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FIRST YEAR NOTES

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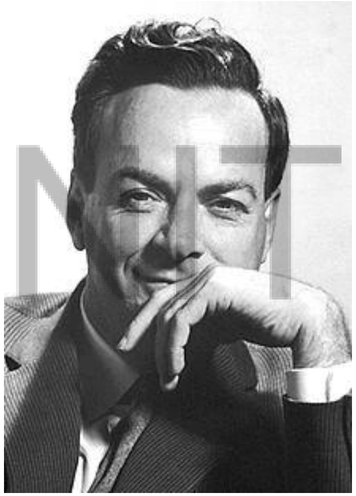
What is Nanoscience?

Way back in 1959, a physicist named Richard Feynman shared his vision of what very small things would look like and how they would behave. In a speech at the California Institute of Technology titled "There's Plenty of Room at the Bottom," Feynman gave the first hint about what we now know as "nanoscience"

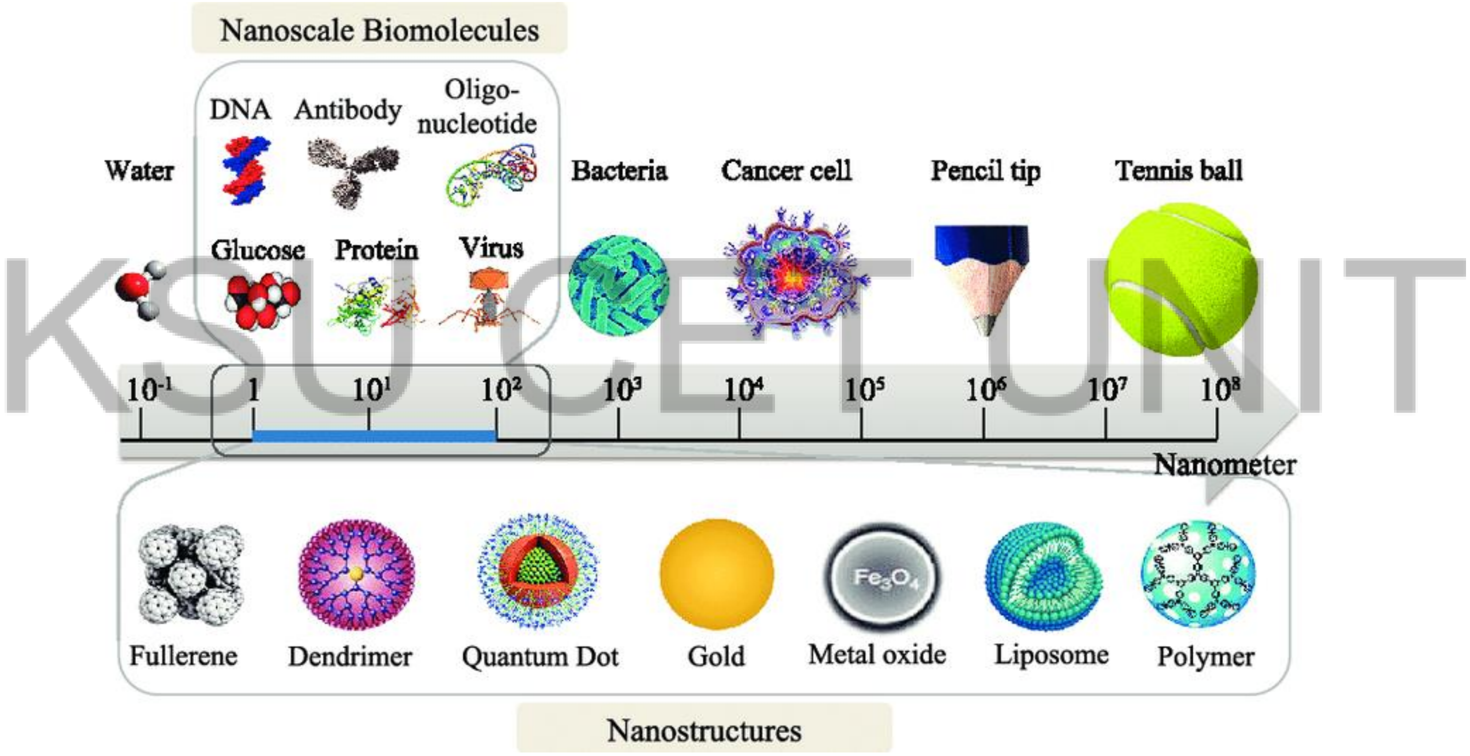
"The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom."



More generally, nanoscience is the study of the behavior of objects at a very small scale, roughly 1 to 100 nanometers (nm). One nanometer is one billionth of a meter, or the length of 10 hydrogen atoms lined up. Nanosized structures include the smallest of human-made devices and the largest molecules of living systems.

How small is Nano?

The word nano has its origin form the greek meaning "Dwarf". It is one billionth of a metre ($1/10^9$)



Hence Nanomaterials are defined as materials with at least one external dimension in the size range from approximately 1-100 nanometers whereas Nanoparticles are objects with all three external dimensions at the nanoscale.

What is the Big Deal About Nanoscience?

You might ask, "What is the big deal with nanoscience? Isn't it just a bunch of really small things?"

It is, in fact, a bunch of small things. But it is a whole lot more. What makes the science at the nanoscale special is that at such a small scale, different laws dominate over those that we experience in our everyday lives.

For example, the element gold (Au) has a nice yellowish-brown color -the color we know as "gold." However, if you had only gold atoms in nm sacle, color would be red.

Color is just one property (optical) that is different at the nanoscale. Other properties, such a flexibility/strength (mechanical) and conductivity (electrical) are often very different at the nanoscale as well.

Two factors that can affect Nano Scale properties

The nanoscopic scale is marked as the point where the properties of a material change;

- **ie, Above this point, the properties of a material are caused by 'bulk' or 'volume' effects, namely which atoms are present, how they are bonded, and in what ratios.**
- **Below this point, two principal factors cause the properties of nanomaterials to differ significantly from Bulk materials:**

1. **Increased relative surface area**
2. **Quantum effects**

These factors can change or enhance properties such as reactivity, strength and electrical characteristics. Hence materials with structure at the nano scale often have unique optical, electronic, or mechanical properties.

Relative surface area

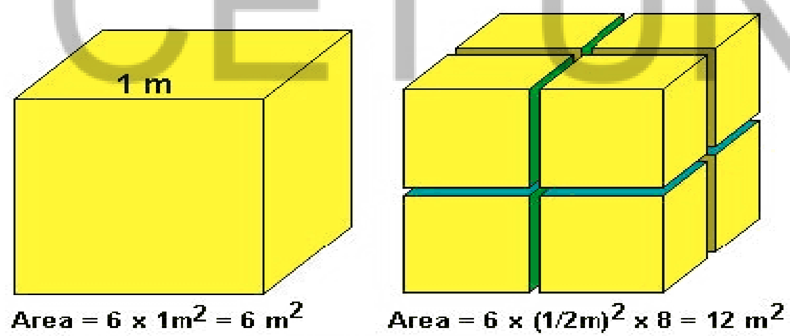
•As a particle decreases in size, greater proportion of atoms are found on the surface compared to those inside. For example of

• size-30 nm -> 5% of its atoms on its surface

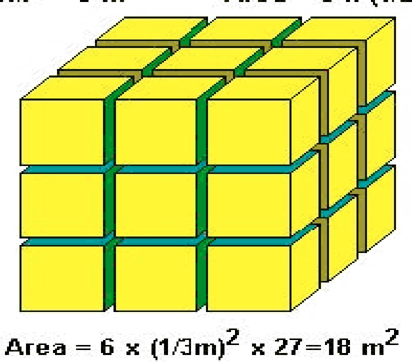
• size-10 nm->20 %of its atom on its surface

• size-3 nm-> 50 %of its atoms on its surface

Thus nanoparticles have much greater surface area per unit mass compared with larger particles.



For eg. See the figure



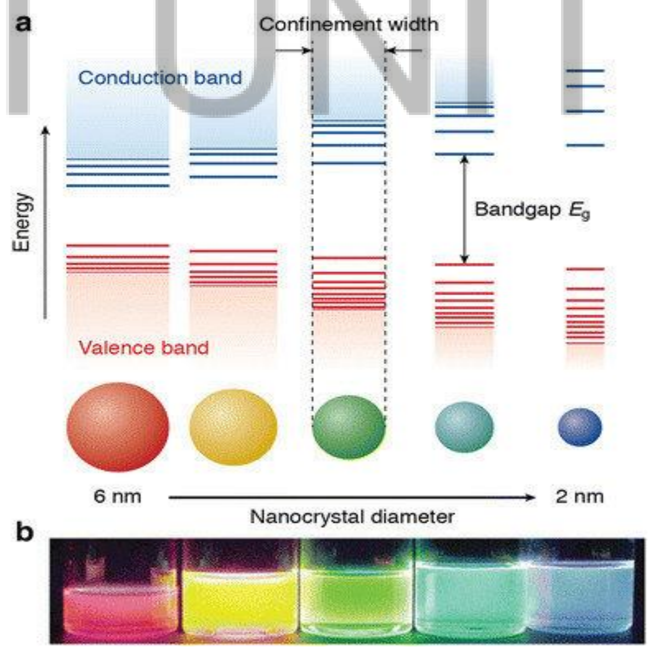
Quantum Effects

The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron.

- To understand this effect we break the words like quantum and confinement.
- The word confinement means to confine the motion of randomly moving electron to restrict its motion in specific energy levels.
- And quantum reflects the atomic realm of particles.

So as the size of a particle decrease till we a reach a nano scale, the following things happens.

- the decrease in confining dimension makes the energy levels discrete and this increases or widens up the band gap and ultimately the band gap energy also increases. See the fig.



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Sources of nanomaterials

(additional information, not in syllabus

Natural

Biological systems often feature natural, functional nanomaterials. The structure of viruses, natural colloids (blood and milk),horny materials (skin,beaks, feathers etc), paper, cotton, corals, and even our own bone matrix are all natural *organic* nanomaterials.

Engineered

Engineered nanoparticles are intentionally produced and designed with very specific properties related to shape, size, surface properties and chemistry. These properties are reflected in aerosols, colloids, or powders.

Incidental

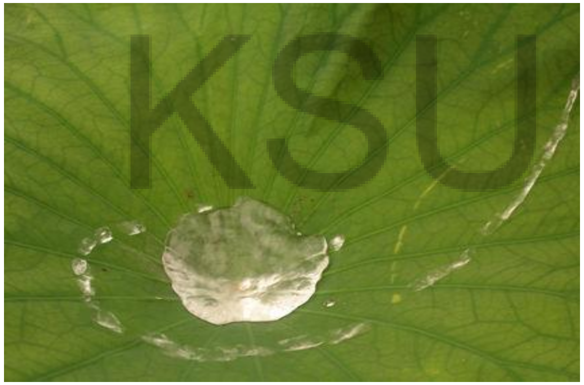
Nanomaterials may be incidentally produced as a byproduct of mechanical or industrial processes. Sources of incidental nanoparticles include vehicle engine exhausts, welding fumes, combustion processes from domestic solid fuel heating and cooking. For instance, the class of nanomaterials called fullerenes are generated by burning gas, biomass, and candle.It can also be a byproduct of wear and corrosion products.

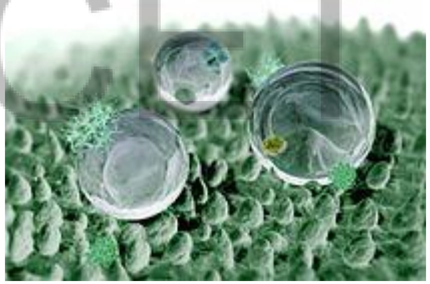
Natural Sources contd

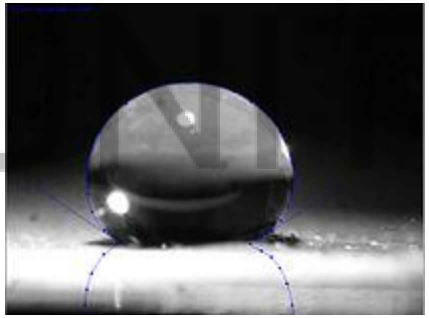
(additional information, not in syllabus

Lotus Effect

It refers to self-cleaning properties that are a result of ultrahydrophobicity as exhibited by the leaves of "lotus flower". Dirt particles are picked up by water droplets due to the micro- and nanoscopic architecture on the surface, which minimizes the droplet's adhesion to that surface







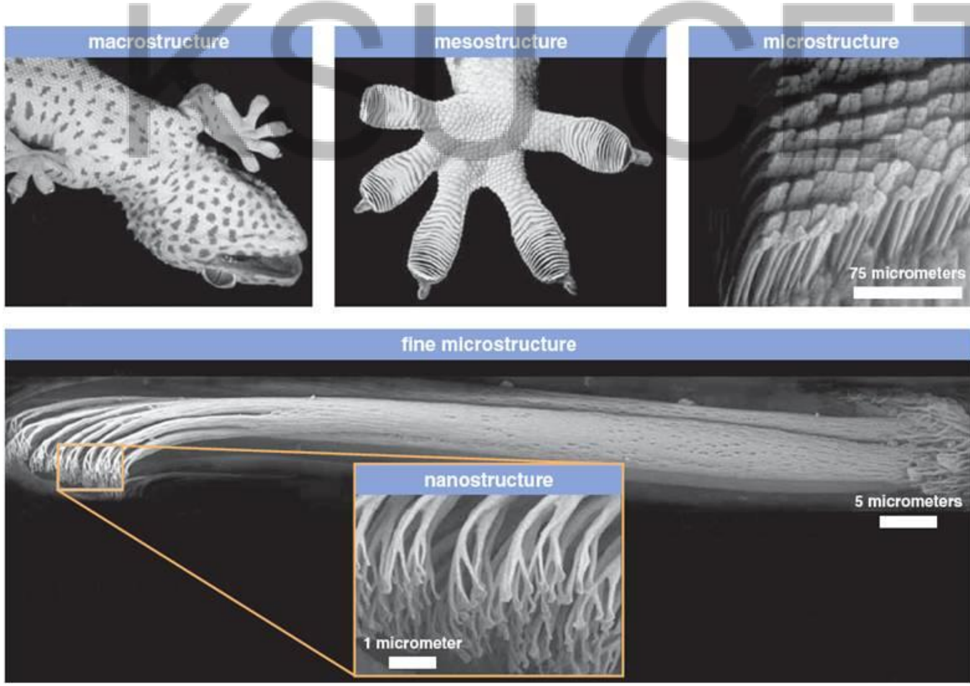
Application

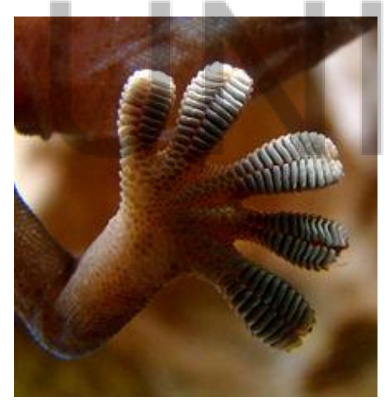
Nanotechnologists have developed treatments, coatings, paints, roof tiles, fabrics and other surfaces that can stay dry and clean themselves by replicating in a technical manner the self-cleaning properties of plants, such as the lotus plant. This can usually be achieved using special fluorochemical or silicone treatments on structured surfaces or with compositions containing micro-scale particulates.

Natural Sources contd

(additional information, not in syllabus

The interactions between the **gecko's feet** and the climbing surface are stronger than simple surface area effects. On its feet, the gecko has many microscopic hairs, or setae (singular seta), that increase the Van der Waals forces - the distance-dependent attraction between atoms or molecules - between its feet and the surface. These setae are fibrous structural proteins, which is made of β-keratin, the basic building block of human skin.

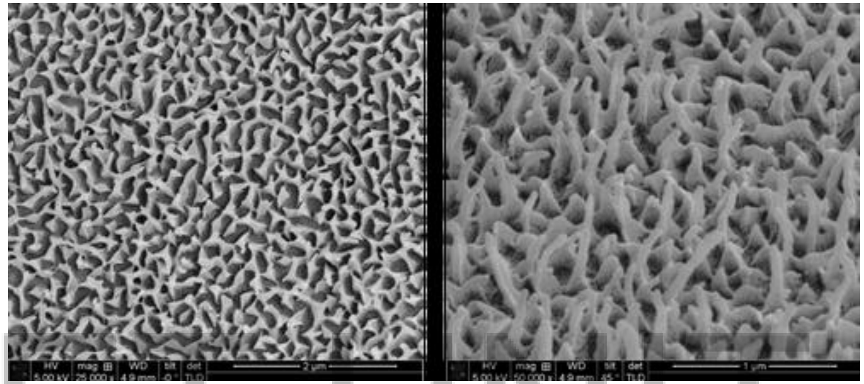




Natural Sources contd

(additional information, not in syllabus

Nanostructures in butterfly wings



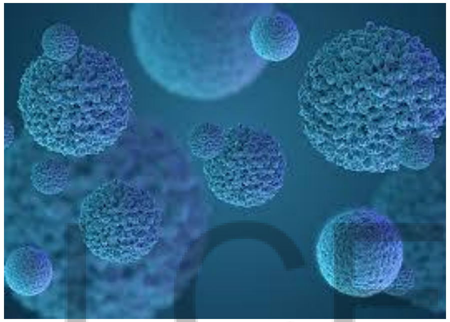
Glass wing butterflies have sections of their wings that are see-through. These "glass" sections confuse their predators while they fly. This property is called optical transparency, which means all the light that goes into the wing continues out the other side, just like with real glass. But what makes this possible? When you look at the transparent parts of a glass wing butterfly under a scanning electron microscope, you can see a lot of randomly sized nano-pillars. It is the random size and shape of the pillars that makes the glass wing butterflies transparent from any direction.

Note: Iridescence is the phenomenon of certain surfaces that appear to gradually change color as the angle of view or the angle of illumination changes. Examples of iridescence include soap bubbles, feathers, butterfly wings .

Classification based on Dimension

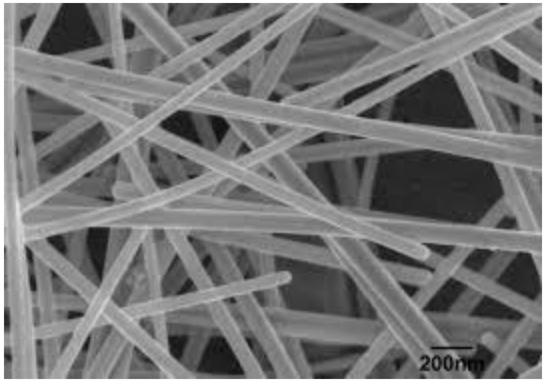
1. **Zero Dimension(0-D):** Here all the three dimensions are in the nanometric range.

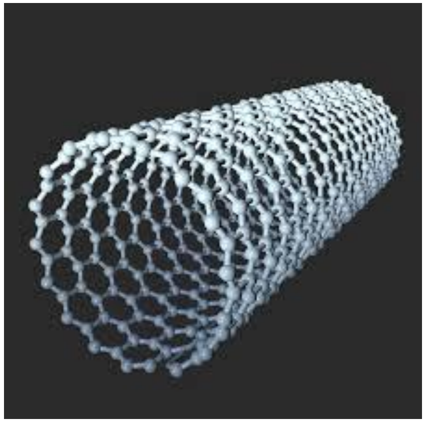
eg: nanoparticles



2. **One Dimension (1-D):** Here one of the dimensions is outside the nanometric range and the other two are within the range. eg: nanowires, fibres and tubes.

Silver nanowires

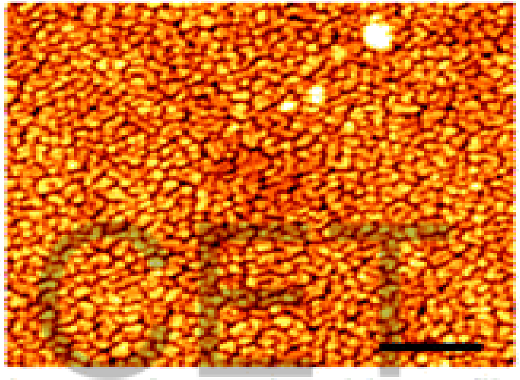




Carbon nanotubes

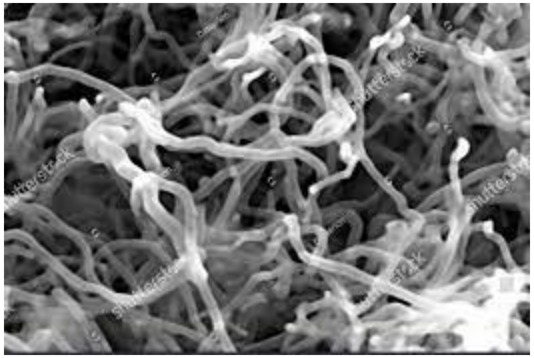
Classification based on Dimension

3. Two Dimension (2-D): Here two of the dimensions are outside the nanometric range and one is within the range. eg: Nanofilms, layers and coatings.



Thermo-plasmonic gold nanofilm

4. Three Dimension (3-D) : Here all the dimensions are outside the nanometric range (>100 nm). eg: bundles of nanowires and tubes, multinanolayer.

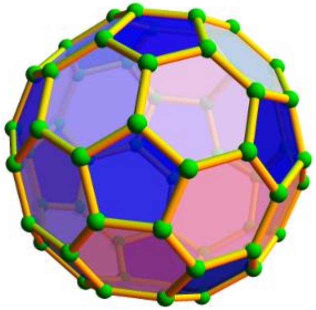


Nanotube bundles-SEM image

Classification based on Materials

1.Carbon based Nanomaterials:

Materials in which the nano component is pure carbon.



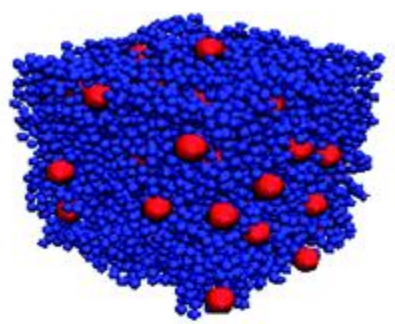
eg: CNT, wires, spheres(fullerenes).

2. Metal based nano materials:

Made of metallic nanoparticles like gold, silver metal oxides etc. Eg: Titanium dioxide.

3. Nano composites:

Composite materials contain a mixture of simple nanoparticles or compounds such as nanosized clays within a bulk material. The nano particles give better physical/chemical properties.

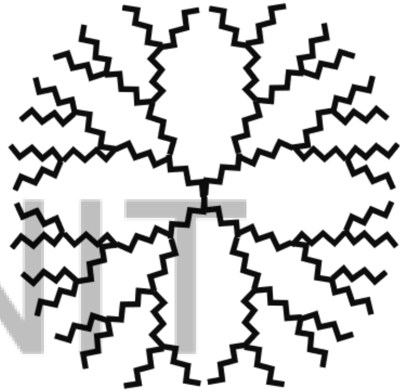


Snapshot of polymer nanocomposites

Classification based on Materials

4. Nano polymers or dendrimers:

they are nano sized polymers built from branched units. These are tree like molecules with defined cavities. They can be functionalized at the surface and can hide molecules in their cavities (drug delivery).



5. Biological Nanomaterials:

they are of biological origin. The important features are (1) self assembly properties. (2)Specific molecular recognition.
eg DNA nano particles, nanostructured peptides.

Chemical Synthesis of nanoparticles

Synthesis of nano particles can use physical or chemical methods. Two important chemical methods are discussed here, Hydrolysis and Reduction.

1. Hydrolysis

Nano particles of metal oxides can be prepared by hydrolysis of their alkoxide solutions under controlled conditions. Commercially important nanoparticles of SiO2, TiO2 and Al2O3 are prepared by this method.

$$Ti(OR)_4 + 2H_2O \longrightarrow TiO_2 + 4ROH$$

a) Hydrothermal synthesis

- **Process involves the heating a solution inside a steel bomb under high pressure (between 1 atm and 1000 atm) and temperature (100 to 1000^{o}C) that facilitates the interaction of precursors during synthesis.**

- **If water is used as the solvent, the method is called hydrothermal synthesis. Synthesis under hydrothermal condition usually performed below the supercritical temperature of water (374^{o}C)**

Chemical Synthesis of nanoparticles

- It can be used to prepare nanoparticles of various geometries including thin films, bulk powders, single crystals and nanocrystals.

- The morphology of the crystals (Sphere(3D), Rod(2D) or wire 1(D) can be controlled by the solvent super saturation, concentration and kinetic control.

b) Sol-Gel Method

➢ The sol-gel method is based on the phase transition of a sol into a gel.

➢ A sol is a colloidal system of nano solid particles dispersed in a liquid.

➢ A gel is a colloidal system in which liquid droplets are dispersed in a network of solid nano-particles.

➢ Hydrolysis of metal alkoxides or metal salts can give a sol at a suitable temperature and pH. The sol contains many impurities. In order to remove impurities, sol is transformed to a gel by changing the pH or other factors.

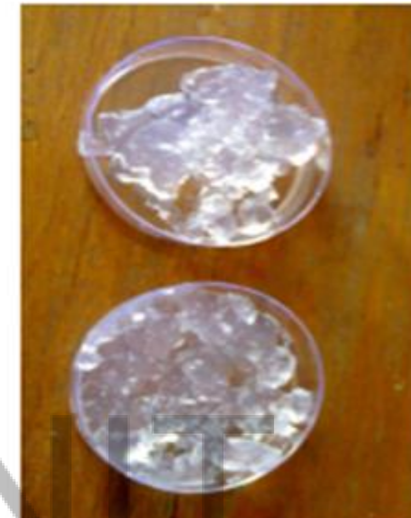
➢ The gel can be purified by filtration and washing with suitable solvents. The purified gel on drying give solid nanoparticle.

Chemical Synthesis of nanoparticles

Eg: Aluminium oxide nanoparticles are obtained by hydrolysis of Aluminium Alkoxide by sol-gel technique.

$Al(OR)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3ROH$

Sol



Gel

- **A sol is a colloidal or molecular suspension of solid particles of ions in a solvent.**
- **A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network .**

Chemical Synthesis of nanoparticles

2. Reduction

- Prepared by the reduction of their respective solutions.
- Reducing agents used: NaBH4, Ascorbic acid, Glucose etc.
- Protective agents: Thyol, Gucose etc.
- Classified in to two Reduction using Reducing Agent & Electro reduction.

Preparation of silver nano particles

a) Reduction using Reducing Agent

Take 60mL of 1mM $AgNO_3$ solution in a beaker covered with a watch glass

↓ Heating (hotplate) Stirring (Magnetic Stirrer)

On Boiling 6mL of 10mM Trisodium citrate added dropwise@one drop/sec

↓

The beaker is then closed and kept for sometime till the colour of the solution changed to a light golden colour. The solvent is removed by freeze drying.

Chemical Synthesis of nanoparticles

b) Electro Reduction

Eg: Cu nano particles have ben prepared by electro reduction process using copper plating bath containing homogeneously acidified copper sulphate solution. The nanoparticles are formed as spongy black coloured layers of ball structures at the cathode. The spongy layers of copper can be easily separated to give fine particles.

In conclusion, Nanoscience is the study of extremely small things which are in the nano range and Nanotechnology is the application of these materials in various fields such as in medicine, industries, electronics, textiles etc.

Applications of Nanotechnology

- Magnetic nano-composites are used as ferrofluids (It is a liquid that becomes strongly magnetised in the presence of a magnetic field), high density information storage and magnetic refriferation.

- Nanostructured metal-oxide thin films are used as gas sensors (for CO, CO_2 etc)

- Nano semiconductors are used as window layers in solar cells.

- carbon nanotubes based transistors used for miniaturizing elctronic devices.

- carbon nanotubes are used for making paper batteries.

- A mixture of carbon nanotubes and fullerenes is used for making solar cells.

- Nanomedicine is the medical application of nanotechnology where nanoparticles based treatment are used for tumours.

- Nano-cadmium-telluride exhibit different colour depending upon its size. It can be used for dyeing fabrics such as nano colourants never fades.

Model questions

1. Discuss the classification of nanomaterials?
2. Discuss the classification of nanomaterials based on dimension?
3. Explain hydrothermal synthesis of metal oxide nanoparticles?
4. Write a note on sol-gel method?
5. Explain elctro reduction and chemical reduction methods for the production of nanoparticles?
6. Give different chemical methods of preparation of nanoparticles?
7. Give the properties and application of nanomaterials?