UNIT-5 NANO MATERIALS

a. NANO MATERIALS

Introduction - concept of nanomaterials - quantum confinement and surface volume ratio - catalytic property and mechanical properties.

Types of Nanomaterials: carbon nano tubes, quantum dots, nanowires, nano crystals.

Synthesis of nano materials: top down and bottom up approachesmechanical grinding by ball milling, sol gel method.

Carbon Nanotubes: single walled carbon nanotubes (SWCNTs). Multi walled carbon nanotubes (MWCNTs), synthesis of CNTs- arc discharge and laser ablation methods, applications.

LECTURE-1

Introduction

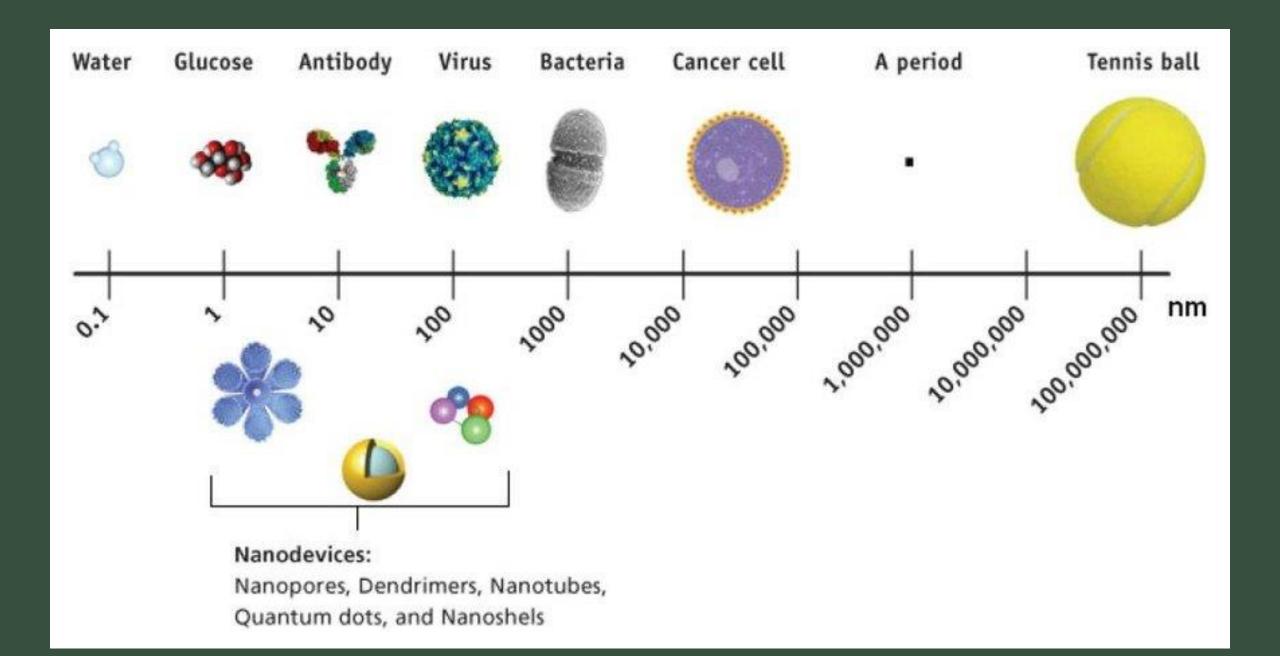
Concept Of Nanomaterials

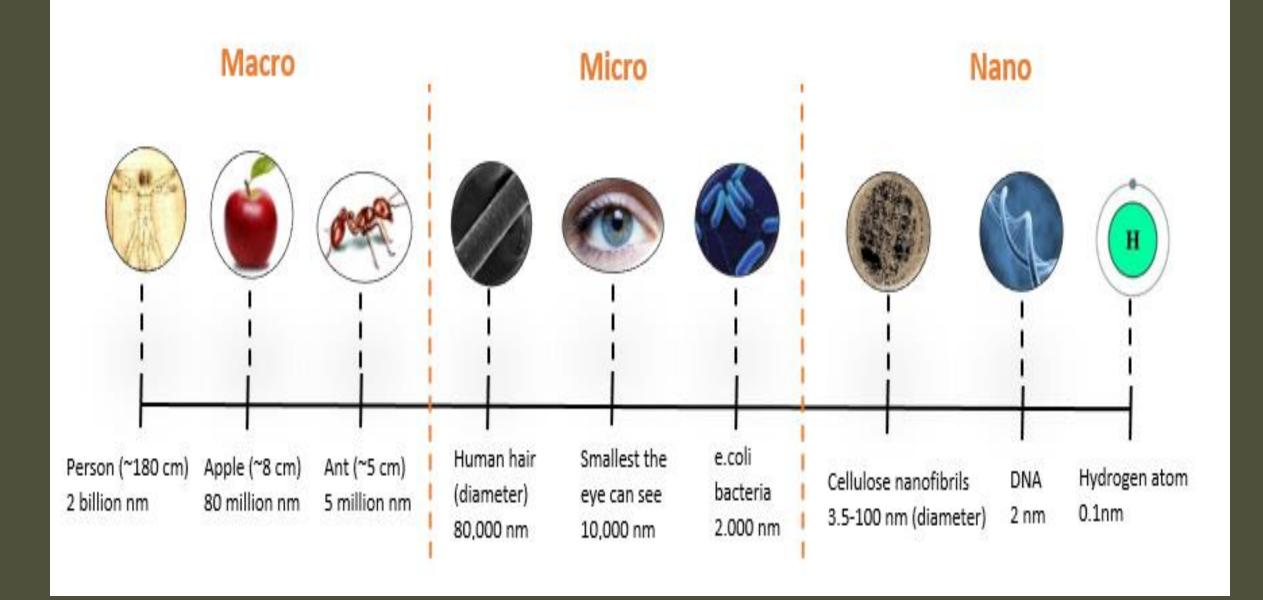
Surface - Volume Ratio

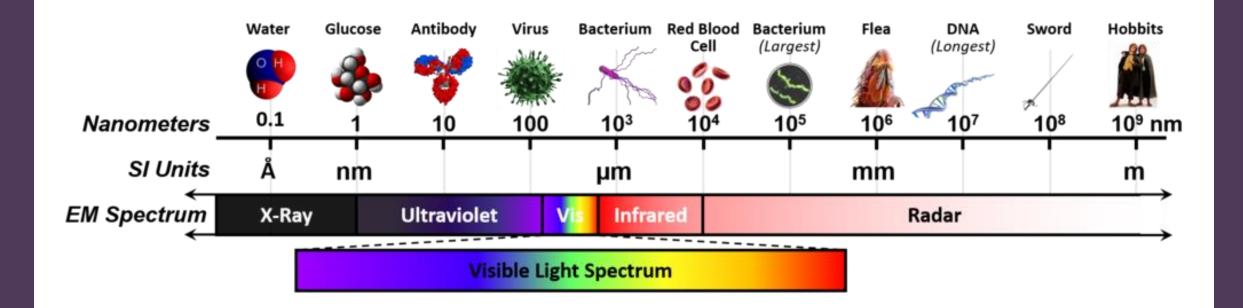
Quantum Confinement

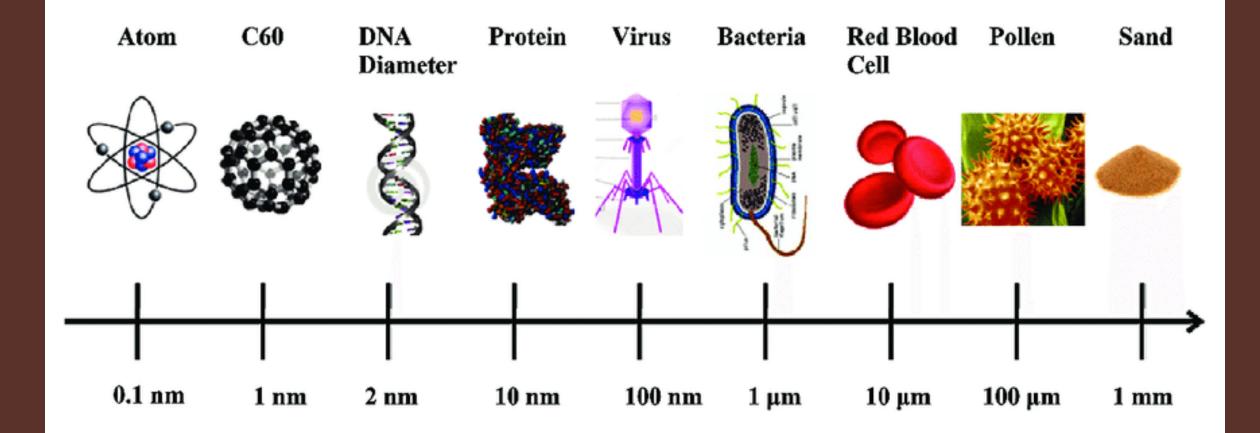
Catalytic Property

Mechanical Properties.









WHAT IS NANO MEANS?

https://youtu.be/zbFHYjaqjzw

Some interesting applications of nano materials

https://youtu.be/nRMiQRiK5GY

Generally properties of materials depend upon :

1. Chemical composition

2.Structure

Also on particle size of the material

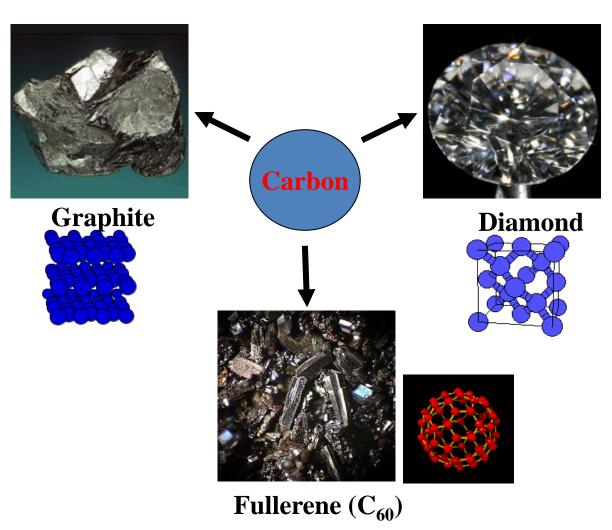
We required different materials to satisfy the needs of mankind

Properties of materials depend upon:

Chemical composition



Different Structures



WHAT IS NANO?

- The term 'nano' is a Greek word meaning 'dwarf'.
- Word 'nano' means 10⁻⁹ or one billionth part of a meter 1 nanometer= one billionth (10⁻⁹) of a meter.
- Nano scale size range between 1 to 100 nm.

NANOMATERIALS

Nanomaterials regarded as the materials which are in the **nanometer range** (**1-100 nm**) at least in **one dimension** and they can be considered to constitute a bridge between single molecules and infinite bulk systems.

The structure and properties of nanomaterials differ significantly from those of atoms and molecules as well as the bulk materials.

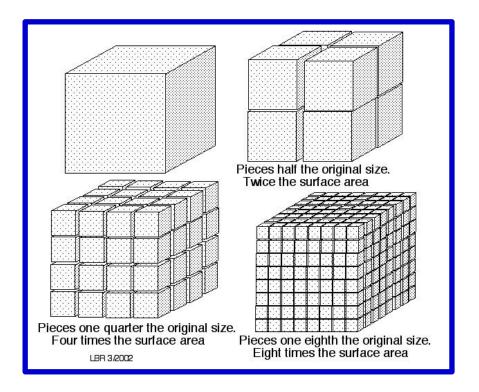
Properties of nanomaterials are significantly different from those of atoms as well as those

of bulk materials?

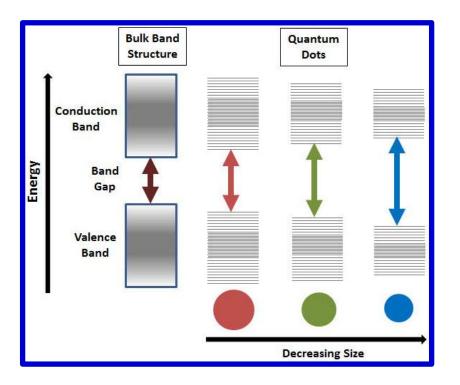
Why?

The main reasons are

1.Large Surface area-to-volume ratio



2.Quantum confinement



Properties of nanoparticles

The causes of these differences in their properties are:

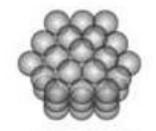
- The large increase in the surface area, which leads to large increase in the number of surface atoms.
- The quantum confinement of the electrons inside the nanoparticle (new quantum effect).

Properties of nanoparticles

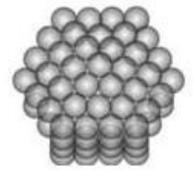
Variation of the surface area in nano clusters



13 atoms (12 atoms on Surface) 92%

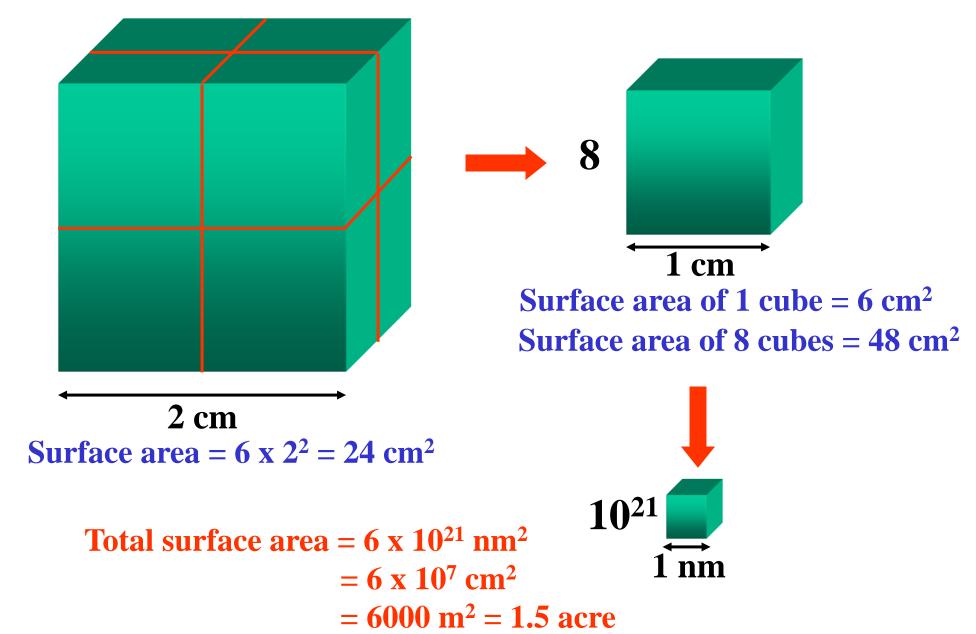


55 atoms (45 atoms on Surface) 76%



147 atoms (93 atoms on Surface) 63%

Large Surface area





Surface area of 10 g of nanoparticles is equivalent to that of a cricket stadium.

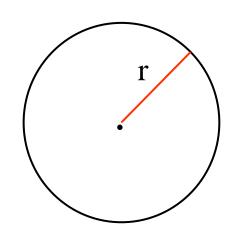
Surface Area to volume ratio

Let us assume a spherical particle, whose radius is r

Its surface area = $4\pi r^2$

Its Volume
$$=\frac{4}{3}\pi r^3$$

Surface Area to volume ratio = $3 r^{-1}$



Hence, as particle size (particle diameter, r) decreases, the surface area to volume ratio increases which indicates the fraction of atoms/molecules on the surface will increase. This leads to a drastic changes in properties of the nanomaterials as their size changes.

Quantum confinement

Another most direct effects of reducing the size of materials to the nanometer range is the appearance of quantization effects due to the confinement of the movement of electrons. This leads to discrete energy levels depending on the size of the structure as it is known from the simple potential well treated in introductory quantum mechanics.

For a confined particle of mass m, in 1-dimensional space of length L, its energy can be

represented as
$$E_n = \frac{n^2 h^2}{8mL^2}$$

Energy gap between two successive levels $\Delta E_{n-(n-1)} = \frac{n^2h^2}{8mL^2} - \frac{(n-1)^2h^2}{8mL^2}$

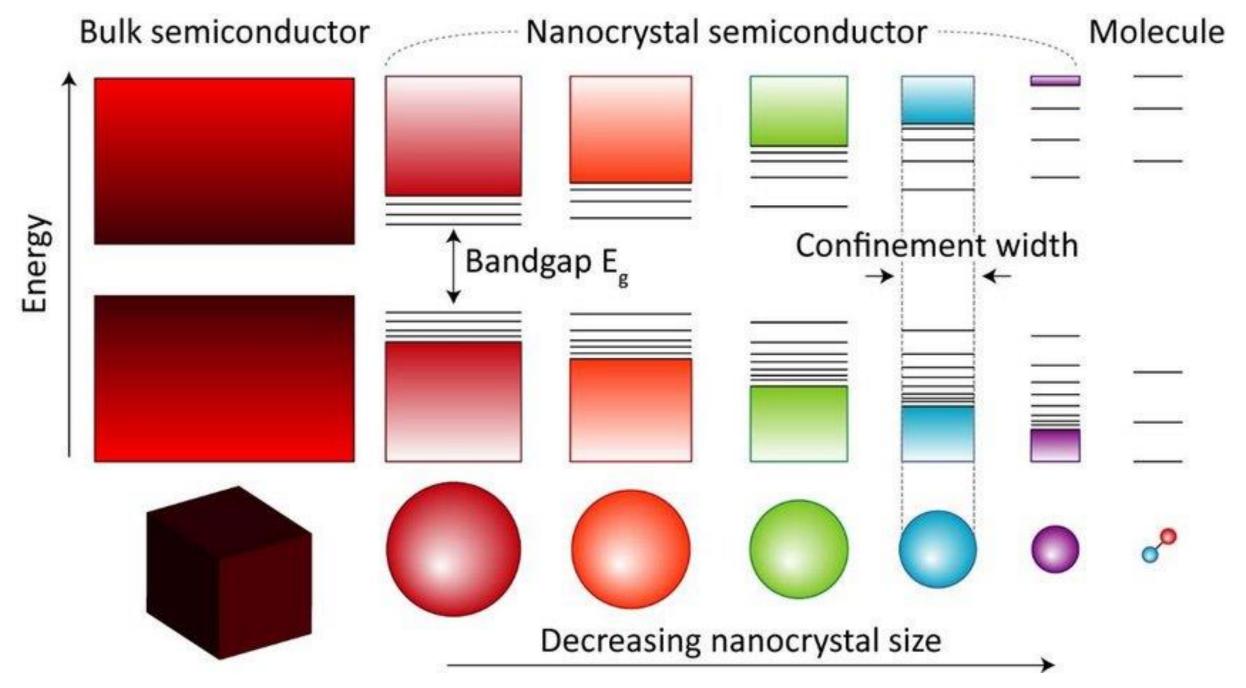
$$\Delta E_{n-(n-1)} = \frac{(2n+1) h^2}{8mL^2} \qquad h = planck's constant$$

$$\Delta E_{n-(n-1)} = \frac{(2n+1) h^2}{8mL^2} \qquad h = planck's constant$$

From this, as L increases the gap between energy levels will decrease and as L decreases the energy levels will be increased and at very low L all energy levels become discrete.

Here, the electrons are confined in the particle of size L, as particle size decreases the energy levels become more discrete.

In simple words, bulk materials have the continuous electronic energy levels such as bands but nanoparticles has non-continuous and discrete (finite density of states) electronic energy levels because of the confinement of the electrons to the physical dimensions of the particles. This phenomenon is called as Quantum confinement.



Ref: Quinten A Akkerman et al. DOI: 10.13140/RG.2.2.23651.81442,

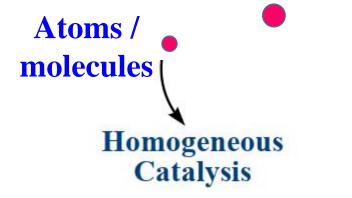


This 'micro-carnation' is actually a catalyst vanadium containing phosphorus and (V(OH)PO₄.½H₂O). It is a selective catalyst used in a natural gas purifying process (changing normal butane into maleic acid anhydride). The petal structure of the flower surface increases and area improves performance of the catalyst.

Catalytic properties

Increased surface area means more efficient chemical reactions when used as a catalyst

- ➤ Noble metals such as gold, silver are inert in their bulk form.
- ➤ But, nanoparticles of them are good catalysts for many reactions.
- Nanoparticle catalysts can combine the advantages of homogeneous and heterogeneous catalytic processes, as they are highly efficient and reusable.
- nano particles are widely used as catalysts in many reactions like oxidation, reduction, C-H activation, oxidative esterification, asymmetric synthesis etc.



Merits:

- 1. High activity
- 2. High chemo-and regioselectivity

Demerits:

Cumbersom product purification and difficulty in catalyst recovery

1-10 nm Nanomaterials

Nano-Catalysis

High activity

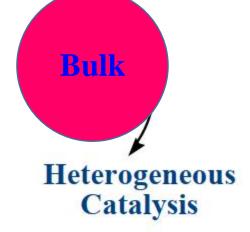
High selectivity

Excellent stability

Easily separable

Energy efficient

Atom economy



Merits:

- 1. Excellent stability
- 2. Easy accessibility
- 3. Easily seperable

Demerits:

Inferior catalytic activity relative to their counterpart homogeneous and requires more reaction time. High surface area

Efficient Recovery

Nanocatalysts

Low preparation cost

Excellent activity

Mechanical properties

The nano-materials have less defects compared to bulk materials, which increases the mechanical strength.

- (i) Mechanical properties of polymeric materials can be increased by the addition of nano-fillers.
- (ii) As nano-materials are stronger, harder and more wear resistant and corrosion resistant, they are used in spark plugs.

EXAMPLES

Nano-crystalline carbides are much stronger, harder and wear resistant and are used in micro drills.

Mechanical properties

- > Nanomaterials and their composite materials exhibit high mechanical strength. Carbon nanotubes and related structures are well known for their strength.
- > The inclusion of nanomaterials in composites is normally meant to improve the impact resistance and Young's modulus.
- > Improvement is expected in properties such as tensile strength, Young's modulus, bending strength, fracture properties, and impact resistance.
- > The fatigue strength increases with a reduction in the grain size of the material.
- ➤ Nanomaterials provide such a significant reduction in the grain size over conventional materials that the fatigue life is increased by an average of 200-300%.

LECTURE-2

Types of Nanomaterials: carbon nano tubes, quantum dots, nanowires, nano crystals.

Synthesis of nano materials: top down and bottom up approaches- mechanical grinding by ball milling, sol gel method.

Types of nanomaterials

Different nanoparticles according to the spatial dimensions:

☐ Zero dimensional (0-D): These nanomaterials have Nano-dimensions in all the three directions. Diameter of particles: 1-50 nm. Most of these are spherical. Examples: clusters.

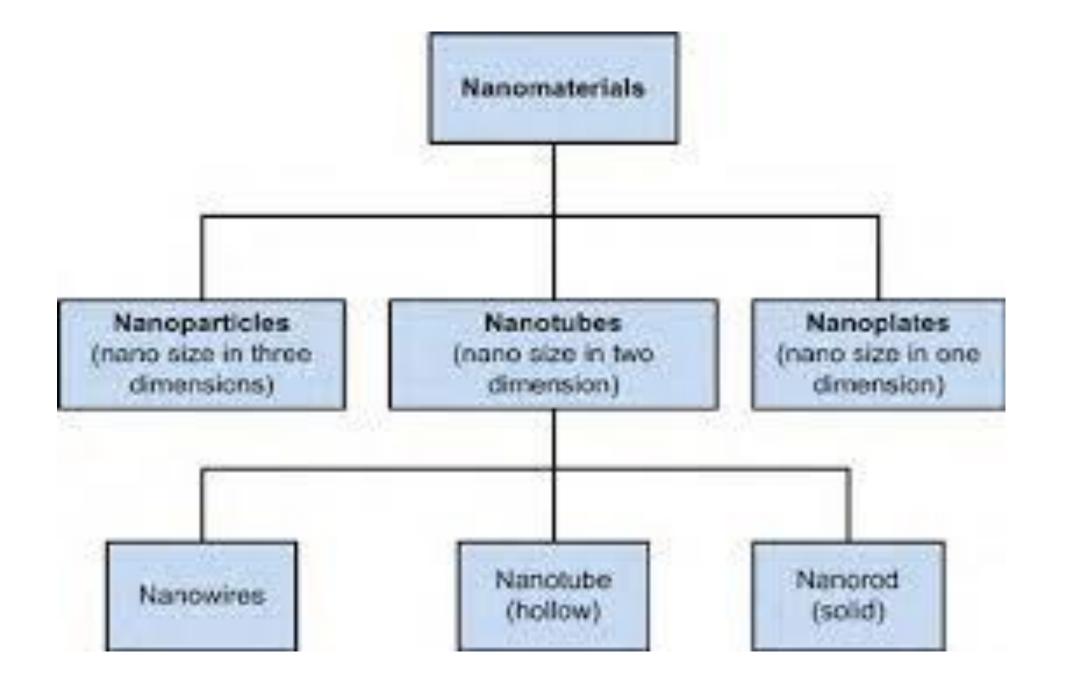
☐ One dimensional (1-D): one dimension of the nanostructure will be outside the nanometer range. Examples: nanowires, nanotubes, fibers and rods).

Classification of nanoparticles

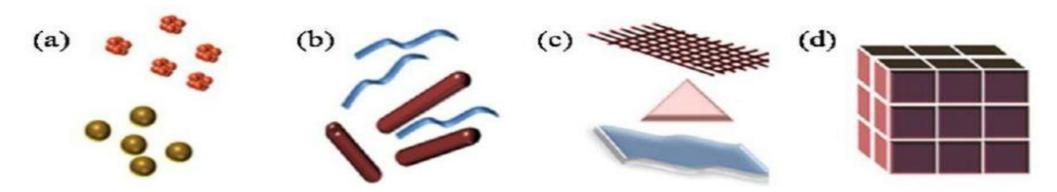
Different nanoparticles according to the spatial dimensions:

☐ Two dimensional (2-D): In this type of nanomaterials, two dimensions are outside the nanometer range. Examples: nano films, nano sheets.

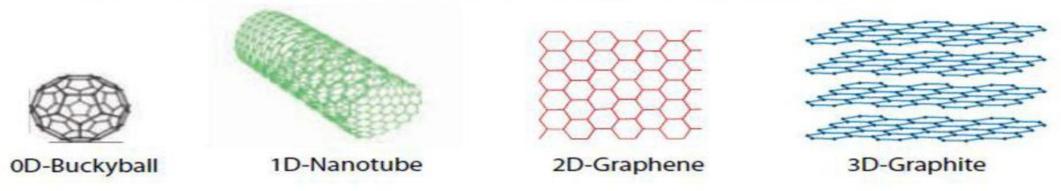
☐ Three Dimensional(3-D): All dimensions of these are outside the nano meter range. Examples: nanocrystals, nano-elctrodes etc...



Classification of nanomaterials

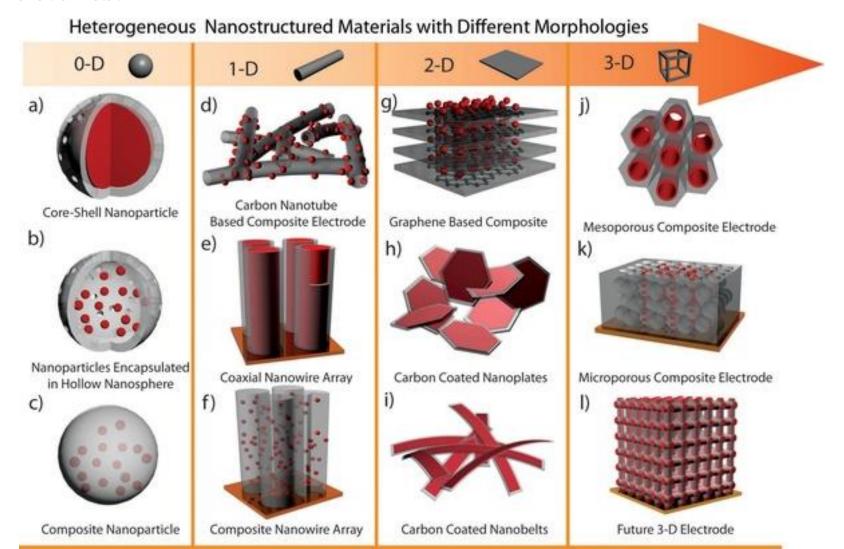


 Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.



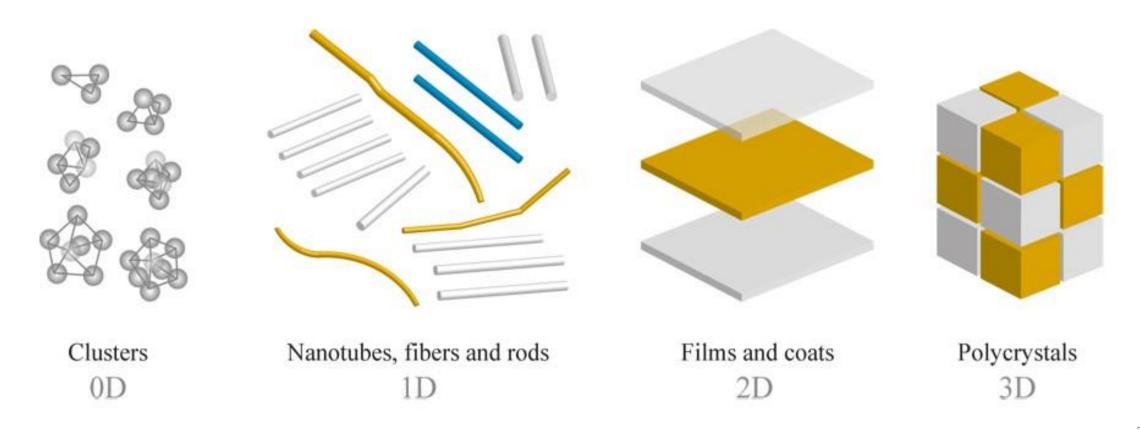
CLASSIFICATION OF QUANTUM CONFINED STRUCTURES

Based on confinement of electrons, nanoparticles are classified as zero dimensional, 1-D, 2-D and 3-D nanostructures.



Classification of nanoparticles

Different nanoparticles according to the spatial dimensions:



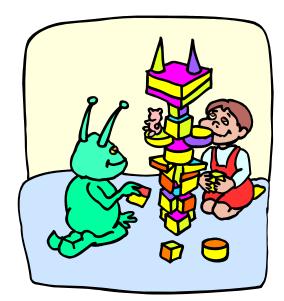
Manufacturing Methods:

Two General Approaches to Nanoparticle Synthesis

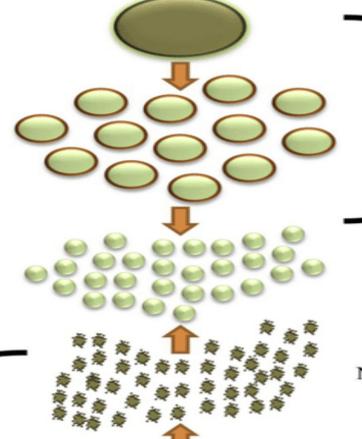
- \triangleright Top \Rightarrow Down:
 - Start with the bulk material and "cut away material" to make the what you want



- \triangleright Bottom \Rightarrow Up:
 - Building what you want by assembling it from building blocks (such as atoms and molecules).
 - Atom-by-atom, molecule-bymolecule, or cluster-by-cluster



Bulk Material



Top Down Approach

- Mechanical Milling
- Etching
- Laser Ablation
- Sputtering
- Electro-explosion

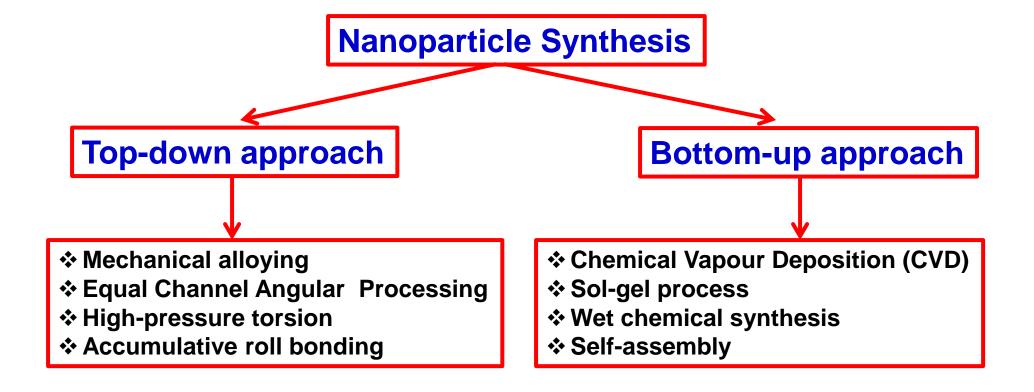
Nanoparticles

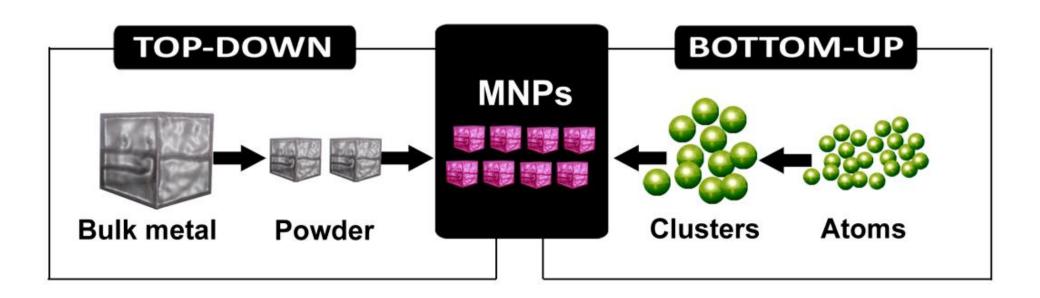
Bottom Up Approach

- ❖Supercritical Fluid Synthesis
- Spinning
- Sol-gel Process
- Laser Pyrolysis
- Chemical Vapour Deposition
- Molecular Condensation
- Chemical Reduction
- Green Synthesis

Nuclei and its growth

Molecular/Atomic Level

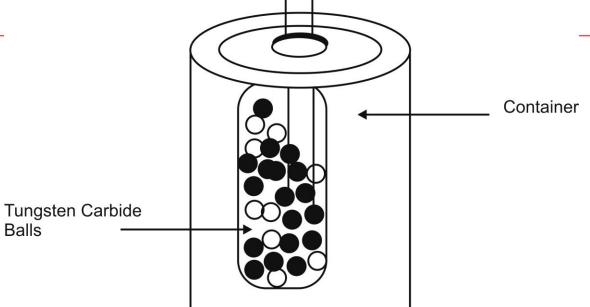




Ball Milling

Principle: Small hard balls allowed to rotate inside a container and then it is made to fall on a solid with high force to crush the solid into nano materials.

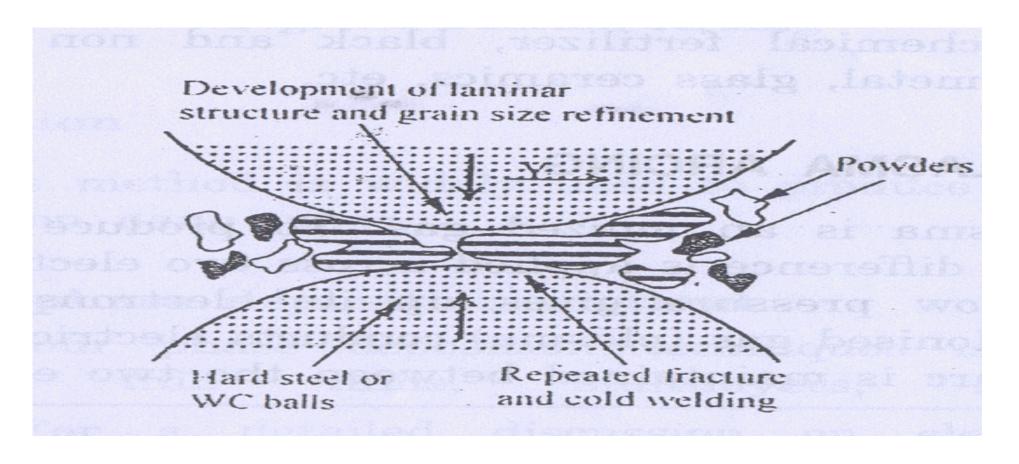
Construction and Working: Hardened steel or tungsten carbide balls are put in a container along with powder of particles ($50\mu m$) of a desired material. The container is closed with tight lids.



Ball Milling

When the container is rotating around the central axis, the material is forced to press against the walls. The milling balls impart energy on collision and produce smaller grain size of nano particle.

Ball milling is also known as Mechanical alloying or crushing



Advantages of Ball Milling

- •Few mg to several kgs of nanoparticle can be synthesized in a short time.
- •This technique can be operated at large scale.

Applications

- Ball milling method is useful in preparation of elemental and metal oxide nano crystals like Co, Cr, Al-Fe, Ag-Fe and Fe.
- · Variety of intermetallic compounds of Ni and Al can be formed.
- Ball milling method is useful in producing new type building materials, fire proof materials, glass ceramics, etc.
- Ball milling animation https://youtu.be/L6sgGXXYdEU.

Sol-gel Method:

This method involves two types of materials 'Sol' and 'Gel'

Principle:

- o Sol-Gel method involves formation of 'sols' in a liquid and then connecting the sol particles to form a network.
- o By drying the liquid, it is possible to obtain powders, thin films etc.,

Methods for sol-gel formation: Sol can be obtained by,

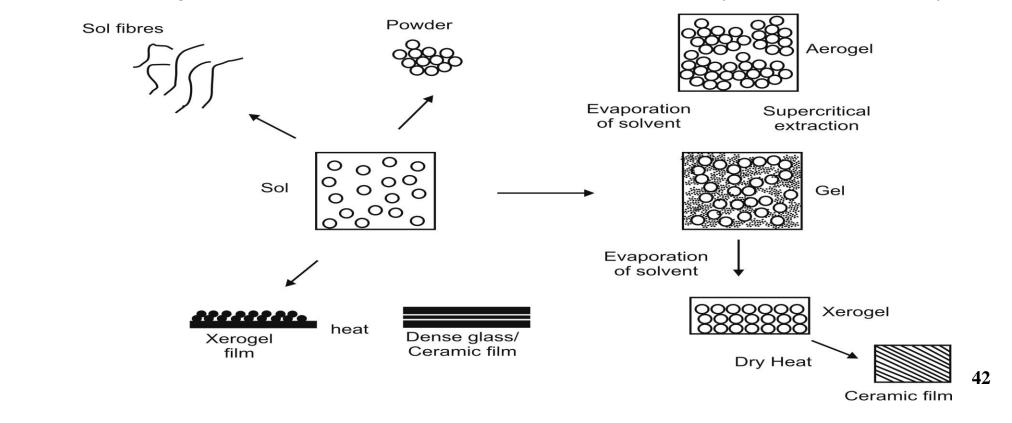
- •Hydrolysis
- •Condensation and Polymerization of monomers to form particles
- •Agglomeration of particles
 After the formation of sol, formation of network (gelation) which extends throughout the
 liquid medium is obtained to form a gel.

https://youtu.be/3uMWO9EPU8c



Sol-gel Method

- > Synthesis of sol-gel involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes (shown in the Figure).
- > Precursors (starting chemicals) are to be chosen such that they have a tendency to form gels.



Sol-gel Method

Rate of hydrolysis and condensation reactions are governed by various factors such as

- ✓ pH
- ✓ Temperature
- ✓ Molar ratio
- ✓ Nature
- ✓ Concentration of catalyst
- ✓ Process of drying

Finally, at proper conditions spherical nanoparticles are produced.

Applications:

Mostly useful in synthesis of metal oxide nanoparticles

LECTURE-3

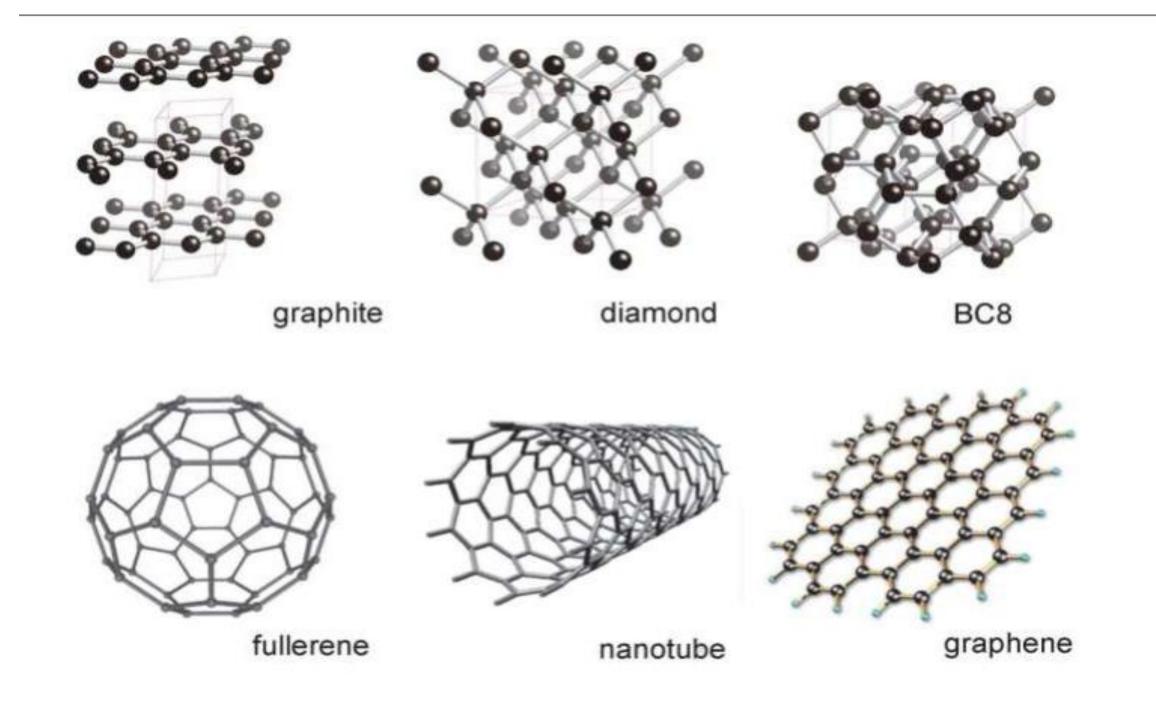
CARBON NANOTUBES:

single walled carbon nanotubes (SWCNTs).

Multi walled carbon nanotubes (MWCNTs),

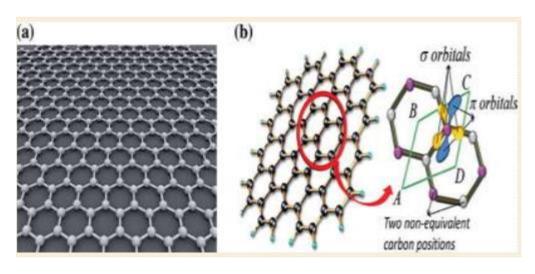
synthesis of CNTs- arc discharge and laser

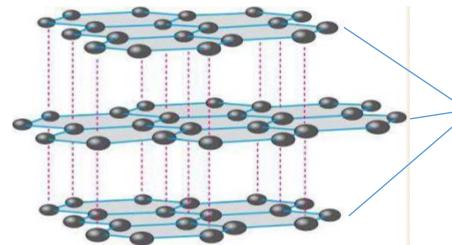
ablation methods, applications.



GRAPHENE

- > Graphene is basically a 2D single layer of graphite.
- > Graphene is stronger and stiffer than diamond. It, however, can be stretched like rubber.
- The C–C bond(sp2) length in graphene is ~0.142 nm. The graphene sheets stack to form graphite with an inter planar spacing of 0.335 nm,





Layer of graphite

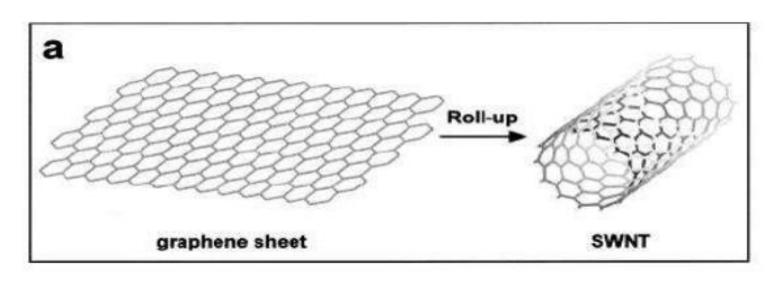
If single layer atom
thickness is
prepared, then it is
called as graphene

CARBON NANOTUBE

- > The discovery of carbon nanotubes (CNTs) in 1991, Iijima (japan) opened up a new area in materials science.
- ➤ A carbon nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale, with length-to-diameter ratio of up to 132,000,000:1.
- > Allotropes of carbon with a cylindrical structure.
- > Can be capped on the ends with bucky balls or open ended
- > Composed entirely of sp² bonds
- > Geometrically,

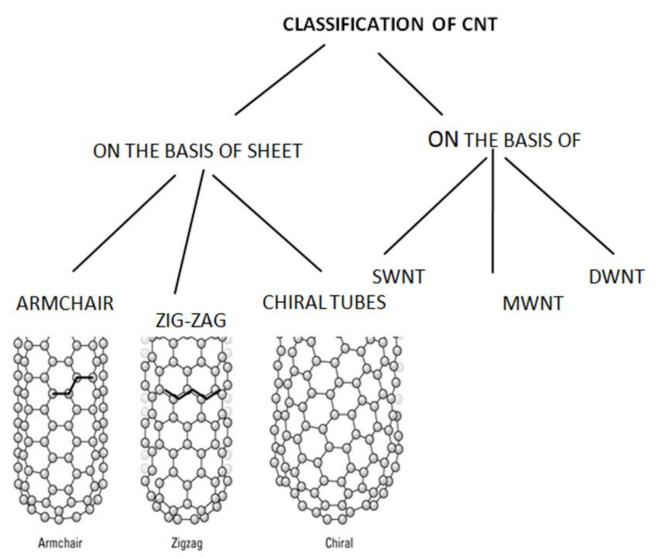
Roll-up Graphene







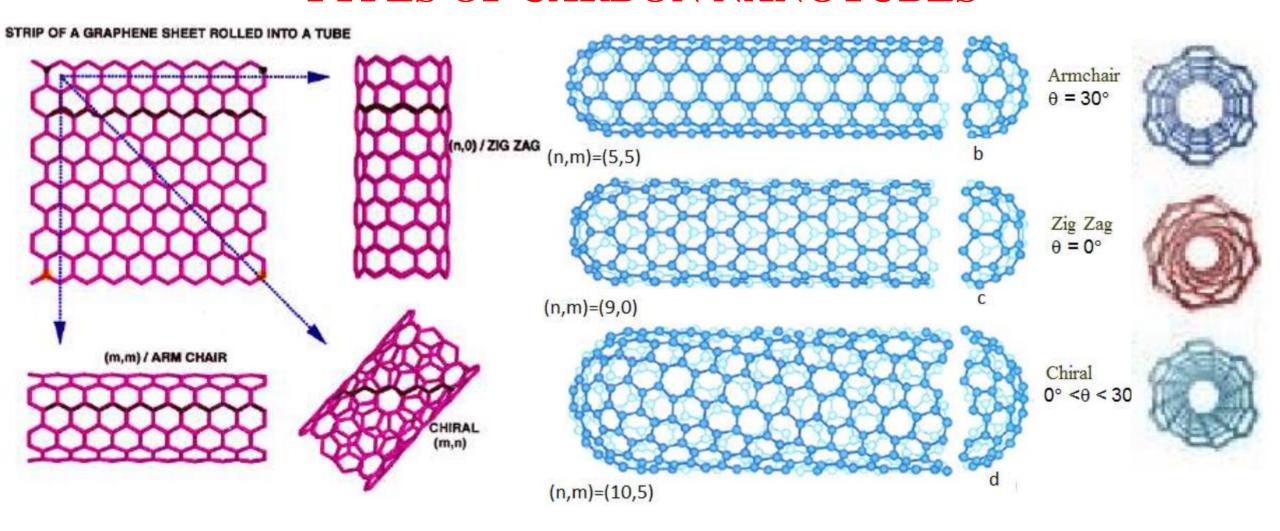
Classification of carbon nanotubes



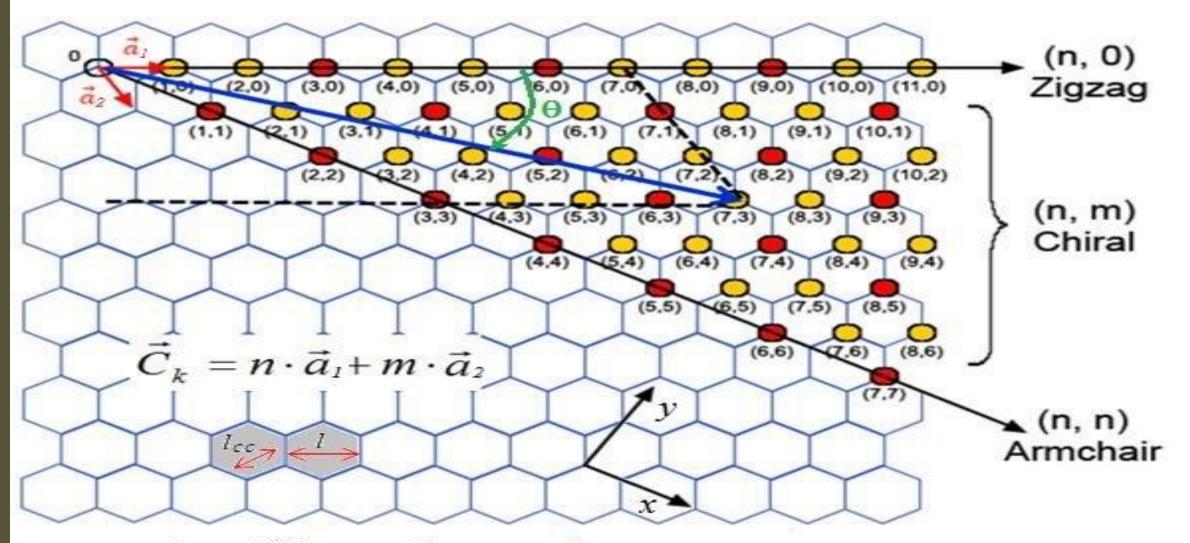
Ekta Singh et al. Carbon Nanotube: A Review on Introduction, Fabrication Techniques and Optical Applications. Nanoscience and Nanotechnology Research, 2017, Vol. 4, No. 4, 120-126. doi:10.12691/nnr-4-4-1,

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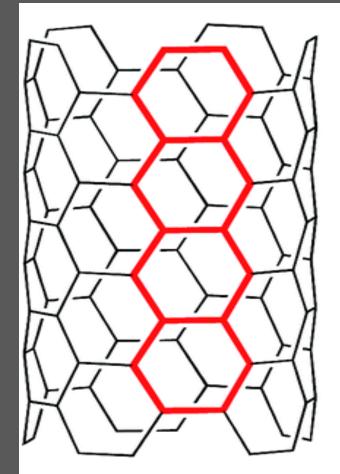
TYPES OF CARBON NANOTUBES



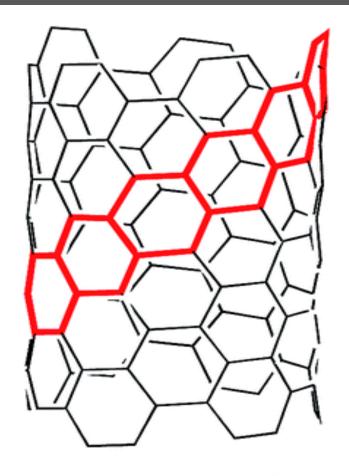
Their electrical characteristics differ depending on these variations, and variations in diameter acting either as metals or as semiconductors.



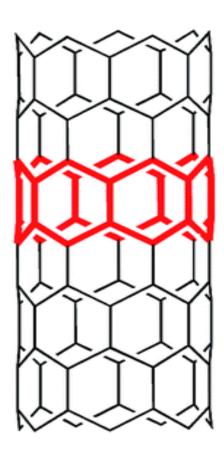
- represents metallic properties: n-m = 3p
- o represents semiconductor properties



[5,5] CNT Armchair Metallic



[7,5] CNT Chiral Semiconducting

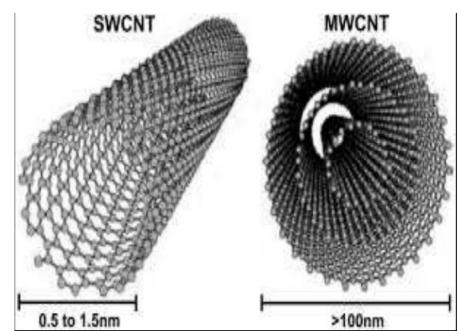


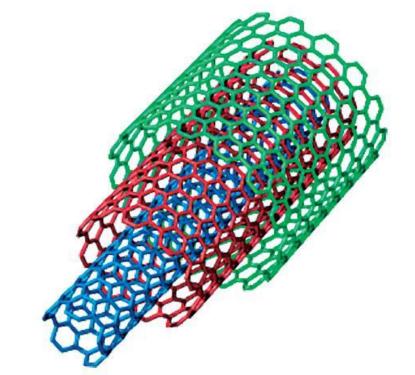
[7,0] CNT
Zigzag
Semiconducting

CARTEGORIES:

Carbon Nanotubes can be categorized by their structures:

- ➤ A Single-walled Nanotube (SWNT) may be thought of as a single atomic layer thick sheet of graphene rolled into a seamless cylinder.
- ➤ Most single-walled nanotubes (SWNT) have a diameter of close to 3 nanometer, with a tube length that can be many 10⁴ times longer.
- > Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene.
- ➤ MWCNTs can have OD ~ 20nm, ID ~ 3nm length can be 10⁴ times longer.





There are two structural models of multi-walled nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube).

In the Parchment model, a single graphene sheet is rolled around itself multiple times, resembling a rolled up scroll of paper.

Multi-walled carbon nanotubes have similar properties to single walled nanotubes, yet the outer walls on multi-walled nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials. Multi-walled nanotubes also have a higher tensile strength than single-walled nanotubes

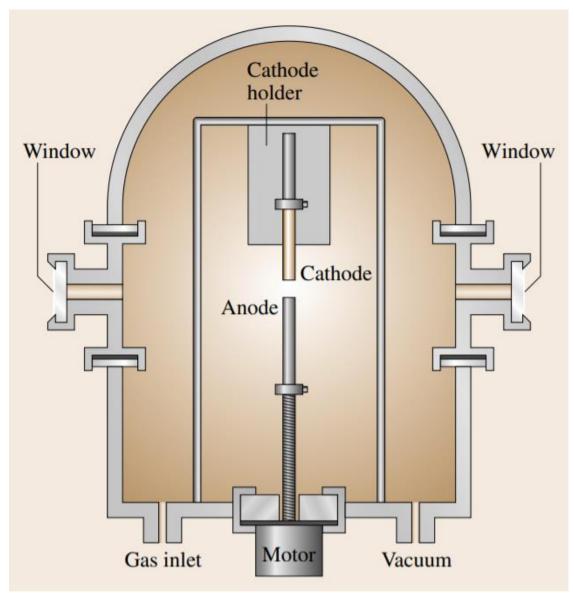
Synthesis of Carbon Nanotubes

Techniques have been developed to produce nanotubes, including **arc discharge**, **laser ablation**Most of these processes take place in vacuum or with process gases. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

- SWNTs and MWNTs are usually made by carbon-arc discharge, laser ablation of carbon,.
- Nanotube diameters range from 0.4 to 3 nm for SWNTs and from 1.4 to at least 100 nm for

MWNTs. Nanotube properties can thus be tuned by changing the diameter.

Arc discharge method for CNT preparation



WORKING PRINCIPLE

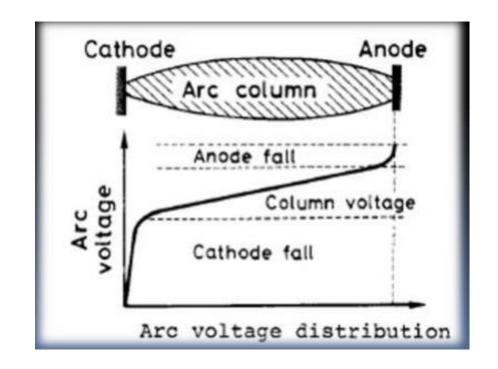
It is based on the vaporisation and cooling of electrode material which is done by thermionic emission of electrons from the electrodes supporting the arc.

Thermionic emission is the heat-induced flow of charge carriers from a surface. This occurs because the thermal energy given to the carrier overcomes work function of the electrode material.

ARC PROPERTIES

The arc consists of three major parts as:

- 1. The arc column,
- 2. The cathode region and
- 3. The anode region.

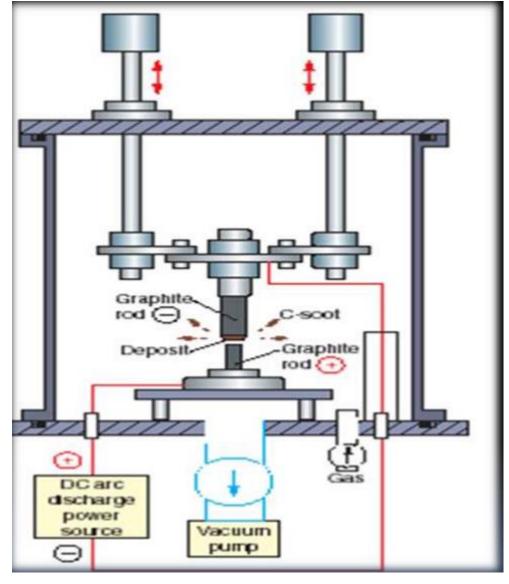


The arc column has the charge equilibrium, the low electric field and high temperature, so that it plays fundamental role in heating the gas.

While the cathode and anode regions, where the transition between metallic and gaseous condition occurs, have positive and negative space charges with high electric field respectively, and also have high temperature gradient.

https://youtu.be/7WGZq1EY6no

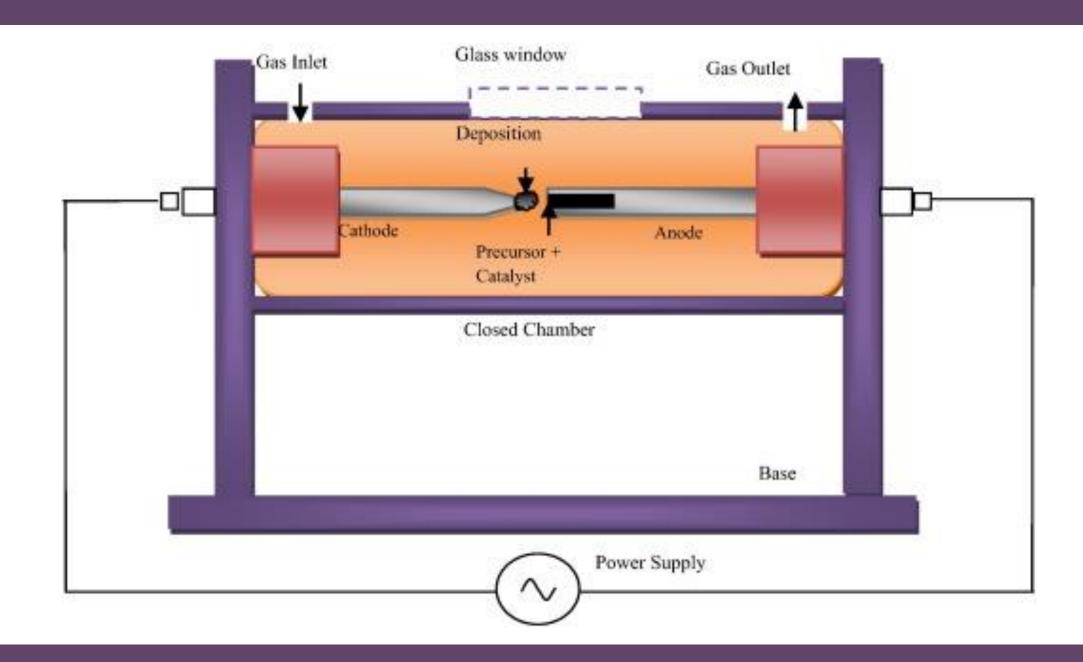
- The principle of this technique is to vaporize carbon in the presence of catalysts (iron, nickel, cobalt, yttrium, boron, gadolinium, and so forth) under reduced atmosphere of inert gas (argon or helium).
- After the triggering of the arc between two electrodes, a plasma is formed consisting of the mixture of carbon vapor, the rare gas (helium or argon), and the vapors of catalysts.
- > The vaporization is the consequence of the energy transfer from the arc to the anode made of graphite doped with catalyst.
- The anode erosion rate is more or less important depending on the power of the arc and also on the other experimental conditions.

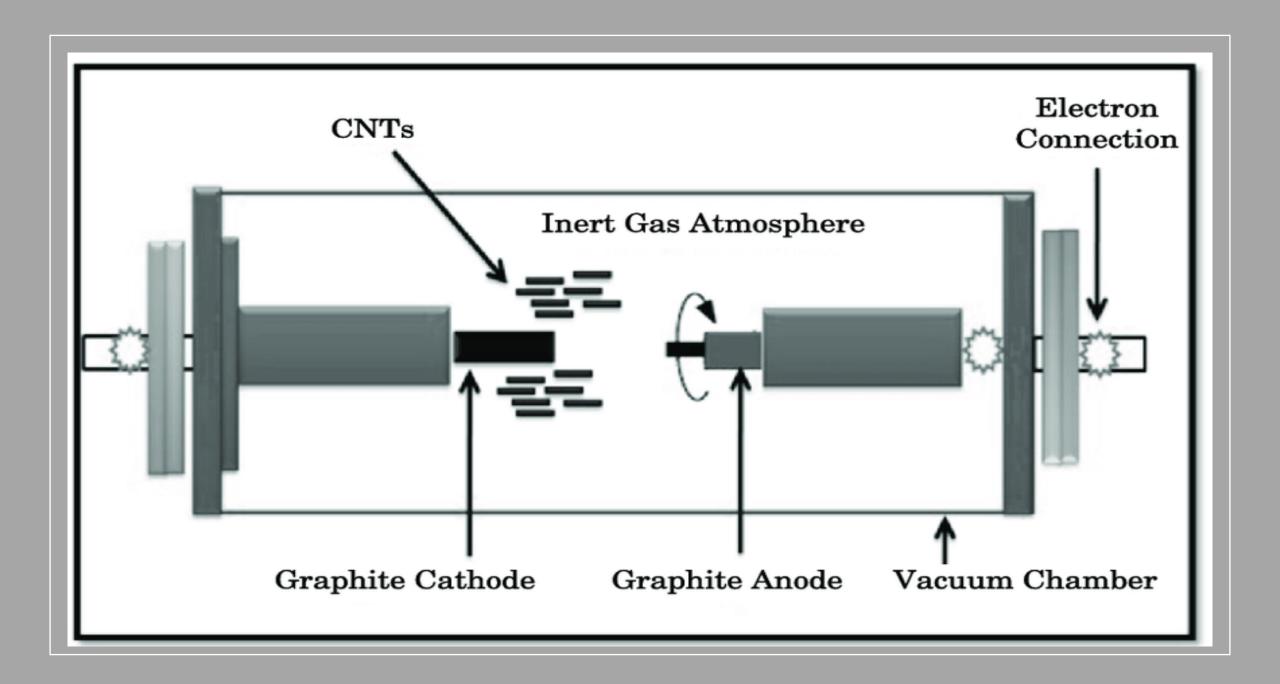


SCHEMATIC DIAGRAM OF

ARC-DISCHARGE APPARATUS

- This apparatus must be connected both to a vacuum line with a diffusion pump, and to a helium supply.
- The electrodes are two graphite rods, usually of high purity.
- ➤ Typically, the anode is a long rod approximately 6 mm in diameter and the cathode a much shorter rod 9 mm in diameter.
- Efficient cooling of the cathode has been shown to be essential in producing good quality nanotubes.
- ➤ In the arc discharge method, a DC bias of 20–30 V is applied between two carbon electrodes in a helium atmosphere.
- Carbon atoms are ejected from the anode, and accumulate in the form of nanotubes on the cathode.
- Arc discharges tend to produce narrower and shorter tubes than those obtained from laser ablation.





EXPERIMENTAL CONDITIONS MAINTAINED IN THE ARC DISCHARGES FOR SWNTs

- \triangleright The potential drop between electrodes is V = 20 V.
- \triangleright The current density is j =150 A/cm.
- \triangleright The inter electrode distance during the stationary period of discharge d \leq 1 mm.
- \triangleright The average temperature of an inter electrode plasma is T ~ 4 x 10³ K.
- The deposit rate on the cathode surface is 1 mm/min= 16 μ m/s. Assuming the average material density of the deposit to be 1.5 g/cm, and a deposit area of 0.5 cm, this corresponds to 6.25 x 10¹⁹ carbons/s (the flux density of carbons is 1.3 x 10²⁰ cm⁻²s⁻¹).
- The pressure of the helium fill in the discharge chamber is P = 500 Torr. Thus the number density of helium is $n_{He} = 6.4 \times 10^{18}$ cm (Tpl/300 K), where T_{pl} is the plasma temperature in K.
- The electrodes are carbon rods with flat surfaces approximately parallel to each other (the cathode surface is larger than that of the anode).

If SWNTs are preferable, the anode has to be doped with metal catalyst, such as Fe, Co, Ni, Y or Mo.

□ A lot of elements and mixtures of elements have been tested by various experiments and it is noted that the results vary a lot, even though they use the same elements.

☐ The quantity and quality of the nanotubes obtained depend on various parameters such as the

metal concentration, inert gas pressure, kind of gas, the current and system geometry.

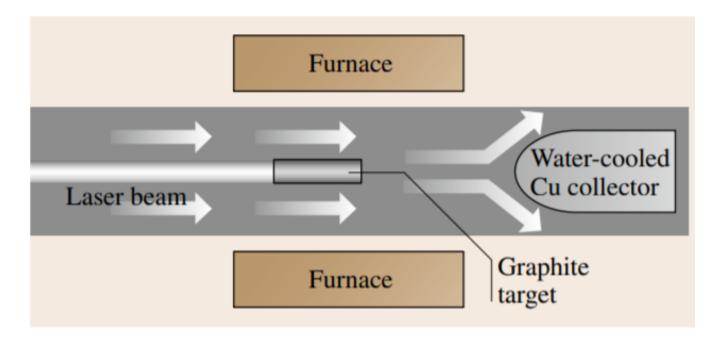
APPLICATIONS OF ARC DISCHARGE METHOD

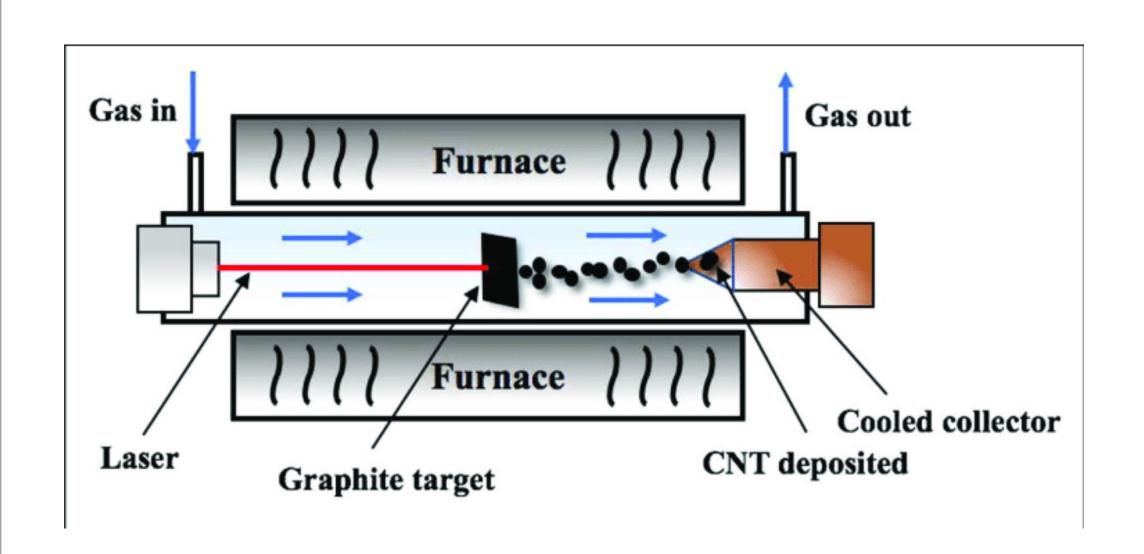
- > Synthesis of metal nanoparticles, nano metal oxides, carbon-coated metal particles (core shell) can also be prepared.
- > Synthesis of nanowires (e.g. Ag nanowires.)
- > Production of carbon nanotubes.
- ➤ Simple method of preparing graphene flakes., Filling of carbon nanotubes with metal is done by arc discharge method.

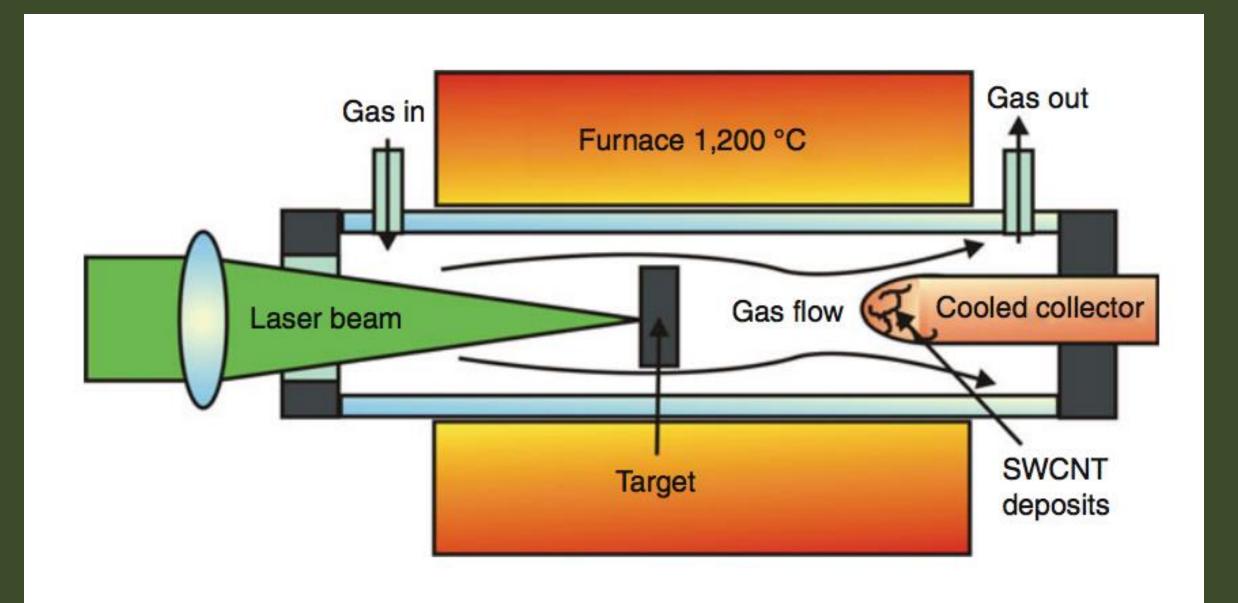
LASER ABLATION METHOD

In laser ablation, a laser vaporizes the graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes. For animation click the link https://youtu.be/iEaYt3rGkXY

In 1996, Smalley *et al.* successfully developed this laser ablation method for the "mass production" of SWNTs. Other improvements were made by Thess *et al.* and Rao *et al.* using double beam laser.







- An efficient route for the synthesis of bundles of SWNTs with a narrow distribution is the laser evaporation technique. In this method, a piece of graphite target rod with 1:1 catalyst mixture of Co and Ni is vaporized by laser irradiation under high temperature in an inert atmosphere (Argon).
- > MWNTs were produced when a pure graphite target was used.
- ➤ The quality and yield of these products have been found to depend on the reaction temperature. The best quality is obtained at 1200°C reaction temperature. At lower temperature, the structure quality decreases and the CNTs start presenting many defects.
- The yield of SWNTs strongly depends on the type of metal catalyst used and is seen to increase with furnace temperature, among other factors
- The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter.
- > Nanotubes produced by laser ablation have higher purity (up to about 90% pure)

CARBON NANOTUBES

Advantages:

- Extremely small and lightweight, making them excellent replacements for metallic wires
- Resources required to produce them are plentiful, and many can be made with only a small amount of material
- Are resistant to temperature changes, meaning they function almost just as well in extreme cold as they do in extreme heat

Disadvantages

- Despite all the research, scientists still don't understand exactly how they work
- Extremely small, so are difficult to work with.
- Currently, the process is relatively expensive to produce the nanotubes
- Would be expensive to implement this new technology in and replace the older technology in all the places that we could
- At the rate our technology has been becoming obsolete, it may be a gamble to bet on this technology

Strength Properties

- Carbon nanotubes have the strongest tensile strength of any material known.
- It also has the highest modulus of elasticity.



Material	Young's Modulus (TPa)	Tensile Strength (GPa)	Elongation at Break (%)
SWNT	~1 (from 1 to 5)	13-53 ^E	16
Armchair SWNT	0.94 ^T	126.2 ^T	23.1
Zigzag SWNT	0.94 ^T	94.5 ^T	15.6-17.5
Chiral SWNT	0.92		
MWNT	$0.8-0.9^{E}$	150	
Stainless Steel	~ 0.2	~ 0.65−1	15-50
Kevlar	~ 0.15	~ 3.5	~ 2
Kevlar [⊤]	0.25	29.6	

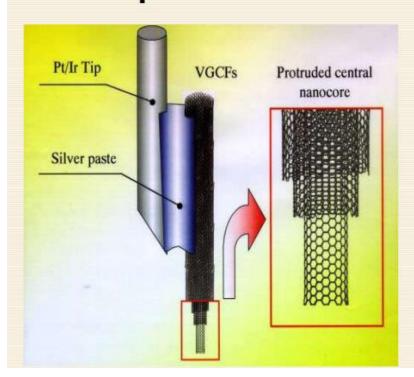
APPLICATIONS:-

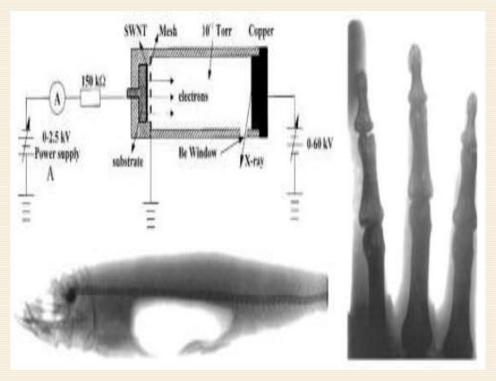
- Conductive plastics
- Structural composite materials
- Flat-panel displays
- Gas storage
- Antifouling paint
- Micro- and nanoelectronics
- Radar-absorbing coating

- Technical textiles
- Ultra-capacitors
- Atomic Force Microscope (AFM) tips
- Batteries with improved lifetime
- Biosensors for harmful gases
- Extra strong fibers

Electronic Applications of Carbon Nanotubes

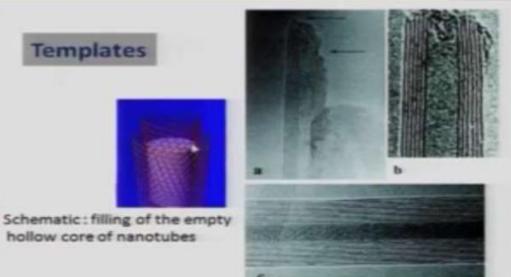
- Conductive
 Composites
- Electron
 Emitters
- Nanoprobes





>Sensors

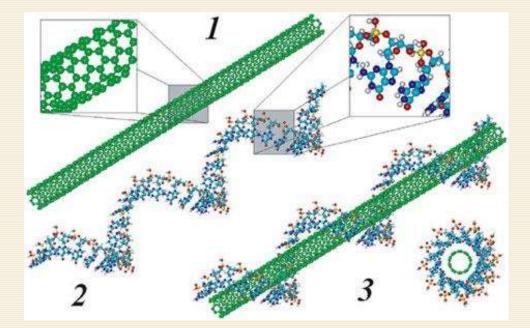
- Biomedical Industry
- Automotive Industry
- Food Industry
- Environmental Monitoring
- >FED Display
- >Template





CNT in Medical

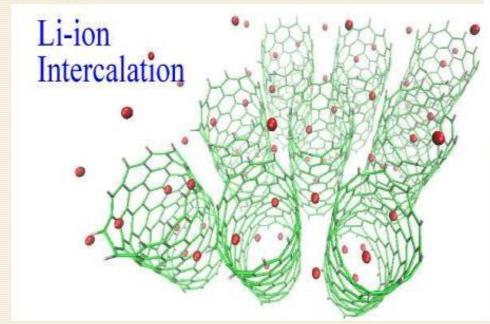
- □CNTs in Drug Delivery and Cancer Therapy
- □ CNTs as Biosensors
- CNT Network Bio-Stress Sensors
- Glucose detection biosensors
- DNA detection biosensors

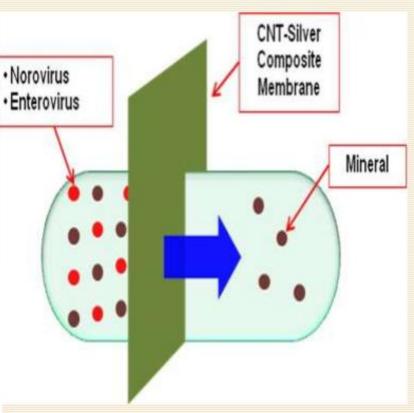


Other applications of CNTs

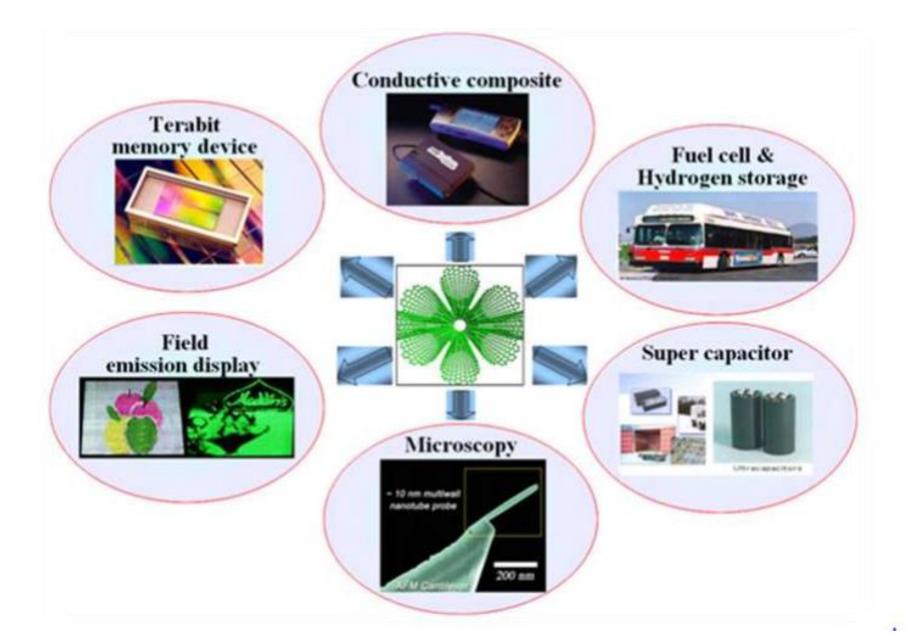
- > CNTs Thermal Materials
- CNTs Air and Water Filtration
- Hydrogen Storage
- Energy Storage

> ...





In Conclusion



https://youtu.be/k5Tjy_90WBUhttps://youtu.be/H-a2dC9Bgak

https://youtu.be/F8_M61AjeOE