Introduction of Nano chemistry

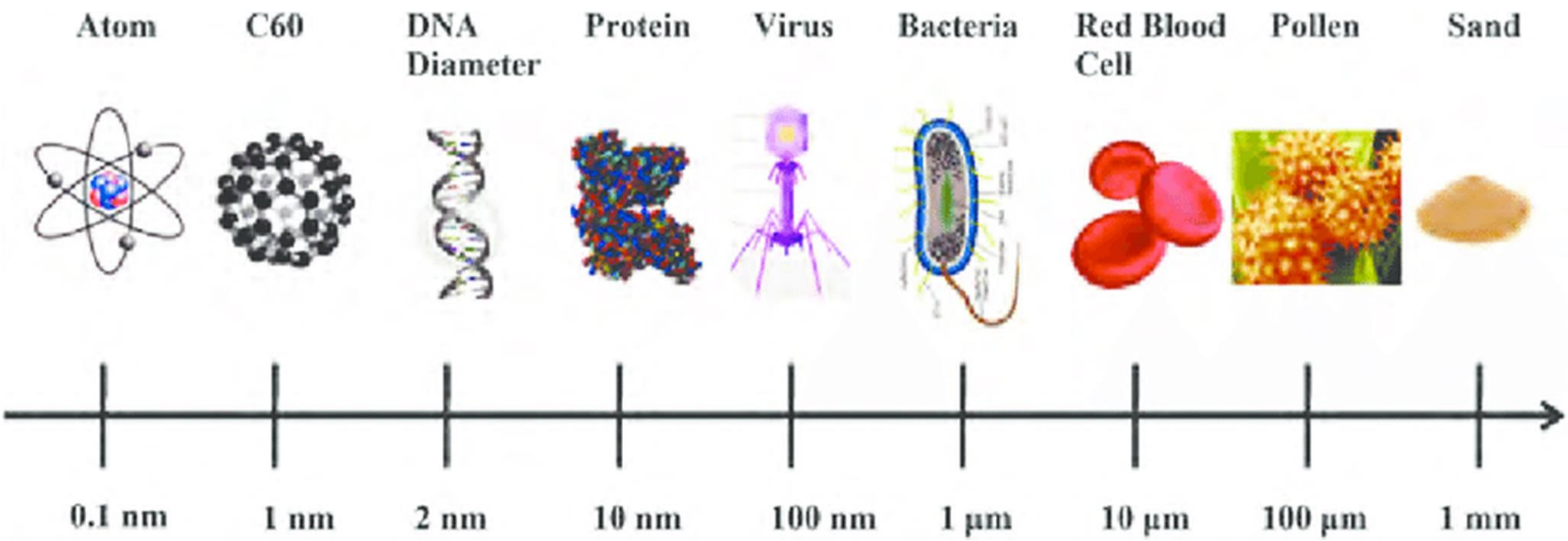
Nanochemistry: Nanochemistry is defied as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales at nano scale (1-100 nm) [1 nm=10^{-9} m]

Nanotechnology: Nanotechnology is defined as the design, characterization, production and applications of structures, systems and devices by controlling size and shape at nano scale (1-100 nm) [1 nm=10^{-9} m].

The conception of nanotechnology was first introduced by Prof. Richard Feyman in 1959.

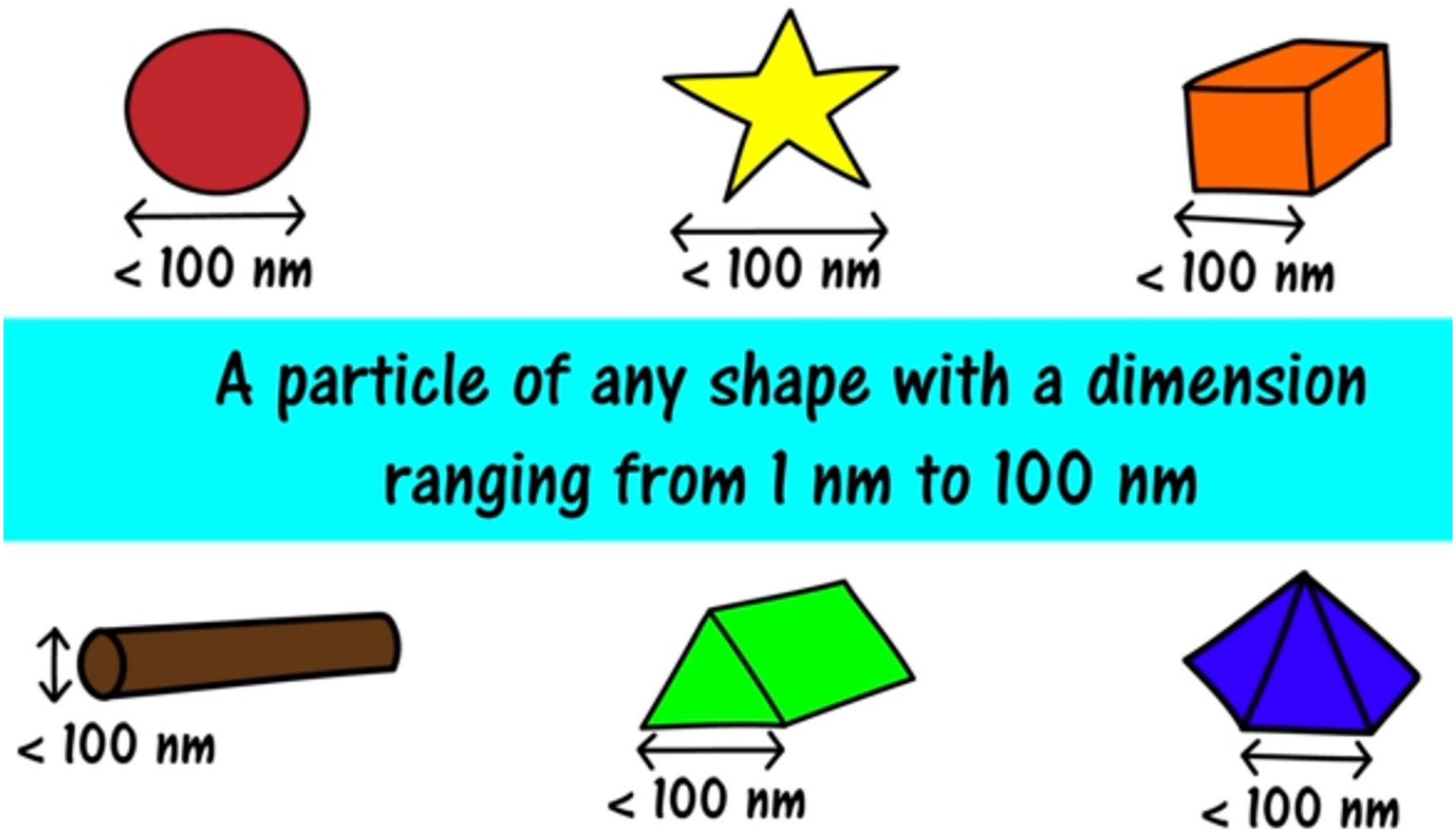
Prof. Richard Feyman

Nanomaterials: The materials having at least one dimension in nano scale (1-100 nm) [1 nm=10^{-9} m], are called nanomaterials.



A human hair is approximately 80,000- 100,000 nm wide

What are Nanomaterials????



Distiguish between nanomaterials and bulkmaterials

1. The sized of nanoparticle are in <100 nm in diameter, where as bulk materials are larger than one micrometer (1 micrometre = 10^{-6} meters).

2. Molecules is a collection of atoms, nanomaterial are collections of few molecules, which are less than 100 nm. Bulk material contains thousands of molecules.

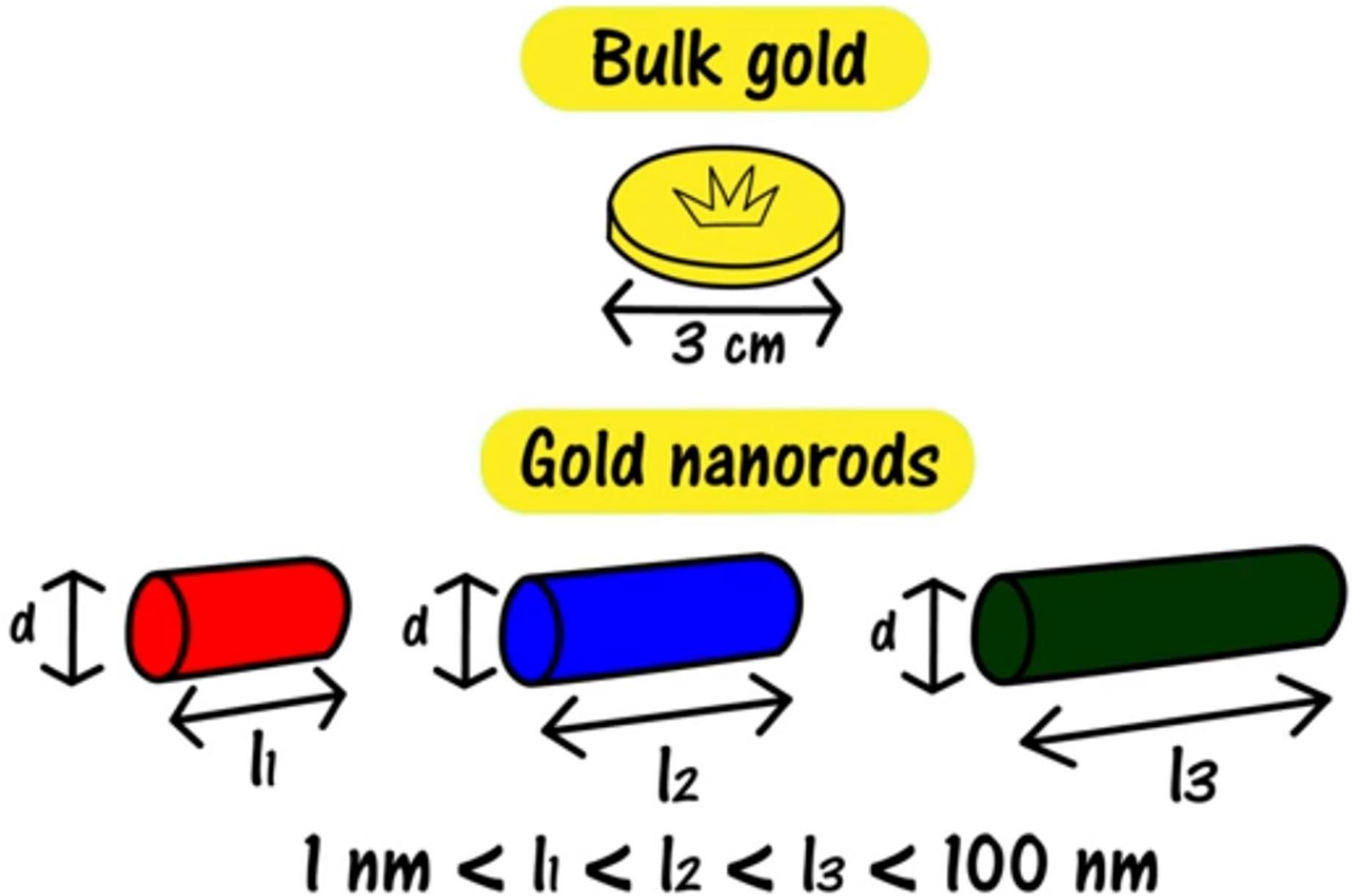
3. **Surface area of nanomaterials is more than the bulk material.** That's why; the interesting and sometimes unexpected properties of nanomaterial are observed.

Some examples-When bulk material are reduced to nanometer size?

When bulk material are reduced to nanometre size (1 nm-100 nm), the properties exhibited by these nanomaterial are drastically changed.

1. Opaque material become transparent (Copper)
2. In fact, in normal scales gold is chemically innert, but in nanoscale, they are served as potential chemical catalyst

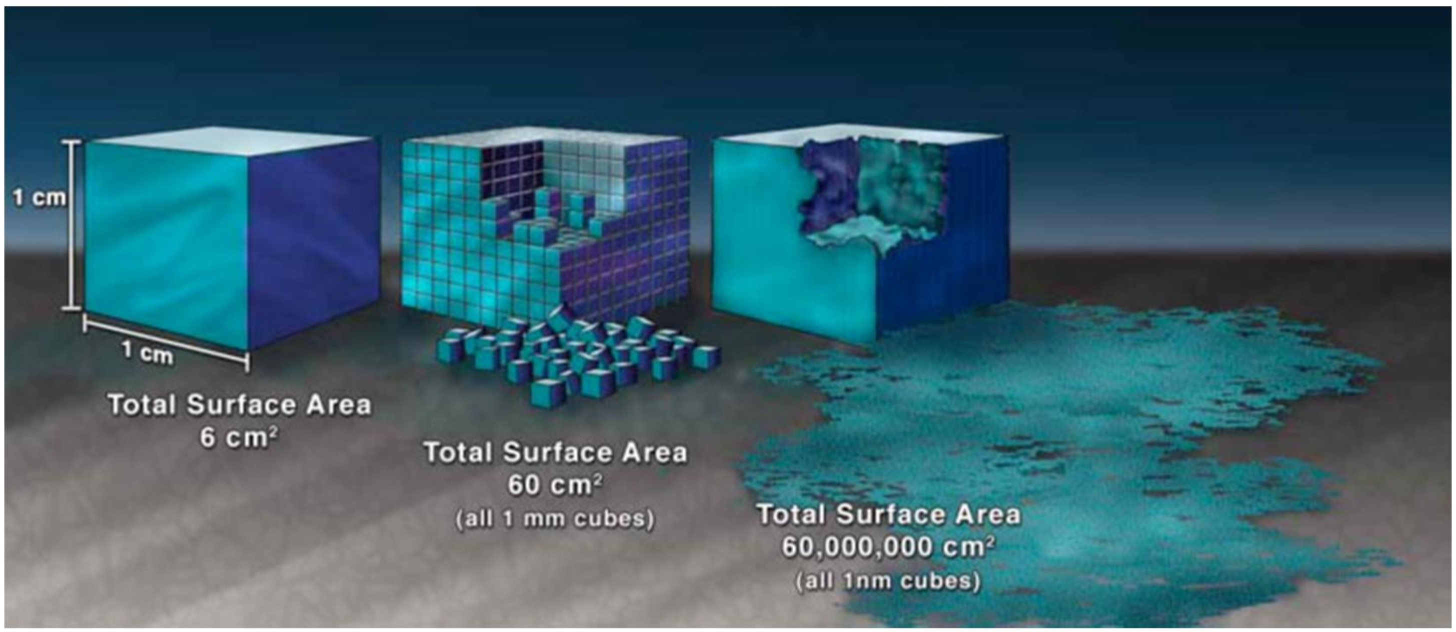
Examples……..



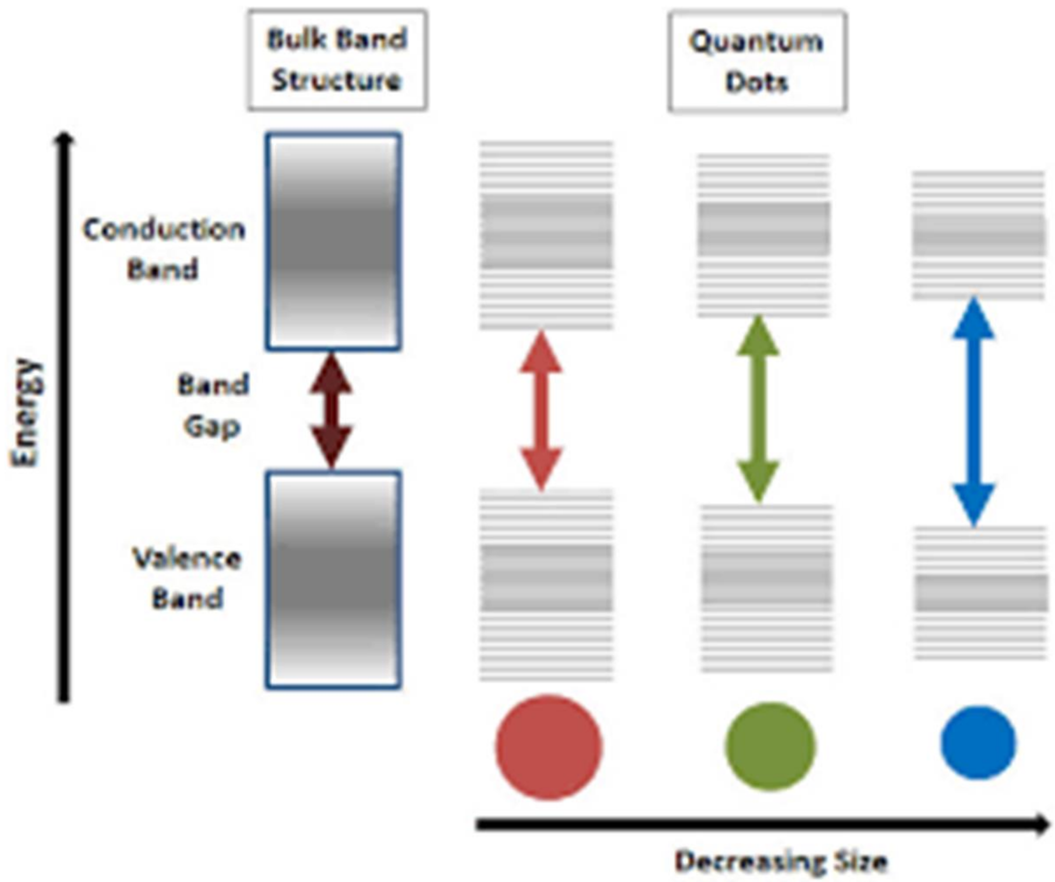
Why the properties of nanomaterial changes drastically when it converted to nano scale size?

Two primary factors cause nanomaterials to behave significantly differently than bulk materials:

1. The **surface area to volume ratio** of nanomaterial is relatively larger than that of bulk materials of same mass, which increases the chemical reactivity, affects, strength and electrical properties of material.



2. Quantum confinement is change of electronic and optical properties when the material sampled is of sufficiently small size, typically 10 nm or less. The band gap increases as the size of the nanostructure decreases, which changes the optical, electronic and magnetic properties.



Nanomaterial classification

Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm):

(a) zero-dimensional (0-D),

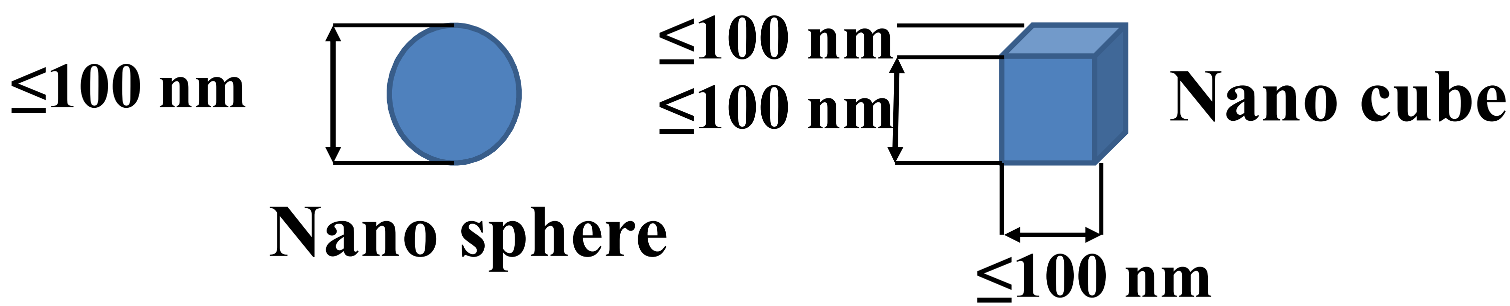
(b) one-dimensional (1-D),

(c) two-dimensional (2-D), &

(d) three-dimensional (3-D).

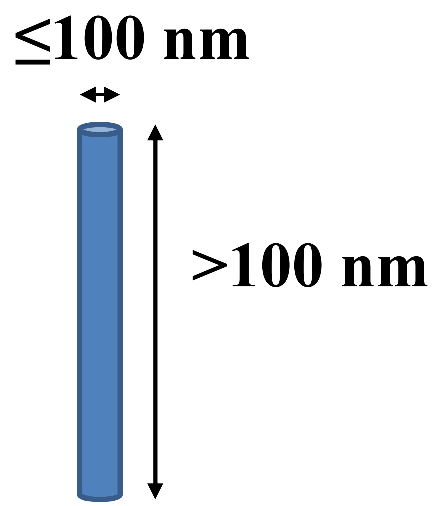
Zero dimensional (0-D) nanomaterials

- Materials with all the dimensions are measured in nanoscale (no dimensions are larger than 100 nm);
- The most common representation of zero-dimensional nanomaterials are nano sphere, nano cube etc.



One dimensional (1-D) nanomaterials

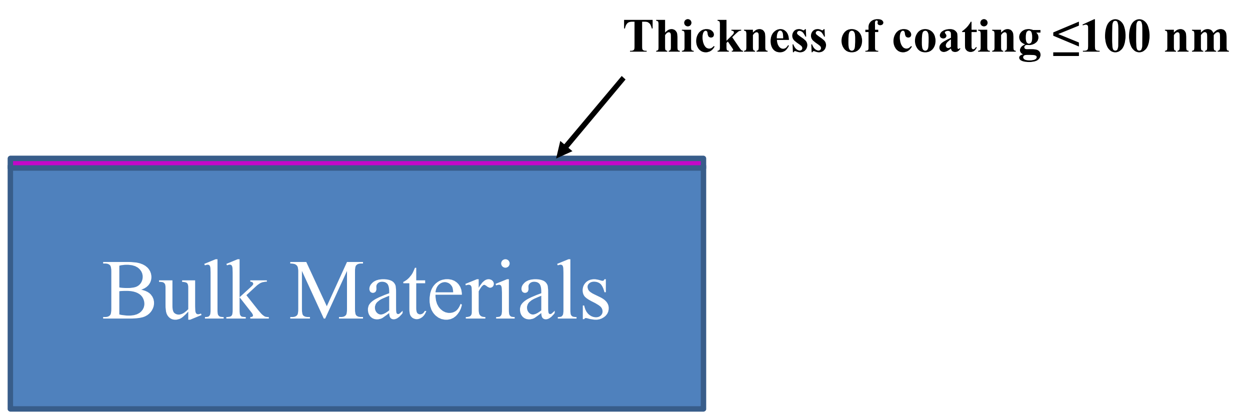
- ❖ One dimension that is outside the nanoscale;
- ❖ 1-D nano-materials include nanotubes, nanorods, and nanowires



Nanotube or nanorod

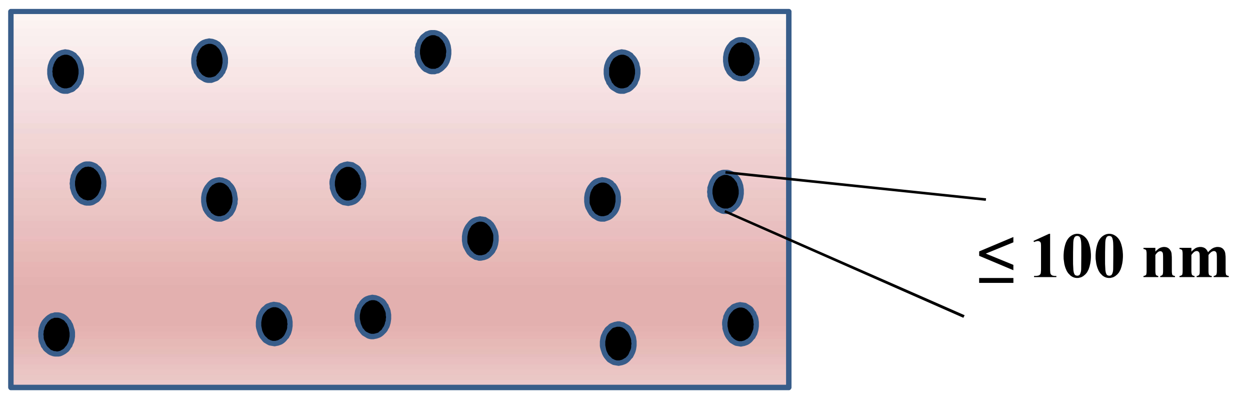
Two dimensional (2-D) nanomaterials

- ✓ Two of the dimensions are not confined to the nanoscale;
- ✓ 2-D nanomaterials exhibit plate/sheet-like shapes;
- ✓ Two-dimensional nanomaterials include nano-films, nano-layers, and nano-coatings, graphene, etc.



Three dimensional (3-D) nanomaterials

- Bulk nanomaterials are materials are not confined to the nanoscale in any dimension.
- 3-D nanomaterials can contain dispersions of nanoparticles.



Nanocomposite

Few Applications of nanomaterials….

1. In semiconductor devices, such as Nano capacitors
2. Nano medicine for cancer treatments
3. In targeted drug delivery
4. In agriculture
5. In electronics
6. In fuel cells
7. In chemical and biosensors
8. In solar cells
9. Nano-optics
10. Waste-water treatment
11. Green nanotechnology

General methods for the synthesis of nanomaterials:

1. **Top-down approach**
2. **Bottom-up approach**

Top-down approach: It refers to successive cutting of a bulk material to get nanoparticles.

Example: Ball milling technique is used in this approach.

Comparison…..

Rock

Statue

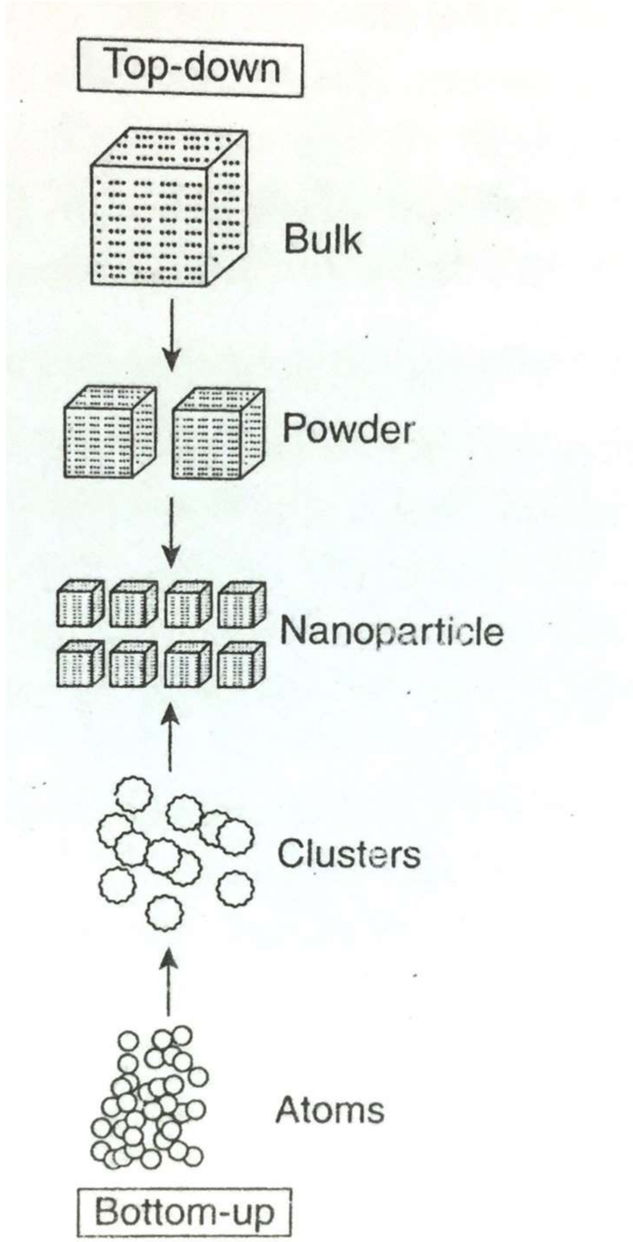
Bottom-up approach: It is the building up a material from the bottom *i.e.* atom by atom, molecule by molecule or cluster by cluster.

Example: Colloidal dispersion methods is one of the example used for the synthesis of nanomaterial.

Comparison.....

Brick

Building



Schematic representation of the building up of nanostructures

Difference between Top-down and bottom-up approach for the synthesis of nanoparticles:

Top-down	bottom-up
1. It involves the particle size reduction to nano size.	1. It involves the growth of nanoparticles from atomic size particles to nano size.
2. The process is used only for hard and brittle materials.	2. The process is used for gas, liquids and solids as well.
3. The Nano crystalline material prepared by this process may be contaminated by milling tools and atmosphere.	3. Less chances of contamination.
4. All particles of precursor may not break down to the required particle size.	4. More control over particle size.
5. Ball-milling	5. Sol-gel , Gas condensation methods

Disadvantages of top-down approach over bottom-up approach for the synthesis of nanomaterials:

1. **All particles of the precursor may not break down to the required particle size (Top-down).**

2. **The Nano crystalline materials prepared by the process (Top-down) may be contaminated by milling tools and atmosphere.**

Different processes for Bottom-up and Top-down approaches:

Bottom-up

1. **Sol-gel process**
2. **Liquid-solid reaction (Precipitation)**
3. **Gas Vapor Condensation (GVC)**
4. **Laser Ablation**
5. **Gas Condensation Pricessing (GPC)**
6. **Hydrothermal synthesis**
7. **Thermolysis**
8. **Solvothermal synthesis**
9. **Electro deposition**

Top-down

Ball-milling process

What are the techniques adopted for the characterization of nanoparticles?

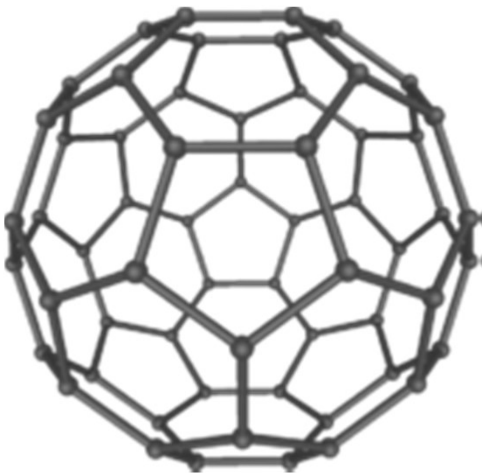
1. **Electron microscopy [Transmission electron microscopy (TEM); Scanning electron microscopy (SEM)]**
2. **Atomic Force Microscopy (AFM)**
3. **Dynamic light scattering (DLS)**
4. **X-Ray photoelectron spectroscopy (XPS)**
5. **X-ray diffraction (XRD)**
6. **FT-IR**
7. **MALDI-TOF mass spectrometry**
8. **UV-*vis* spectroscopy**
9. **NMR**

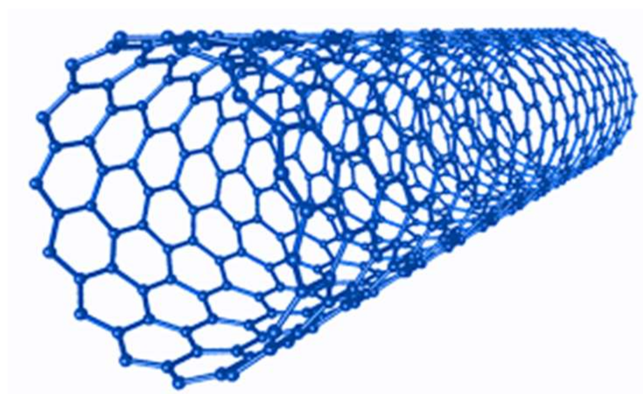
Introduction of Fullerenes-

it’s types, characteristics, properties, structures and uses of fullerenes

What is Fullerene?

A Fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes.





Buckminster fullerene C_{60} (left) and carbon nanotubes (right) are two examples of structures in the fullerene family.

Discovery of first Fullerene : C60

- **The name *Buckminster fullerene* comes from the inventor; Richard Buckminster Fuller**

- **Fullerenes was first isolated from soot of chimneys and extracted with solvents as red crystals**

- **Other fullerenes with C20, C70, C76, C84, and even C100 carbon atoms have also been prepare later on.**

- **The first form is C60 and second form is known as nanotube form**

Structure of C60

- **Fullerenes consists of hexagonal rings and alternation pentagonal rings of carbon closed in *the form of hollow spheres (like foorball*) or ellipsoid or *tubes (carbon nanotubes*)**

- ***12 pentagons and 20 hexagon* are arranged in form of Buckminster fullerene C60**

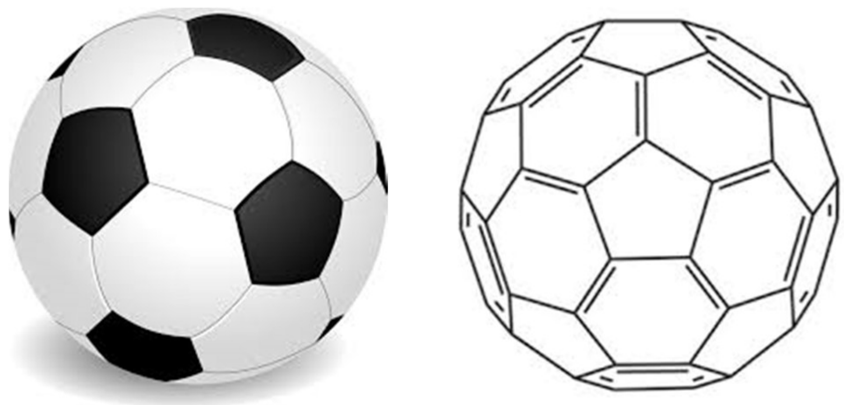
- **The hybridization of the carbon atoms are proposed to be in between *Sp2 hybridization*, having totally *symmetrical structure* with *all bond lengths and angles being equal.***

Properties of Fullerenes

- **Fullerenes (C60) is fine black powder having a density of 1.65 g/cm3 and sublimes at 800 K. It exist as brittle.**
- **They are electrical insulators as there is no movement of electrons from one molecule to another.**
- **Individuals molecules are held together by weak van der Waals forces**
- **Fullerenes are sparingly soluble in many organic solvents, for example, benzene, toluene, methyl benzene and carbon disulphide. Solution of fullerenes in toluene is bright red in colour**

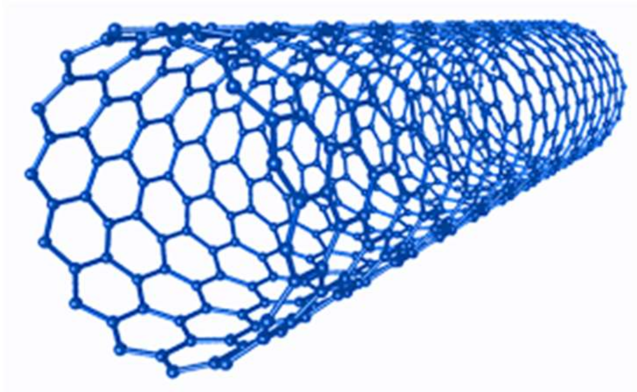
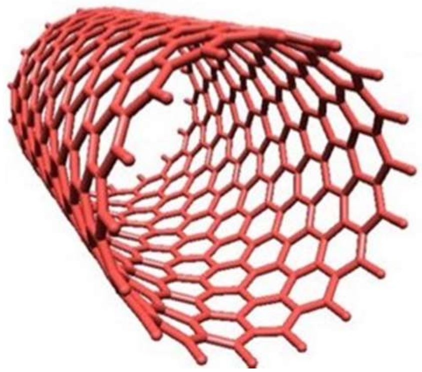
Different types of Fullerenes: 8 different types of fullerenes are known

1. Buckyball clusture:

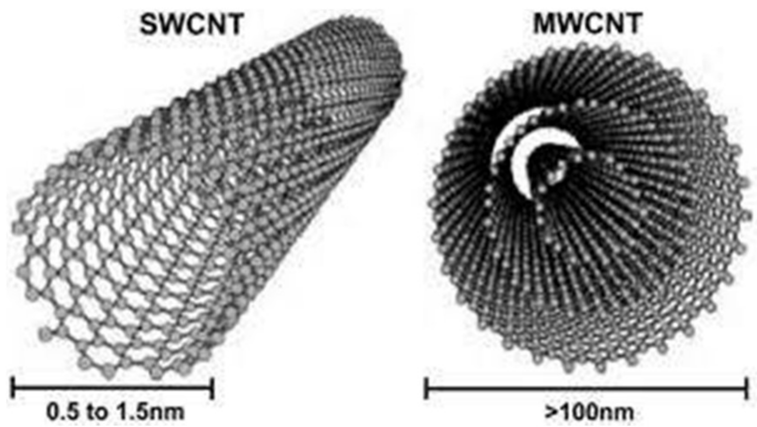


- Fullerenes having less than 300 carbon atoms are known as bucky-balls
- Fullerene wilh smallest member of carbon is C_{20} (found in soot of coal)
- Most common and abundant fullerene is C_{60}, named as buckminster fullerene

2. Nanotubes:

Nanotubes are hollow cylindrical tubes of carbon of which are of a few <u>nm in diameter and few macrons in length.</u>

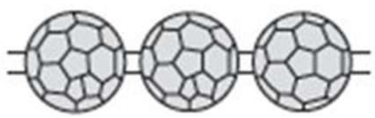


SWCNT: single-walled carbon nanotube;
MWCNT: multi-walled carbon nanotube

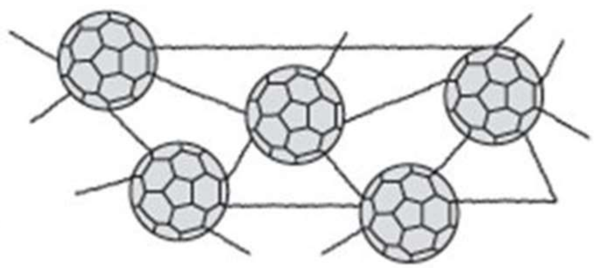
3. Megatube:

- ❖ **These are tubes with larger diameter than nanotubes. Their walls are made of varying thickness**

4. Polyfullerenes:



Directly linked to each other

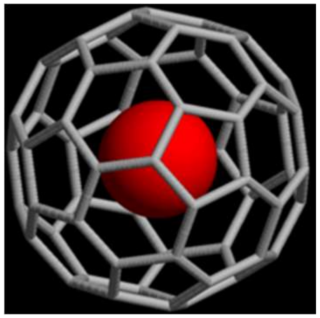


Cross-linked

linked through polymer backbone

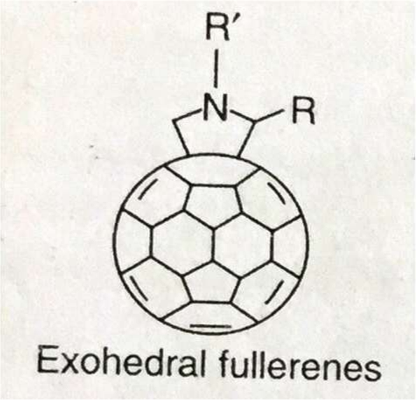
- ❖ **Polyfullerenes are made of C_{60} and C_{70} balls by covalent bonds in different ways. For example, Directly linked to each other, cross-linked, and linked through polymer backbone**

5. Endohedral:



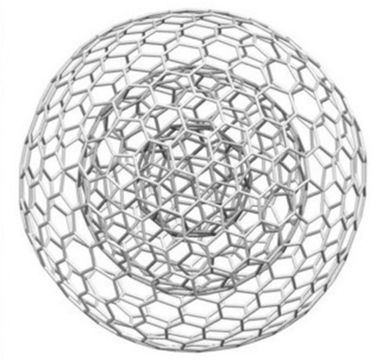
- Fullerene derivatives with various atoms are enclosed with inside. For example, when metal atoms are enclosed they are called metallo-fullerenes

6. Exohedral:



- Exohedral fullerenes are fullerenes that have additional atoms, ions, or clusters attached their outer spheres

7. Nano-onions:



❖ **The structures consisting of carbon spheres of increasing diameters layered on top of each other. Due to their layered design these are called nano-onions.**

8. Fullerenerings:

❖ **These types of fullerenes are made of 13-membered ring hole through which small molecules can pass through or get included.**

Characteristics of Fullerenes

- **C60 is highly symmetrical fullerene. Each carbon atoms bonds with three other adjacent atoms using *Sp2* hybridization**

- **Fullerenes are chemically stable. Breaking the balls require 1000 ºC.**

- **Fullerenes are reactive, as they possesses π -electrons, which are responsible for chemical reactions such as addition and redox reaction.**

- **Fullerenes are not soluble in water, sparingly soluble in toluene and carbon disulphide**

- **Fullerenes are non-toxic, but some of the derivatives are harmful to the health**

Applications of Fullerenes

- Fullerenes are powerful antioxidant. So, they can find application in health and personal care areas.
- Fullerenes nanotubes are promising as chemical molecular sensor. They had wide applications as coating materials on some chemical sensors.
- Fullerenes can react readily with free radicals, thus preventing cell damage.
- The fullerenes can control Alzheimer's and HIV
- Fullerenes derivatives can be used in targeted and controlled drug delivery.
- Endofullerenes are capable of being applied in MRI and X-ray imaging application.
- Other applications of fullerenes in organic reactions, water purification are also being used.

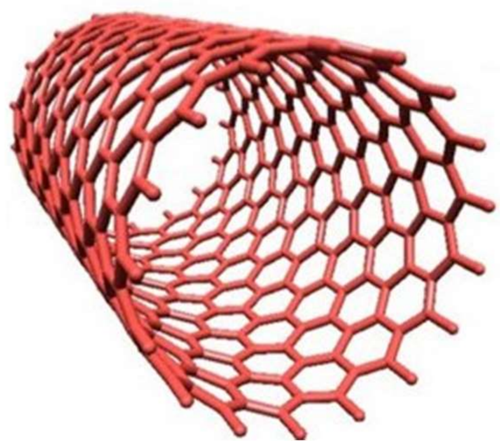
Introduction of carbon nanotubes (CNTs)

Carbon Nanotubes (CNTs)

- **Carbon nanotubes (CNTs; also known as buckytubes) are allotropes of carbon with cylindrical nanostructure.**

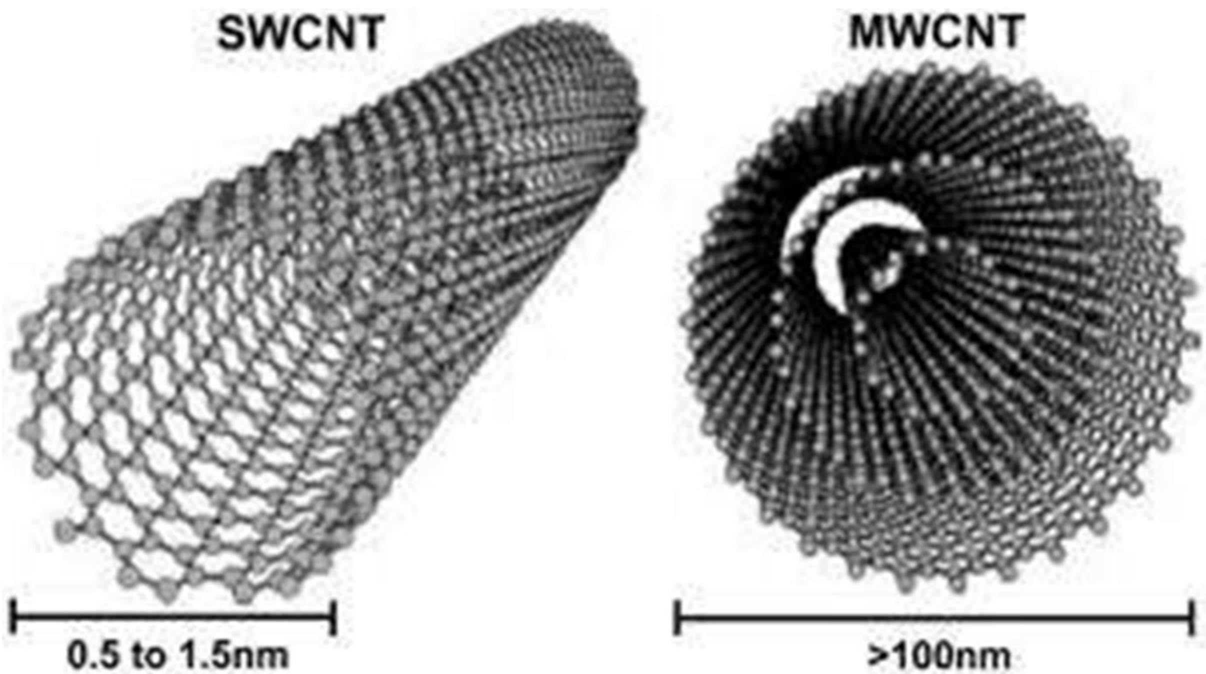
- **CNTs have been synthesized with length-to-diameter ratio upto 132,000,000 : 1, which is significantly larger than any other material.**

- **CNTs have extraordinary strength and stiffness in the fields of materials science.**



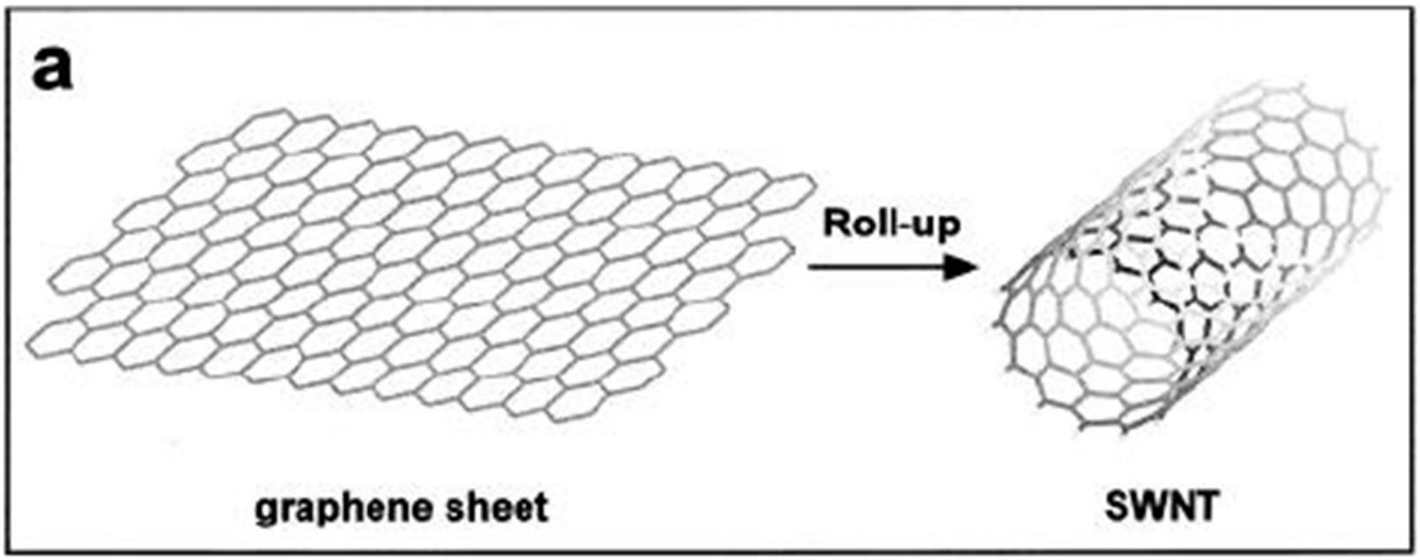
Types of Carbon Nanotubes (CNTs)

(i) SWCNT: single-walled carbon nanotube;
(ii) MWCNT: multi-walled carbon nanotube



Single-walled carbon nanotube (SWCNTs)

- Have a diameter of ~ 1 nm, with tube length many million times longer.
- The structure of SWCNTs can be imagined to be wrapping/rolling of a graphite (graphene) sheet to form a tube



Multi-walled carbon nanotube (MWCNTs)

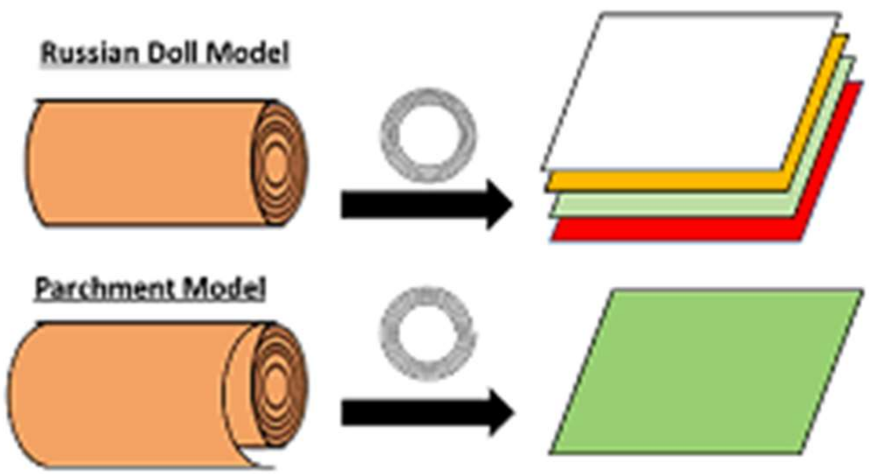
- Consist of multiple rolled layers of graphite.

- The interlayer distance of MWCNTs is 3.4 A°, Which is approximately equal to the distance between two graphene layers.

- To describe the structure of MWCNTs, there are two models

  1. Russian Doll model (sheets of graphite are arranged in concentric cylinders with in a large-walled nanotubes)

  2. Parchment model (a single sheet of graphite is rolled in around itself, similar like a rolled paper)



Properties of CNTs

- **Strength:** The chemical bonding of nanotubes involves entirely *sp^2*-hybrid carbon atoms. These bonds are similar to those of graphite and provide nanotubes with their unique strength. That's why; CNTs are strongest and stiffest material.

- **Hardness:** A super-hard material as compared to *diamond and boron nitride* can be synthesized by compressing SWNTs.

- **Kinetic:** In MWCNT, an inner nanotube core may slide within outer nanotube wall almost without friction. Hence, it is used in molecular technology.

- **Thermal:** All CNTs exhibit good thermal conducting properties along the tube, but they are good insulators laterally to the tube axis.

- **Chemical resistance:** They are extremely good resistant to chemicals.

- **Mechanical and electrical property:** The mechanical and electrical properties can be modified by breaking the C=C bond.

Applications of CNTs

- ***Application in the field of energy…..***

- **CNTs find application in nanoelectronics.**
- **A paper battery is made of paper-thin nanotube, which can provide a long and steady power output comparable to conventional battery (Li-battery).**
- **The efficient soar cells have been developed by a mixture of CNTs and Carbon buckyballs.**
- **CNTs may be used to improve the efficiency of ultracapasitors.**

Applications of CNTs in material science……

(i) CNTs find applications in composite polymer materials, where they are used to add the strength of the polymers.

(ii) As CNTs have high mechanical strength, they are being explored stab-proof and bullet-proof material.

(iii) Carbon nanotubes are used for making aircraft structures.

Application in the field of medicine………………

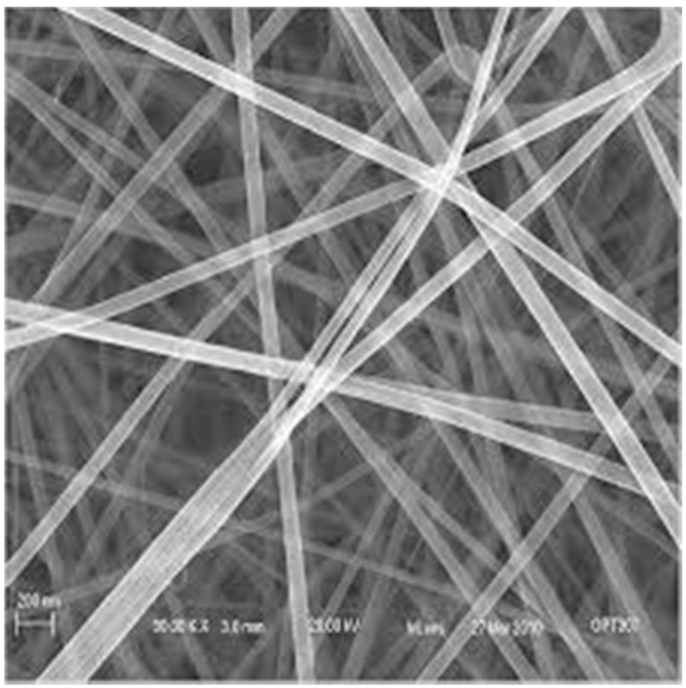
(i) SWNTs have been used as *in vivo* Nano scale capsules.

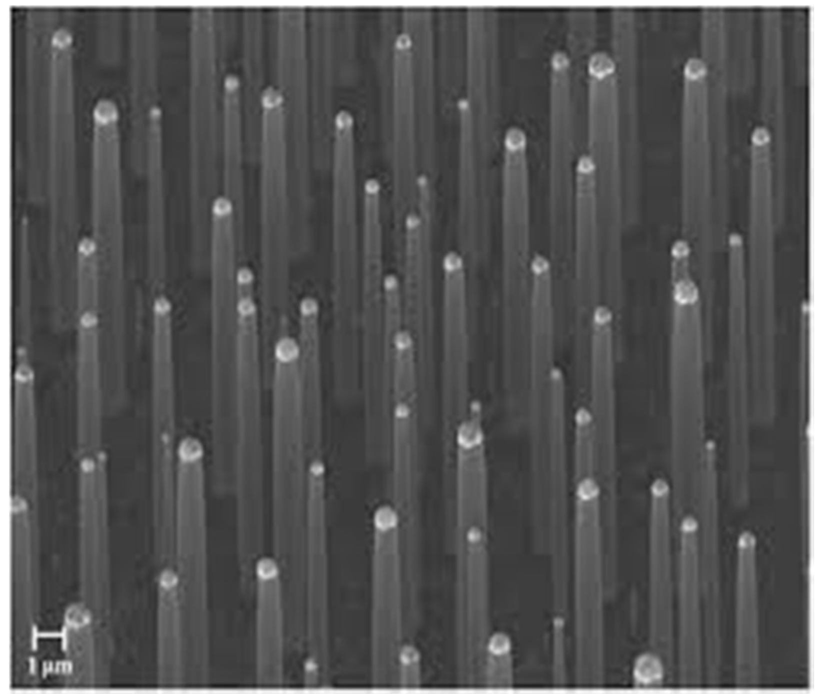
(ii) In cancer research, SWNTs inserted around cancerous cells and excited with radio waves results in killing the cancerous cells.

Introduction of Nanowire

What is Nanowire?

A nanowire is a wire with diameter of the order of nanometer (10^{-9} meters) and an unconstrained longitudinal size.





Properties of Nanowire

1. **Nanowires could be metallic (Ni, Pt, Au), semiconducting (Si), and insulating (SiO_2, TiO_2).**

2. **Nanowires have high excitation binding energy.**

3. **Nanowires have high density, high surface to volume ratio.**

4. **This all make unique in their electrical, magnetic, optical, thermoelectric, and chemical properties.**

Applications of Nanowire

- They find a lot of applications in the fields of electronics, optics, sensor devices, etc.
- They are used in magnetic information storage medium.
- They find potential use in electronic applications, such as junction diodes, memory cells, switches, transistors, and LEDs, etc.
- In medical field, silicon nanowires are used in "tissue engineering"

What are Biological nanomaterials? How are they potentially useful?

Biological nanomaterials are biological systems which are inherently nano in size. They serve as models and help in understanding the behaviour of nanomaterials in general and lead us to approaches like biomimicking.

There are many nanophase materials in biological systems.

For example,

1. **Living systems produce mineral material of the bone in the nanometer scale, which could be used as direct source of novel materials *in vivo* procedures and *in vitro* manipulations.**

2. **Some examples of biological nanomaterials are ferritins and related iron-storage proteins, which are used to investigate iron metabolism in living organisms.**

Application of nanomaterials in the field of catalysis, Energy science and medicine

Application of nanomaterials in the field of catalysis:

1. **Nano-sized ruthenium/platinum catalysts could potentially be used for the purification of hydrogen for hydrogen storage.**

2. **Palladium nanoparticles can catalyse the oxidation of CO and NO to control in air pollution in the environment.**

3. **Carbon nanotube supported can be be used as a cathode catalytic support for fuel cells.**

4. **Carbon nanotubes are promising candidates for methanol fuel cells.**

5. **Gold nanoparticles exhibit catalytic properties, despite the fact that bulk gold is unreactive.**

6. **Iron oxide and Cobalt nanoparticles are used to convert into liquid hydrocarbon from CO and H2 using Fischer-Tropsh process.**

Application of nanomaterials in the field of Energy science

1. **Nanomaterial are used in photovoltaic cells.**
2. **A plastic solar cell made-up with nanomaterials can turn the sun power into electrical energy even on a cloudy day.**
3. **CNTs are used to make super capacitors.**
4. **Nanomaterial are added to solid polymer gel to enhance the conductivity and storage capacity.**
5. **Nanotechnology can enhance the safety and capacity of Li-ion batteries greatly..**
6. **Pt-nanoparticles are used instead of solid Pt, increase efficiency of fuel cell.**
7. **SWCNTs are solving the storage problem for hydrogen-fuel cars and trucks.**
8. **Solar water splitting is considered as most efficient and cleanest way to produce hydrogen.**

Application of nanomaterials in the field of Medicine

1. **Drug and medicine:** **Nanotechnology deliver medicine or drugs into the specific parts of human body (Targated drug delivery) thereby making more effective and less harmful to the other parts of the body**

2. **Tissue repair:** **Nanotechnology can help to regenerate or repair damaged tissues by using suitable nanomaterials and the technique is called "tissue engineering".**

3. **Medical robotics:** **Nanorobotics have useful and variety of applications, such as diagnosis, monitoring diabetics and health care, etc.**

4. **Gold nanoparticles are useful to kill the cancer cells.**