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UNIT-III
Nano Materials
(From the Academic year 2022-23 onwards)

Introduction: Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimetre, approximately 100,000 times smaller than the diameter of a human hair. One nanometre is one billionth (1/1000000000) of a metre i.e. 1 nm = 10^{-9} m.

Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Nanomaterials can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials are nanotubes, dendrimers, quantum dots and fullerenes.

Types of Nanomaterials
I. Based on materials
Mainly there are four types of Nanomaterials: carbon based materials, metal based materials, dendrimers and composites.

1. Carbon based materials: These nanomaterials are composed mostly of carbon and are available in the form of a hallow sphere, ellipsoids or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. They are used for the improved coatings of stronger and lighter materials and in electronics.

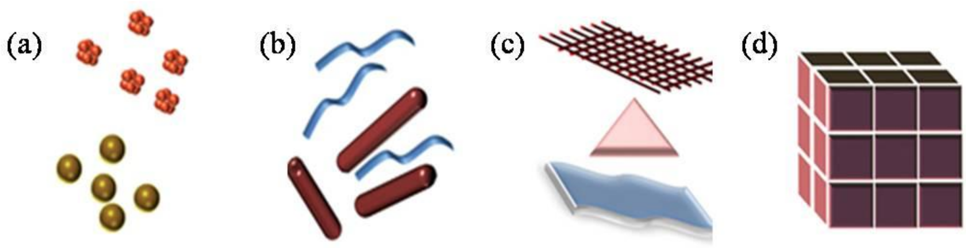
2. Metal based materials: These nanomaterials include quantam dots, nanogold,nanosilver and metal oxides, such as titanium oxide. A quantum dot is a closely packed semiconductor crystal comprised of thousands or hundreds of atoms, and whose size is in the order of a few nanometers to a few hundred nanometers. Changing the size of the quantum dots changes their optical properties.

3. Dendrimers: These nanomaterials are nanosized polymers built from branched units. (The surface of a dendrimer has numerous chain ends, which can be tailored to perform specific chemical functions). This property could also be useful for catalysis.
3- Dimensional dendrimers contain interior cavities into which other molecules could be placed; they may be useful for drug delivery.

4. Composites: Combined nanoparticles with other nanoparticles or with larger nanoparticles, such as nanosized clays, are already being added to products ranging from auto parts to packing materials to enhance their mechanical, thermal barrier and flame retardent properties. The unique properties of these various types of nanomaterials give them novel electrical, catalytic, magnetic, mechanical, thermal or imaging features that are highly desirable for application in commercial, medical, military and environmental sectors. These materials may also find their way into more complex nanostructures and systems.

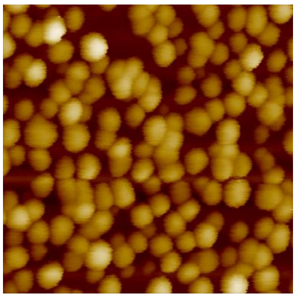
II. Based on dimensions

According to Richard W. Siegel, nanostructured materials are classified as zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

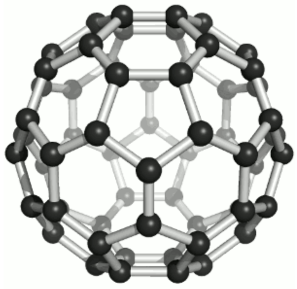


0D spheres and clusters | 1D nanofibers, wires, and rods | 2D films, plates, and networks | 3D nanomaterials

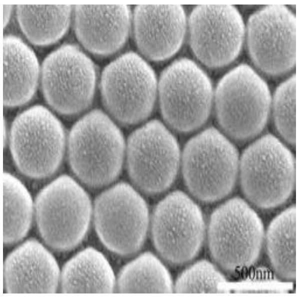
Gold, carbon, metals, metal oxides and alloys are some of the nanomaterials with variety of morphologies (shapes) and their pictures are show below.



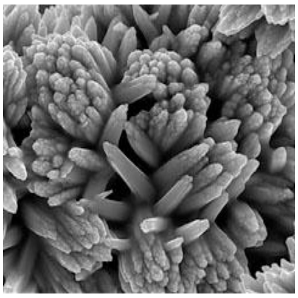
Au nanoparticle



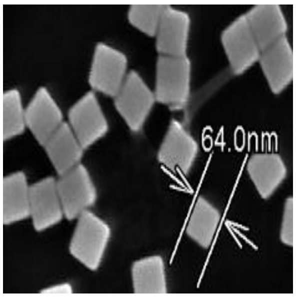
Buckminsterfullerene



Fe-Pt nanosphere



Titanium nanoflower



Silver nanocubes

SnO_2 nanoflower

Nanomaterials with a variety of morphologies

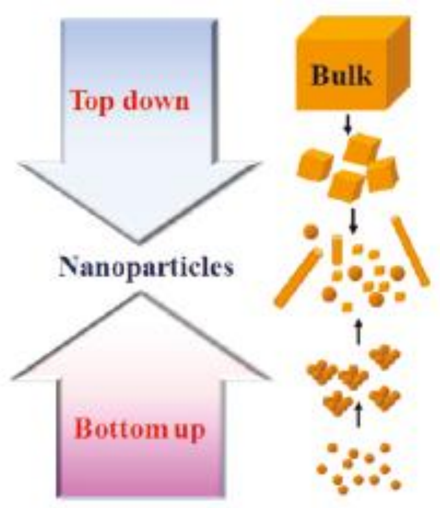
Production of Nanomaterials

There are two approaches for synthesis of nanomaterials and the fabrication of nano structures. They are (i) Top down process and (ii) Bottom up process

(i) Top down process: Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle. Attrition or Milling is a typical top down method in making nanoparticles.

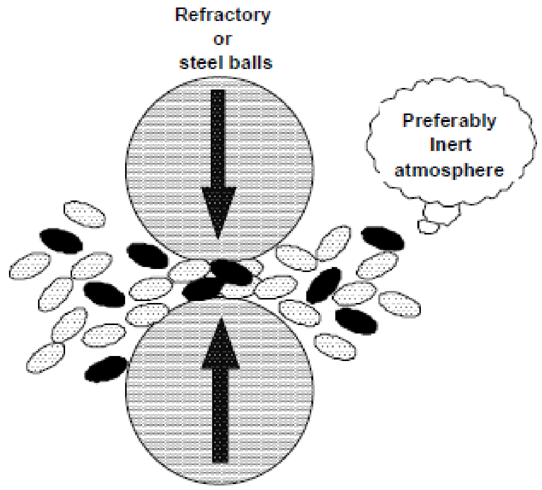
(ii) Bottom up process: Bottom up approach refers to the build-up of a material from the bottom i.e., atom by atom, molecule by molecule or cluster by cluster. The colloidal dispersion is a good example of bottom up approach in the synthesis of nanoparticles.

Both approaches play very important role in modern industry and most likely in nano technology as well. The bottom up approach plays an important role in the fabrication and processing of nano structures.



Schematic illustration of the preparative methods of nanoparticles

Mechanisms for the formation of nanocrystalline structures:



Schematic representation of the principle of mechanical milling

Mechanical milling is typically achieved using high energy shaker, planetary ball, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanoparticles are produced by the shear action during grinding.

Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed.

Synthesis of nano metal oxides

Synthesis Nano ZnO by Solution combustion method

Solution combustion synthesis is an efficient, inexpensive method for the production of a variety of industrially useful materials. This method is used for the synthesis of nanocrystalline oxide powders with high crystalline quality. This process involves a reaction of different oxidants and fuels. Usually the metal nitrates are used as oxidizers and urea, glycine *etc*., as fuels. In this method, a silica crucible containing an aqueous redox mixture is kept in a pre-heated muffle furnace and is brought to boil until it ignites. As a matter of fact, water is used to prevent the direct contact of the oxidant and fuel. During the combustion water from the redox mixture is evaporated, the solution becomes viscous generating large number of air bubbles. At this point, the oxidant reacts with the fuel generating intense heat and gases such as N_2, CO_2 and H_2O resulting in a dry nanocrystalline oxide powders.

Procedure: ZnO nanoparticles are prepared by mixing of 2 g of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] as a precursor and 0.34 g of urea [NH_2CONH_2] as a fuel. These two starting materials are dissolved in 10 mL distilled water, stirred thoroughly to obtain the homogeneous solution and then transferred to silica crucible. The solution is heated to 450 ^oC in muffle furnace for 30 min and then calcined at 550 ^oC for 3 hours to obtain ZnO nanoparticles in good yield.

$$Zn(NO_3)_2 \cdot 6H_2O + 2\ NH_2CONH_2 + \tfrac{1}{2}\ O_2 \rightarrow ZnO + 2CO_2 + 10H_2O + 3N_2$$

Nano TiO_2 by hydrothermal method

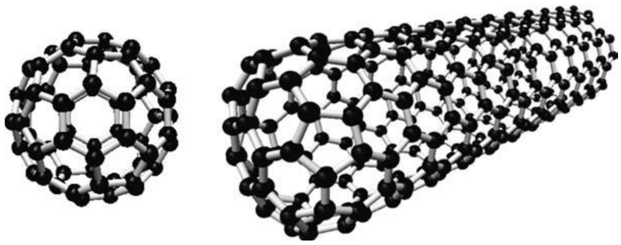
In a sealed steel pressure vessel (bomb, autoclave *etc*.), water can be brought to temperatures well above their boiling points by the increasing the autogenous pressures resulting from heating. Performing a chemical reaction under such conditions is referred to as hydrothermal process. The critical point of water lies at 374 °C and 218 atm. Above this temperature and pressure, water is said to be supercritical. Supercritical fluids exhibit characteristics of both a liquid and a gas.

Procedure: Known quantity (5 mL) of $TiCl_4$ is transferred to 35 mL capacity Teflon tube which contains 25 mL double distilled water. Brisk effervescence is observed indicates the liberation of HCl with the formation of white colored precipitate. The formed white precipitate is stirred for 10 min using magnetic stirrer. The Teflon lined autoclave is kept in hot air oven and maintained at constant temperature (Eg: 180 °C) for known duration (24 h). When the reaction completes, autoclave is cooled to room temperature naturally. The formed white coloured product is retrieved from centrifugation, washed with distilled water several times to remove impurities followed by washing with ethanol. The obtained milky white TiO_2 is dried using hot air oven for overnight at 60 °C. The dried nanostructured TiO_2 is stored in airtight cover for further characterization and application.

$$TiCl_4 + 4\,H.\,OH \xrightarrow[-\,4\,HCl]{180\,°C,\ 24\,h} Ti\,(OH)_4 \longrightarrow TiO_2 + 2\,H_2O$$

Carbon Nanotubes

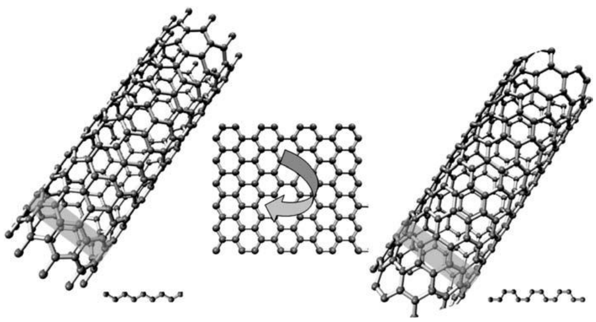
In 1996, Harry Kroto, Robert Curl, and Richard Smalley were awarded the Nobel prize in Chemistry for the discovery of a spherical molecule composed entirely of carbon atoms.



Molecular models representing a C60 fullerene (left) and a single-walled carbon nanotube caped on one end (right).

Fullerenes are closed-cage clusters relatively stable in gas phase, whereas nanotubes are elongated structures that can nowadays reach several micrometers in length but still have very small diameters (in the few nanometers order). The end cap of the nanotube can be thought as an incomplete fullerene.

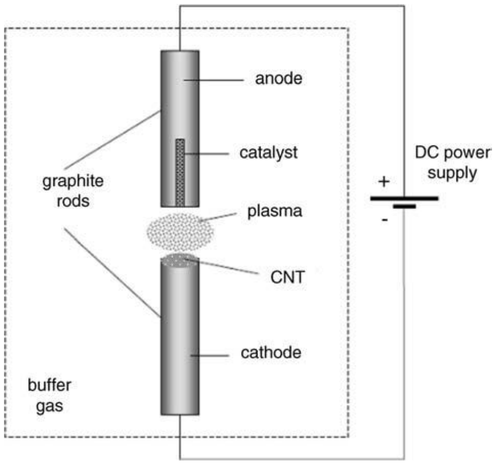
Definition: Carbon nanotubes (CNTs) are cylindrical molecules that consist of rolled-up sheets of single-layer carbon atoms (graphene). They are single-walled (SWCNT) with a diameter of less than 1 nanometer (nm) or multi-walled (MWCNT), consisting of several concentrically interlinked nanotubes, with diameters reaching more than 100 nm.



A single-walled carbon nanotube can be pictured as a rolled graphene sheet. Nanotubes are classified according to the rolling direction as zigzag, armchair, and chiral. Multi-walled nanotubes can be pictured as a set of concentric single-walled nanotubes differing from them in their properties.

Synthesis of carbon nanotubes by Arc Discharge method

The carbon arc-discharge method is a high temperature process that is used for the production of nanotubes. The derived product and the yields are mainly dependent on the atmosphere and catalysts utilized. In the carbon arc-discharge method, an arc is ignited between two graphite electrodes in a gaseous background (usually argon/hydrogen). The arcing evaporates the carbon and meanwhile it cools and condenses that some of the product forms as filamentous carbon on the cathode. This filamentous product comprised of multi-walled carbon nanotubes. The optimization of metals being included in the anode led to the growth of single-walled carbon nanotubes. This in turn, stimulated the successful use of metal catalysts in other techniques for both single-walled and multi-walled carbon nanotube synthesis.



Schematic diagram of an arc-discharge method

Applications:

1. Carbon nanotubes used for applications in energy storage, device modelling, automotive parts, boat hulls, sporting goods, water filters, thin-film electronics, coatings and electromagnetic shields.
2. Epoxy resins strengthened with carbon nanotubes.
3. Windmills with lightweight blades made with an epoxy containing carbon nanotubes.
4. Bicycle components that use a resin containing carbon nanotubes to fill gaps between carbon fibers and reinforce the composite material.
5. Nanotube based transparent conductive film for use in applications such as LCD displays and e-paper.
6. Carbon nanotube based sensors for detecting chemical vapors.

7. Sensor based upon enzyme coated carbon nanotubes for analyzing chemicals in liquid samples.
8. Nanotube based X-ray systems.
9. Nanotube based plastic molding compounds.
10. Nanotube based epoxy resins, coatings and conductive plastics.
11. Nanotube based cathodes, AFM probes and x-ray tubes.

Techniques used in characterization of nanomaterials

FTIR analysis: Infrared radiation has a property of bringing about the changes in the vibrational frequency of the molecules. This change in the vibrational frequency of a molecule would occur only when the natural frequency of vibration of a molecule correspond with that of a particular wave length of IR radiation. This change in vibrations of a molecule is caused by the absorption of IR radiation.

X-ray diffraction (XRD) technique: XRD is non-destructive analytical technique which reveals information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization and wavelength or energy.

Scanning electron microscopy (SEM): It is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that gives information about the sample's surface topography, composition, and other properties such as electrical conductivity.

Note: a raster scan, or raster scanning, is the rectangular pattern of image capture and reconstruction in television.

Transmission electron microscopy (**TEM**): It is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen and the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film.

Questions

1. What are nanomaterials? Explain the different types of nanomaterials.
2. Distinguish between Top down process and Bottom up process.
3. Explain the synthesis Nano ZnO by Solution combustion method.
4. Explain the synthesis of nano TiO_2 by hydrothermal method.
5. Discuss the production of carbon nanotubes by arc discharge method.
6. What are carbon nanotubes? Discuss the applications of CNTs.
7. Describe the various techniques in Characterization of Nanomaterials.

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