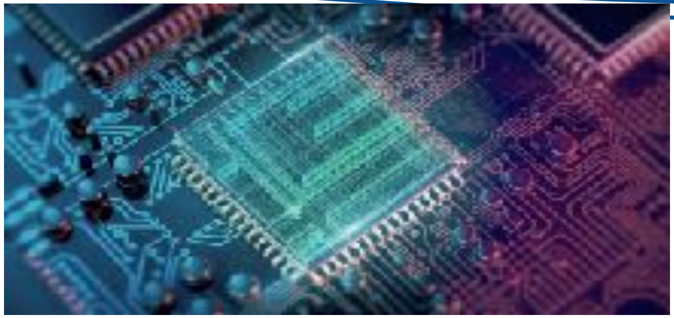
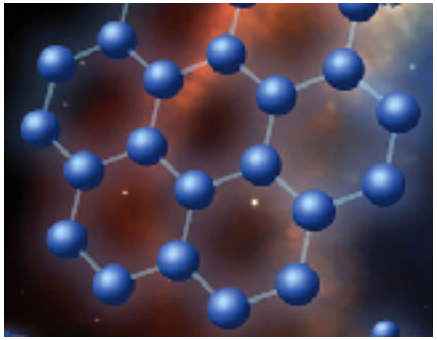
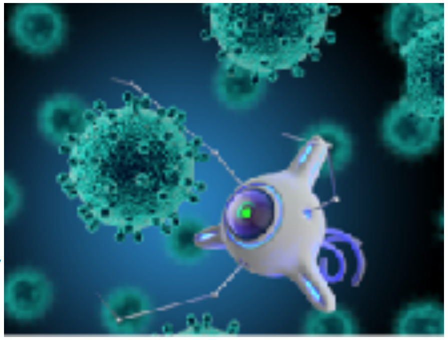
CHRIST
(DEEMED TO BE UNIVERSITY)
BANGALORE, INDIA





Nano Materials & Nanotechnology



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Syllabus:

Unit 1 – Introduction

Unit 2 – Synthesis of Nanomaterials

Unit 3 – Characterization of Nanomaterials

Unit 4 – Nanomaterials

Unit 5 – Applications.

Text Books:

- 1. Processing & properties of structural naonmaterials -Leon L. Shaw, Nano chemistry: A Chemical Approach to Nanomaterials, Royal Society of Chemistry, Cambridge UK 2005.
- 2. Nanoparticles: From theory to applications – G. Schmidt, Wiley Weinheim 2004.
- 3. Advances in Nanotechnology and the Environment, Juyoung Kim, CRC Press, Taylor and Francis Group.
- 4. W. Gaddand, D.Brenner, S.Lysherski and G.J.Infrate (Eds), Handbook of nanoscience, Engg. and Technology, CRC Press,2002.
- 5. G. Cao, Naostructures and Nanomaterials: Synthesis, properties and applications, Imperical College Press, 2004.
- 6. Ghuzang G.Cao, Naostructures and Nanomaterials: Synthesis, properties and applications, Imperical College Press, 2004

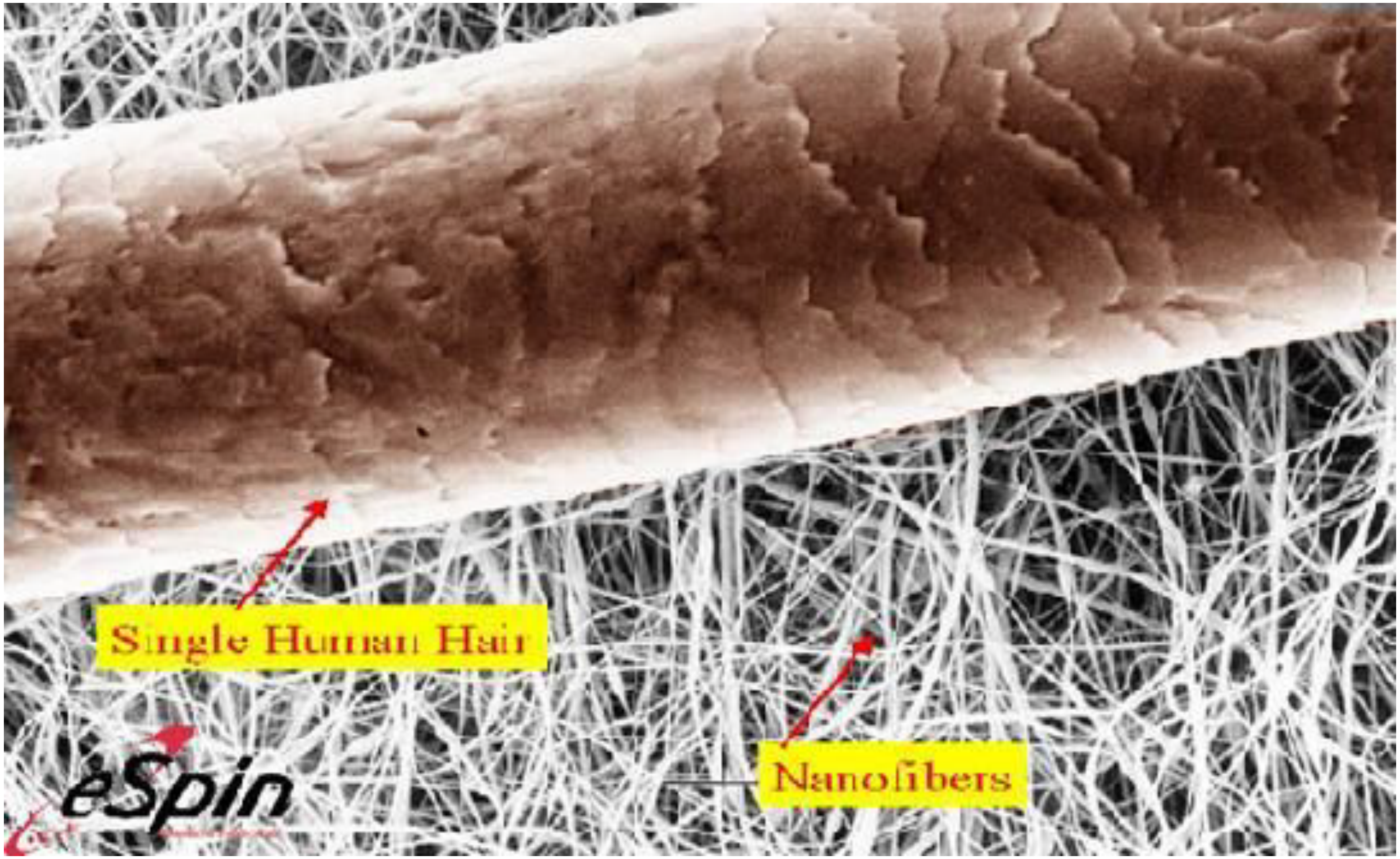
EVALUATION PATTERN:

- **CIA I - 20 Marks - 2 components**
  Test 1 - UNIT 1 - 10 Marks
  Test 2 - UNIT 2 - 10 Marks

- **CIA II - Mid Semester Exam - 50 marks**

- **CIA III - 20 Marks - project**

Size comparison :

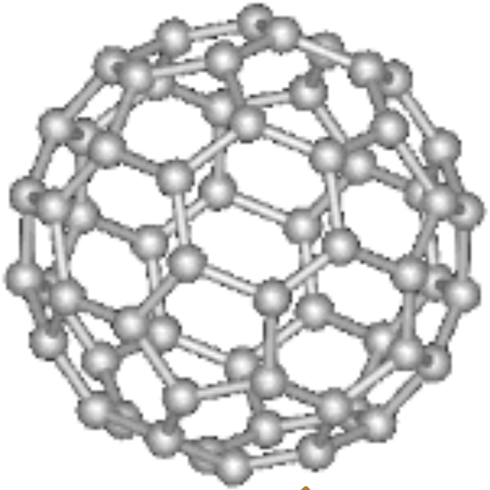


What is Nanoscale?
1nm = 10^{-9} m

12,756 Km

22 cm

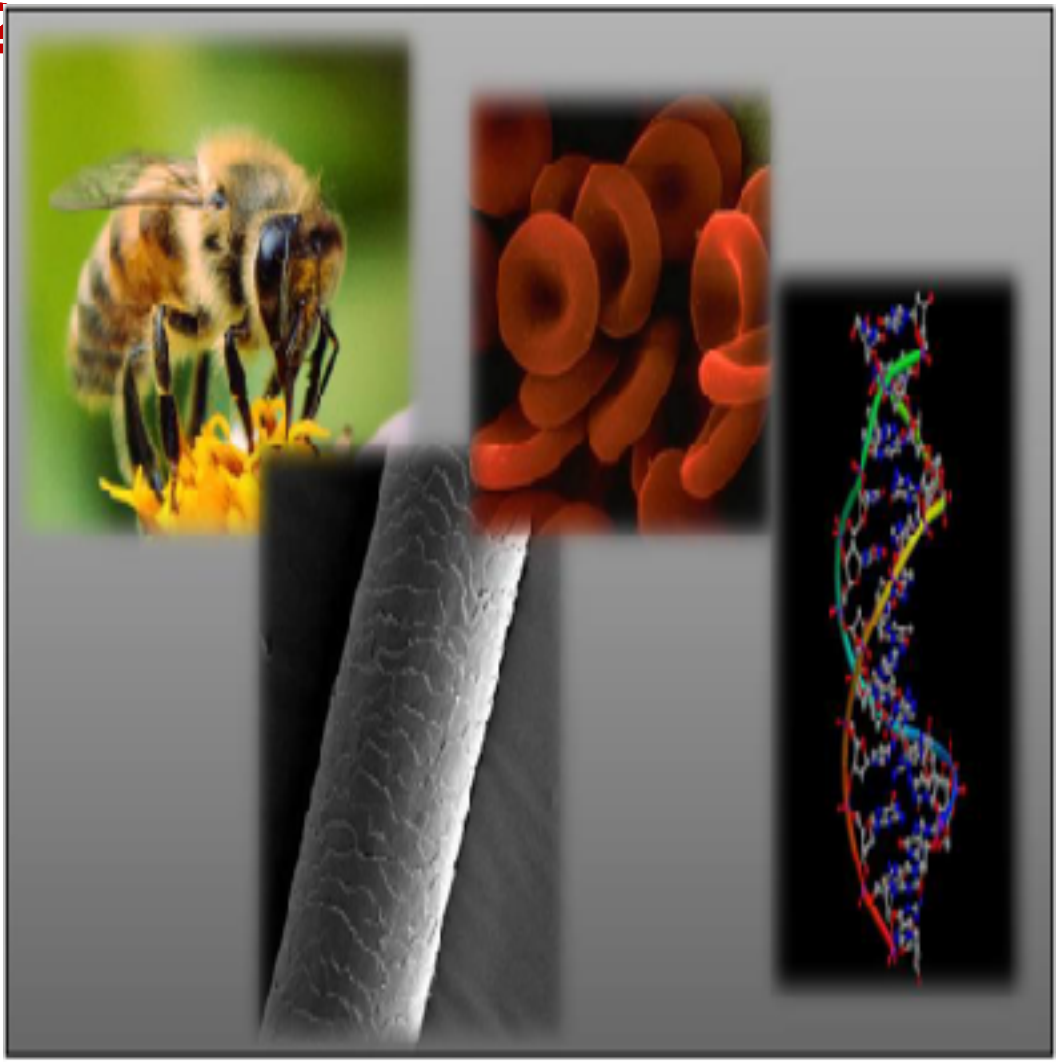
0.7 nm



10 millions times smaller

1 billons times smaller

Macro, Micro, or Nano?

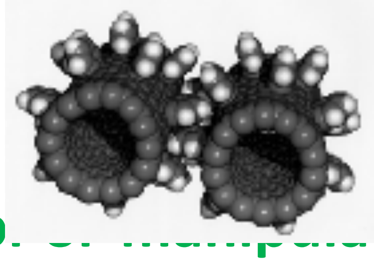


- A honey bee is approximately 12 mm long
- A human hair is 60 to 100 µm in diameter
- A red blood cell averages 7 µm in diameter
- The DNA helix is 0.002 µm wide or 2 nm wide.

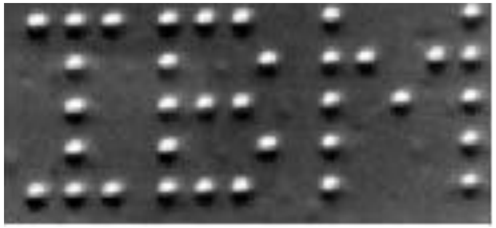
What is Nanotechnology?

1. Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 - 100 nanometre range.

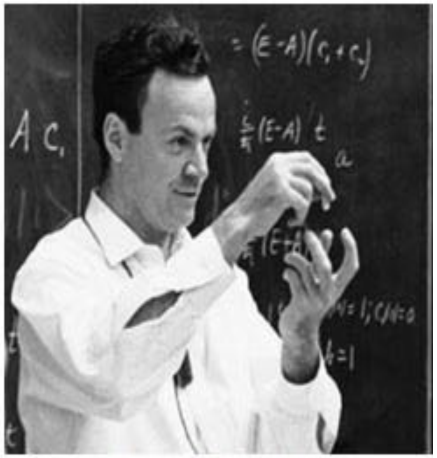
2. Creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.



3. Ability to control or manipulate the properties of matter at the atomic or molecular scale.

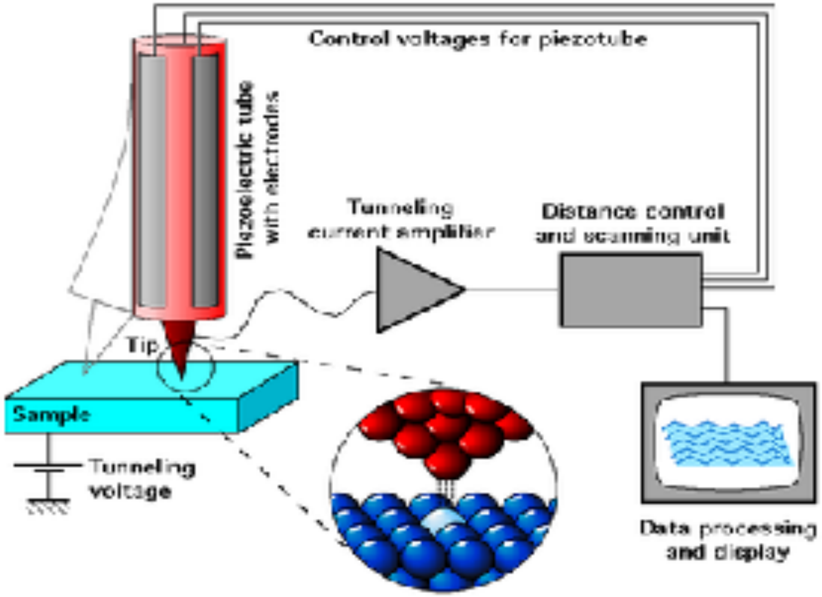


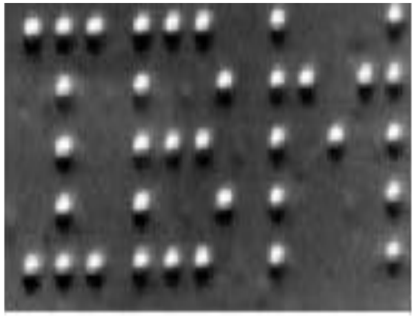
Nanotechnology: History & Origin?



Conceptual origins:

Physicist Richard Feynman: "There's Plenty of Room at the Bottom", lecture at American Physical Society,



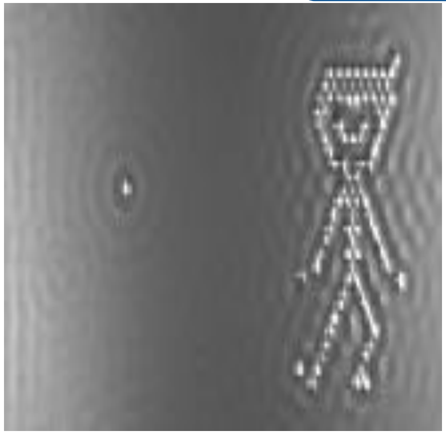


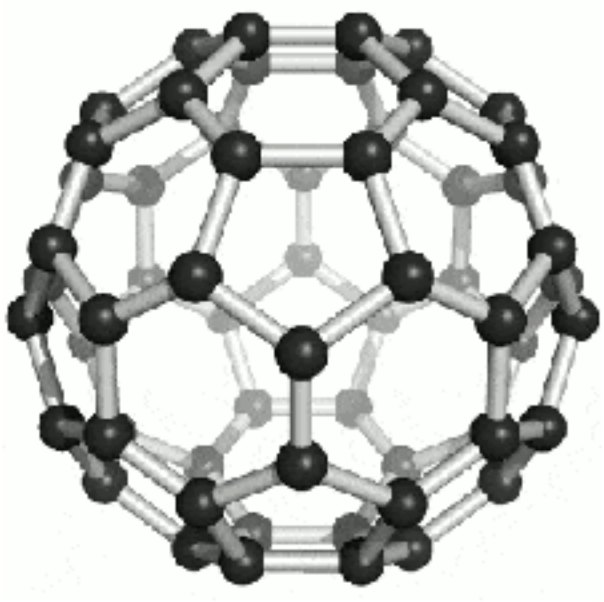
Norio Taniguchi, Tokyo University of Science, *First to use the term "nano-technology"*.

Arranged 35 individual xenon atoms on a substrate of chilled crystal of nickel to spell out the three letter company initialism. It was the first time atoms had been precisely positioned on a flat surface

A Boy and His Atom:

Is a 2013 stop-motion animated short film released on YouTube by IBM Research.





New carbon family - Fullerenes. ball shaped, cage-like molecules, characterized by the symmetrical C60

In 1980, K. Eric Drexler developed and popularized the concept of nanotechnology

Nano Tech in Real Life:

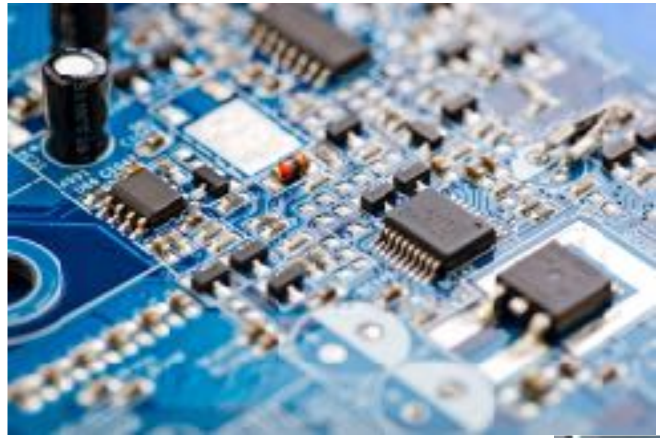
- ***Sunscreen:*** **Nanoparticles have been added to sunscreens for years to make them more effective. nanoparticles commonly added to sunscreen are titanium dioxide and zinc oxide. These tiny particles are effective at blocking UV radiation.**
- ***Antibacterial agent*: Silver nano particle used as antibacterial agents**
- ***Tennis balls* : Clay nano particles helps tennis balls keep their bounce for longer, and CNT make tennis racquets more stronger**
- **Clothing: When used in textiles, nanoparticles of silica can help to create fabrics that repel water and other liquids.**

Nano Tech in Fiction:

- ➢ **Terminator –Judgement Day T -1000 robot which could alter its shape and heal itself.**

2018 film *Avengers:* Infinity War , where Tony Stark taps a panel on his chest to release a billion tiny robots, which rapidly assemble into an Iron Man suit around him.

This kind of self-assembling nanotechnology is a very real and exciting field of research.



<u>Nano-Tech, Nanomaterials are everywhere !!!!!</u>

Why Nanotechnology ?

- It offers the possibility of creating materials with novel combination of properties.

- Devices in the nano-scale, needs less material to make them and it also uses less energy.

- It offers a universal fabrication technology.

Size Effect:

Three important ways in which Nano scale materials may differ from macro scale materials

- ➢ Gravitational forces become negligible and electromagnetic forces dominate.

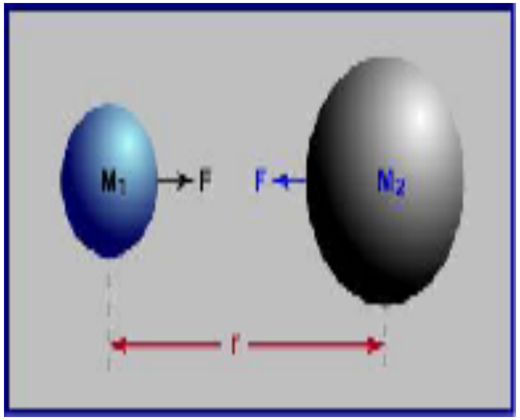
- ➢ Quantum mechanics is the model used to describe motion and energy instead of the classical mechanics model.
- ➢ Greater surface to volume ratio.

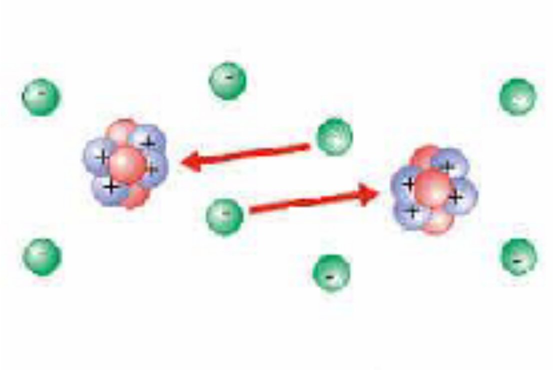
- ➢ Random molecular motion becomes more important.

Dominance of Electromagnetic Forces

- Gravitational force is a function of mass and distance and is weak between (low-mass) Nano sized particles.

As things get smaller, gravity would become less important, surface tension molecule attraction would become more important.

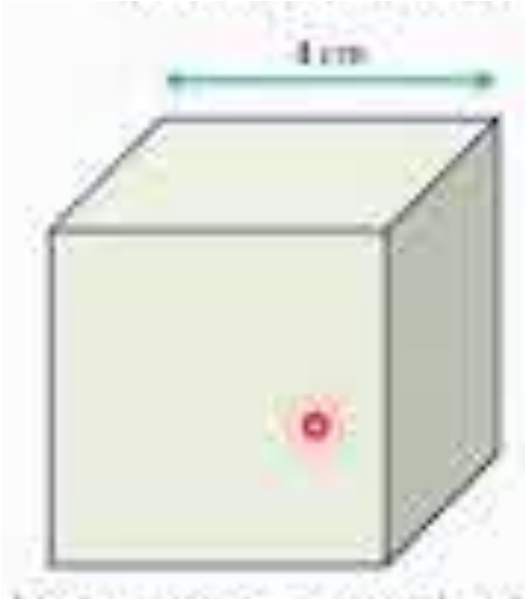




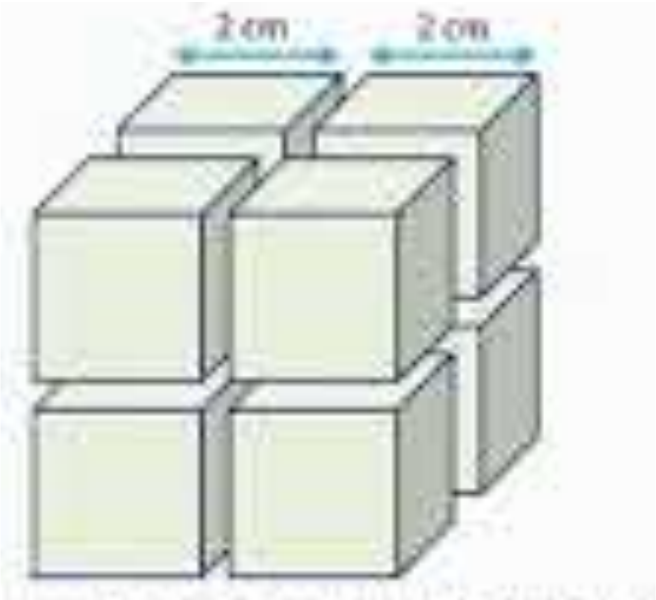
- Electromagnetic force is a function of charge and distance is not affected by mass, so it can be very strong even when we have Nano sized particles.

The electromagnetic force between two protons is 10^{36} times stronger than the gravitational force!

Surface Area to Volume ratio

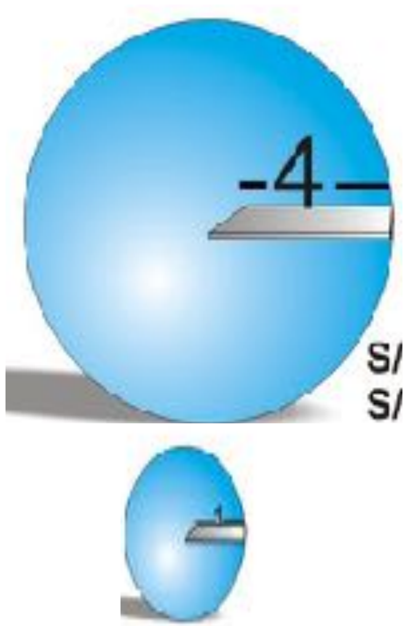


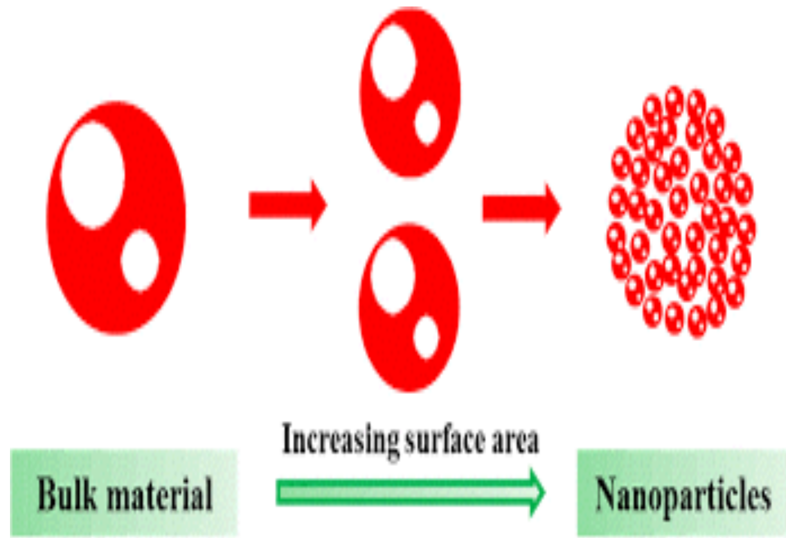
Surface Area = $6a^2$
Volume = a^3



Surface Area = $8 * 6a^2$
Volume = a^3

Surface to Volume ratio:

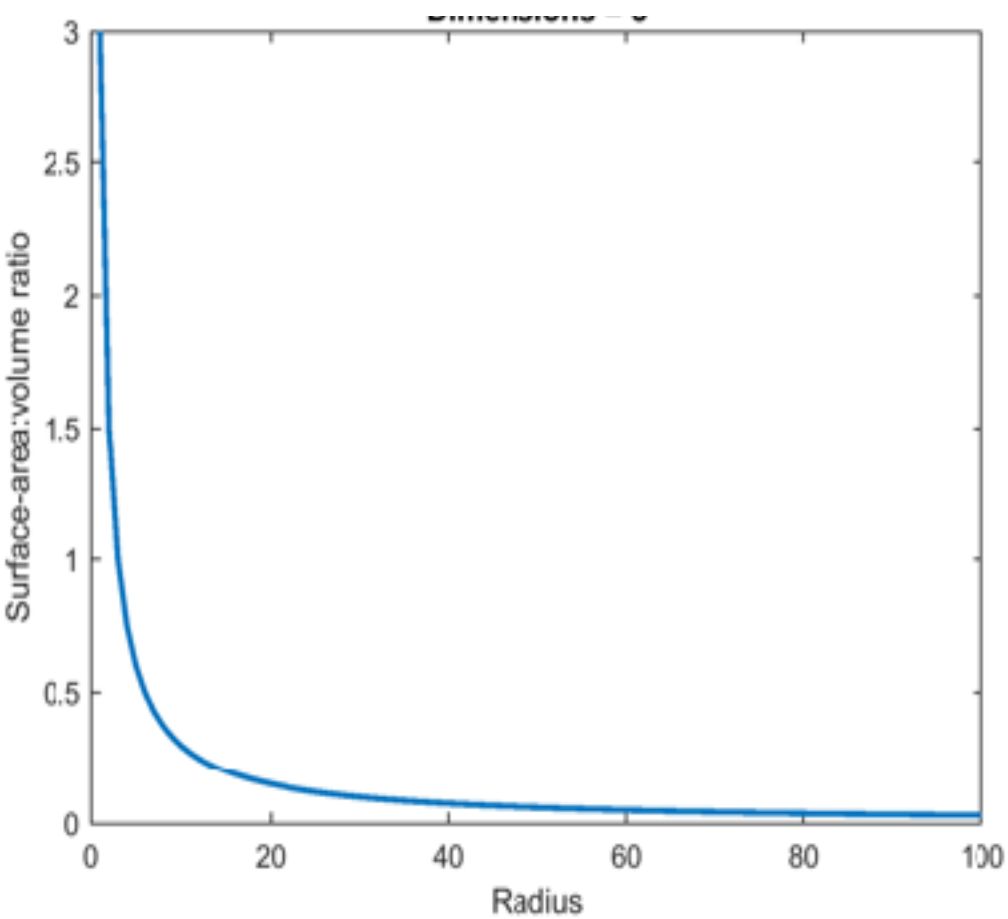




Surface area of sphere $=4\pi R^2$
Volume of the sphere $= 4/3\ \pi R^3$
A/V=?

For Cylinder,
S.A=$2\pi r.$ H
V=$\pi r2.$H
A/V=?

Surface to Volume ratio:

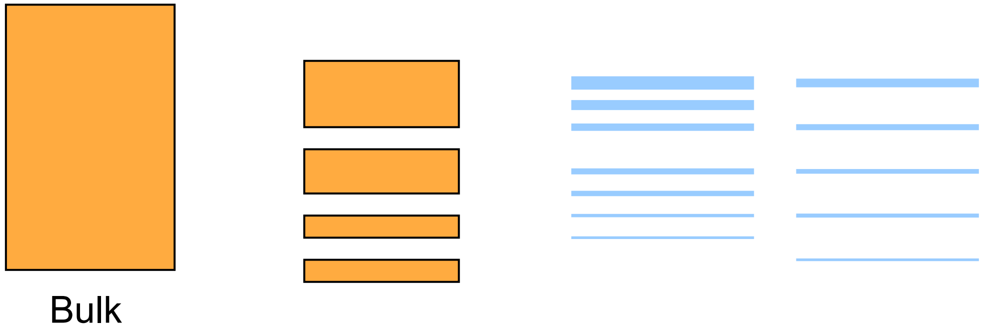


- ➢As surface area to volume ratio increases – A greater amount of a substance comes in contact with surrounding material –

- ➢This results in better catalysts, since a greater proportion of the material is exposed for potential reaction

Quantum Size effect:

❑ Quantum mechanics better describes phenomena that classical physics cannot – The probability (instead of certainty) of where an electron will be found.



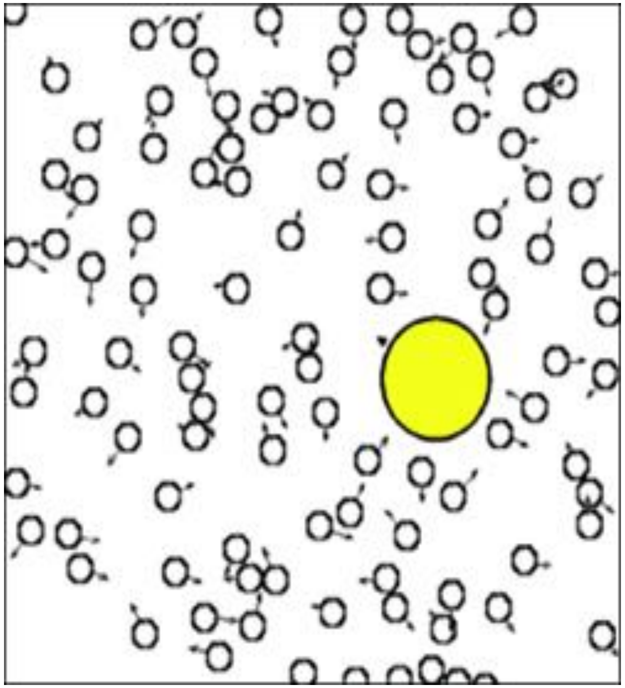
- Energy band to Energy level.
- Discreteness of energy

(DOS) Energy states decreases as size reduces

❑ For extremely smaller particle with very small mass- wave nature becomes pronounced . $\lambda = \frac{h}{mv}$

Random Molecular Motion is Significant

- At macro-scale random molecular motion is the movement of molecules in a substance , it is due to their K.E. This motion increases at higher temperature.
- At macro-scale motions is very small when compared to size of the objects and thus it is not very influential in how the particle behave.
- At nano-scale random motions can be on the same scale as the size of the particle and thus it influence the behaviour of the particle.



A grain of pollen colliding with water molecules moving randomly in all directions as a result of heat energy.

Properties that change at the nano scale

The dominance of electromagnetic force, the presence of quantum mechanical phenomena, the large surface area to volume ratio and the importance of random kinetic motion cause nano scale sized particles to often have very different properties than their macro scale counterparts.

- ✓ *Reactivity*
- ✓ *Optical property*
- ✓ *Melting point*
- ✓ *Magnetic property*
- ✓ *Thermal property*
- ✓ *Electrical property*

Reactivity:

Nanoparticles are more reactive, because they have more surface area than macro scale particles.

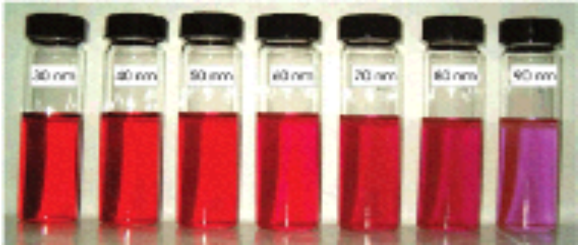
- **Aluminum (Al) is the shiny pliable metal used to make soda cans. At the nano scale, aluminum particles are extremely reactive and will explode.**

- **Gold at Macro scale is inert but gold at nano scale is extremely reactive and can be used as catalyst to speed up the reactions.**

Optical property:

As we go in nano range, number of atoms decreases, hence the band gap is more. Optical properties such as colour and transparency are observed to change at nano scale level.

- **Bulk gold appear yellow in colour while in nano-size gold appear red in colour.**



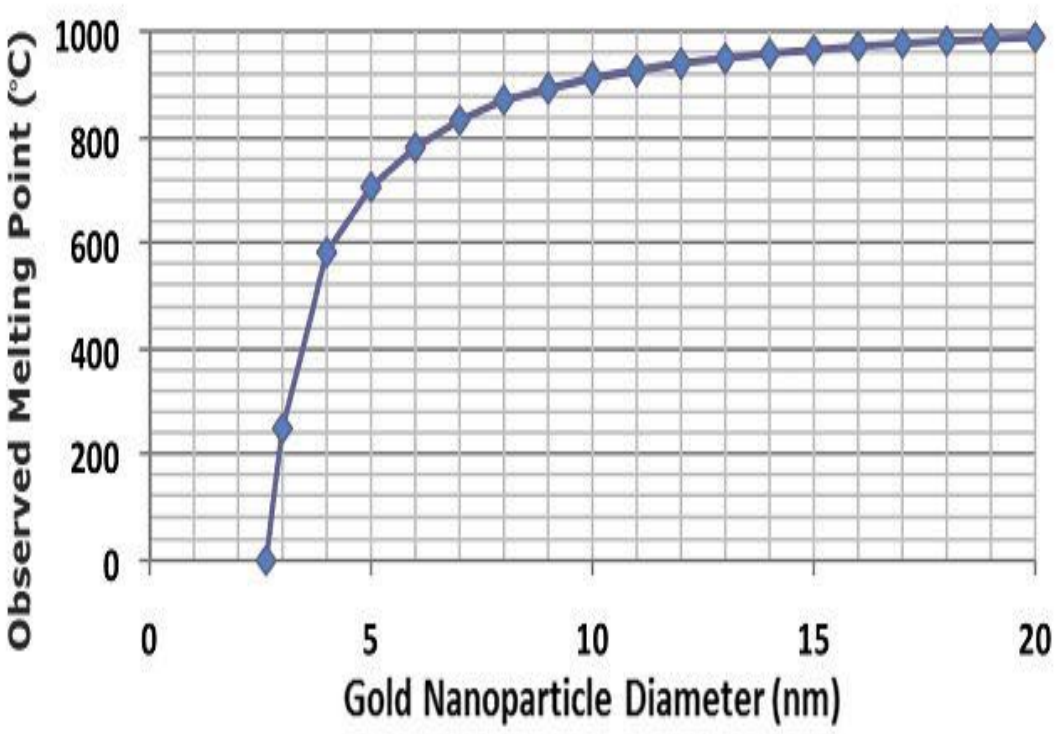
- **Bulk silicon appears grey in colour while nano sized silicon appears red in colour.**
- **Zinc oxide gives white appearance while nano scale zinc oxide appears transparent.**

Optical properties of nanomaterials are due

➢**to increase in energy level spacing- quantum size effect.**

➢ **Surface Plasmon resonance (SPR)**

Melting point:



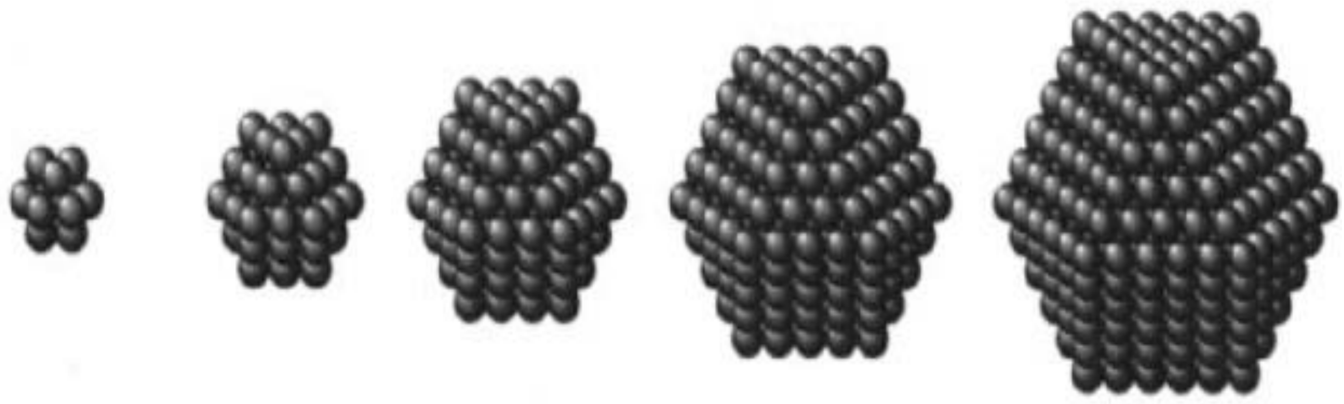
As the particle size decreases , the MP decreases due to the increase in surface energy with increase in surface area.

- **The dominance of electromagnetic force,**
- **The presence of quantum mechanical phenomena,**
- **The large surface area to volume ratio.**
- **Random (Brownian) motion**

So these all are main reasons which causes nano-scale sized particles to often have very different properties than their macro scale counterparts

Structure of nano materials:

- Nano particles of a atomic species can form stable configurations of structures when the inner layer of atoms are covered with one more layer of atoms.
- The optimal number of atoms that forms the stable configuration is called structural magic number.
- The total number of atoms required to form such particles is given by $N = 1/3(10n^3-15n^2+11n-3)$ where n= 1, 2, 3….. (FCC closed packing)



Structure of nano materials

If the cluster is spherical in shape then we can estimate the no of atoms on the surface of the cluster

$$= \frac{surface\ area\ of\ the\ cluster}{cross\ sectional\ area\ of\ the\ atom} = \frac{4\pi R_C^2}{\pi r_a^2}$$

$$volume\ of\ the\ cluster = no\ of\ atoms\ in\ the\ cluster \times volume\ of\ the\ atom$$

$$\frac{4}{3}\pi R_C^3 = N_a \times \frac{4}{3}\pi r_a^3 \qquad N_a = \frac{R_C^3}{r_a^3}$$

$$Surface\ area\ of\ the\ cluster = 4\pi R_C^2$$

$$\therefore no\ of\ atoms\ on\ the\ surface\ of\ the\ spherical\ cluster\ is = 4N_a^{2/3}$$

Estimation of Total number atoms & surface atoms:

Example:

Estimate the number of total number atoms and surface atoms in FCC gold nano particle with diameter 0.288 nm with 2 and 4 shells.

Total no of atoms $N = 1/3(10n^3 - 15n^2 + 11n - 3)$ **where** $n = 2, 4$

$N = ?$

Total number surface atoms $N_s = 10n^2 - 20n + 12$

$N_s = ?$

Estimation of Total number atoms & surface atoms:

Example:

Estimate the number of total number atoms and surface atoms in FCC gold nano particle with diameter 0.288 nm with 2 and 4 shells.

Total no of atoms $N = 1/3(10n^3 - 15n^2 + 11n - 3)$ **where n= 2, 4**

$N = ?$

Total number surface atoms $N_s = 10n^2 - 20n + 12$

$N_s = ?$

Estimation of Total number atoms & surface atoms:

- *n=1 gives N=1 where 100% of the atom on the surface.*
- *n=2 gives N=13 where 12 atoms (92%) are on the surface.*
- *n=3 gives N=55 where 42atoms (76%) are on the surface.*
- *n=4 gives N=147 where 92 atoms (63%) are on the surface.*

Example:

If 147 atoms are used in creating 13 atom nano particles . How many nano particles can we make ? How many atoms are at the surface? Which will have higher reactivity?

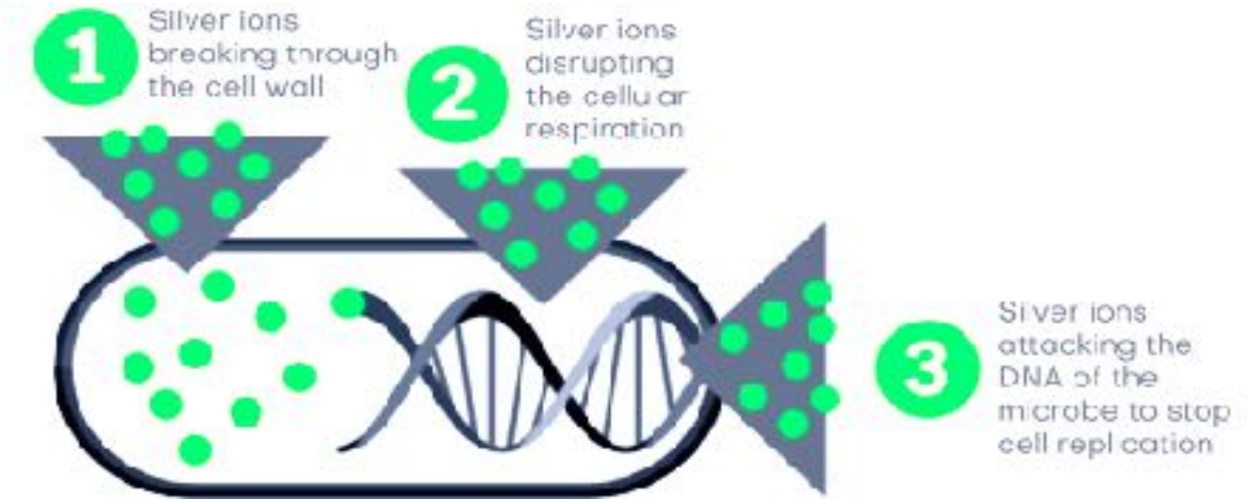
Positive impact of Nanomaterials:

- Some of the nanomaterials such as carbon nano-tubes (CNTs), zeolites, nanoparticles of zero valent iron (ZVI), silver nanoparticles can be used for remediation of water.
- nanomaterials like zinc oxide (ZnO), titanium dioxide (TiO_2), tungsten oxide, serve as a photo-catalyst. These photo-catalysts can oxidize organic pollutants into harmless material.
- To clean oil spills in the water bodies, a nano-fabric paper towel has been developed which are woven from tiny wires of potassium manganese oxide that can absorb oil 20 times its weight.
- A mixture of CNTs with gold particles helps adsorb toxic gases like NO_X, SO_2 and CO_2.
- A sensor called nano contact sensor has been developed which can detect the heavy metal ions and radioactive elements. These sensors have a small size, are inexpensive and are easy to use on-site.

Challenges of nanoscience and nanotechnology (negative Impact):

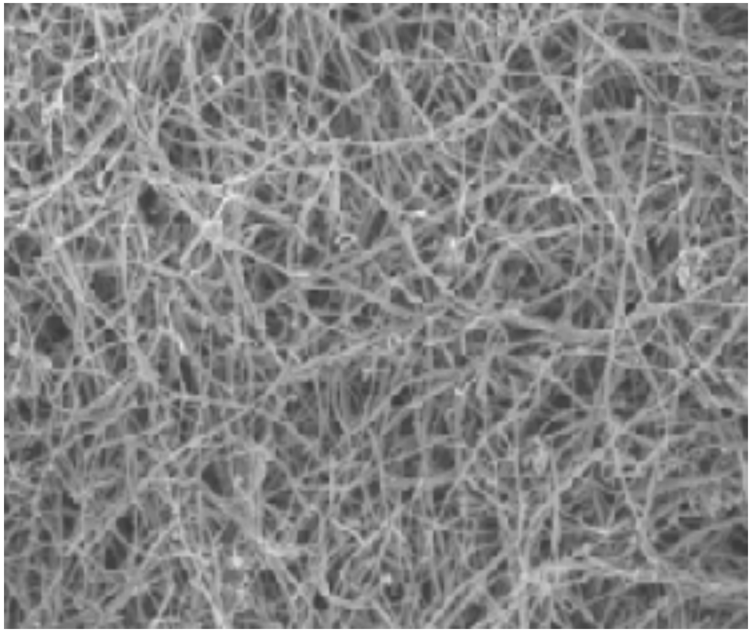
Effect of industry scale manufacturing of nanomaterials and nanotech on human health and environment??

Example: Bacteriostatic Silver Nanoparticles in your socks & shoes.



When released out, these nano particles are destroying bacteria's which are critical component of natural ecosystems, Farms and Waste treatment

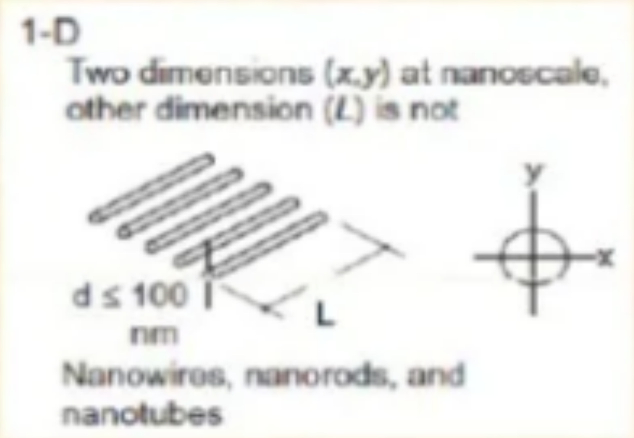
Nano-fibres:

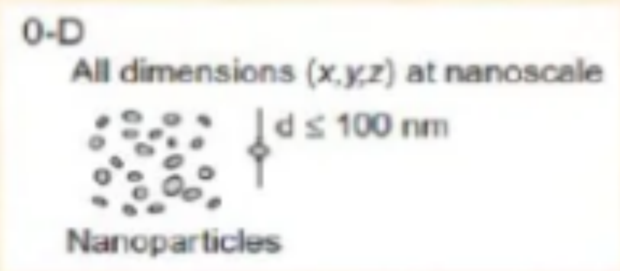


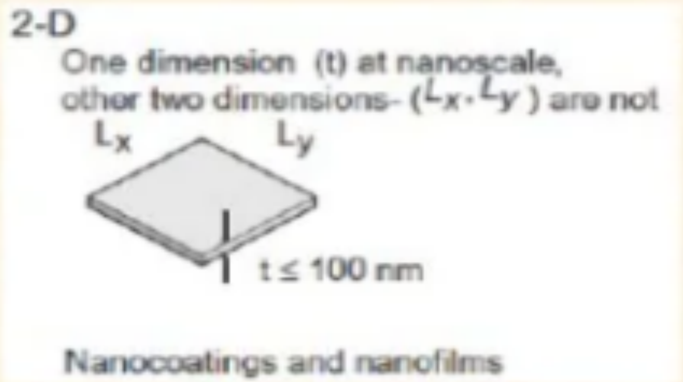
Mesothelioma is a malignant tumour that is caused by inhaled asbestos fibres' and forms in the lining of the lungs, abdomen or heart. CNT tubes also have similar effect like the asbestos .

CLASSIFICATION OF NANOMATERIALS:

- Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).
- (1) zero-dimensional (0-D),
- (2) one-dimensional (1-D),
- (3) two-dimensional (2-D), and
- (4) three-dimensional (3-D).







CLASSIFICATION OF NANOMATERIALS:

- Zero-dimensional (0D) nanomaterials all the dimensions are measured within the nano scale (no dimensions are larger than 100 nm). Example: 0D nanomaterials are nanoparticles, quantum dot.

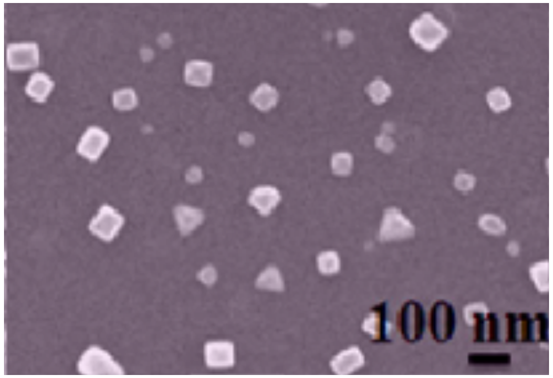
- One-dimensional nanomaterials (1D), one dimension is outside the nano scale. Example: nano-tubes, nano-rods, and nano-wires.

- Two-dimensional nanomaterials (2D), two dimensions are outside the nano scale. Example: graphene, nano-films, nano-layers, and nano-coatings.

- Three-dimensional nanomaterials (3D) are materials that are not confined to the nano scale in any dimension. Example: bulk powders, dispersions of nanoparticles, bundles of nano-wires, and nano-tubes as well as multi-nano-layers.

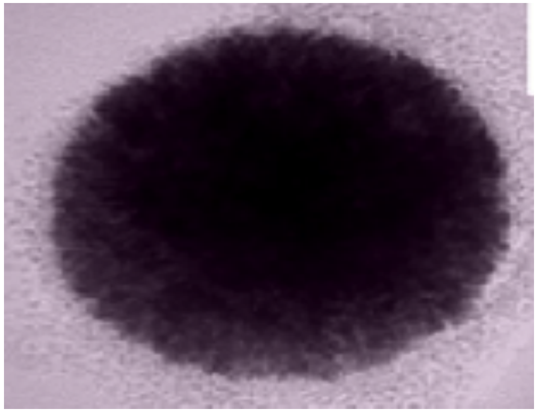
Zero-dimensional (0D) nanomaterials:

Zero-dimensional (0D) nanomaterials: **all the dimensions are measured within the nano scale (no dimensions are larger than 100 nm)**
Example: nanoparticles, Nanospheres



nanoparticles

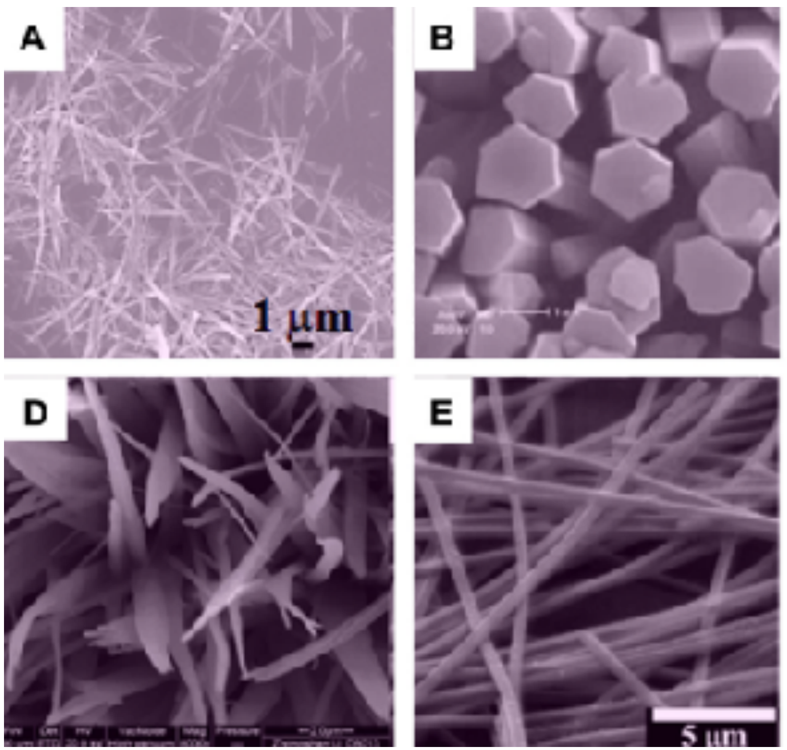
- Nanoparticles can:
- Be amorphous or crystalline
- Be single crystalline or polycrystalline
- Be composed of single or multi-chemical elements
- Exhibit various shapes and forms
- Exist individually or incorporated in a matrix
- Be metallic, ceramic, or polymeric



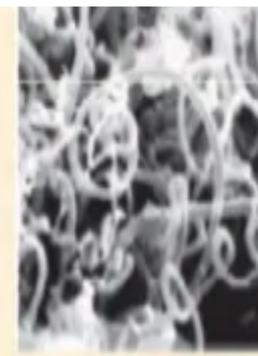
nanospheres.

One-dimensional nanomaterials (1D):

- One dimension that is outside the nanoscale.
- This leads to needle like-shaped nanomaterials.
- 1-D materials include **nanotubes, nanorods, and nanowires**.

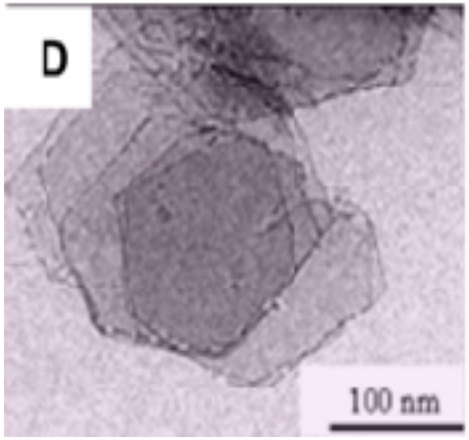


- 1-D nanomaterials can be
- Amorphous or crystalline
- Single crystalline or polycrystalline
- Chemically pure or impure
- Standalone materials or embedded in within another medium
- Metallic, ceramic, or polymeric



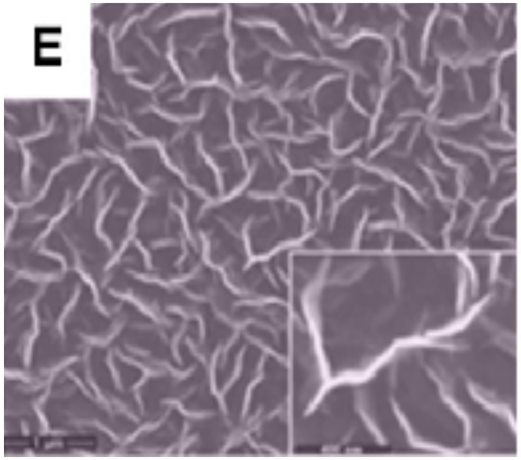
Two-dimensional nanomaterials (2D):

- Two of the dimensions are not confined to the nanoscale.
- 2-D nanomaterials exhibit plate-like shapes.
- Two-dimensional nanomaterials include **nanofilms, nanolayers, and nanocoatings.**



nanosheets

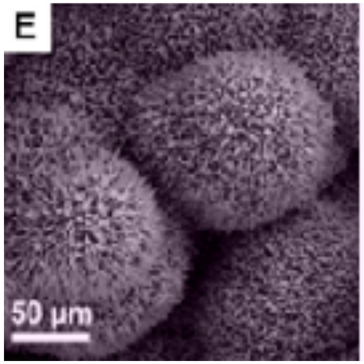
- **2-D nanomaterials** can be:
- Amorphous or crystalline
- Made up of various chemical compositions
- Used as a single layer or as multilayer structures
- Deposited on a substrate
- Integrated in a surrounding matrix material
- Metallic, ceramic, or polymeric



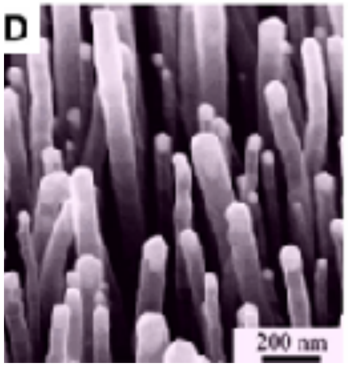
nanowalls

Three-dimensional nanomaterials (3D):

- **Bulk** nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.
- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple **arrangement of nanosize crystals**, most typically in different orientations.
- With respect to the presence of features at the nanoscale, **3-D nanomaterials** can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

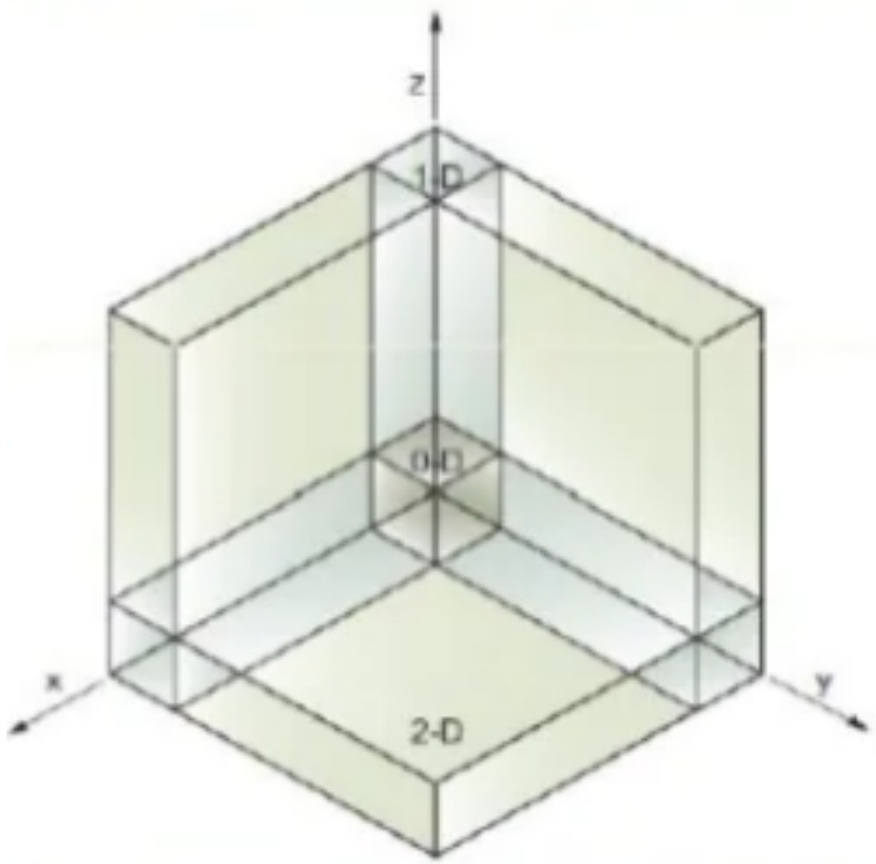


nanoflowers



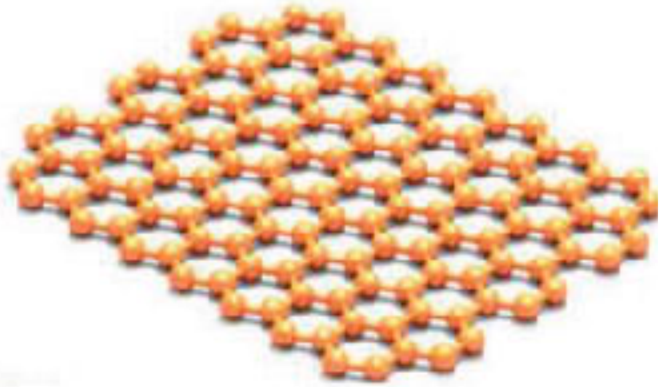
nanopillers

3 Dimensional Space – Showing the relation among 0D, 1D, 2D and 3D nanomaterials

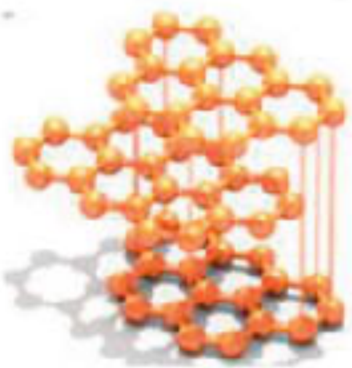


Allotropic forms of Carbon:

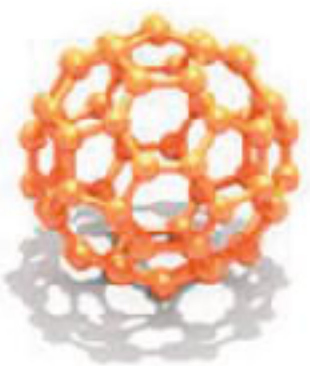
Nanotube



Graphene



Graphite



Fullerene

a) diamond
b) graphite
c) lonsdaleite (hexagonal diamond)
d) - f) fullerenes (C60, C540, C70);
g) amorphous carbon
h) carbon nanotube