

Nanotechnology is the study of the control of matter on an atomic scale. Generally, Nanotechnology deals with structures of the size 100 nanometres or smaller and involves developing materials or devices within that size. These are known as Nanostructures.

Nanomaterials could be defined as those materials which have structural components with size less than 100nm at least in one dimension.

- Materials that are Nano scale in one dimension (and are extended in the other two dimensions) are layers, such as thin films or surface coatings.
- Materials that are Nano scale in two dimensions (and are extended in one dimension) include nanowires and nanotubes.
- Materials that are nanoscale in three dimensions are particles, for example, precipitates, colloids, and quantum dots (tiny particles of semi-conductor devices)

Surface area to volume ratio

Surface area to volume ratio in nanoparticles have a significant effect on the nano particles properties. Firstly, nanoparticles have a relative larger surface area when compared to the same volume of the material.

For example, let us consider a sphere of radius r :

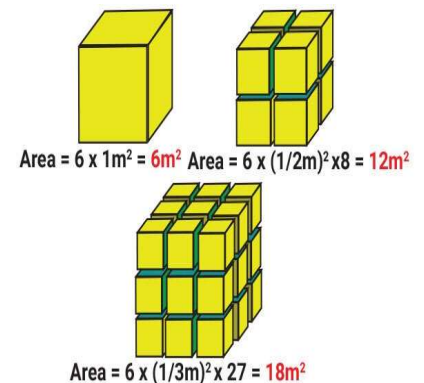
The surface area of the sphere will be $4\pi r^2$.

The volume of the sphere = $\frac{4}{3} \pi r^3$

Therefore, the surface area to the volume ratio will be $\frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

- It means that the surface area to volume ration increases with the decrease in radius of the sphere and vice versa.
- Similarly, as shown in figure, surface area increases with decrease in size of cube.
- It can also be concluded here that when given volume is divided into smaller piece, the surface area increases.
- Therefore, as particle size decreases, a greater portion of the atoms are found at the surface compared to those inside.

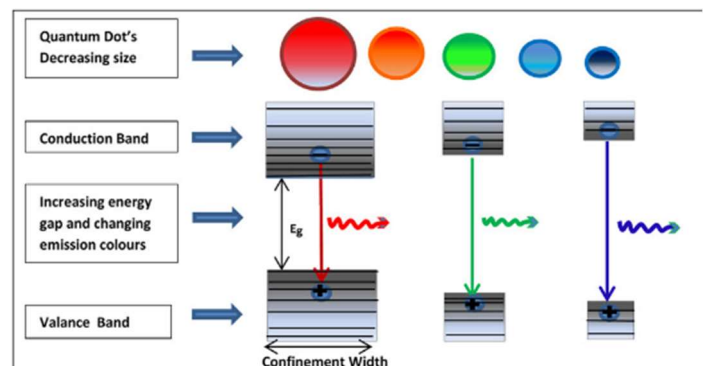
A particle of size 3 nm has 50% of its atoms on its surface, at 10 nm 20% of its atoms and at 30 nm has 5% of its atoms on its surface. The materials which are inert in their bulk form are reactive when produced in their nanoscale form.



Quantum Confinement:

Quantum Confinement is the spatial confinement of electron-hole pairs (excitons) in one or more dimensions within a material and electronic energy levels are discrete.

- Firstly, the high surface to volume ratio that results in the presence of many atoms at the surface in the crystalline lattice.
- Secondly, the electronic bands are spilt up into discrete energy levels and three-dimensional confinement of the charge carriers occurs.
- This leads to quantum confinement of charge and results in the increasing bandgap with decreasing particles size.
- If the dimensions of potential wells or potential boxes are of the order of the de Broglie wavelength of electrons (mean free path of electrons), then the



energy levels of electrons change, and the electron will remain confined to a small region of the material.

Physical properties of Nano Materials:

At the macro scale, the physical and chemical properties are not dependent on the size of the material, but at the nanoscale, everything, including colour, melting point and chemical properties will change, compared to what they exhibit on a macro scale.

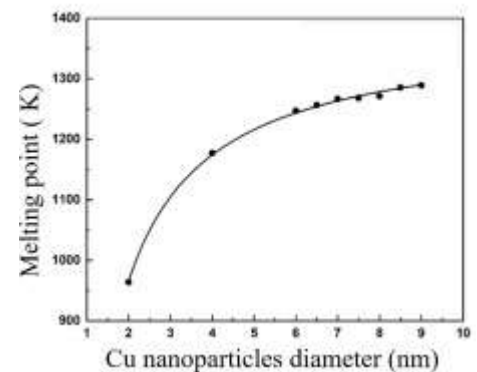
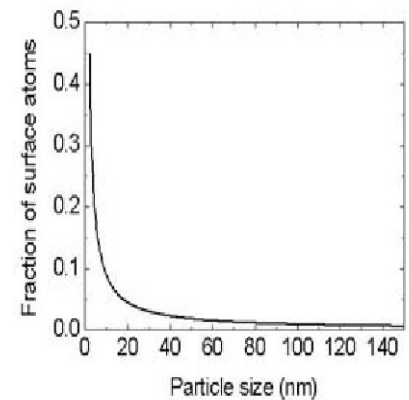
Interatomic spacing:

In nanoscale the reduction in particle size creates more surface sites and surface to volume ratio increases. The change in surface pressure results in change in the inter particle spacing.

The interatomic spacing decreases with size.

Melting Point:

The change in surface to volume ratio and interatomic spacing results in variation of surface free energy and thermal properties. Therefore, **decrease in interatomic spacing results in decrease in melting point.** The melting point of nanogold decreases from 1200K to 800K as the size of the particles decreases from 300 Å to 200 Å. For example, when the crystallite size of gold is reduced to around 2 nm, its melting point reduces from 1064°C to about 500°C



Production of Nanomaterials:

Nanomaterials can be produced by a number of ways. Nanomaterials can be synthesized by “**top down**” techniques, producing very small structures from large pieces of the material. One way of doing this is, mechanically crushing of the solid into fine nano powder (ball milling). Nanomaterials may also be synthesized by “**bottom up**” techniques, atom by atom or molecule by molecule. One way of doing this is to allow the atoms or molecules, arrange themselves into a structure, due to their natural properties. Ex: crystal growth.

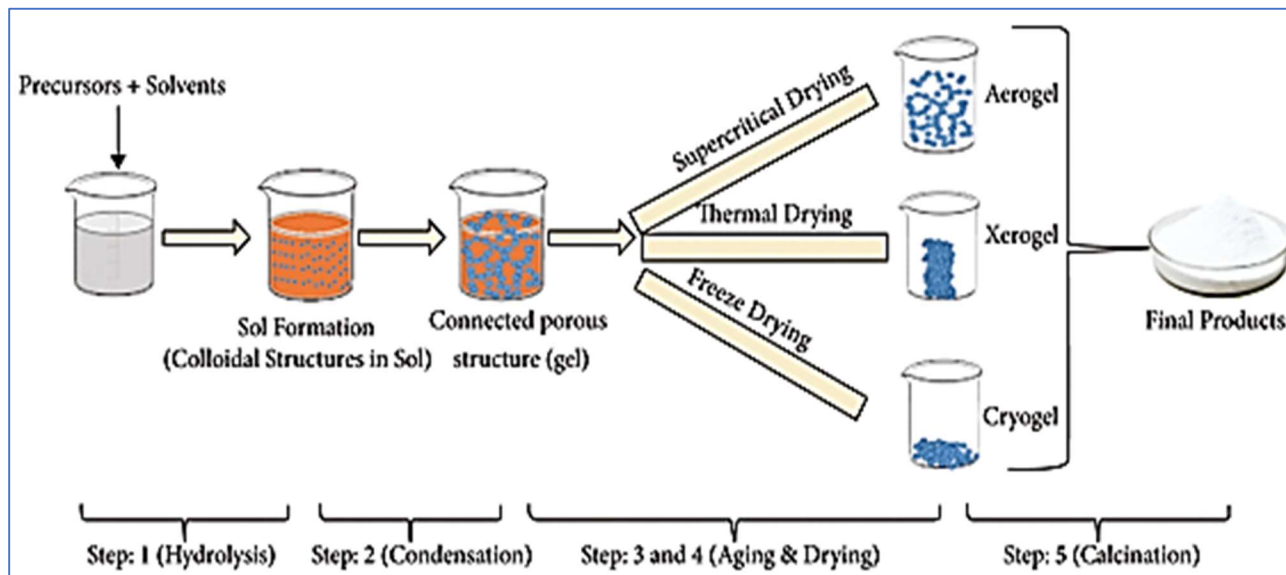
Bottom-up approach of nanomaterial synthesis:

Sol-Gel method

- The sol-gel process is a wet chemical method for the synthesis of various nanostructures, especially metal oxide nanoparticles.
- In solutions, nanosized molecules are dispersed randomly whereas in colloids, the molecules have diameters in the range of 20µm-100µm and are suspended in the solvent. So, the colloid appears cloudy.
- A colloid that is suspended in a liquid is called a **Sol**. The gelation of the sol in the liquid to form a network is called gel. Gel is the suspension that keeps its shape.

Sol-gel formation occurs in different stages.

In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis.



Step-1: Hydrolysis

- During hydrolysis reaction, a larger molecule forms two (or more) smaller molecules and water is consumed as a reactant and sol is formed.

Step-2: Condensation and polymerization

- During Condensation, the vapours are condensed and during polymerization, smaller molecules, called monomers or building blocks, are chemically combined to create larger molecules. Agglomeration of particles which is the process of forming powdered and particle-based materials into a larger mass.

Step-3: Aging

- During being aged, the sol will continue to react chemically, and sol particles agglomerate to become larger which eventually crosslink to form a **colloidal gel**.

Step-4: Drying

- The water and other liquids entrapped within the pores of the gel structure are removed during this stage.
- Drying the gel by means of low temperature treatments (25–100 °C), it is possible to obtain porous solid matrices called xerogels.
- Aerogels are formed when frozen at -70°C and dried under a vacuum. Cryogels are formed in normal frozen conditions.

Step-5: Calcination:

- In this stage, the morphology of nanomaterials will be improved.
- Calcination is performed at increased temperatures varying within the range 750-1470°F (400-800°C)

Step-6: Final powder in nano size.

- The final gel is powdered and collected.

Characterization of Nanomaterials

The characterization technique that is employed for the characterization of Nanomaterial depends on the type and application of the nanomaterial. For all Nanomaterials, particle size determination is essential, and this can be done using X-ray diffraction and Electron microscopy.

X-ray Diffraction Method:

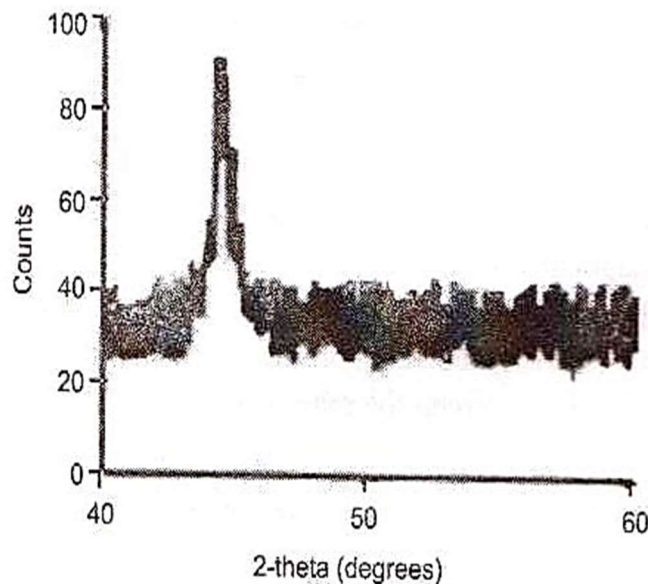
- Phase identification using X-ray diffraction lies mainly on the position of the peaks in the diffraction profile and to some extent on the relative intensities of these peaks.
- The shape, particularly the width of the peak is a measure of the amplitude of thermal vibrations of the atoms at their regular lattice sites.
- It can also be a measure of any deviations from the normal structure.

Ex: Plastic deformation, impurity doping, second phase addition to the host phase. When X-ray powder pattern is taken on poly crystalline powders, the crystallite size causes peak broadening. The crystallite size is easily calculated as a function of peak width, specified as Full Width at Half Maximum (FWHM), peak position and wavelength.

The average crystallite size 'L' is given by,

$$(L)_{\text{Vol}} = \frac{K\lambda}{W \cos \theta_B}$$

Where, θ_B is the Bragg's angle W is FWHM of the diffraction peak; K (0.91) is a constant and λ is the wavelength of X-rays used.



Scanning Electron Microscopy (SEM)

The image in scanning electron microscope is produced by scanning the sample with a focused electron beam and detecting the secondary and back scattered electrons. Electrons and photons are emitted at each beam location and subsequently detected.

Schematic representation of SEM

- 1) The electron gun produces a stream of monochromatic electrons.
- 2) The electron stream is condensed by the first condenser lens. It works in conjunction with the condenser aperture to eliminate the high angle electrons from the beam.
- 3) The second condenser lens forms the electrons into a thin, light coherent beam.
- 4) Objective aperture further eliminates high angle electrons from the beam.
- 5) A set of coils acting as electrostatic lens scans and sweeps the beam in a grid fashion (as in television)
- 6) The objective lens focuses the scanning beam onto the part of the specimen.
- 7) When the beam strikes the sample, interaction occurs. The intensity of display is determined by the interaction number. More interactions give a brighter pixel.
- 8) This process is repeated until the grid scan is finished and then repeated. The entire pattern can be scanned 30 times per second.

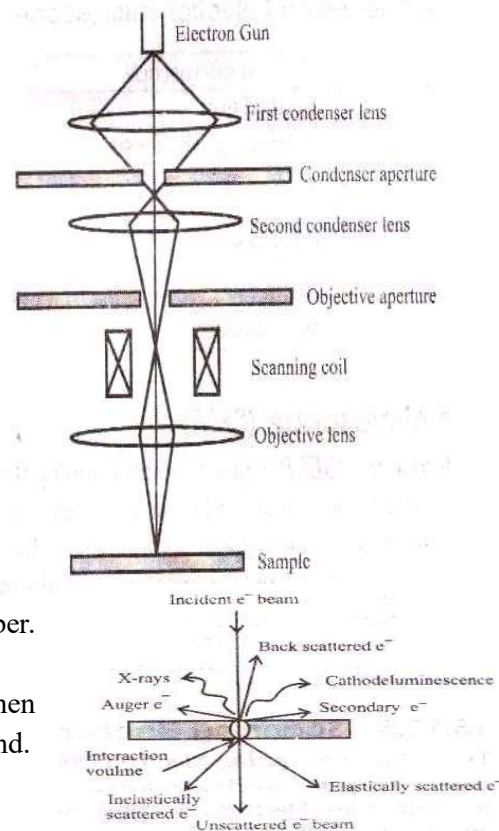


Fig.3.5 Specimen interactions in SEM

SEM gives useful information on

- 1) **Topography:** The surface features of an object or “how it looks,” its texture, detectable features, limited to a few nano meters.
- 2) **Morphology:** The shape, size and arrangement of particles making up the objects that are lying on the surface of the sample or have been exposed by grinding or chemical etching, detectable features limited to a few nano meters.
- 3) **Composition:** The elements and compounds the sample is composed of and their relative ratios, in areas approximately 1 micrometer in diameter.
- 4) **Crystallographic Information:** The arrangement of atoms in the specimen and their degree of order, only useful on single-crystal particles >20 μms .

Applications of Nanotechnology**1. Electronics industry**

- Reduction in size of electronic components leads to faster switching times.
- Nanotechnology includes fabrication of nanowires used in semiconductors.
- Porous silicon emits visible light. So, it finds application in optoelectronics.
- Quantum dot laser emits good quality laser beam compared to semiconductor laser diodes. They are cheaper and the emitted wavelength depends on the diameter of the dot.
- Materials like nanocrystalline selenide, zinc sulphide, lead telluride and cadmium sulphide synthesized by sol-gel method improve the resolution of the image in television or in a monitor. The resolution depends on the size of the pixel made of phosphors. The resolution increases as the size of the pixel reduces.
- Batteries made of nanocrystalline nickel and metal hydrides are long lasting and require minimal recharging.

2. Industry

- Nanocrystalline materials such as tungsten carbide, titanium carbide are harder than conventional materials. They are more wear resistant and erosion resistant. So, they can be used in cutting tools and drilling bits.
- Nanocrystalline silicon nitride and silicon carbide are used in the manufacturing of high strength springs, ball bearings and valve lifters.
- Nanocrystalline ceramics such as zirconia are easily pressed and sintered into various shapes at lower temperatures, because they are softer than conventional materials.

3. High power magnets

- The magnetic strength of a material is directly proportional to the surface area per unit volume.
- The magnetic nanocrystalline yttrium-samarium-cobalt possesses very high magnetic properties due to large surface area.
- The high-power rare-earth magnets are used in submarines, generators, electric motors, automobile alternators, magnetic resonance imaging (MRI) instruments and in ultrasensitive analytical instruments.

4. Motor vehicles and aircraft

- The wastage of thermal energy generated in engines is reduced by coating the cylinders with nanocrystalline ceramics such as zirconia and alumina.
- In aircraft, by decreasing the grain size of the materials, the fatigue strength increases as much as 300 %. The components made of nanomaterials are stronger and operate at higher temperatures. So, aircraft can fly faster using the same amount of aviation fuel.

5. Aero gels

- Aero gels are nanocrystalline and porous. Hence, air is trapped at the interstices. These materials can be used in offices and homes to reduce cooling and heating bills by saving power. These are also used for smart windows so that the materials become darkened when the sun is too bright and lightened when the sun is not shining brightly.

6. Energy efficiency

- Energy consumption can be greatly reduced by using quantum edged atoms or LEDs instead of ordinary filament bulbs.
- Nanostructures have increased solar energy conversion efficiency as compared to ordinary semiconductor solar cells.
- In hydrogen fuel cells, nanostructured catalyst material is used on carbon supported noble metal particles, with diameters between 1 & 5nm.
- For hydrogen storage, CNTs, zeolites etc., are used.

7. Medical field

- Nanomaterials are used in the development of diagnostic devices, drug delivery vehicles, and analytical tools and in physical therapy applications.
- The genetic sequence of a sample can be detected by tagging gold nanoparticles with short segments of DNA.
- Magnetic nanoparticles are used to label molecules, structures or micro organisms of an antibody.
- Iron nanoparticles are used in cancer treatment. Nanotechnology is used to repair or to reproduce damaged tissue.

8. Textile industry

Clothes made of nanofibers are water and stain repellent and wrinkle free. They can be washed less frequently at low temperatures.

9. Information technology

Nanoscale fabricated magnetic materials are used in data storage. Quantum computers use fast quantum algorithms and have quantum bit memory space (qubit). So, it involves several computations at the same time.

10. Cosmetics

- Sunscreens based on mineral nanoparticles such as titanium-di-oxide offer several advantages. They have high UV protection compared to the bulk material. In addition to these, there are quantum dots, suntan lotion, nanotubes, and protective coatings.
- Fullerenes (C_{60}) are used as lubricants (molecular ball bearings), diamond seeding, diamond protection, xerographic materials, photo chronic goggles etc.