Nanochemistry

Nanoparticles:- (1–100 nm)

If the particle sizes are in the range of 1–100 nm, then they are generally called as nanoparticles or Nanomaterials i.e, $1 nm = 10 Å = 10^{-9} m$

These nano particles possess large surface atoms per unit volume.

Mathematically, spherical particles :-

$$\text{area of sphere} = 4\pi r^2$$

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

$$\text{Surface / Volume} = 3/r$$

These may have one dimensional structure (e.g. nanorods, nano wires)

2 – D " (eg. surface films)

3 – D " (eg :- particles)

0 – D " (eg:- Quantum dots, clusters)

* Different Nanomaterials :

1. **Carbon based materials :**
   eg:- Carbon nano-tubes, graphite, graphene

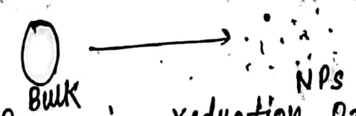
2. **Metal based materials :**
   eg:- Silver nanoparticles, Gold nanoparticles, Cu nanoparticles, TiO_2, ZnO, CuO, Co_3O_4, Fe_2O_3, Fe_3O_4, Ag_8SnS_6, Ag_2S, ZnS, etc.

3. **Dendrimers:** These are hyper branched polymers.
   eg:- Polyamidoamine dendrimers (PAMAM)
   Various drugs:- Antiinflammatory, antimicrobial, anticancer drugs

4. **Composites:** It consist of two or more phases in which one of the phase is called matrix and the other is called reinforcement. The function of matrix is to protect the reinforcement from environment whereas reinforcement enhances the matrix properties. • In composites, when one of the phase has dimension 1–100 nm then that particle is called nano-composites. The unique properties of the composites nano-particles give them noble electrical, optical, magnetic, catalytic, mechanical, thermal or imaging feature that are highly desirable for application in commercial, medical, military and environmental sectors.

Synthesis of Nanoparticles

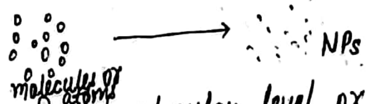
Top-down Approach | Bottom up approaches



* **Top-down Approach:-**

Nanoparticles are generated from size reduction of Bulk materials by using Physical methods.

This is done by Mechanically grinding or milling process.



* **Bottom up approach:-**

The Nanoparticles are generated from molecular level or atomic level by using physical and chemical methods.

This is done by pyrolysis.

1. Gas phase synthesis :-
   Ex:- Chemical vapour deposition material. (CVD)

2. Liquid phase synthesis:-
   (i) Precipitation method.
   (ii) Sol-gel method.
   (iii) Hydrothermal synthesis.
   (iv) Solvothermal synthesis.
   (v) microwave assisted synthesis.
   (vi) microemulsion.

2. Liquid Phase Synthesis :

(i) **Precipitation method** :- In this method, metal precursors such as metal Chlorides, sulphates, acetate are dissolved in water. The metal cations are precipitated out by adding base like NH_4OH, $NaOH$ and Urea.

Eg:- Fe_3O_4

$FeCl_2 + FeCl_3$ (1:2) $+ NH_4OH$
(dissolved in H_2O)

$\downarrow$ stirring & heating

$Fe(OH)_2 \cdot Fe(OH)_3$
Precipitate $\xrightarrow[\text{washed dried}]{\text{centrifuged}}$ $FeO \cdot Fe_2O_3$ or Fe_3O_4

Reaction:-

$$Fe^{2+} + Fe^{3+} + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O$$

$FeCl_2 + FeCl_3$ + Urea + ethylene glycol (solvent)
(1 : 2)
B.P. 182°c

$\downarrow$

$Fe(OH)_2 : Fe(OH)_3$

washed & dried | centrifuged

$\downarrow$

$FeO \cdot Fe_2O_3$ or Fe_3O_4

$FeCl_2$ is replaced by $CuCl_2$

$CuFe_2O_4 \downarrow$

" " " $ZnCl_2$

$ZnFe_2O_4$

" " " $MnCl_2$

$MnFe_2O_4$

" " " $CaCl_2$

$CaO\,Fe_2O_3$

" " " $MgCl_2$

$MgO\,Fe_2O_3$

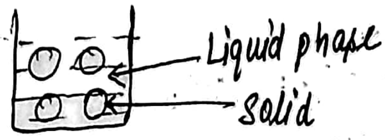
* Advantages of Bottom-up approach over Top-down:

Bottom-up approach provides more homogeneous chemical composition, less effects and better ordering. This is because the bottom of approach is driven by the reduction of Gibbs free energy also that nano-structures or nano ~~particles~~ materials such produced are in a state closer to thermodynamic equilibrium state.

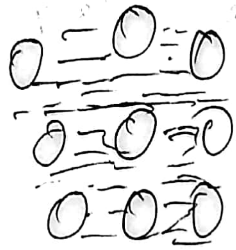
Whereas top down approach most likely introduces and internal stress in addition to surface contamination.

(ii) Sol-gel method :

Sol.



gel



Porous, three dimensional solid network enclosing continuous liquid phase.

Metal alkoxides

$Ti(OBu)_4$, $Si(OC_2H_5)_4$

+

H_2O

↓

gel formation $\xrightarrow[\text{dried}]{\text{washed}}$ Calcined at elevated temperature

Sol-gel method is one of the most popular solution processing method for preparing metal oxides nano-particles. In this method, metal recursions such as metal alkoxides are hydrolysed with water and hydrolysed species are allowed to condense with each other to form precipitate of metal oxides. The obtained precipitate is then washed and dried and finally calcined at an elevated temperature to form metal oxides nano-particles.

$$M-(OR)_4 + H_2O \longrightarrow (OR)_3-M-OH + R-OH$$

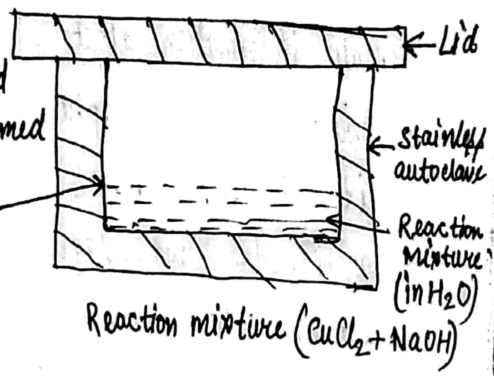
$$(OR)_3-M-OH + HO-M-(OR)_3 \longrightarrow (OR)_3-M-O-M-(OR)_3 + H_2O$$

$$(OR)_3-M-OH + (OR)_4-M \longrightarrow (OR)_3-M-O-M-(OR)_3 + R-OH$$

Scanned by CamScanner

(iii) Hydrothermal synthesis and solvothermal synthesis :

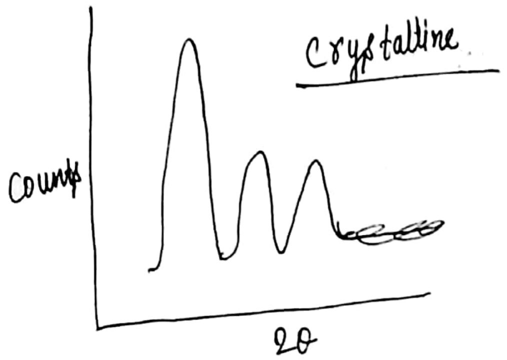
In hydrothermal synthesis, water is employed as a solvent. All the precursors are dissolved in water and the chemical reactions are performed in a closed teflon lined stainless steel autoclave above the boiling point of water.

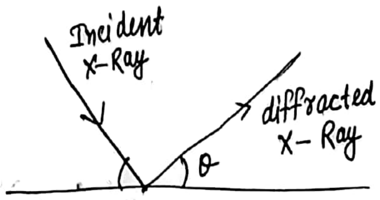


(iv) In solvothermal synthesis, all the precursors are dissolved in organic solvent and the chemical reactions are performed in closed teflon lined stainless steel auto clave above the boiling point of the solvent.

- Characterizations :-

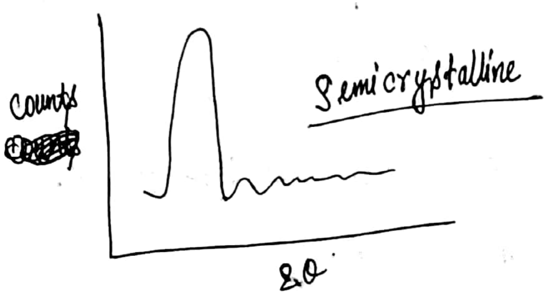
1. X-ray diffraction (XRD) :

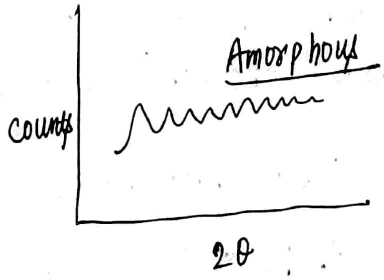




Bragg's law

$n\lambda = 2d\sin\theta$





- Debye Scherer Eq^n,

crystallite size $D = \dfrac{K\lambda}{B\cos\theta_B}$; K = Scherer constant (0.89)

λ = X-ray wavelength

B = full width of height maximum at a diffracted peak.

θ_B = angle of diffraction.

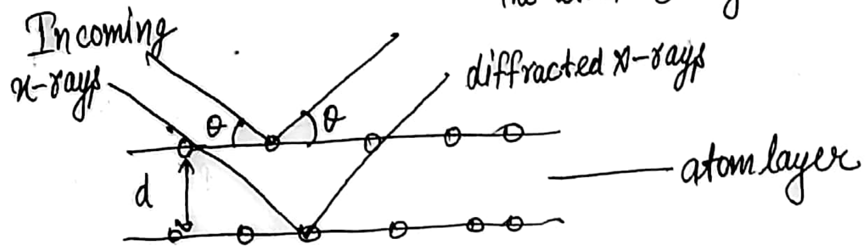
• X-Ray diffraction is a non-constructive rapid analytical technique which reveals information about chemical composition, phase identification of crystalline materials, crystallographic structure. It also provides information about unit cell dimension. Since each crystalline solid has unique atomic architecture and consequently had unique characteristic X-ray powder pattern. These patterns can be used as finger print for the identification of solid phases. In X-ray diffraction, X-ray beams is incident on the specimen and is deflected by crystalline phases present in the sample according to Bragg's Law which is

$*\; n\lambda = 2d\sin\theta$; where n is an integer

λ = X-ray wavelength

d = spacing between two atomic planes or layers.

θ = angle between the incoming X-rays and the atom layer.



These diffracted rays are detected, processed and counted by scanning the sample through the range of 2θ angle.

Crystallite size of nanoparticles can be estimated ~~by~~ from the peak width by using Debye Scherer eqn.

$* \; D = \frac{K\lambda}{B\cos\theta_B}$, K = Scherer constant (0.89)

λ = X-ray wavelength

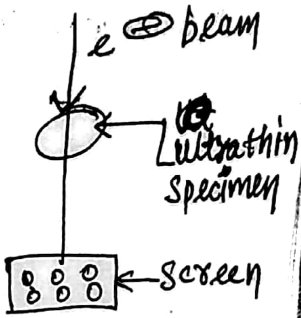
B = Full width of height maximum at a diffraction peak.

θ_B = Angle of diffraction.

2. Transmission electron microscopy :-

e.g. of sample :-

Powdered $CaCO_3$ + Ethanol $\xrightarrow{\text{dried \& put on Ni plate}}$ 



It uses beam of electrons rather than visible light.

The transmission electron microscopy is a microscopy technique whereby a beam of electrons is passed by an ultrathin specimen and interacts as it passes through the sample. The image is formed from the e⊖ that are transmitted through the sample which is then focused and magnified by objective lens and the image appears on the screen.

e.g. of sample :-

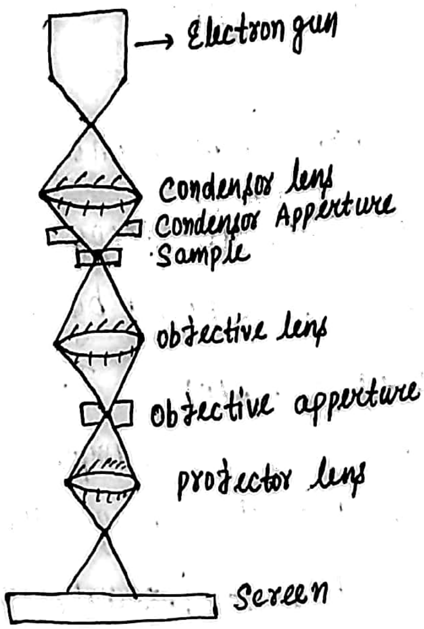
It is used to observe finer details of internal structures of microscopic objects.

Limitation :-

1) Live specimens cannot be observed.

ii) As the penetration power of e⊖ beam is very low, the object should be ultrathin.

* Schematic diagram of TEM :-



• Properties of nanomaterials :-

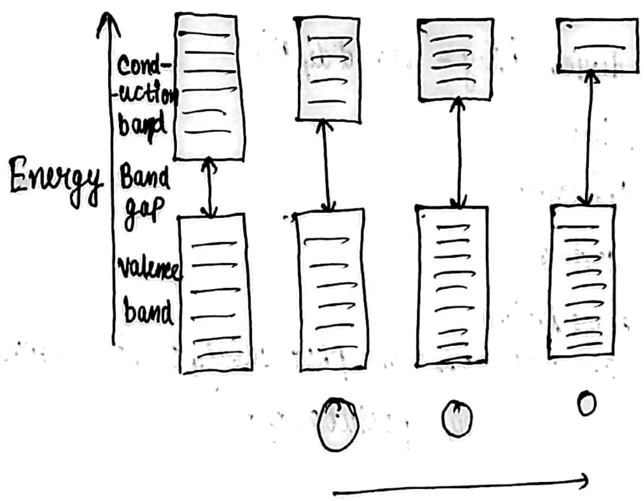
(i) Surface area
(ii) Melting point
(iii) Crystal Structure
(iv) Optical property (Band gap)
(v) Magnetic property
(vi) Catalytic property
(vii) Electrical property

(i) Surface area :- The surface area of nanomaterials is large than that of bulk materials.

(ii) Melting point :- Melting point decreases as the particles size get reduced.

(iii) Crystal structure :- Crystal structure of nanomaterials remains same as that of bulk structure with different lattice parameters.

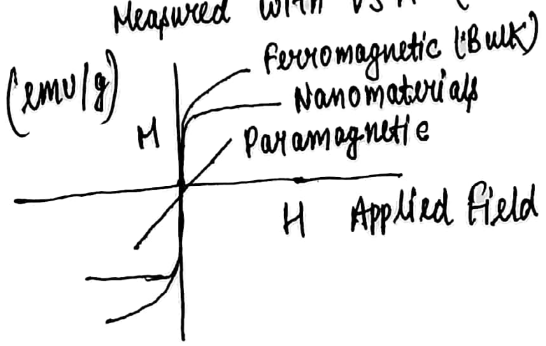
(iv) Optical property :- Band gap is the energy needed to promote an electron from valence band to conduction band. Band gap energy increases as the particle size get reduced.



Electronic structure of Quantum dots varies with size of dot.

(v) Magnetic property :- For magnetic materials such as Fe, Co, Ni, Fe_3O_4, etc., magnetic properties are size dependent. Magnetic moment of nanoparticles is found to be very less when compare them with bulk size.

Measured with VSM (Vibrating Sample Magnetometer).



(vi) Catalytic property :- The large surface [illegible] variations on geometry and electronic structure of nanomaterials have strong effect on catalytic properties.

(vii) Electrical property → The electrical properties of nanomaterials varying between metallic to semi-conducting materials. It depends on the diameter of ~~nano~~ particles.

- Application of Nanomaterials :-

Nanomaterials find applications in :-

1. Energy storage devices (e.g.- Solar cells, batteries, Fuel cells, Super capacitors, etc.)
2. Memory storage devices (e.g.- Hard disk)
3. Microwave absorption
4. Electromagnetic Shielding
5. Anti-corrosive Coatings.
6. Environmental remedation
   Ex:- TiO_2-used as photocatalyst for removal of aqueous pollutants.
7. Anti-oxidants
8. Inorganic chemical transformation reactions.