

NANOMATERIALS

Introduction :- The prefix nano means one billionth. One nanometer (1 nm) is $\frac{1}{10^9}$ that a meter which is close to $\frac{1}{10^{9\text{ th}}}$ of a yard. To get a sense of nanoscale, a human hair measures 50,000 nanometers across, a bacterial cell measures a few hundred nanometers across. The smallest things seeable with the unaided human eye are 10,000 nanometers across, just 10 hydrogen atoms in a line make up one nanometer across.

Nanoscale is at its simplest form, the study of fundamental particles of molecules and structures with at least one dimension roughly between 1 to 100 nanometers. These structures are known perhaps as nanostructures. Nanotechnology is the application of these nanostructures into useful nanoscale devices.

Hence materials having structured components with at least one dimension less than 100 nm are known as nano materials. Nanoparticles can display properties significantly different from the bulk material because at this level quantum effects may be significant. Simply we can say the mechanical, electrical, optical, electronics, catalytic, magnetic etc. properties of solids are significantly altered with great reduction in particle size. Hence it also explained as nanoparticles have high surface to volume ratio.

- Examples
- ① Gold nanoparticles are deep red in colour but its bulk material (gold pieces) is gold-coloured.
 - ② Silver foil does not react with dil. HCl but silver nanoparticle rapidly react with dil. HCl.
 - ③ Gold and silver both are chemically inert but their nanoparticles show catalytic property.

CLASSIFICATION OF NANOMATERIALS :- There are several ways of classifying nanomaterials. The two extreme classifications are

- ① classification focusing on the macroscopic dimensions
- ② classification reflecting their composition

Classification on the basis of macroscopic dimensions

According to Siegel, nanostructured materials are classified as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials.

(i) Zero-dimensional nanomaterials (0D) :- Here all the dimensions (x, y, z) are at nanoscale, i.e. no dimensions are greater than 100nm. It includes nanospheres and nano-clusters, which are considered as a point like particles.

(ii) One-dimensional nanomaterials (1D) :- Here two dimensions (x, y) are at nanoscales and the other dimension is outside the nanoscale i.e. length larger than 100nm in one direction only. This leads to needle shaped nanomaterials. It includes nano-fibers, nano-tubes, nanorods and nanowires.

(iii) Two-dimensional nanomaterials (2D) :- Here one dimension (y) is in nanoscale and the other two dimensions are outside the nanoscale i.e. length larger than 100nm in two directions. The 2D materials exist as plate like shapes. It includes nanofilms, nanolayers, nanocoatings with nanometer thickness. It ~~consists~~ uses films, plates, multilayers or networks.

(iv) Three-dimensional nanomaterials (3D) :- These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100nm. The bulk (3D) nanomaterials are composed of a multiple arrangement of nanosize crystals in different orientations. It includes dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multi-nanolayers (polycrystals) in which the 0D, 1D and 2D structural elements are in close contact with each other and form interfaces.

② Classification reflecting their composition:- It is possible to classify nanomaterials in families reflecting their composition. There are classified the following four different categories

(i) Carbon-based nanomaterials

(ii) Metal-based nanomaterials

(iii) Dendrimers

(iv) Composite nanomaterials.

① Carbon-based nanomaterials:- These are composed of mostly carbon, taking the form of a hollow spheres, ellipsoids or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes while cylindrical forms are called nanotubes. These particles have many potential applications including improved films and coatings. These are stronger and lighter materials and applied in electronics.

② Metal-based nanomaterials:- These include quantum dots, manogold, manosilver and metal oxides like TiO_2 . A quantum dot is a closely packed semiconductor crystal comprising hundreds or thousands of atoms and whose size is in the order of a few nanometers to a few hundred nanometers. changing the size of the quantum dots changes their optical properties. TiO_2 nanoparticles are extensively used in applications such as paint, sunscreen and toothpaste.

③ Dendrimers:- Dendrimers are relatively branched molecules. The name comes from the Greek word "dendron" (tree). These nanomaterials are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can perform specific chemical functions. This property could also be useful for catalysts. 3D-dendrimers contain interior cavities into which other molecules could be placed, that's why they can be used for drug delivery. Dendrimers are also be used in molecular recognition, nanosensing, light harvesting and opto-electrochemical devices.

④ Composite nanomaterials:- composites are combination of nanoparticles with other nanoparticles or with larger, bulk-type materials. Nanoparticles like nanosized clays are added to the products (auto parts, packaging materials etc.)

to enhance physical, mechanical, thermal, chemical and flame-retardant properties.

Applications of some specific nanomaterials

① FULLERENE :- The fullerenes (allotropes of carbon) are graphene sheets rolled into tubes or spheres. It is a cage like molecule composed of 60 carbon atoms (C_{60}) joined together by single and double bonds to form a hollow sphere with 20 hexagonal and 12 pentagonal faces (as design resembles a football). It was named as buckminsterfullerene or buckyball. It is a spherical molecule of about 1nm in diameter. The different applications of fullerene are as follows.

- ① Fullerenes (C_{60}) and their derivatives have potential antiviral activity and may be used for the treatment of HIV-infection.
- (ii) They have potential medicinal uses i.e can bind specific antibiotics and target certain types of cancer cells such as melanoma.
- (iii) They are used as biological oxidants. The antioxidant property of fullerenes is due to the presence of large no. of conjugated double bonds. Due to this property major pharmaceutical companies are exploring the use of fullerene in controlling the neurological damage of such diseases which are a result of radical damage.
- ④ It is used as MRI agents in medical work.
- (v) They are also used as a potential photosensitizers in photodynamic therapy.
- (vi) Fullerenes can incorporate with sulphides of tungsten and molybdenum exhibiting excellent solid-lubricating property.
- (vii) since fullerenes have potential ability to transfer hydrogen, there are used as catalyst for hydrogenation.
- (viii) Fullerenes can be added to polymer structures to create new copolymers with specific physical and mechanical properties.

Q11) Fullerenes are used as proton-exchange membrane for fuel cells.

Q12) Nanotubes :- The carbon nanotubes (CNTs) are elongated form of fullerenes. It is a tube-shaped material made up of carbon having a diameter ranging from 1nm to 50nm. Simply we can say that CNTs are cylinders of one or more layers of graphene. It is of two categories

(a) single-walled carbon nanotubes (SWCNTs)

(b) Multi-walled carbon nanotubes (MWCNTs)

CNT technology can be used for a wide range of new and existing applications, which are as follows

① Nanotubes can potentially replace indium-tin oxide in solar cells to generate photocurrent.

② SWCNTs are used in solar panels due to their strong UV-absorption characteristics.

③ SWCNTs are used in transistors because of their low electron scattering and their bandgap.

④ It is used in making conducting polymers.

⑤ MWCNTs are used in Lithium ion batteries to enhance cycle life.

⑥ parallel CNTs have been used to create loudspeakers.

⑦ CNTs can be serve as a multifunctional coating materials and used to make waterproof and tear-resistance fabrics.

It also used to make the jacket that can stop bullets.

⑧ CNTs can be used to produce manowines.

⑨ CNT in concrete increases it's tensile strength and halt crack propagation.

⑩ It can be used to increase the tensile strength of material (used in aeroplane and automotive structures)

⑪ CNT may be able to replace steel in suspension and other bridges.

⑫ CNTs are also used for application in energy storage, automotive parts, boat hulls, water filters, thin-film electronic coatings, ultra-capacitors, biosensors for harmful gases, extra strong fibers etc.

③ Nanowires:— They may be defined as the structures which have the diameters of the order of a nanometer and an unconstrained length i.e. nanowires are much longer than their diameter. These are also called "quantum wires" because at this scale they have different quantum mechanical effects.

There are different kinds of nanowires such as Carbon nanowires, molecular nanowires, metallic nanowires, Semiconducting nanowires and insulating nanowires.

The different applications of nanowires are as follows:

- ① These are used to prepare active electronic components like p-n junction, logic gates etc.
- ② They have potential applications in high-density data storage either as magnetic read heads or as patterned storage media.
- ③ They may also be used or useful in digital computing.
- ④ Graphene coated with ZnO nanowires are used in solar cells.
- ⑤ Silver chloride nanowires are used as photocatalysts to decompose organic molecules in polluted water.
- ⑥ Because of their high Young's modulus, they are used for enhancing mechanical properties of composites.
- ⑦ Since nanowires appear in bundles, they may be used as tribological additives to improve frictional characteristics and reliability of electronic transducers (electric or electronic devices that transform energy from one manifestation into another) and actuators (devices such as valves and switches that perform actions such as turning things on or off or making adjustments in an operational system).

④ Nanocones:— Carbon nanocones are conical structures made from carbon and have at least one-dimension of the order of one micrometer or smaller. These are obtained from the wrapped

graphene sheets. These are different from nanowires as nanocones have height and base diameter of the same order of magnitude. From electron microscopy it is clear that the opening angle (apex) of the cones is not arbitrary but has preferred values of approximately 20° , 40° and 60° .

The applications are as follows :-

- (i) These are used in chemical sensors, biosensors, SPR Spectroscopy.
- (ii) They may have interesting applications in nanolithography.
- (iii) They may also be used as electrode material in lithium ion batteries.
- (iv) Nanocope can be used a bare polymer or in diluted form both in the catalyst and in the cross-linker component.
- (v) Nanocane surface can be used widely as affinity-based separation.

⑤ Quantum Dots :- These are the semiconductor nanoparticles between 10 and 100 atoms in diameter. The properties of quantum dots can vary depending on the shape and size. Some of the important applications of quantum dots are as follows

- (i) These are used in transistors, solar cells, diode lasers, LEDs etc.
- (ii) These are also significant for optical applications like amplifiers, biological sensors. This is due to high extinction coefficient.
- (iii) These may increase the efficiency of silicon photovoltaic cells.
- (iv) These are used as photocatalysts.
- (v) They have potential applications in spectroscopy, and fluorescent biomedical imaging.

⑥ Nanocluster :- It is a grouping of a no. of nanoparticles in a narrow size distribution having at least one-dimension between 1 to 10 nm. simply these are fine aggregates of atoms or molecules.

Nanoclusters contains a couple of 100 atoms but the larger aggregates containing more than 1000 atoms are called Nanoparticles. The number of atoms in the clusters of critical size with higher stability is called magic number. Some important applications are

- (i) It has potential applications in microelectronics, telecommunications, sensors, transducers, electroluminescent displays, catalysis etc.
- (ii) It is also used in biotechnology and pharmacology.

④ Graphene :- Graphene is a crystalline allotrope of carbon with two-dimensional, atomic scale, hexagonal pattern. Here each carbon atom forms four bonds, i.e. three σ -bonds (sp^2 hybridization) with its three neighbours and one π -bond oriented out of the plane. It is called as mother of all carbon nanomaterials.

Some important applications of graphene are as follows

- (i) They are commonly used in semiconductors and batteries
- (ii) They are used in many electronic devices
- (iii) They are used in composite materials in many industries

Some General Applications of Nanomaterials :-

Nanotechnology has a tremendous potentiality to cater the necessity of modern society with user friendly as well as eco-friendly approach. It is used in different fields and some of the important fields are as follows

- (i) **In Medicine :-** (i) Bioavailability refers to the presence of drug molecules where they are needed in the body and where they will do the most good.
- (ii) Increasing bioavailability is seldom as simple as increasing the amount of drug that is used. In chemotherapy the drugs used are actually toxic and increasing the amount of drug used could adversely affect on even kill a person. On the other hand if the drug could be delivered directly to the site

of the affected tissues without interacting with the rest of the body, chemotherapy could become more effective and much less unpleasant. Nanotechnology and nanoscience are very useful in developing entirely new schemes for increasing bioavailability and improving drug delivery system.

(iii) Much more complex drug delivery schemes have also been developed, such as the ability to get drugs through cell walls and into cells. Efficient drug delivery is important because many diseases ranging from sickle cell anemia to Wilson's disease depend upon processes within the cell and can only be interfered with by drugs delivered into the cell.

(iv) Many drug molecules that cannot pass through the membrane that surrounds the cell because of difficulty associated with putting polar molecules into the non-polar membrane but nanotechnology drug delivery system can do this.

v) The carrier in nanodrug delivery may be coated solid-particles, vesicles, liposomes, micelles, polymers or solid-lipid nanoparticle.

In addition to these nanomaterials are used for the following medical applications

i) Fluorescent biological labels

ii) Drug and gene delivery

iii) Bio detection of pathogens

iv) Detection of proteins

v) Probing of DNA structure.

vi) Tissue engineering

vii) Tumor destruction via heating (hyperthermia)

viii) separation and purification of biological molecules and cells.

ix) MRI contrast enhancement.

x) Phagokinetic studies.

③ Nanomaterials for sensing Applications :- VU

i) The field of sensors encompasses a wide variety of materials and devices used for monitoring

to measurable output signals. Nanomaterials may be used as active sensing elements or receptors as transducing components and even as electrodes in electronic circuit and power systems.

(i) The nanomaterials-based sensors offer inexpensive alternatives to costly and bulky optical detectors.

The main competing selective gas sensitive technology under development on/off nanosensor devices have been demonstrated that may detect from bacterial infection to diabetes and even lung cancer. Using bio-doped nanostructured oxides (unlike in MoO_3) on bionanocomposite (PANI/peptides) as sensing elements.

(ii) The nanomaterial forms the different sensors as follows

(a) Integration of CNT-Based chemical sensors and Biosensors in Microfluidic systems.

(b) Graphene-based chemical and Biosensors

(c) Molecular Imprinting technique for Biosensing

(d) Gold Nanostructure LSPR-Based Biosensor for Biomedical Diagnoses

(e) DNA sensors Employing Nanomaterials for Diagnostic applications

(f) optical chemical sensor and Electronic Nose based on porphyrin and phthalocyanine

(g) Nanotechnology to improve detection sensitivity for Electrochemical interfacial devices.

(3) Sunscreens and cosmetics :- The traditional

UV-protection approach suffers from the loss of long-term stability. A sunscreen based on mineral nanoparticles such as TiO_2 often

mineral nanoparticles such as TiO_2 often

several advantages. TiO_2 (Titanium oxide) nanoparticles have a comparable UV-protection property. Nanosized TiO_2 and ZnO are currently used in some sunscreens as they absorb and reflect UV-rays. Nanosized iron oxide is present in some "lipsticks" as a pigment.

(4) Paints :- Incorporating nanoparticles in paints could improve their performance by making them lighter and giving them different properties. Thinner paint coating in nanoscale used in aircraft and would reduce their weight, which could be beneficial to the environment.

(5) Displays :- The huge market for large area, high brightness, flat-panel displays as used in television screens and computer monitors is driving the development of some nanomaterials. Nanocrystalline Zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol-gel technique are candidates for the next generation of light-emitting phosphors.

(6) Batteries :- With the growth in portable electronic equipment (mobile phones, laptop computers, remote sensors) there is a great demand for light weighting, high-energy density batteries. Nanocrystalline materials synthesized by sol-gel techniques are candidates for separator plates in batteries because of their aerogel like structure, which can hold considerably more energy. Ni-metal hydride battery made of nanocrystalline Ni and metal hydrides are long lasting and require less frequent recharging due to large surface area.

⑦ Catalysis :- In general, nanoparticles have a high surface area, and hence provide higher catalytic activity. Nanoparticles serve as an efficient catalyst for some chemical reactions due to extremely large Surface to Volume ratio. platinum nanoparticles are now being considered in the next generation of automotive catalytic converters because of very high surface area. Some chemical reactions are also carried out using nanomaterials.

⑧ Agriculture :- Applications of nanotechnology have the potential to change the entire agriculture sector and food industry from production to conservation, processing, packaging, transportation and even waste treatment.

⑨ Food :- Nanotechnology can be applied in the production, processing, safety, and packaging of food. A nanocomposite coating process could improve food packaging by placing antimicrobial agents directly on the surface of the coated film. According to the company information posted PEN's web site, the canola oil by Shemen Industries of Israel contains an additive called "nanodrops" designed to carry Vitamins, minerals and phytochemicals through the digestive system and urea.

⑩ Construction : ① Nanotechnology has the potential to make construction faster, cheaper and safer. The silica (SiO_2) is present in conventional concrete as a part of the normal mix but when nanosilica is added to the concrete the particle packing can be improved mechanical properties.

② The addition of nanosilica to cement based materials can also control the degradation of the fundamental C-S-H (calcium silicate hydrate) reaction of concrete caused by calcium leaching in water as well as block water penetration and therefore lead to improvements in durability.

③ The strength of concrete can also be increased by the addition of nanohematite (Fe_2O_3).

- iv) The nano size steel produce stronger steel cables which can be used in bridge construction.
- v) The glass is an important material in construction. TiO_2 nanoparticles are used to coat glazing because it has both sterilizing and anti-fouling properties.
- vi) Most of glass used in construction is on the exterior surface of buildings, so the light and heat entering through the glass into the building is to be prevented.
- vii) Coatings are extensively used to paint the walls, doors and windows. Coating should provide a protective layer which is bound to the base material to produce a surface of the desired protective or functional properties. Nanotechnology is being applied to paints to obtain the coating having self-healing capabilities and corrosion protection under insulation. Since these coatings are hydrophobic and repels water from the metal pipe and can also protect metal from salt water attack.

Other applications: Some commercial products on the market today utilizing nanomaterials include stain resistance textiles and reinforced tennis rackets. Companies like Kraft foods are heavily funding nanomaterials based plastic packaging. Food will stay fresh longer if the packaging is less permeable to atmosphere. Coors Brewing company has developed new plastic beer bottles that stay cold for longer periods of time.