Nanotechnology & Nanochemistry

Materials having size between 1-100 nm are called **Nano meterials**. [1 nm = 10^{-9} m]

The science dealing with study of nanomaterials is called **Nano science**

Nano-chemistry :- deals with synthesis and charaterisation of materials at Nano scale [1-100 nm].

Nanotechnology :- The study of design, production, charaterisation and application of nanomaterials.

It utilises the behaviour of nano materials in various production processes. Application of science and scientific knowledge at nano scale.

Nanometer = 1000000000 th part of a meter.
[one billionth of meter]

e.g.

human hair - 100,000 nm wide

DNA (Human - 2.5 nm "

Water molecule - 0.3 nm across.

wavelength of visible light - 400nm-700nm.

c.

1. meter - m
2. Centimeter - cm $\frac{1}{100}$ m
3. millimeter - mm $\frac{1}{1000}$ m.
4. micrometer (micron) - μm - $\frac{1}{1000000}$ m
5. nanometer - nm - $\frac{1}{1000,000,000}$ m (10^{-9} m)

"Nobel Laureate Richard P. Feynman was the first person, who envisioned remarkable properties of materials at miniature scale"

Switches in computers - Electrical component that can break the electrical circuit interrupting the current or diverting it into other conductor. Nanoswitch - 100 nm wide.

Syllabus: Nanochemistry, Nanomaterials, Properties, Synthesis. Surface characterisation techniques TEM BET. Applications of Nanotechnology.

Nanomaterials examples:

(1) Carbon-nanotubes (CNTs) — ~~Sing~~ Two types SWNTs & MWNTs
(Singlewalled) (Multiwalled)

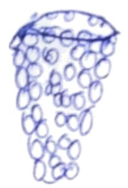
Nano-sized ~~carbon~~ sheets of atomic carbon having hexagonal symmetry known as graphene

~~It has a 2D~~

The graphenes have 2 dimensions. and when such sheets are rolled into cylindrical shapes called carbon-nano tubes

The Nano tubes are 1D. [∵ Aspect ratio is >> 20 length is much larger than width]

Posses Very unique Propertis



- Highly strong, rigid but flexible.
- Very very light
- High conductivity etc

Uses:- ~~as~~ aeroplanes, nanoelectronics, display devics sports goods, reinforced plastics etc

(2) Nanocrystals: Inorganic entities having crystalline arrangement of atoms having size < 100 nm.
used in solar cells, medical imaging, drug manufacture electronic pannels, infrared-lasers etc.

(3) Quantum dots: Nanocrystalline ~~par~~ materials having size < 10 nm are termed as nano dots or Quantum dots.
Mostly inorganic in nature
Uses: electronics, solar cells, biological labbeling in medical diagnosis, environmental pollution control etc.
(eg CdS, ZnO, CO)

(4) Nano wire: Aspect ration > 1000, length is much more than their breadth. These are refered as 1Dimentional. Can be organic like DNA, or inorganic like metal silicate. Uses: Electronics, computers, nano robots,

Classification of Nanomaterials: Based upon their dimensions

1D - only one parameter length, or breadth or height
eg. Film, sheets, surface coatings.

2D - only length and breadth
eg. Nano tube, nano wire

3D - It has all parameters (l, b, h).
eg Nanoparticles, nanocolloids, nanocluster

[~~Nanowires~~, ~~Nanotubes~~, Nano balls bucky balls]

Aspect Ratio — $\frac{\text{length of nanomaterial}}{\text{width of Nanomaterial}}$.

If AR is 1–20 = Nanorod. [overall size = 10-100 nm].
" " > 20 = Nanowire

~~Nan~~ Properties of Nanomaterials:

Nanomaterials derive their importance from their special behaviour/properties in comparison to their corresponding bulk materials. Their properties show huge difference in their properties as their size changes to nanometers.

The nanosize increases their surface area as compared to bulk, and it has a marked effect on their electrical, optical, catalytical, magnetic properties. eg.

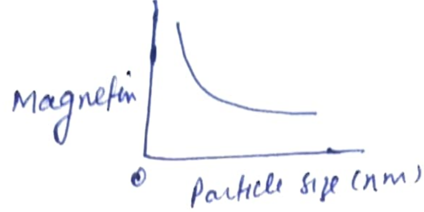
① Fall in melting points:- The melting point of nanomaterials are considerably lower than their bulk forms.
eg. M.Pt of Gold = $1064^{0}C$
" " Nanogold = $300^{0}C$.

The m.pt decreases dramatically as the particle size goes below 5nm.

② Optical properties: The nanomaterials show very interesting optical properties as compared to their bulk materials. The optical properties vary as the size, shape, surface chemistry of material changes. eg CdS nano particles show remarkable flourescent emission. It is red in bulk but 6nm CdS is orange, 4nm CdS is yellow and 2nm CdS. appears white. [Band gap increases with decrease in size]
ZnO (zinc oxide) particles are white and it scatters visible light.
Nano ZnO particles appears clear and it doesnot scatter white light. Both can block UV light.
Nano ~~ZnO~~ ZnO finds use in sunscreen creams

③ Magnetic Properties:- Non magnetic bulk substances like Gold, Pt, Au, become magnetic at nano size. The ferromagnetic behaviour due to uniform orientation of bulk changes to

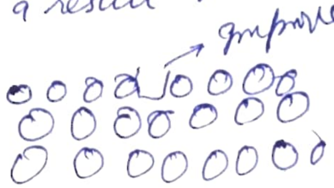
Super paramagnetism owing to random orientation in nano-size



(4) <u>Mechanical Properties</u>:- Nano-materials generally have very high tensile strength, elasticity, flexibility fracture resistance

Flexibility is measured by young modulus. It becomes 10 times greater than that of steel.

nano-materials have less defects; as a result their mechanical strength increases.



(5) <u>Electrical properties</u>; The conductivity decreases from bulk to nanomaterial. It changes from conductors to semiconductors to insulators as size changes. This is due to increases surface scattering and decreased delocalization.

(6) <u>Chemical properties</u>:

water resistance, chemical resistance, and corrosion resistance increase

Total surface area increases

No. of atoms on surface increases

Catalytic activity increases [Due to increased no. of reactive sites]

Synthesis of Nanomaterials:

Two approaches: Top-down - Bulk —— Nano-level
(slicing of Bulk

Bottom up. - Atomic level —— Nanolevel

(A) Top-Down:. Mechanical grinding, cutting, etching, ball milling, lithographic technique (Photolitho-graphy, Electron beam lithography). It is less expensive but causes environmental pollution.

(2) wet chemical synthesis:. It is also top-down approach wherein a single crystal is etched into nano size in aqueous solution. eg Porous silicon is synthesised by electrochemical Etching.

Bottom up synthesis :- It consists of assembling very small particles (like atomic level) and binding them to desired size in nanometers. (1–100 nm).

The Bottom up approach is based on the principle of self assembly.

Self assembly creates ordered patterns or arrays of atoms which enables them to perform some desired functions. The components aggregate without external forces.

SAMS: Self assembled monolayers; eg. alkanethiols on gold colloids.

Self Assembly

Molecular Self assembly
assembling of molecules, spontaneously into stable and structured aggregates by forces like Vanderwalls forces, ~~Material self assembly~~ hydrogen bonds, π-π- interactions
It can be intermolecular or intra molecular

Self Assembly

Material self assembly:- Various nano sized blocks self assemble.

SAM:- Self assembled monolayer. adsorption of an active surfactant on a solid surface.

MESA :- Mesoscale self assembly. Size varies from 10nm–10mm

forces:- capillary, electrostatic, magnetic, optical gravitational etc.

Preparation of Nanomatereals:

No. of ways are employed for preparation of Nanomaterials

① Mechanical grinding:- Based on top-down technology/approach larger particles are cut to size in range of nano-scale (< 100nm) using ~~vario~~ mechanical mills. The larger particles break into smaller sizes, by grinding between the mills.

— ~~Diso~~ Disadvantages:- Enviromental Pollution

② Wet chemical etching:- Top-down approach. Larger crystals are chemically etched into nano-scale sized
eg electrochemical etching of silicon to form nano-silicone having special properties.

③ Wet-chemical synthesis: Bottom up approach, Small particles are allowed to come together and form nano-sized agglomerates under different reaction conditions

④ Solgel process: Bottom up approach. Metals are dispersed in an acid or water forming a gel (solvation)
The solvated gel undergoes condensation leading to gelation.
The gel is solidified, during which small particles agglomerate to form larger particles, of nano size.

~~The gel is dryed to remove volatile liquids~~

~~The gel~~

⑤ Gas-phase synthesis:- This general method involves synthesis of nano-materials involving gas or vapour phase. eg chemical vapour deposition CVD
[Vapours of the materiel are diffused under thermophoretic forces and deposited on the cold surface in nano-size, which can be scrapped off as nano-powder

Surface Charaterisation Techniques

Properties of nanoparticles are dependent largely upon the size and structure of their particles. Their behaviour towards various stimuli & their physiochemical properties are determined by their structure.

As they find application in Medical, Environmental Engineering & technological fields. It is very important to understand their structure.

Most important properties are, their surface properties like ① arrangement of surface atoms, ② surface area ③ surface composition, ④ surface electronic structure play a prominent role in deter. their properties & in addition to bulk properties like ① shape ② size, ③ phase ④ crystallinity.

Methods or Techniques of surface characterisation

① BET, Brunauer - Emmet - Teller :- It helps to find surface area, pore size, and pore size distribution of nanomaterials.

Steps: surface — cleaning [heating, degassing, flushing with inert gas] → Cooling to a low constant Temperature [Dewar flask with liquid N_2]

→ Controlled doses of adsorbate gases admitted into cleaned surface chambers. [Adsorption of gas on surface takes place]

→ desorption of gas.

Amount of gas adsorbed is obtained by noting variation of pressure. By knowing volume of gas occupied by one molecule of adsorbant gas, we can know ~~that~~ the total surface area of adsorbate surface.

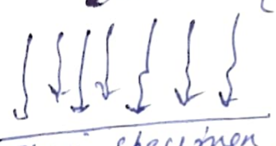
(Tungsten cathode, LaB_6 rods.

electron beam irridiation (density 60-150) keV.

2 TEM Model.

(Transmission electron Microscopy)

used to observe the features of very small specimens.



Thin specimen of nanoparticle

The electron beams get scattered as they pass through the sample.

- & scattered electrons are focussed by objective lens - amplified — to produce image on an

Image recorded system. (Flouresent screen)

Pattern of scattering (elastic / inelastic) gives idea about grain boundaries, defects, dislocations, etc. on the surface of the nanomaterial.

Very thin slice of nanomaterials are used.

Applications of Nanomaterials

① **Medicine** - diagnosis, treatment, medicine as carriers
Large surface area allows them to load drug on them
small size helps to transport drugs into cellular level
Biodegradable nanoparticles carry antibiotics to specific sites

② **Catalysis** Large surface area provide larger sites for reaction which leads to higher catalytic activity.

③ **Environmental technologies**: Control Environmental pollution (Nanoparticles on powder supports are used as catalytic systems for removal of VOCs in chimneys; IC engines (for flue gases) etc. CO_2 sequestering

④ **Electronics**: Electronic circuits, in TVs, radios, telephones, aeronautics. These are preferred ~~owing~~ owing to their small size

⑤ **Mechanics** ~~Tyr~~ Tyres, ceramics, alloys for increased mechanical strength. Increased flexibility, and light weight.

⑥ **Surface nano engineering**: Self cleaning surfaces, (hydrophobic nano particle coating on surfaces of glass)

⑦ **Food packaging**: Indicate deterioration of food by undergoing colour changes (Smart packaging)

⑧ **Lubricant** — Being nano-sized, they act as very effective lubricant

⑨ **Magnetic materials**