsed or continues laser is used to vaporize a graphite target in an oven at 1200^{o}C
- The main difference between continues and pulsed laser, is that the pulsed laser demandsmuch higher intensity.
- A very hot vapour forms, then expands and cools rapidly.
- The nano tubes develop on the cooler surface (water cooled copper collector) of the reactor asthe vaporized carbon condenses
- This method has an yield of 70 % and mainly produces SWNTs with controllable diameterdepending on reaction temperature
- However, it is more expensive than arc discharge or CVD

Chemical Vapour Deposition



- A substrate is prepared with metal catalyst particles (Ni, Co, Fe or a combination). The diameter of CNTs will depend on size of metal particles. This can be achieved by patterned or masked deposition of metal, annealing or etching of a metal layer.
- The substrate is heated to approximately 700^0 C
- To initiate growth of CNTs, two gases are fed into the reactor.
- Process gas: ammonia, nitrogen and hydrogen
- Carbon containing gas: *CO, acetylene, Methane, ethanol* etc.
- Using thermal annealing or chemical etching results in cluster formation on the substrate.

- The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900^{o}Crange.
- The typical yield for this CVD method approximately 20-100%

Properties of CNTs:

- It is the strongest, stiffest in terms of tensile strength and elasticity property. This strengthresults from the covalent sp2 bonds formed between the individual carbon atoms.
- Thus CNTs are used as probe tips for high resolution scanning probe microscopy.
- High Electrical Conductivity
- Very High Tensile Strength
- Highly Flexible- can be bent considerably without damage
- Very Elastic ~18% elongation to failure
- High Thermal Conductivity
- Low Thermal Expansion Coefficient
- Good Field Emission of Electrons
- Highly Absorbent
- High Aspect Ratio (length = ~1000 x diameter)

Engineering Applications of Carbon Nanotubes:

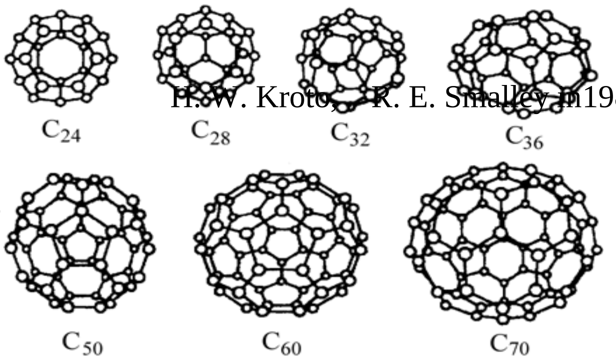
The small dimensions, strength and the remarkable physical properties of these structures makethem a very unique material with a whole range of applications

- They find application in conductive and high strength composites, energy storage and energyconversion devices, sensors and nano meter sized semiconductor devices.
- They are used as Nano probes in meteorology and biological and chemical investigations.
- Hydrogen can be stored in the carbon nanotubes, which is in turn used for the fuel cells.
- CNTs can replace platinum as the catalyst in fuel cells, which could reduce fuel cells overallcost.
- A catalyst having CNTs makes a reaction safer and selective.
- CNTs are used for the electrochemical reaction of oxygen
- Carbon nano tubes are being highly used in the fields of efficient drug delivery and biosensing methods for disease treatment and health monitoring.
- Carbon nanotubes can be used as multifunctional biological transporters and near-infraredagents for selective cancer cell destruction.

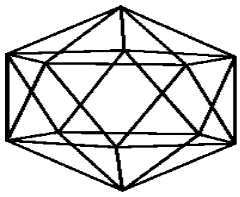
Introduction to Nano materials - Fullerenes

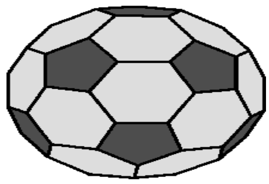
Fullerenes are CNTs are allotropic forms of carbon. The diamond and graphite structures of carbon are well known and main allotropes of carbon with tetrahedral and planar arrangement of carbon atoms respectively.

- **Fullerenes** (C_{60} and others) were discovered by R. F. Curl. H. W. Kroto, R. E. Smalley in 1985 and th



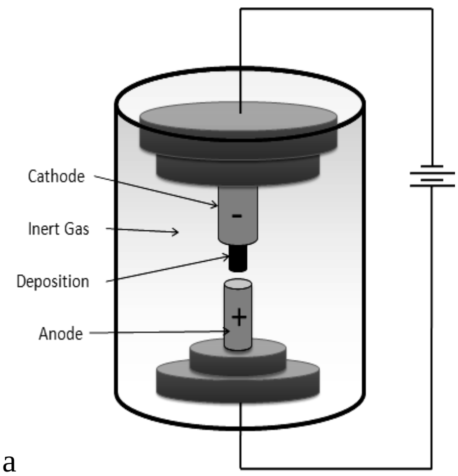
- They are closed structures of only carbon atoms, each bonded covalently by sp^2 hybridization(one double bond, two single bonds).
- The double bonds are usually given for hexagons only
- C_{60} is a polygon (truncated icosahedron) with 12 pentagons and 20 hexagons (like a soccerball). Diameter = 1 - 2 nm (Icasohedron)





Preparation of Fullerenes:

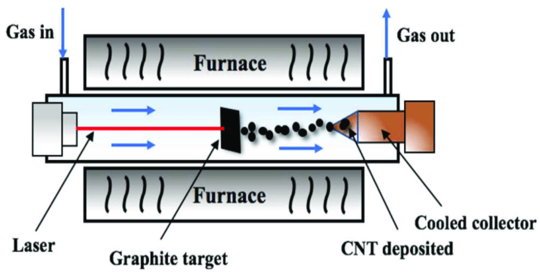
Arc discharge method (Krotschmer and Huffman method, 1990)



- Electrical discharge between graphite electrodes (mixed with metal catalyst like (Fe, Co, Ni etc.) in an atmosphere of Helium, argon at low pressure 50 -700 mbar produces carbon nano tubes along with other carbon mass.
- A direct current of 50-100 A and voltage of 20V creates high temperature arc between the electrodes.
- The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod.
- The resulting soot (on the graphite cathode, inner walls of evaporation chamber) is scraped and dissolved in polar organic solvents. The metal catalysts are separated by treating with mild acid/base and then dissolved in aromatic organic solvent (colored solution).

2. Laser ablation method

- In this method, a high energy pulsed laser vaporizes a graphite target in a high



temperaturereactor, while an inert gas like He or Ar is fed into the chamber (500 Torr).

- A pulsed or continues laser is used to vaporize a graphite target in an oven at 1200^{o}C
- The main difference between continues and pulsed laser, is that the pulsed laser demandsmuch higher intensity.
- A very hot vapor forms, then expands and cools rapidly.
- The Nano tubes develop on the cooler surface (water cooled copper collector) of the reactor asthe vaporized carbon condenses
- However, it is more expensive than arc discharge or CVD

Properties of Fullerenes

- Physical properties: C_{60} is a mustard colored solid. When the thickness of the film. increases,it appears brown to black.
- It is moderately soluble in the common organic solvents, especially aromatic hydrocarbons.
- Mechanical Properties: It has high tensile strength and also highest packing density of allknown structures.
- Thermal properties: Thermally stable upto 600 ^{o} C. it undergoes sublimation under.
- Electrical Properties: It has high electrical conductivity, when doped with alkali metals; theyshow even superconductivity (Eg. KC_{60}).
- They are difficult to oxidize.
- They are good acceptors of electrons (used in polymer solar cells) and electronic energy.

Engineering applications of fullerenes:

- Fullerenes can easily accept electrons; hence they may be used as charge carrier in batteries.
- Fullerenes can be used as organic photovoltaic.
- Alkali metal fullerenes are super conductors.
- It can also be used as a soft ferromagnetic.
- Its spherical structure makes it suitable for the use as lubricant.

Sol-gel Process for the Preparation of Nanomaterials

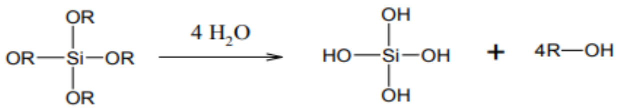
The sol–gel process is a wet-chemical technique used for the fabrication of both glassy and ceramic materials. In this process, the sol (or solution) evolves gradually towards the formationof a gel-like network containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid. The precursor used in sol-gel process for the synthesis of nanoporous materials are metal alkoxides M(OR). They readily react with water to form gels. Examples: Tetra methoxysilane $Si(OCH_3)_4$ Tetra ethoxy silane $Si(OC_2H_5)_4$,

Process (Synthesis of silica aerogel)

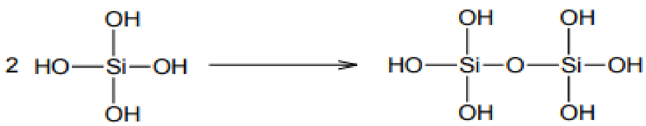
This process consists of four main steps.

1. Hydrolysis of precursors
2. Condensation
3. Poly condensation
4. Drying

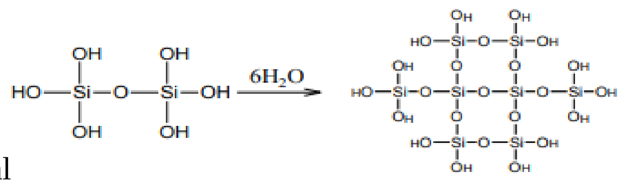
1. **Hydrolysis:** It occurs by the addition of water to any one of the precursor material to formMetal Hydroxide particles.



2. **Condensation:** The self-condensation of metal hydroxide groups produces M-O-M linkages filled with byproducts of water and alcohol.



3. **Poly condensation:** The condensation process continues to form poly condensed M-O-M linkages.

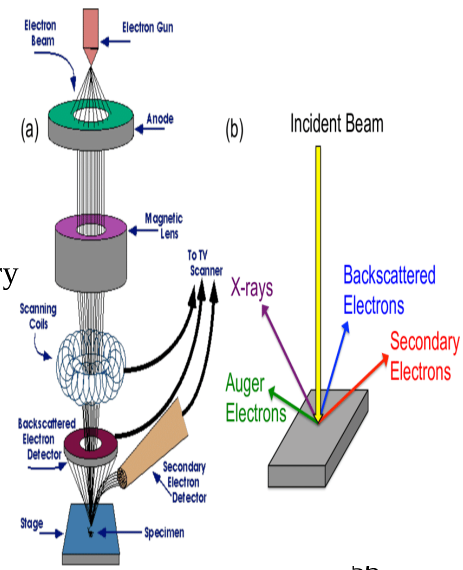


4. **Drying:** The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78 bar and 294°C respectively in order to remove liquid fromsilica gel to form the network structure of silica aerogel.

Scanning Electron Microscope (SEM) Construction and Working

Scanning electron microscope is an improved model of an electron microscope. SEM is used to study the three dimensional image of the specimen.

Principle: When the accelerated primary electrons strike the sample, it produces secondary electrons. These secondary electrons are collected by a positive charged electron detector which in turn gives a 3- dimensional image of the sample.



Construction: It consists of an electron gun to produce high energy electron beam. A magnetic condensing lens is used to condense the electron beam and a scanning coil is arranged in- between magnetic condensing lens and the sample. The electron detector is used to collect the secondary electrons and can be converted into electrical signal. These signals can be fed into CRO (Cathode Ray Oscilloscope) through video amplifier.

Working: Stream of electrons are produced by the electron gun and these primary electrons are accelerated by the grid and anode. These accelerated primary electrons are made to be incident on the sample through condensing lenses and scanning coil. These high speed primary electrons on falling over the sample produce low energy secondary electrons. The collection of secondary electrons is very difficult and hence a high voltage is applied to the collector. These collected electrons produce scintillations on to the photo multiplier tube are converted into electrical signals. These signals are amplified by the video amplifier and are fed to the CRO (Cathode Ray Oscilloscope). By similar procedure the electron beam scans from left to right and the whole picture of the sample is obtained in the CRO (Cathode Ray Oscilloscope) screen.