Unit - II

Chemistry of nanomaterials & Nano Science

Introduction →

The term nano originated from the greek nanos which means dwarf. if it one billionth of a meter. ∴ whenever we think about nanoscience or nanotechnology. very small object come to the mind.

This branch of science & technology deals with materials at least one spatial dimension in the size range of 1 to 100nm.

Terminology →

(DEF - The body of terms used with a particular technical application in a subject of study profession).

Nanoscale Nanomaterial is any material that has a dimension on the scale of 1 to 100 nm: a more exclusive definition is that a nanomaterial is a sub that exhibits properties absent in both the molecular & bulk solid state on account of it having a dimension in this range.

Nano object: material confined in one, two or three dimensions at the nanoscale.

This includes nanoparticles (all three dimensio

is the nanoscale). nanofibres (two dimensi... is the nanoscale & nanoplates (one dimen... is the nanoscale.

- A nanomaterial is taken to be a solid ma... that exists over the scale of 1 to 100 n... & exhibits novel properties that are related to its scale.

Likewise,

Nanoscience is also sometimes restricted to the study of the new effects that arise only in materials that exists on the nanoscale.

Nanotechnology is similarly restricted to the procedures for creating new functionalities that are possible only by manipulating matter on the nanometre scale.

Humans have, practised nanotechnology for centuries, it is only recently that the chemistry of nanosized particles has engendered such high levels of interest & research funding.

ex gold & silver comp have been used to

to produce red & yellow stained glass. In stained glass, the gold & silver metal atoms exist as nanoparticles (known as "colloidal particles") with optical properties that depend strongly on their size.

- metalic nanopigments are now becoming a focal point of biomedical nanotechnology bcs they can be used to tag DNA & other active nanoparticles.
- other classical examples of nanotechnology includes the photosensitive nanosized particles in silver halides emulsions used in photography, nanoparticulate TiO_2 pigments & the nanosized carbon granules in the carbon black used for reinforcing tyres & in printers ink.

- There are two basic techniques for the fabrication of nanoscale entities.
The first entities is to make a nanoscale (or microscale) object & carve out nanoscale patterns methods of this sort are called top down approaches.
Physical interaction are used in top-down

(Is a material defined interaction with electromagnetic radiation in the visible light).

optical properties of nanomaterials

- Nanomaterials having small particles size exhibit enhanced optical emission as well as nonlinear optical properties due to the quantum confinement effect.
Synthesis, characterization & measurement of optical properties of nanomaterials with the different anisotropic shape have also drawn significant attention.

- (confinement effect → is observed when the size of the particle is too small to be comparable to the wavelength of the $\bar{e}$).

- optical properties appears in nanoparticles as a result of confinement effect & are being exploited for information, biological sensing, & energy techniques.

9) Semiconducting techniques →
The colour of quantum dots is dictated by quantum confinement phenomenon & particle localisation; quantization of the HOMO - LUMO bands leads to new optical effect involving interband & intraband transition.

the conduction band (LUMO state) are called interband transitions. & the minimum energy for these transition is increased in QDs relative to those in Bulk semiconductors.

- The wavelength of interband transition depend on the size of the dots, & is possible to tailor their luminescence simply by changing their size.
ex → QD material is cdse. by varying the size of the cdse nanoparticle it is possible to tune emission over the entire visible spectrum, making them ideal for LED & Fluorescent display technologies.
Another use of QDs is chromophores for biogas

- QD chromophores materials have been used to image - cancer cells & nerve cells to track small - molecule transport to the specific organelles.

- The second manifestation of quantum confinement is that the available quantized energy levels inside a QD have no

Introduction of Electronic compound with the regions

net linear momentum & ∴ transition being do not require any momentum transfer. As, result transition probabilities between any two states are high.

- Transition of e⁻ between states in the LUMO band or holes in the HOMO band. relatively intense intraband transitions are typically in the infrared regions of the spectrum & are currently exploited to make device such as infrared photodetectors, sensors & lasers.

b) Metalic nanoparticles → The optical properties of metalic Nanoparticles arise from a complex electrodynamic effect that is strongly influenced by the surrounding dielectric medium.

- Light impinging on metalic particles causes optical excitation of their e⁻. the principle type of optical excitation that occurs is the collective oscillation of e⁻ in the valence band of the metal.

such coherent oscillations occurs at the interface of a metal with a dielectric medium & are called surface plasmons.

- In bulk particles, the surface plasmones are travelling waves & are characterized by a linear momentum. to excite plasmons using photons in bulk metals, the momenta of the plasmon & the photon must match.
This matching is possible only for very specific geometries of the interaction between light & matter & is weak contributor to the optical properties of the metal.

- The characteristics as well of plasmon absorption depend strongly on the metal & the dielectric surrounding as well as on the size & shape of the nanoparticles.
To control the dielectric surroundings, so called core- shell composite nanoparticles

- metalic nanoparticles & metalic nanoshells are used as dielectric sensors bcs their optical properties change when they come into cotact with different dielectric materials.

classmate
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characterization method

- The important characterization method in nanoparticles is microscopy. scanning probe microscopy methods generate image of individual nanoparticles to characterize their shape, size & location.

- spectroscopy which measures the particles interaction with electromagnetic radiation as a function of wavelength, is useful for some classes of nanoparticles to characterization concentration, size & shape.

- The characterization of Nanoparticles is a branch of nanometrology that deals with the characterization of physical & chemical properties of nanoparticles.

- The characterization of materials is significant when it comes to understanding their overall properties. in order to introduce nanomaterials to various applications. characterisation of their optical, morphological, electrical, thermal & magnetic properties are needed.

Energy Dispersive X-ray analysis

energy Dispersive X-ray analysis is a technique to analysis near surface element & estimate their proportion at different position thus, giving an overall mapping of the sample. This technique is used in the conjugation with SEM.

II) microscope method → microscope method such as scanning electron microscope can generate image individual nanoparticle to characteristics their shape, size & location.

III) Ultraviolet - visible spectrophotometer → can provides information about concentration, size & shape.

IV) Transmission Electron microscopy → It is a microscopy technique whereby a beam of e^- is transmited through an ultra thin specimen & interact as passes through the sample.

V) High- Resolution transmission Electron microscopy It is an imaging mode of the transmission

typical formula → It gives Properties of element present in comp

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ix) X-ray photoelectron spectroscopy It is a quantative spectroscopic surface chemical analysis technique used to estimate the emprical Formula or elemental composition, chemical state & electronic state of the elements on the surface (up to 10nm)

1] Top-down Fabrication (It is process to manufacture or inventing)

It is a substrative process in which material is removed to it.

Top down approaches produces features of a controlled shape & size

eg- lithography in the micro-electronic industry.

The advantages of top-down is the ability to put the desired feature & entity in an exact location.

- Top-down approaches refers to successive cutting of a bulk material to get nano-sized particle. (dry material which one powdery carbon nanotubes,
- The most top down Fabrication techniques is a nanothiography in this process required material is protected by a mask &

material is etched away.
Depending upon the level of resolution required for features in the final product etching of the loase material can be done chemicaly using acids or mechanica using UV x-rays or ē beam.

This technique applied to manufacturing of the computer chips.

- A top-down approaches also known as stepwise design & in some cases used as synonym of decomposition is essentialy the breaking down of a system to gain insight into its compositional sub-system in a reverse engineering fashion.

2] Bottom-down Fabrication

- It is a build up of material from the bottom atom by atom molecule by molecule or cluster by cluster.

- Bottom up-Fabrication is an additive proc in which atom & molecules are used to

build up the desired object.

ex: nanowires, nanodots.

- These approaches includes the miniaturiza
- tion of materials components (up to atomic level) with further self-assembly process leading to the formation of nanostructure.

- During self-assembly the physical forces operating nanoscale are used to combine basic units into larger stable ste.

- This approaches rely on the molecular self assembly phenomenon in micro & nanofabricati
- on we mean pattern transfer.

- A bottom-up- approaches is the piecing together of system to give rise to more complex system thus making the original system sub-system of the emergent systems.

Fibres are filament from vegetable tissues
cellulose, lignin, pectin.

Simply are fibres with diameters in nm

templated synthesis using frameworks

Template synthesis is a method using a nanoporous membrane as a template to make nanofibres from various materials, semiconductors & carbon, metals, etc.

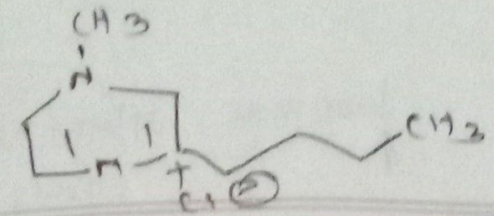
(template means a guide to make something)
(Framework → means supporting structure of building.)

1] metal-organic frameworks → It is a class of compound consisting of metals ions or cluster coordinated to organic ligand to form one, two, three dimentional etc of nanomaterials.

(methyl imidazolium pentane

- metal organic framworks made in is organic-io-organic hybrid crystals porous materials that consist of regular array of the charged metals ions surrounded by organic linker molecules.

- molecular organic framworks are useful in nanoprous materials for gas storage, separa



luminescence magnetic materials & catalysis.
- mof as precursors for the synthesis of nanomaterials with various morphologies they can be used as template for formation of nanomaterials.

- The synthesis of nanomaterials such as copper oxide, zinc oxide, hematite & other nanomaterials from MOF.

2] covalent organic framework (COF) → covalent-organic framework are used in nanomaterials for different application. such as - gas storage, catalysis, electronic devices. etc.

3] inverse micelle framework → It is used for the synthesis of nanoparticles. micelle means. It is a lipid molecules. inverse micelle it is hydrophilic heads of molecules surround the water droplet & hydrophobic tails contact the non-polar solvent which acts as dispersed medium. (hydrophilic means → molecules forming in ionic bond with H_2O molecules).

building block of strong covalent bond.

benzene, ether, hexane
↑ CH_2Cl_2 etc

hydrophobic means non-polar molecules that repels to H_2O-molecules.

inverse micellar consist of H_2O - phase dispersion of immiscible liquid such as H_2O & oil.
Nanoparticles formed by this technique is Cu Fe, Au, Co, & core-shell particles such as Fe/Au.

3] Physical method deposition → PVD is a process used to produce a metal vapour that can be deposited on electrically conductive materials as thin.
PVD is widely used for the fabrication of Nanomaterials.

4) Pulsed-laser deposition → It is a technique that can be used to synthesis a wide variety of high-quality thin film.

5] Chemical vapour deposition → It is widely used method to synthesised ceramic Nanopowder.
It is used to fabrication of oxides.

Control of Nanoarchitecture

Nanoarchitecture is the art or Practice of designing & constructing buildings for doors

It is the design of nanotechnology devices i.e machines that have sizes within the ranges of nanometers.

1) one-dimensional control

Dimensionality plays a crucial role in determining the properties of nanomaterials.
Nanomaterials describes, in principle materials of which a single unit sized in atleast one dimension.

one dimensional nanomaterials is outside the nanoscale. this class includes nanotubes, nanotubes & nanowires. has been studied extensively bcs one-dimensional system are the lowest-dimensional str that can be used for efficient transport of e^- & optical excitation.

There are also many application where

one- dimensional Nanostructures including nanoelectronic, very strong & tough composites functional nano- structured materials & novel scanning probe microscopy tips.

- A key class of nanomaterials is carbon. nanotubes. It is a best example of new nanostc faboricated through bottom- up approaches

- These new nanomaterials have applications as chemical sensors, fuel cells, field- effect transistors, electronic interconnects, & mechanical reinforces.

- carbon- nanotubes may be synthesised using a variety of techniques. Such as Laser. vaporization method. It is process to separate comp in mix.

The definition of one- dimensional is having only one main quality or concern. Dimensional control in the building industry can be defined as the operational techniques & activities that are necessary for the assurance of the predefined dimensional quality of building.

one or more form of element is allotrope
ex → graphite & diamond

The nanotubes can be eighter semiconductor or metalic conductors. when oriented in the chair configuration, carbon nanotubes exhibit high electrical conductivity
electron can travel through the micrometere length nanowires with zero scattering & zero heat dissipation.

- carbon nanotubes also have very high thermal conductivity to the best thermal conductors brice such as their counterparts, diamond graphite & graphene.

- carbon nanotube make the appealing as io-organic nanowires.

2] ~~A It having height & width only so know~~ two-dimensional control
It is composed of thin layers that may have a thickness of atleast one atomic layer.
The most famous of two-dimensional control structure is graphine. It is a single sheets of carbon atoms forming a hexagonal net of a single sheets of the graphite are.

two-dimensional control is used for the graphite → It is paired in three other carbon atoms by

width → It measured at to side to side
Distance between →

grey crystaline allotrope of carbon.
investigation & developing novel applications in sensors, photocatalysis, nanocontainers, nanoreactors & templates for 2D etc of the other materials.

graphene is the 2D sheets of carbon atoms that is one atomic layer thick so it is best example.
2D have attracted extensive interest due to excellent properties such as high mobility high conductivity & high mechanical strength & long spin diffusion length for spintronics device.

graphene is producing in large oriented sheets on substrates mainly involve CVD chemical vapour deposition.
- graphene is an excellent electron conductor & should theoretically display a resistivity lower than that of best simple metal such as silver. It is also used in the thermal conductivity, at R.T, a value better than those exhibited by carbon nanotubes, graphite & Diamond.

↓

It occurs in mirered in some rock

covalent bond

graphite is soft & diamond is hard

This is potentially imp for any future electronic applications based on graphene-containing components.

- most metals & graphite, graphene can adsorb various atoms & molecules - for example NO_2, NH_3, K & H_2O/OH. These adsorbate species act as donors or acceptors to the graphene layer & lead to the changes in the Nbr of mobile e^- in the film.

2D Nanomaterials are considered to be the thinnest Nanomaterials due to their thickness & dimensions on macroscale / Nanoscale-graphene, hexagonal boron Nitride (hBN) metal dichalcogenides (MX_2) it is used in electronic, optoelectronics, catalysis, energy storage Facilities, sensors, Solar cells lithium batteries, composities etc.

- graphene is the top-down technique in Nanotechnology by which a longitudional or transverse stress is created on the surface of layered etc materials.

graphite is used in lubricant in oil, It is good conductors of electricity

ex → bulk - powders

↑ bundles of nanocoines nanorubes-

3) Three-dimensional control

Three-dimensional control are materials that are not confined in nanoscale in any dimension. (area or volume)

The design & synthesis of three-dimensional supramolecular architecture with tunable nanoporous, open-channel are have attracted bcs of their potential applications as molecular sieves, sensors, size-selective separators & catalysis.

- The ability to Fabricate mesoporous materials with pore sizes considerably larger than those achievable with zeolites are best -known- is an imp advance in the Nanomaterials area.

An imp class of three-dimensionally ordered nanomaterials is mesostructured nanomaterials, which includes mesoporous materials.

mesoporous materials is a material containing pores with diameters between 2 & 50 nm, mesoporous materials are well known in heterogenous catalysis

pores → minute particles in surface.

- mesoporous inorganic nanomaterials are synthesised in a multistep process based on the initial self-assembly of surfactant molecule & block co-polymers that self-organize into supramolecular str which are crystalise assemblies of cylindrical, spheric lamellar micelles.

- These supramolecular framework serve as str-directing templates for the growth of mesostructured inorganic materials (silica, titania).

- mesoporous nanomaterials are routes to functionilize pores to increase catalytic activity & selectivity.
They useful in organometallic complexes, polymers, & metal complexes

- In-organic-organic nanocomposites are a class of three-dimensional, ordered materials whose chemical & physical properties can be tuned by association of organic & inorganic components of nanoscale. these hybrid materials originated in the paint & polymer industries, where

Bioinorganic Nanomaterials

- Bioscience & Nanoscience together bioactive or biocompatible hybrid system & composite Nanomaterials with neco structural organisation properties & system.

- Bio-inorganic is a field that examines the role of metals in biology.

- The interface of biology & in-organic material represents one of the fastest growing & most promising area of Nanotechnology.

- The physico-chemical characterisation of Nanomaterials & the understanding of their interaction with biological media are essential for optimizing Nanoparticles properties.

Nanoscience & Bioscience are neco technique & methods for structural & functional studies with improved spatial resolution down to the nano-scale & high sensitivity

Nobel metal nanoparticles → It is used in the labeling detection, bactericidal materials & coating therapy.
Biomolecules - nobel metal nanoparticles conjugate are applicable for diagnostics & analytics using optical or electrical detection techniques.
nanowires & & networks formed via DNA metalization.

magnetic nanoparticles, generally iron nanoparticle Biogenic & Synthetic magnetic iron oxide nano-particles (usually Superparamagnetic due to their small size with appropriate surface modification & functionalization have been used in magnetic resonance imaging contrast enhancement

- The electronic & optical properties of nanocrystalline quantum dots may lead to future application of electrotopic device & biomedical imaging.

(metals are used in preparation of drug).
(Na, K, Mg, Ca, are imp in human body).
(Zn & Cu are used in metabolism.
(Fe is used in Hemoglobin)

C:

DNA & Nanomaterials

- DNA - Deoxyribonucleic acid
DNA is used in to make a variety of nanomaterials device. including molecules that change shape & molecules that can walk along a DNA sidewalk.

- DNA is recognised as a nanomaterials not as a biological materials, in the research field of nanotechnology.
This articles reviews recent research on nanowires, nanoarchitecture, computing, aptamer biocatalysist, devices & machines using DNA.

- in these works, the characteristics of DNA including facile synthesis by the solid-phase method, self-assembly, electro-conductivity, information elements, amplification, switching molecular recognition, & catalytic functions, appropriately applied.

- ∴ The combinations of functional sequences of DNA can produce unique materials.
The DNA molecule is one of the most

DNA assembly → method of physically joining multiple fragments of DNA to create a synthetically designed DNA sequence.

Promising functional nanomaterials.
Biological molecules such as DNA have shown great potential in fabrication & construction of nanostructures & devices. DNA molecules can be used for devices assembly & computional elements, for the assembly of interconnects. or as the device element itself. There are several advantages to use DNA for these constructions.

- DNA is the basic building block of life. Hereditary information is encoded in the chemical language of DNA & reproduced in all cells of living organisms.
The double stranded helical str of DNA is key to its use in self-assembly applications. each strand of the DNA is about 2nm & composed of linear chain of four bases Cadenine, cytosine, guanine & thymine.

- DNA-based techniques to organise gold nanocrystals into spatially defined str. In their work, gold particles were attached to either 3 or 5 end of

Volanic sac → combination of fine particles of

ocean spray → spray (liquid drop) from the ocean

Signals or as sensors to detect the concentrations of chemicals or biological materials such as DNA.

Natural & artificial nanomaterials & bionanocomposites

- Naturally occuring nanoparticles can be found in volcanic ash, ocean spray, fine sand & dust & even biological matter

ex → viruses.

- Naturally occuring nanoparticles of inorganic, elemental sulfur, are found in mineral wells rich in Hydrogen Sulfide, such as ~~Elisenbrunnen in Aachen.~~

- Naturally produced nanomaterials of natural biological product such as nanoscopic particles elemental selenium coated with microbial proteins which are formed by bioreductive or oxidative metabolism in bacteria & fungi.

- Natural product of nanomaterials can show their own particular chemical & physical

rock thin strand of supercooled lava.

properties, biological activities & promise for applications.

- Nanoparticles are used in variety of health product & medical treatment as well. product like sunscreen, deodorant & cosmetics all employ nanoparticles & nanotechnology. household product such as stain removers degreasers, & air filters & purifiers,
  ex- alcohol (remove in mat or spot
- nanoparticles catalyst can also be used to improve fuel production efficiency. reducing fuel consumption in vehicles. as well reduced fuel consumption in power plants.

Natural sources of nanoparticles includes combustion product, forest fires, volcanic ash etc.

Synthetic Nanomaterials →

Synthetic Nanomaterials including carbon nanomaterials has many application in the industries, & nanofibres ~~cellulose & synthesi~~ & science.

- Carbon Nanomaterials such as CNT (carbon nanotube) & CNF (carbon nanofibres) are made up from sp2 carbon atoms with one dimensions etc. CNF have cylindrical nano-etc with different stacking arrangements of graphene sheets, such as stacked platelet, ribbon, or herringbone,

- CNF & CNT with 1000. density & high aspect ratio. as well as extraordinary mechanical thermal, electrical & electrochemical properties have produced a amount of activity in most areas of science & engineering.

- Artificial nanomaterials are the ones that are fabricated by different experiment. These nanomaterials include quantum dots nanogold, nanosilver & metal oxides such as

Titanium dioxide.

- Synthetically produced nanoparticles play an imp role in nanotechnology. they are basis for many applications currently, used as large scale, & they are a great potential in the development of new materials.

- The diversity of synthetic nanoparticle is considerable. they are distinct in their properties & applications. in addition to their size, synthetic nanoparticles vary in chemical composition, shape, surface characteristics & mode of production.

- Synthetic nanoparticles find use in many applications. this includes dispersions in gases (eg as aerosols), as ultrafine powders, for films, distributed in fluids (ex.- ferrofluids) or embedded in a solid body (nanocomposites).

- Liposomes, micelles & vesicles which are soluble nanoscale organic comp & also fall into the category of nanoparticles.