INTRODUCTION:

Nonmaterial is defined as the material with any external dimension in the nanoscale i.e. length range approximately from 1 nm to 100 nm. This includes both nano-objects and nanostructured materials, which have internal or surface structure in the range of 1 to 100 nm at least one spatial direction.

Richard P. Feyman –Father of Nano Technology.

The properties of nanomaterials are significantly different from those of atoms and bulk materials. This is mainly due to

- High surface volume ratio
- High surface energy
- Spatial confinement.
- Reduced imperfection.

which do not exist in the corresponding bulk materials. When the materials are nono size, their electronic and optical properties deviate substantially from those of bulk materials.

For Example: 1 : Gold is diamagnetic and conductor but nano size Au is magnetic & semiconductor.
Au is solid but nano size Au is liquid at room temperature
2: Au, Pt are inert material but nano size Au, Pt are catalyst.
3: Si is insulator but nano size Si is conductor.
4: Cu is opaque but nano size Cu is transparent.

→Nano- materals exhibit change in the properties which include greater material strength, enhanced reactivity better catalytic function and high conductivity.

→Nano- materials show unique electronic and optical properties different from their bulk due to modified energy band structure and charge carrier density.

→The uses of nano- materials play a considerable role in Next generation computer chips, phosphors for HDTV, tougher and harder cutting tools, high power magnets, long lasting medical implants, killing cancer cells, ductile and machinable ceramics, large electro chemical display devices, elimination of pollutants, high energy density batteries, automobiles with greater fuel efficiency, aerospace components with greater performance etc.

Nano materials are classified as 0 D, 1 D, 2 D, 3 D etc.

0 D → Cluster

1D → Wires / Tubes, Thin Film, Surface Coating, Computer Chips.

2D → Sheets / Colloids, Nano Wires, Nano Tubes

3D → Complex Shape, Precipitates, Quantum Dots.

0 D :- Zero Dimension Nano Materials

-The materials where all dimensions are at the nano scale the electron is confined in 3-D space. No electron delocalization occurs

-Ultrafine grain size $<$ 50 nm

Example :
Atomic cluster, filament, fullerenes (C_{60}, C_{540} , C_{70}) Spheres and clusters, may be metallic, ceramics or polymeric.
Exist individually or incorporated in a matrix.
May be amorphous or crystalline
Zero Dimension Nano Materials may be composed of single or multi-chemical elements.

1D :- One Dimensional Nano Materials

The smallest possible crystalline wires with cross-section as small as a single atom can be engineered in cylindrical confinement is called as 1D Nanomaterials.

- Needle like-shaped includes nano tubes, nano rods & nano wires.
- May stand alone or embedded within another medium.
- Metallic, Ceramic or polymeric.
- In 1D nano materials, electron confinement and delocalization co-exist.

2D:- Two Dimensional Nano Materials

Two-dimensional (2D) materials, sometimes referred to as single-layer materials, are crystalline materials consisting of a single layer of atoms..

- exhibit plate like shape (nano films, nano layer or nano coating)
- can be amorphous or crystalline
- may be metallic, Ceramics or polymers.
- used as a single or multilayer structure.
- Deposited on a substrate and integrated in a surrounding matrix material.

GRAPHENE: is an one atom thick planer transparent sheet of SP^2 –bonded C-atoms those are densely packed in a honey comb crystal lattice. The C-C bond length is $\approx$ 0.142nm.
Graphene is the basic structural element of some allotropes of carbon (i.e graphite ,carbon nano tube, fullerenes etc),Conduct electrons,Used in computer displays,flat panel TV to ATM touch screen and solar cell.

CARBON NANO TUBE (CNT):-A CNT is made by rolling a grapheme sheet in to a cylindrical shape. The ratio of length to diameter is of the order of 100nm. Hence CNT are considered as 1D structure. These materials have found use in applications such as photovoltaics, semiconductors, electrodes and water purification

PROPERTIES:

CNTS are 100 times stronger and 6 times lighter than steel

Possess very high tensile strength and stiffness.

They have unique electronic and one mechanical properties.

They can with stand large strain and show considerable elasticity and capability of atomic reamangement.

They posses high conductivity, chemical specificity and inertness.

Individual CNTS align themselves through non-bonding interactions such as van derails force,π - stacking to form ropes.

Types of CNT: Two types., Single –walled (SWNT) 2) Multi walled NT (MWNT).

Application of CNT :(high electrical, thermal conductivity, strength, stiffness and toughness) used in the manufacture of reinforced composites sensors, nano electronics and display devices etc.

SWCNTs are used in rein forced plastic, car, aero plane parts, sports goods.

MWCNT have good heat and electrical conductivity used in chemical sensors, conducting paints, hydrogen storage and in the manufacture of composite materials.

SWCNT are used in solar panel (as they absorb UV/visible and near IR light)

ELECTRICALLY CONDUCTING CNT films are used in LCDS, touch screens and photo voltaic devices (displays in computers, cell phone and ATM etc)

MWNT are used in Li-ion batteries and Si- coated CNTS are used as anode for Li-ion batteries.

CNTs are used in water purification.

Quantum dots: size 2 to 10 nm in diameter, semiconductor materials (C_CS_e & ZnS)

Properties:-The optical properties of QD are affected by the nature and area of the surface. Their properties change significantly when an electron leaves the surface. QDS emits photons under excitation and these are visible to human eye as light .By controlling their size, it is possible to monitor their wavelength of emission hence colour of the light.

APPLICATION:

used in photolysis reactions and in the manufacture of dye-synthesized solar cells.

used in the electronic industry and in photo voltaic cell.

used in removal of pollutants from environment (Example - Cds nano crystal , atmospheric CO_2).

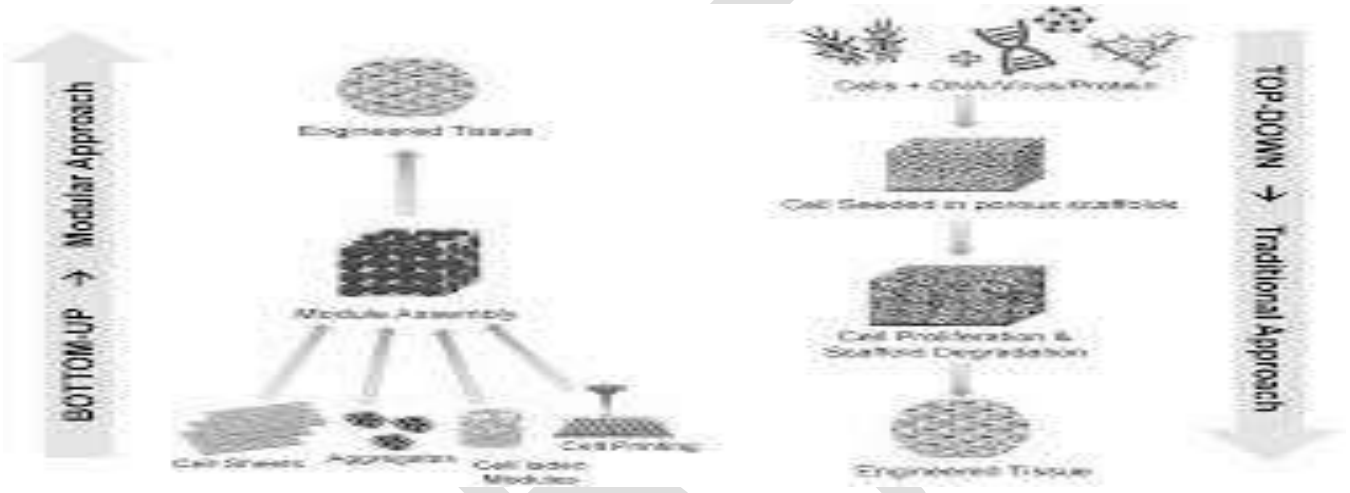
SYNTHESIS OF NANO MATERIALS

For the synthesis of nano materials, the processing conditions need to be controlled in such a manner that the resulting nano materials have following characteristics.

- Identical size of all particles.
- Identical shape of all particles.
- Identical chemical composition and crystal structure.
- Identically dispersed with no agglomeration.

There are two approaches to synthesize nano materials

1) **BOTTOM UP** 2) **TOP DOWN**



TOP DOWN APPROACH: In this approach micro fabrication methods in which externally controlled tools are used to cut, mill and shape materials in to desire shape and order

Ex : Etching, lithography, Deposition etc.

In top down techniques (such as lithography) significant crystallography defects can be introduced to the processed patterns.

Ex: Nano wire, made by lithography are not smooth contains a lot of impurities and structural defects on its surface which reduces conductivity and generates excessive heat on operation.

BOTTOM UP APPROACH: In bottom up approaches the molecular components are arranged themselves in to some useful conformation (regular pattern with lowest energy configuration) using the concept of molecular self-assembly selective growth i.e (atom by atom, molecule by molecule, duster by duster from the bottom (e.g growth of a crystal) Ex: by colloid dispersion.

The main driving force behind the bottom up approach is the reduction in Gibb's free energy. Therefore the materials proceeded are close to their equilibrium state.

The bottom up approach produces nano structures with fewer defects as compared to the nanostructure produced by the top- down approach.

Comparison of Top Down and Bottom Up approaches.

Top Down :- 1) Involves slicing or successive cutting of the bulk material to get nano sized particles.

2) Attrition or Milling is a typical top down method in making nano particles.

3) There are imperfections (defects) of surface structure, internal stress and significant crystal graphic damage to the processed patterns.

Bottom Up :-1) Process involves building up of a material from the bottom i.e atom by atom, molecule by molecule cluster by cluster.

2) Colloidal dispersion is an example of bottom up approach in the synthesis of nano particles

3) There are less defects, and a more homogeneous chemical composition.

SELF –ASSEMBLY (SA):-Self Assembly is the basic principle underlying bottom-up approach that helps to synthesize nanomaterials where small particles aggregate on their own without external force to organize in to a regular patterns with lower energy configuration.

The driving force behind SA is vander waals forces, electrostatic forces, hydrophobic interaction, $\pi - \pi$ interaction, hydrogen bonds, metal- ligand bond etc.

Types of self Assembly: a) Molecular SA , **b)** Material SA **c)** Molecular SA

Molecular SA

- Molecules are assembled spontaneously in to stable and structured aggregates without the aid of any external force, whose properties are different from the individual molecules.
- The driving force behind molecular SA are weak and reversible such as vander waals forces hydrogen bands metal-ligand bond, $\pi - \pi$ interaction etc.

Material SA

- Material SA is formed when the atoms are replaced by nano size blocks from the lattices of a conventional solid.
- These nano size blocks form thermodynamically stable structure with unique electronic, photonic, mechanical, analytical and chemical system for specific application.
- These nano blocks may be organic, inorganic and polymeric.
- Used in switching, amplification.

Nano materials can be synthesized by Mechanical Grinding, Wet chemical synthesis (Sol-gel process), Gas phase synthesis (chemical vapour deposition),

- Chemical vapour deposition is achieved in a number of ways. Furnace heating, Flame-assisted ultrasonic spray pyrolysis, Gas condensation processing (GCP), Chemical vapour condensation (CVC),Sputtered plasma processing,Microwave plasma processing.

→ Important nano materials are carbon nano tubes, nano crystals, nano wires of carbon, quantum dots, nano cones.

Use of Nano Materials (NMS) in Electronics

- Use of NMS helps in reducing the size of the gadgets. NMS are widely used in electronic circuits of TV, computers, radio, telephone, automobiles, aeronautics etc.
- Use of carbon nano tubes in semiconductor chips, light emitting diode (LED) or organic light emitting diodes (OLED)
- Use of quantum dots in lasers.
- Nano materials used in lithium-ion batteries.
- Carbon nano tubes in fuel cell and in solar industries for use in photo voltaic cell.
- Use of NMS to produce lead-free solder as well as in development of solder-free assembly technology.
- Non crystalline ZnSe, ZnS, Cds, PbTe are used to improve resolution of monitors.
  The use of non-phosphors materials reduces the cost of the display and renders high-definition TV and personal computers are in affordable price.
- Next Generation computer chips. Nano technology (miniaturization technology) enables more efficient and smaller computer and electronics, data processing and communications, which require less electrical energy.
- Using quantum dots ultra high definition with more vibrant colors and energy efficient are developed.
- Semiconductor nano membranes, grapheme and cellulosic NMS are being used to develop flexible, flat ,non-brittle highly efficient smart electronic products like flash memory chip for smart phone, ultra-responsive hearing aids , antibacterial coating of key board and phone casing , conductive inks for printing electronics for smart card/smart packaging.
- Silicon germanium quantum dots as infrared optoelectronic devices
- Nano crystalline silicon film is highly transparent contacts in thin film solar cell.
- Nano structured MnO_2 are used for rechargeable batteries for ears or consumer goods.
- Nano structured TiO_2 porous film is used for strong absorption in dye sensitized solar cell for its high transmission and significant surface area.

GREEN SYNTHESIS

Nano technology is bringing a revolution in the industrial sectors like information technology, Electronics, transportation energy, Environmental science, fabrics etc. It is making an impact in all spheres of human life in the modern age.

Large scale production of NMS will bring widespread environmental contamination and exposure of manufacturing workers causes health hazards. Correct disposal options are not yet known Nanotechnology can be a double edged sword it proper care is not been taken in right time .There is a growing need to develop environment friendly processes through Green synthesis and other biological approaches.

At present the researchers are looking in to the development of environment friendly routes, which will be cost effective procedures for producing stable, biocompatible, reproducible nano particles (NPS) and an eco-friendly alternative to existing chemical and physical methods.

The three main steps in the preparation of NPS in Green chemistry are

- Choice of the solvent medium used for the synthesis of NPS.
- Benign reducing agent.
- Non-toxic materials for the stabilization of the NPS.

Ex: 1. Water is used as the solvent.

2. Mill, renewable, inexpensive and non –toxic reducing agent like reducing sugar $\beta - D$ glucose are used.
3. For separation and purification of NPS capillary magnetic field flow traction (MFFF) size exclusion chromatography and Centrifugation methods are used widely.
4. Non-toxic materials are used for the stabilization of NPS .To protect or passivity the NPS surface capping materials are used (Ex: starch is selected as the protecting agent)
5. Bio synthesis of NPS has been proposed as a cost effective and eco-friendly method at ambient temp. and neutral pH. The process required less-energy and generate less waste. Using natural resources like medicinal plants, micro-organisms and algae and other sources (volcanic dust) are under investigation.
6. Use of microwave and ultrasonic radiation assisted green synthesis as these energy sources are safe, energy efficient, clean, increase rate of reaction and does not directly attack the bonds or chemicals undergoing reaction. A large portion of energy goes in to heating the reactor. (Requires less energy, generate less waste, avoid the use of solvent)
7. Green synthesis of Ag, Au NPS of many shapes (spherical, rod shaped, truncated, triangular) are already reported.

KEY- Green synthesis emphasizes on

- Renewable energy sources (solar energy)
- Use of non-toxic solvents and safer chemicals
- Design for energy efficiency.
- Use of selective catalyst to reduce production of by products and waste.
- Design for waste degradation.

Application of nano materials in Environmental field

There are wide spread use of nano materials in sensing and removing/degrading contaminants from environment. The properties of NMS which help to mitigate the environmental pollution are

→ High surface to volume ratio
→ High chemical reactivity of surface atoms.
→adsorption capacity
→ The case with which they could be mounted on solid support.
Example:-Role of NMS in remedying the contaminants.

1. **Sensors:** - rely on the highly active surface to initiate a response with minute change in the concentration of the species to be defected.

(a) Quantum dots (CdSe – ZnS) nano sensor have potential to defect toxins, Contaminants present in the soil and water.

(b) Nano structured metal oxide thin films and metal dusters are used as sensors for the gases (like NO_X ,CO, CO_2 ,CH_4 and aromatic hydrocarbon)

2. **Nano catalyst**: Like Fe, Fe, Au, Ag, TiO_2, MgO etc are used in the removal of pollutants from water and air.

(a) Nano catalyst- Pt is used in catalytic converters of internal combustion engine where burning of gasoline and coal occurs to oxidize CO to CO_2 (Auto mobiles and power generation unit)

(b) NOx is removed by reducing it to N_2 in presence of CO and nano catalyst Rh.

(c) hydrocarbons are oxidized to CO_2 & H_2O using nano catalyst –Pt .

(d) (Ni-Fe) nano particles are used to remove chlorinated hydrocarbon.

(e) Removal of heavy metal like Cr, V, Pt (II) from water by Fe (0) nano particles supported by silica gel or polymeric resins.

(f) Nano catalyst Au, Ag and activated Alumina are used in removal of pesticides, halocarbon (CCl_4 ,$CHBr_3$,CCl_3F

(g) Fe (nano catalyst) used in de-chlorination.

(h) Nano catalysts TiO_2 And ZnO are used for degradation of organic contaminants (Organic dyes , nitrobenzene, nitrophenol etc)

3. Adsorption:

(a) Carbon nanotube and carbon nano fibre are good adsorbants for dioxins and chloro benzenes.

(b) Ceria (CeO_2) molecules are combined with carbon nano tubes and the resulting nano materials show good adsorption of arsenic (As)

(c) Cerium oxide nano particles are used as filter in diesel engines for pollution control as they trap the carbon particles (soot's) formed.

(d) Carbon nano tube can adsorb toxic metal like Pb^{+2}, Ca^{+2} , Cd^{+2} and many other chemicals (Bisphenol-A) from water.

(e) Membrane filtration and nano filtration techniques are useful for the treatment of waste water and ground and surface water purification due to its capacity to remove micro organisms , turbidity and hardness.(Ex: antibacterial activity of MgO nano particles in nano filter)

(f) Use of thin film membrane with nano pures for energy efficient desalination.(eg the molybdenum disulphide MoS_2 membrane filters 2 to 5 times more water than current conventional filter.

(g) Nano scale Biopolymers offer an environmentally benign route for the remediation of heavy metals in water and soil.

Use of Nano-materials in solar PV panels.

Fig: use of solar PV panels to generate electricity for feed-into city grid.

The nanostructures have significant specific heat and quantum confinement effects.

The first generation solar photovoltaic (PV) systems directly convert sunlight (solar energy) in to electrical energy by using silicon diodes.

The 2nd generation: Use of thin film technologies with other semiconducting materials such as Cd Te (Cadmium Telluride) and copper indium Gallium Selenide (CIGS)

3RD Generation: Include quantum dots, nano structured semiconductors and amorphous silicon, Novel technologies like nano wires, quantum dots and radial junctions raise the limit of PV efficiency. Sunlight can be concentrated in nano wires due to a resonance effect. This effect can result in more efficient solar cells, allowing more of the energy from the sun to be converted to electricity.

Example:

1. Copper Indium selenide supplied quantum dot.
2. Solar cell made from single molecule thick shuts of grapheme and materials such as molybdenum Disulphide.
3. Graphene coated with ZnO nano wires are law coat flexible solar cells at high efficiency.
4. Using light absorbing nana wires embedded in a flexible polymer film is another method to produce low coat flexible solar panels.
5. CdS nano wires coated with CuS.
6. Combining Ag-nano wires, TiO_2 nano particles and a polymer that absorbs Infrared light to make a solar cell 70% transparent to visible light used in windows.
7. Flexible layer of nano porous germanium to produce light weight solar cells for mobile applications.

These PV panels not only can be plugged in to existing grid infrastructure once converted to AC, they also can be used for off-grid applications like portable charger and space applications. By combining with energy storage techniques' PV panels can be considered a major energy storage in remote housing.

QUESTIONS & ANSWER

Q-1. What are nano materials?

Ans:-Materials which are smaller than 100 nm at least in one dimension

- Spherical structure (e.g. fullerenes, nano particle)
- Fibrous structure (e.g.nano tubes)
- Extremely thin layer (e.g. nano platelets grapheme)

Q-2. Are there any safety or Environmental issues with the Nanotechnology is use today?

Ans:-Large scale production and use of nano materials will bring wide spread environmental contamination and exposure of manufacturing worker's health hazards. Correct disposal options are also not yet known. Nano technology can be a double-edged sword if proper care is not been taken in right time

Q-3. Why are nano materials so special?

Ans:-NMS are greater material strength, enhanced reactivity better catalytic functions and high optical and electrical properties. NMS are strong, light weight for better fuel economy, hence used in aerospace ,targeted drag delivery for safer and more effective cancer treatments ,clean drinking water, computers with more memory capacity, self cleaning surface, efficient solar panels, safer food packaging ,good sensor etc.

Q-4. Explain why bottom up approach is better method of nano material synthesis than top down approach.

Ans:-In top down techniques a bulk material is cut down to nano size material by externally controlled tools. This technique introduces crystallographic defects, contains lots of impurities on its surface. Which reduces conductivity and generates excessive heat on operation. In bottom up approach involves building up of a nano material from bottom i.e. atom by atom, molecule by molecule, and duster by duster in a regular pattern with lowest energy configuration. Hence there are less defects and a more homogeneous chemical composition. Hence bottom up approach is a better option for nano material synthesis.

Q-5. What are nano materials? Do they exist in Nature? & what are the applications of nms?

Ans-:

Nano Materials are material having size from 1- 100 nm at least in one dimension. Spherical structure (e.g. fullerenes, nano particle),Fibrous structure (e.g.nano tubes), Extremely thin layer (e.g.nano platelets grapheme).

Nano Materials exist in nature in different forms such as paper, cotton, nacre, corals etc

Applications:

* Providing renewable clean Energy., * Supplying clean water
* Improving Health and Longevity. * Healing and preserving the environment
* Making information Technology available to all.
* Enabling space Development.

Q-6 .Why properties of NMS are different from the same balk material?

Ans:- High due to surface to volume ratio, High surface energy, Spatial confinement Modified energy band structure and charge carrier density. Reduced imperfection.

ASSIGNMENTS

1. What are the types of NMS? Give examples.
2. Give use of Nano Materials in Electronics.
3. What is self Assembly? How many types of self Assemblies' are there? Explain.
4. Short notes on:- CNT, Quantum dot, grapheme
5. What is the green synthesis of nano materials?
6. How can nano materials be used in the sustainable development of world.
7. How can nms be used for environmental protection?

ABIT