UNIT-V

NANOMATERIALS

Introduction :

In 1959, Richard Feynman made a statement ‘there is plenty of room at the bottom’. Based on his study he manipulated smaller units of matter. He prophesied that “we can arrange the atoms the way we want, the very atoms, all the way down”. The term ‘nanotechnology’ was coined by Norio Taniguchi at the University of Tokyo. Nano means 10^{-9}. A nano metre is one thousand millionth of a metre (i.e. 10^{-9}m). Nanomaterials could be defined as those materials which have structured components with size less than 100nm at least in one dimension. Any bulk material we take, its size can express in 3-dimensions. Any planer material, its area can be expressed in 2-dimension. Any linear material, its length can be expressed in 1-dimension.

In recent years nanoscience and technology is emerging as one of the most and exciting areas of interest in all fields of science and technology.

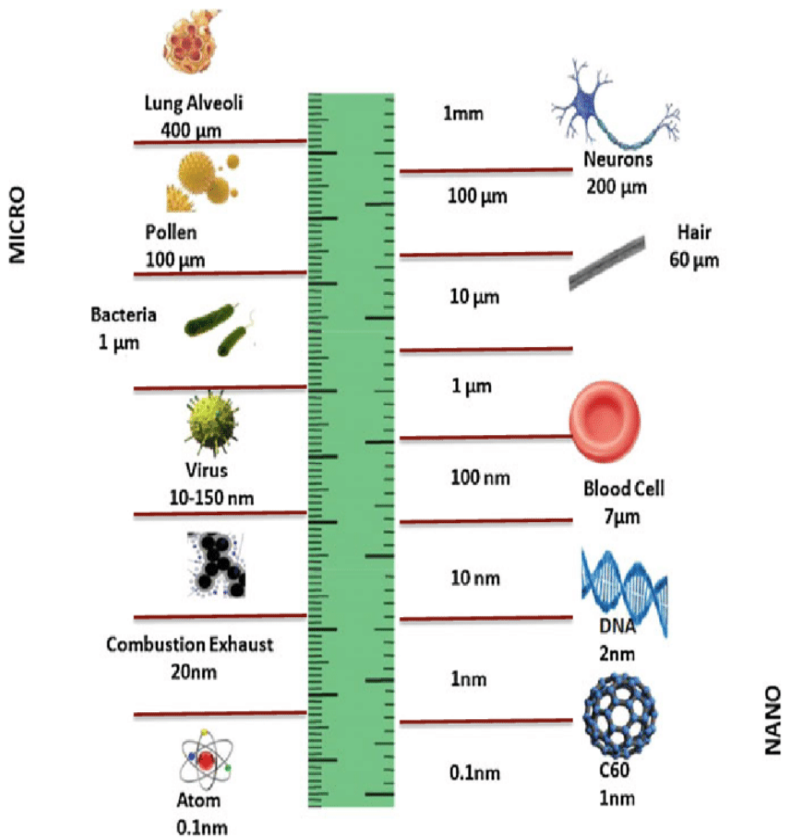
Nanotechnology is designed to provide a novel and improved approach to cancer diagnosis and treatment. Nanoscale devices can interact with large biological molecules on both the surface and inside cells involved in cancer.

Nanotechnology has a vast range of applications, such as in medicine, electronics, biomaterials, solar cells, sporting goods, lasers, displays, aerospace, **nano**-foods, textiles, cosmetics and energy production. **Nanotechnology** can transform vapors escaping from cars or industrial plants into harmless gasses.

5.1 Nanoscale :

Nano means 10^{-9} m, i.e., A nanometre is one billionth of a meter.

- Size of the atom -0.1 to 0.5 nm
- Carbon atom – 0.15 nm
- Water Molecule – 0.3 nm
- Red Blood Cell - 7,000 nm
- Human hair – 50,000 nm-80,000 nm
- Nano Scale : The scale which lies between 1 – 100 nm is called as Nanoscale.



Significance of Nano Scale:

- When the particle size is reduced to nano scale due to increase in surface area to volume ratio and Quantum confinement the properties (Physical, chemical ,optical, electrical, thermal, mechanical, magnetic etc.,) of nano materials are different form bulk materials. Due to this change of properties from bulk nano materials have wide applications in the field of science and technology.

5.2 Nano materials:

- The materials which have structured components with size less than 100 nm at least in one dimension are known as Nano materials.
- **One dimensional Nano materials** : Materials that are in nano scale only in one dimension are known as One dimensional Nano materials. Ex: Thin films ,surface coatings.
- **Two dimensional Nano materials** : Materials that are in nano scale in two dimensions are known as Two dimensional Nano materials. Ex: Nano wires and Nano tubes.

- **Three dimensional Nano materials** : Materials that are in nano scale in all three dimensions are known as three dimensional Nano materials. Ex: Quantum dots, nano crystalline materials.

5.2.1 Classification of Nano materials :

Nano materials are broadly classified into two types. They are

- Fullerenes
- Inorganic nanoparticles (or) Nanoparticles

1.Fullerenes :

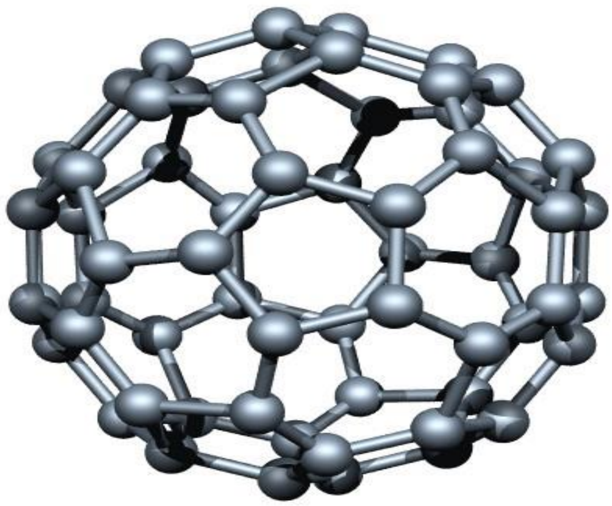
Fullerenes are the allotropes of carbon in which graphene sheets are rolled down into sphere or tubes.

Depends upon the type of rolling fullerenes are classified into two types. They are

- Spherical Fullerene
- Cylindrical Fullerene

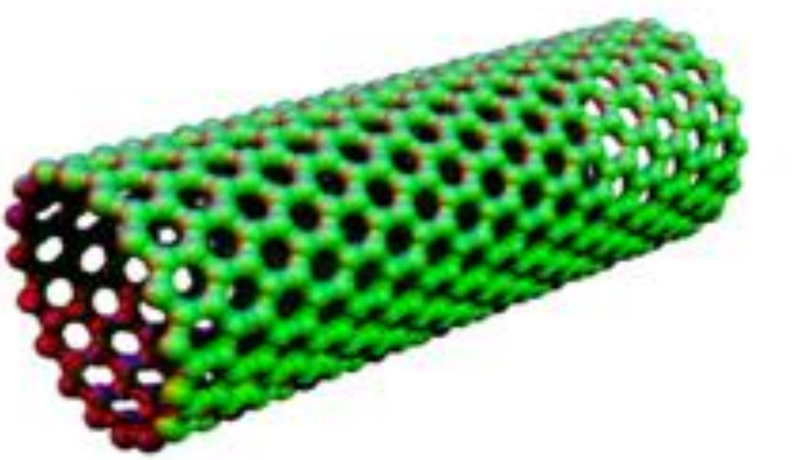
(i) Spherical Fullerene:

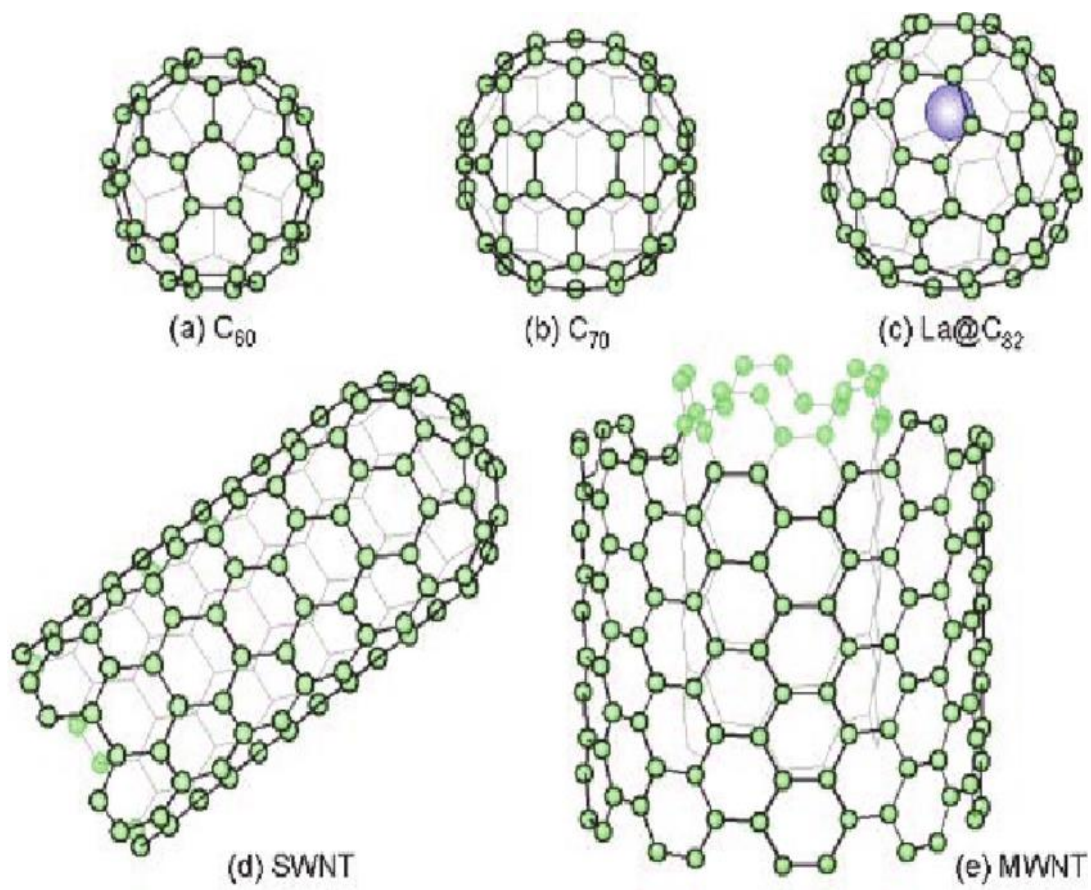
- When the graphene sheet is rolled down in the form of sphere then the spherical fullerenes are formed. They are also known as Bucky balls.
- The first Bucky ball was buckminsterfullerene C_{60} in 1985.



(ii) Cylindrical Fullerene:

- When the graphene sheet is rolled down in the form of cylindrical shape then the cylindrical fullerenes (or) Carbon Nano tubes are formed.
- Carbon nano tubes have novel properties. They exhibit extraordinary strength and unique electrical properties. They are potentially useful in many applications in nanotechnology, electronics, optics and material science.





2.Nano Particles :

Nanoparticles sized between 1 to 100 nm are available in different forms. They are

1.**Nanoclusters**: They have dimension between 1 to 100 nm and a narrow size distribution

2.**Nanopowders**: Agglomerates of nanoclusters.

3. **Nanocrystals:** Nanometre sized single crystals.

4. **Nano colloids** : Nano particles suspended in liquids

5.**Quantum dots**: They are tiny particles of semiconductor materials. They are man-made nanoscale crystals that that can transport electrons. When UV light hits these semiconducting nanoparticles, they can emit light of various colors. These artificial semiconductor nanoparticles that have found applications in composites, solar cells and fluorescent biological labels.

5.3 Basic Principles of Nano materials (Why the properties of nano materials are present from Bulk):

The properties of nanomaterials are different from bulk due to the following two factors

1.Increase Surface area to volume ratio

2.Quantum Confinement.

1.Increase Surface area to volume ratio :

Nano materials have relatively larger surface area when compared to the bulk material of same volume.

Let us consider a sphere

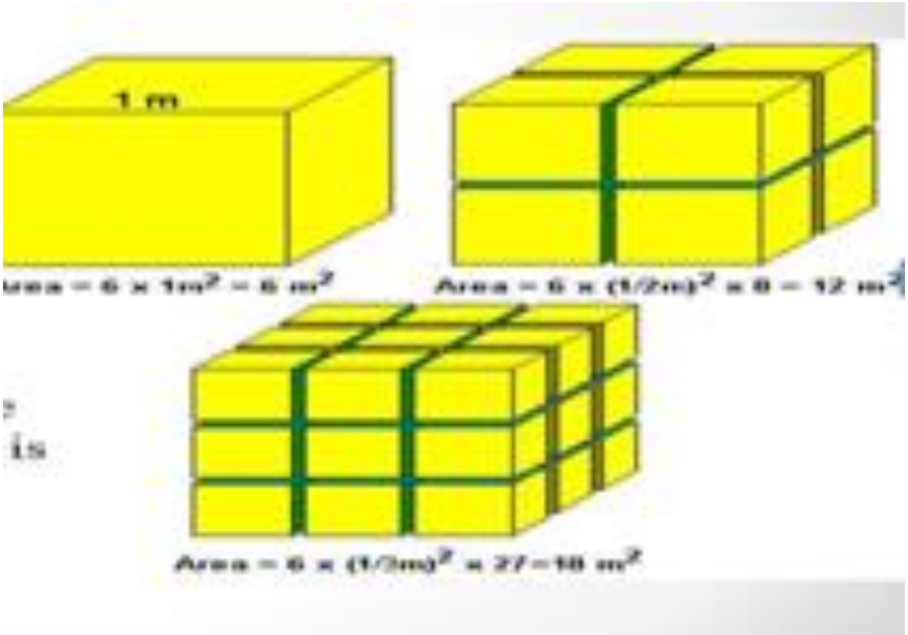
Surface area of sphere = $4\pi r^2$

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

Surface area to volume ratio =$\frac{3}{r}$

That means when the radius of the sphere decreases ,its surface area to volume ratio increases.

Let us consider another example cube of 1 m each side, then surface area of the cube is 6 m^2. If each side of the cube is divided into two equal parts then surface area becomes 12 m^2. If each side of the cube is divided into three equal parts then surface area becomes 18 m^2. If each side of the cube is divided into 'n' equal parts then surface area of the cube becomes n times.



When the particle size decreases a greater proportion of atoms are found at the surface compared to those inside.

For example a particle size is 30 nm then 5 % of atoms are present on its surface. If a particle size is 10 nm then 20% of atoms are present on its surface. If a particle is 3 nm then 50% of atoms are present on its surface.

It makes materials more chemically reactive. As growth and catalytic chemical reactions occur at surfaces, hence nano particles are much more reactive than the bulk.

In some cases materials that are inert in bulk will reactive when the particle size is reduced to nano scale.

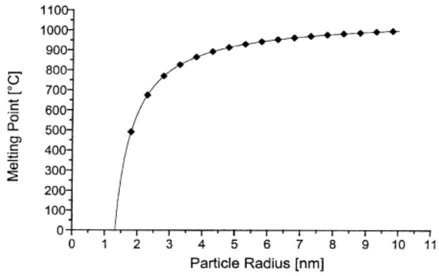
2. Quantum Confinement:

- When atoms are isolated, energy levels are discrete or discontinuous. When very large number of atoms is closely packed to form a solid, the energy levels split and form bands. Nano materials represent intermediate stage.
- When dimensions of potential well and potential box are of the order of De-Broglie wave length of electrons or mean free path of electrons, **then energy levels of electrons changes**. This effect is called Quantum confinement effect.
- These can affect the optical, electrical and magnetic behaviour of materials.

5.4 Properties of nano materials

The physical, optical, magnetic, mechanical and thermal properties of materials depend on size. Small particles behave differently from those of individual atoms or bulk.

Physical properties: The effect of reducing the bulk into particle size is to create more surface sites i.e. to increase the surface to volume ratio. This changes the surface pressure and results in a change in the inter particle spacing. Thus the inter atomic spacing decreases with size.



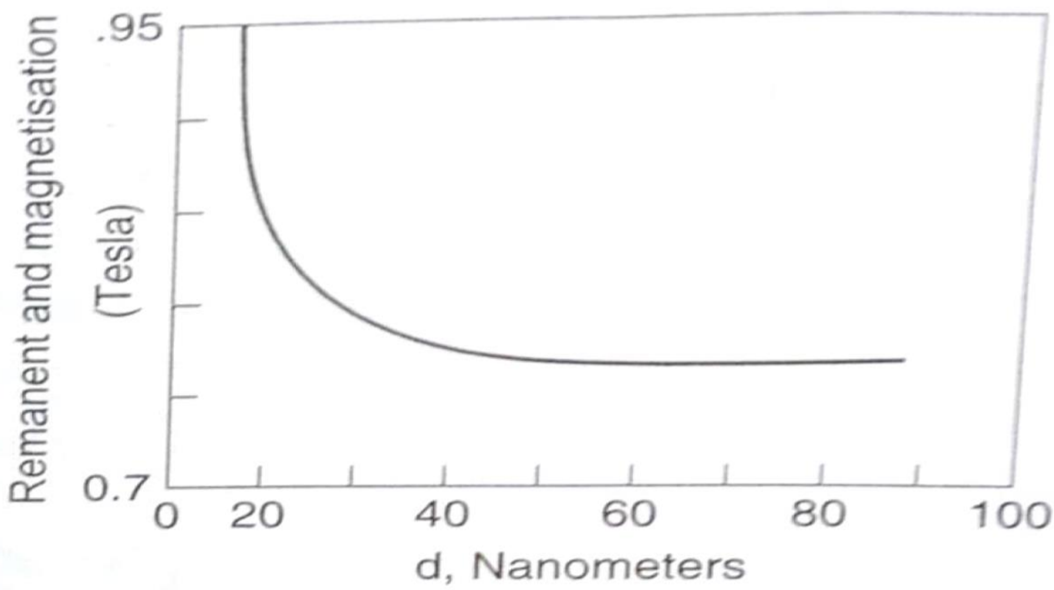
The change in the inter particle spacing and the large surface to volume ratio in particle have a combined effect on material properties. Variation in the surface free energy changes the chemical potential. This affects the thermodynamic properties like melting point. The melting point decreases with size and at very small sizes the decrease is faster.

Another important application is hydrogen storage in metals. Most metals do not absorb, hydrogen is typically absorbed dissociatively on surfaces with hydrogen- to- metal atom ratio of one. This limit is significantly enhanced in small sizes. The small positively charged clusters of Ni, Pd and Pt and containing between 2 and 60 atoms decreases with increasing cluster size. This shows that small particles may be very useful in hydrogen storage devices in metals.

Optical properties: Depending on the particle size, different colors are seen. Gold nano spheres of 100nm appear orange in colour while 50nm nano spheres appear green in colour. If semiconductor particles are made small enough, quantum effects come into play, which limits the energies at which electrons and holes can exist in the particles. As energy is related to wavelength or colour, the optical properties of the particles can be finely tuned depending on its size. Thus particles can be made to emit or absorb specific wavelength of light, merely by controlling their size.

An electro chromic device consist of materials in which an optical absorption band can be introduced or existing band can be altered by the passage of current through the materials, or by the application of an electric field. They are similar to liquid crystal displays (LCD) commonly used in calculator and watches. The resolution, brightness and contrast of these devices depend on tungstic acid gel's grain size.

Magnetic properties: The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume) of the grains.



- Nano particle of even non-magnetic solids are found to be magnetic. It has been found theoretically and experimentally that the magnetism special to small sizes and disappears in clusters. At small sizes, the clusters become spontaneously magnetic.
- Nano materials have size dependent magnetic behaviour. In small ferromagnetic particles, the magnetic properties are different from that of the bulk material. At nanoscale, the magnetic material has a single magnetic domain.

Mechanical Properties:

If the grains are nano scale in size, the interface area with in the material greatly increases, which enhances its strength. Because of the nano size many mechanical properties like hardness, elastic modulus, fracture toughness, scratch resistance, fatigue strength are modified.

Grain refinement leads to an improvement in the properties of the metals and alloys. A reduction in grain size lowers the transition temperature in steel from ductile to brittle.

The average grain size and yield strength are related by

$$\sigma = \sigma_0 + \frac{k}{\sqrt{d}}$$

Similarly hardness and grain size

is given by H= $H_V + \frac{k}{\sqrt{d}}$

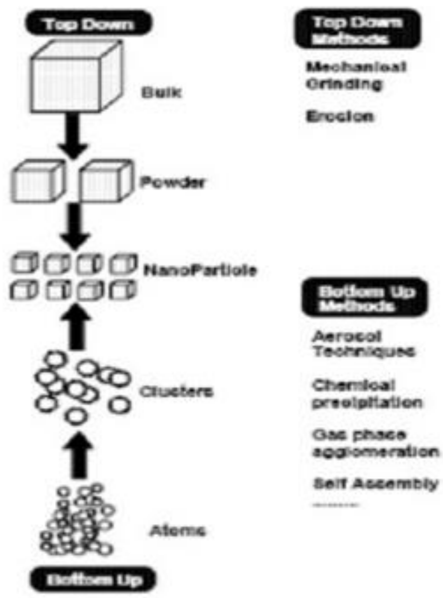
Super plasticity is the capability of some polycrystalline materials to exhibit very large texture deformations without fracture. Super plasticity has been observed occurs at somewhat low temperatures and at higher strain rates in nano crystalline material.

Thermal Properties:

There is a change in thermal properties of some materials as they go from bulk to nano particles.

- The melting point of nanogold decreases from 1200 K to 800 K as the size of the particle decreases from 300 $A^0$to 200 A^0.
- Stable aluminium becomes combustible in nanophase
- Solid gold changes into liquid as it goes bulk to nanomaterial
- Super plasticity occur at lower temperature by reducing grain size.
- The Debye temperature and ferroelectric phase transition temperature are lower for nanomaterials.
- The diffusion co-efficient and solid state phase transition pressure are high for nanomaterials.

<u>5.5 SYNTHESIS OF NANOMATETIALS</u>:



Nano materials can be synthesized by' top down' techniques producing very small structures from larger pieces of material. One way is to mechanical crushing of solid into fine nano powder by ball milling.

Example: 1. Ball milling , 2. Laser sputtering , 3. Plasma arching

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 arranges themselves into a structure due to their natural properties.

Example: 1. Sol-gel method , 2. Electrodeposition, 3. Chemical Vapour deposition.

All the synthesis/deposition techniques are divided into two categories based on the phase of starting material

Top-Down approach

In Top-down techniques, the starting material is solid state

Physical processing methods:

- ✓ Mechanical methods :
  - cutting , etching, grinding
  - ball milling
- ✓ Lithographic techniques:
  - Photo Lithography
  - Electron Beam Lithography

Bottom-Up approach

All the Bottom-up techniques, the starting material is either gaseous state or liquid state of matter

- Physical and chemical processing methods:

Physical techniques-

Physical Vapor Deposition (PVD): involves condensation of vapor phase species
- Evaporation (Thermal , e-beam)
- Sputtering
- Plasma Arcing,
- Laser ablation,

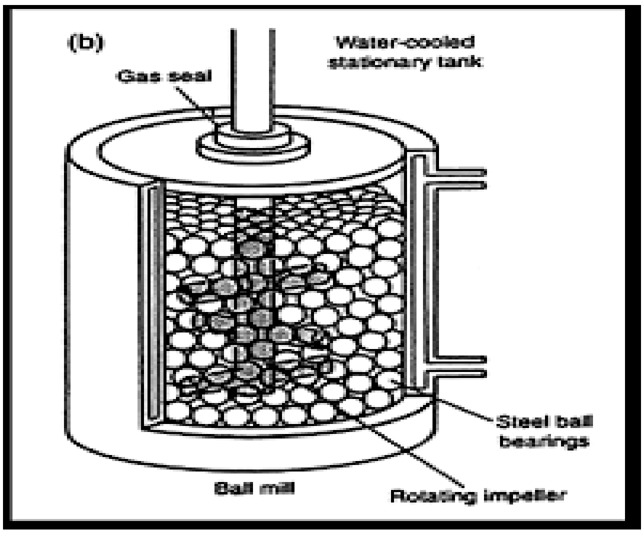
Chemical techniques-

CVD: Deposition of vapor phase of reaction species
- PECVD(RF-PECVD,MPECVD)

Self-assembled Monolayer :
Electrolytic deposition, Sol-gel method, Microemusion route, pyrolysis.

Ball Milling :

Ball Milling (or) Attrition Ball Milling (or) Mechanical crushing method is an example for typical Top-Down fabrication method. Ball milling can be used to prepare a wide range of elemental and oxide powders. Ball milling is the preferred method for preparing metal oxides.



Construction:

1. It consists of stationary steel vessel. The capacity of the vessel is approximately 500 ml.
2. Inside the vessel it consists of shaft and the hardened steel or tungsten balls are attached to it.
3. The shaft is connected to the motor.
4. The vessel is closed with tight lid as shown in the figure.

Principle: The basic principle in this is small hard balls are allowed to rotate inside a container and then it is made to fall on a solid base with high force to crush the solid into nanoparticles.

Working :

1. The material from which nano material has to extract is to be placed in the vessel (or) container.
2. When the balls are rotated around the crystal axis, the material is forced to press against the balls.
3. The milling balls impart energy on collision and produce smaller grain size of nanoparticles.
4. Depends on the number of grinding hours required size of nanoparticles can be obtained.
5. In order to increase rate of reaction surfactants like Ethylene glycol, n-heptane are to be added.

Advantages:

1. Inter metallic oxides of nanoparticles can be extracted.
2. Using this method few milligrams to several kilograms of nanoparticles can be extracted.
3. This technique can be operated at large scale.
4. Operation is very easy.

Disadvantages:

1. Due to long grinding hours vibrations are more and strong foundation is required.
2. Large amount of noise is produced due to long grinding hours.
3. Contamination of product may occur as a result of wear and tear which occurs principally from the balls and partially from the casing.

Applications:

1. This method is useful in producing new types of building materials, fire proof materials, glass ceramics etc.,

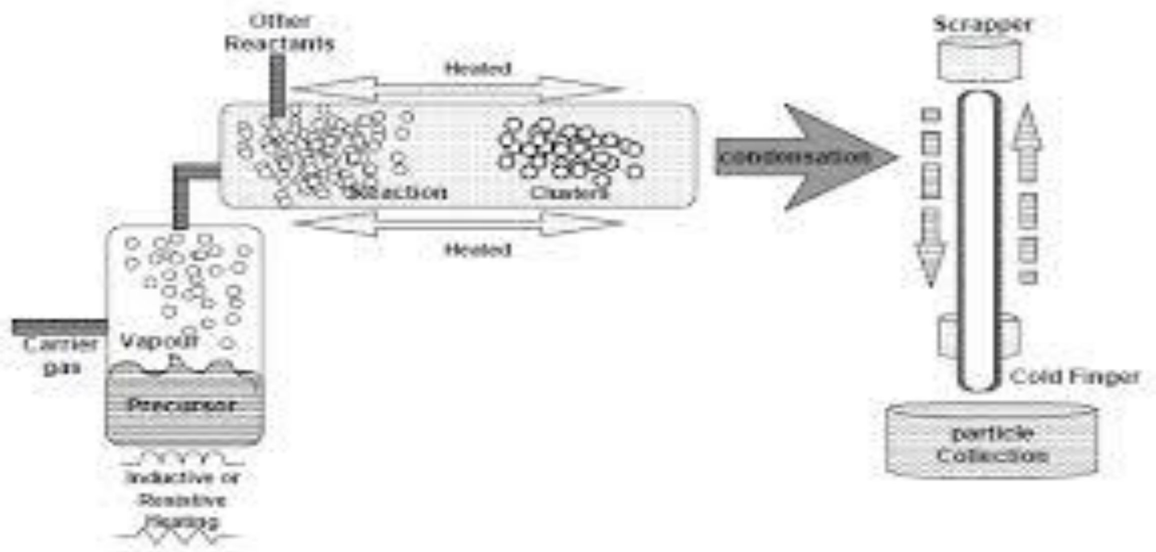
2. This method is useful in the preparation of elemental and metal oxide nanocrystals such as Co, Cr, AlFe etc.,

3. A Variety of intermetallic compounds of Ni and Al can be formed.

CHEMICAL VAPOUR DEPOSITION:

In this method, nanoparticles are deposited from the gas phase. Material is heated to from a gas and then allowed to deposit on solid surface, usually under vacuum condition. The deposition may be either physical or chemical. In deposition by chemical reaction new product is formed. Nano powders of oxides and carbides of metals can be formed, if vapours of carbon or oxygen are present with the metal.

Production of pure metal powders is also possible using this method. The metal is meted exciting with microwave frequency and vaporized to produce plasma at 15000c . This plasma then enters the reaction column cooled by water where nanosized particles are formed.



CVD can also be used to grow surfaces. If the object to be coated is introduced inside the chemical vapour, the atoms/molecules coated may react with the substrate atoms/molecules. The way the atoms /molecules grow on the surface of the substrate depends on the alignment of the atoms /molecules of the substrate. Surfaces with unique characteristics can be grown with these techniques.

The particle size could be controlled by

1. Rate of evaporation (Energy input)
2. Rate of cluster formation (Energy removal rate)
3. Rate of Condensation (Cluster removal from the reaction chamber)

Advantages:

1. A wider range of ceramics including nitrides and carbides can be synthesised.
2. More complex oxides can be formed.
3. Increased yield of nano particles.

Applications:

CVD has applications across a wide range of industries such as:

1. Coatings – Coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection, erosion protection and combinations thereof.

2. Semiconductors and related devices – Integrated circuits, sensors and optoelectronic devices

3. Dense structural parts – CVD can be used to produce components that are difficult or uneconomical to produce using conventional fabrication techniques. Dense parts produced via CVD are generally thin walled and maybe deposited onto a mandrel or former.

4. Optical Fibers – For telecommunications.

5. Composites – Preforms can be infiltrated using CVD techniques to produce ceramic matrix composites such as carbon-carbon, carbon-silicon carbide and silicon carbide-silicon carbide composites. This process is sometimes called chemical vapor infiltration or CVI.

6.Powder production – Production of novel powders and fibers

7. Catalysts

8. Nanomachines

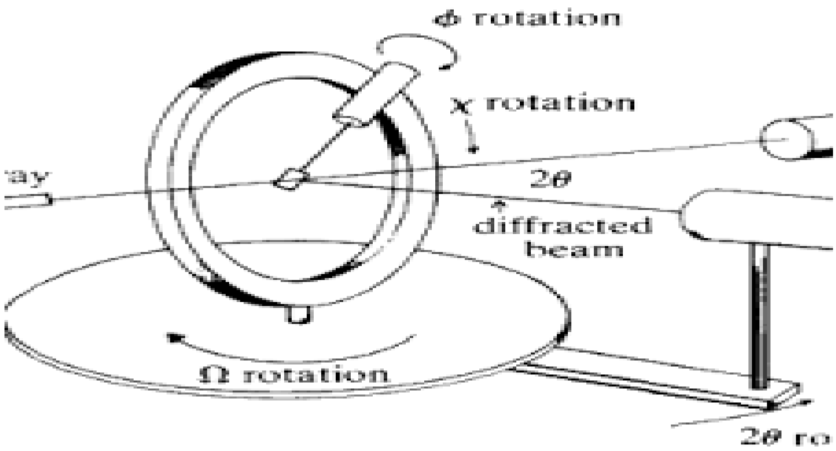
5.6 Characterization of Nanomaterials:

X-Ray Diffraction Technique(XRD)

- XRD is used for characterization of nano powders of any sizes, and the observed changes in positions of diffraction peaks are used to make conclusions on how crystal structure and cell parameters changes with the change in nanoparticles size and shape.

- X-Ray Diffraction, frequently abbreviated as XRD, is a non-destructive test method used to analyze the structure of crystalline materials. XRD analysis, by way of the study of the crystal structure, is used to identify the crystalline phases present in a material and thereby reveal chemical composition information.

X-ray diffraction is used to study structure of crystals which are not obtaining easily in the form of single crystal . Therefore sample used in the form of fine powder containing large number of tiny randomly oriented crystals. This method was developed by Debye and Scherrer so it is called Debye-Scherrer method



Fig(a) shows experimental arrangement used to produce diffraction pattern. It consist a cylindrical camera called Debye-Schreer camera. A strip of photographic film arranged along inner periphery of the camera. The powder specimen is filled in a thin capillary glass tube made up of non-diffracting material and placed at centre of camera.

By passing a beam of monochromatic X-rays through collimated (parallel) mono chromatic X-rays (sharp). The X-rays entered into the camera through collimator and strike the powdered sample. Since specimen contains large no. of small crystals with random orientations all possible diffraction planes will be available for Bragg reflection to take place.

The reflected rays will form a cone whose axis lies along the direction of incident X-ray beam and whose semi vertical angle is equal to twice the glancing angle (θ).

If all crystal planes of inter planar distance'd' reflect at the same Bragg angle(θ) all reflections from a family lie on the same cone. Hence many cones of reflections are emitted by different sets of planes.

The recorded lines from any cone are a pair of arc's that form path of circles as shown in figure (b) and figure(c).

The distance between any two corresponding arcs on the film indicated by's' In this case of cylindrical camera cone angle proportional to 'S'.

Cone angle α s

$$4\theta = S/R$$

$$\theta = S/4R$$

Where R is the radius of camera.

If S1, S_2, S_3 ------------- S_n are the distance between symmetrical lines on the film then $\theta_1 = S_1/4R$, $\theta_2 = S_2/4R$ --------------$\theta_n = S_n/4R$

Using these values of θ_n in Braggs equation that is

$$2d_{hkl} \sin\theta_n = n\lambda$$

The inner planar distance d_{hkl} can be calculated.

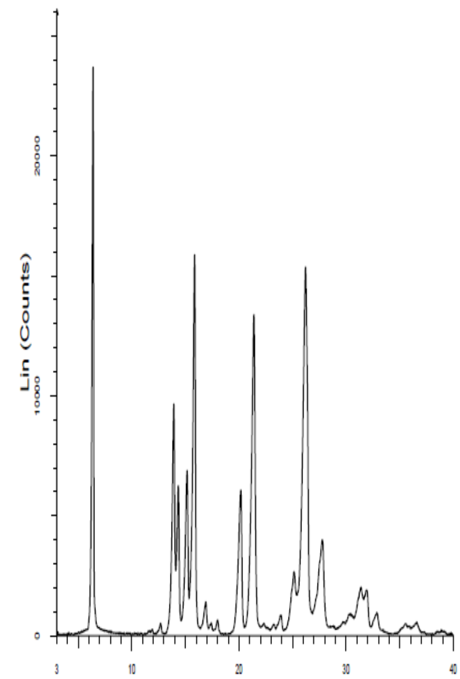


Figure 1: A typical diffractogram.

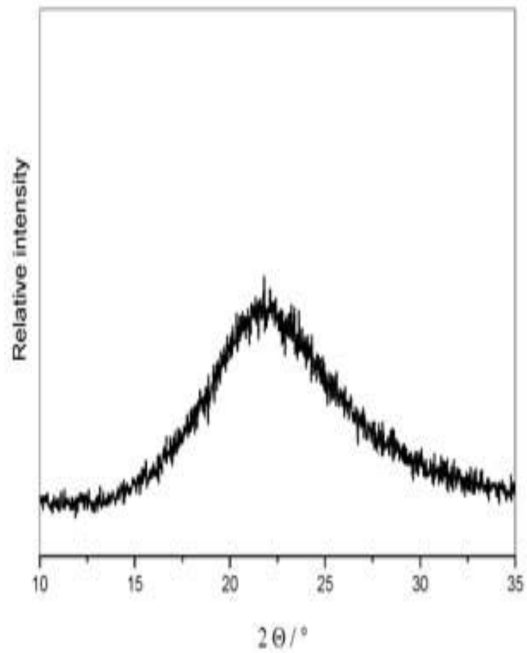


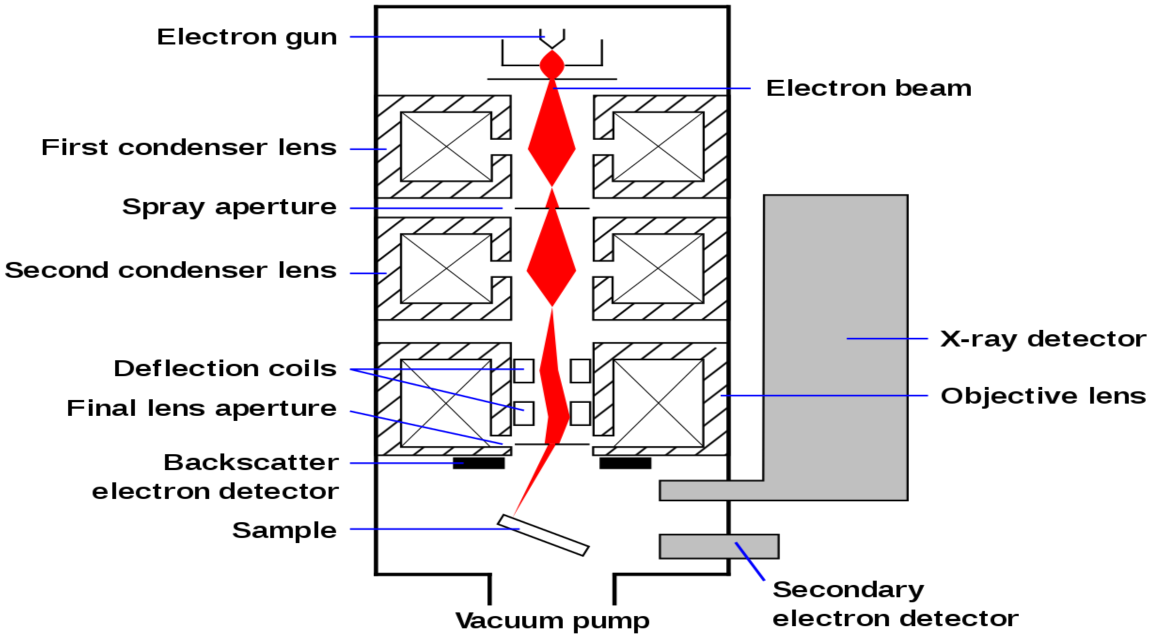
Figure 1: X-ray powder pattern of precipitated SiO_2 with a characteristic amorphous peak

Applications:

1. It is used for characterization of crystalline materials.
2. Identification of fine-grained such as clays and mixed layer clays that are difficult to determine optically.
3. It is used to determine unit cell dimensions
4. It is used to measure sample purity
5. It is used in textural measurements such as orientation of grains in a polycrystalline sample.

<u>**SCANNING ELECTRON MICROSCOPE (SEM):**</u>

- Scanning Electron Microscope (SEM) is made up of two main components, the electronic console and the electron column.
- The electronic console provides control knobs and switches that allow for instrument adjustments such as filament current ,accelerating voltage , focus, magnification, brightness and contrast.
- The image that is produced by the SEM is usually viewed on CRT's located on the electronic console. Images that are captured can be saved in digital format or printed directly.



Scanning electron microscopy (SEM) is a powerful analytical technique to perform analysis on a wide range of materials, at high magnifications, and to produce high resolution images.

Electron Gun:

It is located at the top of the column where free electrons are generated by thermionic emission from a tungsten filament at 2700 K. The filament is inside the Wehnelt which controls the number of electrons leaving the gun. Electrons are primarily accelerated toward an anode that is adjustable from 200 V to 30 Kv.

Condenser Lenses:

After the beam passes the anode it is influenced by two condenser lenses that cause the beam to converge and pass through a focal point so that electron beam is essentially focused down to 1000 times its original size. In conjunction with the selected accelerating voltage the condenser lenses are primarily responsible for determining the intensity of the electron beam when it strikes the specimen.

Apertures:

Depending on the microscope one or more apertures may be found in the electron column. The function of these apertures is to reduce and exclude extraneous electrons in the lenses.

The final lens aperture located below the scanning coils determines the diameter or spot size of the beam at the specimen. The spot size on the specimen will in part determine the resolution and depth of field.

Scanning System:

Images are formed by rostering the electron beam across the specimen using deflection coils inside the objective lens. The stigmator or astigmatism corrector is located in the objective lens and uses a magnetic field in order to reduce aberrations of the electron beam. The electron beam should have a circular cross section when it strikes the specimen however it is usually elliptical thus the stigmator acts to control this problem.

Specimen Chamber:

At the lower potion of the column the specimen stage and controls are located. The secondary electrons from the specimen are attracted to the detector by a positive charge.

Applications of SEM:

- Scanning electron microscopy can be used to identify problems with particle size or shape before products reach the consumer. Finally, industries that use small or microscopic components to create their products often use scanning electron microscopy to examine small components like fine filaments and thin film.

5.7 Applications of Nanomaterials:

- **Material Technology:**

1. Cutting tools made of nanocrystalline materials are much harder, much more wear resistant and last longer.
2. They are used in sensors
3. They are used in high energy-density batteries.
4. They are used in water repellent paints.
5. They are used in scratch resistant watches.
6. They are used in water purification system.
7. They are used in cosmetics like sun screen lotions, lipsticks, talcum powders etc.,
8. Nanoparticles react with pollutants in soil and ground water and convert them into harmless compounds.
9. They are used in car reinforcement tyres.
10. They are used in textile industry.

- **Information Technology:**

1. Nanoscale fabricated magnetic materials are used in data storage.
2. They are used in flat panel displays.
3. They are used for information storage.
4. They are used in optoelectronic devices.
5. Nanophotonic crystals are used in chemical optical computers.

- **Energy Storage :**

1. Nanoparticles are used in hydrogen storage devices.
2. Addition of nanoparticles to diesel fuel improves fuel economy by reducing the degradation of fuel consumption.
3. They are used in magnetic refrigeration.
4. Metal nanoparticles are very useful in fabrication of ionic batteries.

Medical:

1. **Anti-cancer treatment** : Nanotubes, when exposed to infrared light, lend to heat up to 160^0F(70^0 C) in just 120 seconds , if they are placed inside the cancer cells they destroy the cancer cells without having effect on normal cells.
2. **Gene therapy** : Gene therapy could also be improved by using carbon nanotubes. Modified Carbon nanotubes can act as a transporter and change the gene.
3. **Biomolecule sensor**: Carbon nanotubes can be used for sensing the biomolecules or species.
4. **Drug delivery** : Carbon nanotubes can also be used as blood vessels in order to deliver drugs to their target.

- **Biomedical Applications**:

1. Bio sensitive nanoparticles are used for tagging of DNA and DNA chips.

2. They are used in controlled drug delivery.

3. Nanostructured ceramics readily interact with bone cells and hence finds application as an implant material.

4. They are used in the fabrication of artificial heart valves.

Area of application	**Purpose**	**Approaches**
New products	Delivery	• Nano micells for targeted delivery of nutrients (nutrition nanotherapy) • Nanocapsulation for controlled release of nutrients, proteins, antioxidants, and flavors
	Formulation	• Production of nanoscale enzymatic reactor for development of new product. • Fortification of food by omega3 fatty acid, haem, lycopene, beta-carotene, phytosterols, DHA/EPA
	Evaluation	• Enzyme and protein evaluation as nanobiological system to development of new products
	Packaging	• Nanocomposites application as barriers, coating, release device, and novel packaging modifying the permeation behavior of foils, increasing barrier properties(mechanical, thermal, chemical, and microbial), improving mechanical and heat-resistance properties, developing active antimicrobial surfaces, sensing as well as signaling microbiological and biochemical changes, developing dirt repellent coatings for packages
Processing	Nanofiltration	• Selective passage of materials on the basis of shape and size
	Nanoscale enzymatic reactor	• Improved understanding of process
Nanosensors and nanobiosensors	Quality control and food safety	• Detection of very small amounts of chemical contaminants • Monitoring and tagging of food items • Electronic nose and tongue for sensor evaluation • Food born pathogen identification by measurement of nucleic acid, protein or any other indicator metabolite of microorganism