11 Nano Physics

(1) INTRODUCTION

"Nanoscience is defined as branch of physics dealing with study of special phenomena that occur when objects are of size between 1 nm to 100 nm (1 nm = 10^{-9} m) in at least one dimension." The work on nanoscience is on the cutting edge of scientific research and expanding the limits of our collective scientific knowledge.

An exciting but challenging aspect of nanoscience is that matter acts differently when particles are nanosized. This means that many macro level concepts of physics cannot be applied to understand nanoscience. For example we cannot apply principles of classical physics which are otherwise applicable to motion of macrosized objects. At nanoscale level we have to apply quantum mechanical description. Further some times it may not be clear if the macroscale level explanations are applicable or not applicable. For example scientists are still exploring whether models used to describe friction at macroscale are useful in predicting behaviour at nanoscale or not.

Nanoscience is multidisciplinary field and because of this we can some times feel the requirement to draw knowledge in potentially unfamiliar academic fields. One day we may be dealing with nanomembranes and drug delivery systems and next day we may be talking about nanocomputing and semiconductors.

(2) NANO SCALE

"Nanotechnology deals with synthesis and processing of particles on the nanoscale." One nanometer is roughly the distance between two points containing five atoms in contact in an ordinary solid. In order to illustrate nanometer scale we consider following example : If the size of a soccer ball (≈ 30 cm $= 3 \times 10^{-1}\ m$) reduced 10,000 times then we reach the width of human hair ($\approx 30\,\mu m = 3 \times 10^{-5}\ m$). If we further reduce the size of hair by same factor, then we reach the width of a carbon nanotube ($\approx 30\ nm = 3 \times 10^{-9}\ m$). Nanotechnology owes its existence to the astonishing development within the field of micro-electronics. Since the invention of integrated circuit in 1958, there has been an exponential growth in the number of transistors per microchip and an associated decrease in the smallest width of wires in electronic circuits. As a result of this extremely powerful computers and efficient communication systems have emerged with a subsequent profound change in our daily lives. A modern computer chip contains 10 million transistors and the smallest wire width are incredibly small, now entering 100 nm range. Nanotechnology with active components is now part of ordinary consumer products. Conventional nano technology is a top down technology. This means that the nanostructures are fabricated by manipulating large piece of material, typically a silicon crystal using processes like lithography, etching, metalliration etc. Since the mid 1980s a number of very advanced instruments for observation and manipulation of individual atoms and molecules have been invented. Most important amongst this is atomic force microscope (AFM) and scanning tunnel microscope (STM). These instruments had an enormous impact on fundamental science discoveries. These instruments have also boosted a new approach to nanotechnology denoted as "Bottom-Up", where instead of making small structure from a large sample, we make small structures directly by assembling atoms and molecules. This reduces material wastage and increases quality of nanostructures.

(3) ATOMIC FORCE MICROSCOPE (AFM)

Atomic force microscope is a device used to observe and manipulate nanometer sized objects of both conductive and insulating nature in vacuum, air, gaseous and liquid environments."

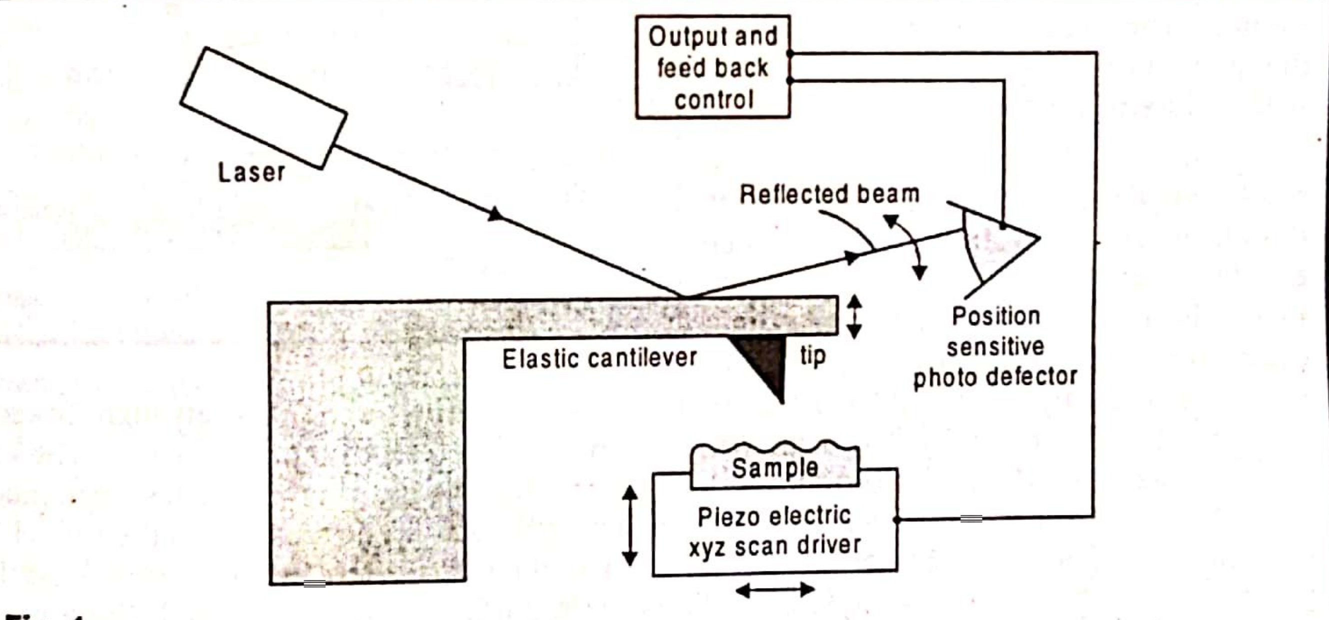


Fig. 1.

A sketch of layout of typical AFM is shown in figure (1). The central component is the nanometer sized tip mounted to an elastic cantilever. By the use of piezo-electric *xyz* scan driver, the tip is scanned across the sample. The distance between tip and sample can be between 0-100 μm. Depending on the contents of the surface of sample, the force acting on the tip changes during the scan due to which position dependent deflection is produced on the elastic cantilever. This deflection is monitored by reflecting a laser beam on the cantilever and recording the movement of reflected beam using a position sensitive photo detector. The signal from photodetector can be used in a feed back loop with *xyz* driver to control the motion of tip. To construct a well functioning AFM following requirements must be fulfilled :

(*i*) The spring constant of cantilever should be small enough to allow detection of minute atomic forces.

(*ii*) The resonance frequency of contilive should be as high as possible to minimise sensitivity to external vibrations.

(*iii*) The tip should be as sharp as possible to allow atomic resolution.

(*iv*) The tip should be as narrow as possible to allow penetration into deep troughs on the surface.

(4) SCANNING TUNNEL MICROSCOPE (STM)

Basic diagram of STM is shown in figure (2). In contrast to AFM, it can scan only conducting surfaces because instrument relies on small tunneling current ($\approx 10^{-9}$ A) that runs between substrate and metal (tungsten) tip. Through a computer controlled feedback loop and a piezoelement, this current controls the height *d* in the z-direction over the substrate. Scans across the surface in *xy* plane are controlled by a piezo electric element. The feedback voltage controlling the height in *z*-direction together with *xy* scan voltage is used as output.

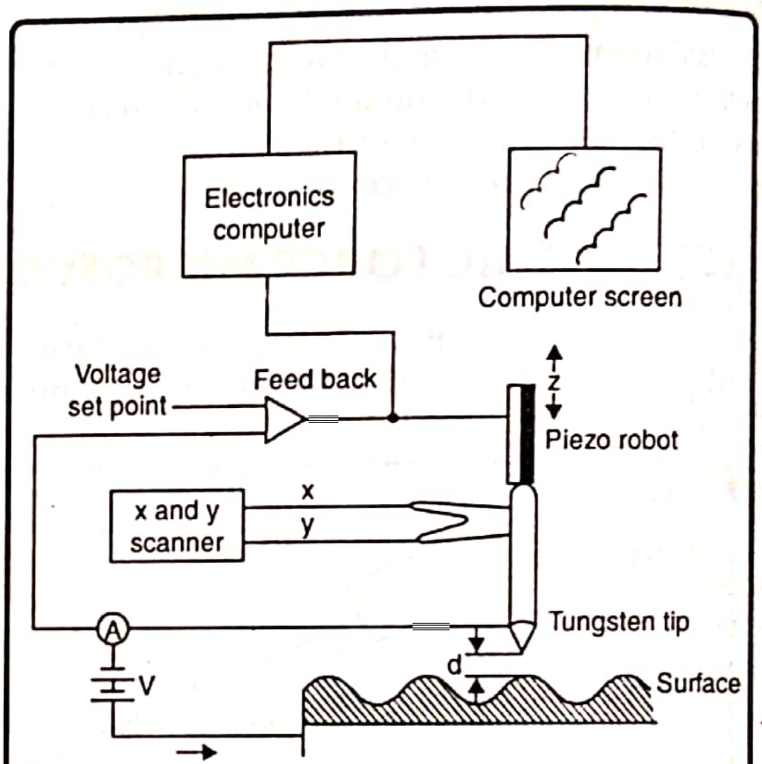


Fig. 2.

With STM one can achieve a resolution of around 0.1 nm. This is better than AFM. The tunneling current reduces by a factor of 10 for every 0.1 nm increase in *d*. This means that over a typical atomic diameter ($\approx$ 0.3 nm), the tunnelling current changes by a factor of 1000. Due to this reason sensitivity of STM is very high. The scan range for a STM is typically upto 1 μm with a scan speed of the order of 1 mm/min. The scan speed depends on the mode used for STM. The constant height mode is fastest scan mode. Here the tip is kept at a fixed vertical position during the scan. The changes in the tunnelling current thus reflects the electronic topology of the surface. Using this mode, there is a risk that the tip will bump into unexpected high regions on the surface and get destroyed. The constant current mode is most widely used STM mode. In this mode, the feed back mechanism ensures that the tunnelling current is kept constant by displacing the tip vertically as the scan proceeds. This is slower than the constant height mode but without risk.

(5) NANOSTRUCTURES

"A nano structure is an object whose size is intermediate between size of an atom (0.1 nm) and size of a microscopic (1 μm sized) object". There are many types of nanostructures depending upon various numbers of nanoscales. For example in case of nanotextured surfaces there is only one dimension on nanoscale and other two dimensions can be quite large *i.e.* only the thickness of surface of object is between 0.1 nm-100 nm while its length and breadth can be much greater. In case of nanotubes there are two dimensions on nanoscale i.e. each of two perpendicular diameters lies between 0.1 nm-100 nm and length can be quite large. Further in case of nanoparticles all three spatial dimensions are on nanoscale. Various types of nanostructures are : Nanocages, Nanocompositics, nanofabrics, nanofoam, nanomesh, nanopillar, nanopin film, nanoring, nanoshell, quantum dot, quantum heterostructure, scuptured thin film etc. A few of these are discussed below :

(*a*) **Nanoring.** "Nanorings are made up of fine nanobelts, that are rolled up as coils layer by layer with as many as hundred loops."

Figure (3) shows a typical nanoring. The diameter of nanoring lies usually in the range 1-4 μm and thickness in the range 10-30 nm.

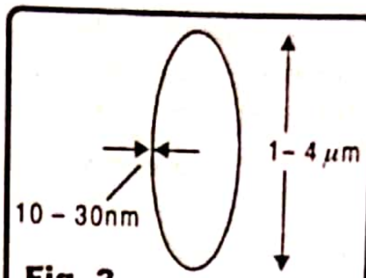


Fig. 3

A nanoring can be made by solid vapour technique from powders of zinc oxide, indium oxide and lithium carbonate in a horizontal tube furnace. The material is heated to 1400°C in argon and it gets deposited on a silicon substrate. Around 20-40% of the deposited material contains nanorings of zinc oxide.

Nanorings of zinc oxide can be used for fabricating piezoelectric based fluid pumps and switches for biotechnology. Nanorings can also be used to measure stress at the scale of a single cell in biotechnology. Nanorings are considered to be future memory storage devices. The basic idea is that current through each ring (due to associated magnetic field) can either be clockwise or anticlockwise. These two directions can be used as 1 and 0 of computer information. Because of small size it can store large memory in small space and further the ring works magnetically, so these rings will not need power to retain information.

(*b*) **Nanorods.** "Nanorods are nanostructures having two spatial dimensions in the nanoscale range". These can be made from metals or semiconductors. Their length is 3-5 times their width. Nanorods are produced by direct chemical synthesis. A combination of ligands act as shape control agents and bond to different facets of the nanorod with different strengths. Due to this, different faces of nano rods grow at different rates, producing an elongated object.

Aggregated diamond nanorods (ADNRS) are a nanocrystalline form of diamond. This material is believed to the hardest and least compressible.

Nanorods have a number of applications :

(*i*) These are used in display technologies. By changing the orientation of nano rods with applied external electric field, the reflectivity of rods can be altered, resulting in superior displays.

(*ii*) The picture elements known as pixels are composed of sharp tipped objects of nanoscale dimensions. These can improve picture quality of a television.

(*iii*) Thin film computers are nanorod based.

(*c*) **Nanoparticles.** "A nanoparticle is defined as a small object having all three spatial dimensions in nanometer scale and behaves as a single unit in terms of its transport and other properties."

These are further classified in 2 catagories. Ultra fine particles (UFP) are nano particles having size between 1 nm-100 nm while fine particles have dimensions in the range 100 nm-250 nm. Nanoparticles have great scientific interest as these act as bridge between bulk materials and atomic/molecular structures. The physical properties of a bulk material are constant, independent of size, but at nanoscale range the physical properties become size dependent. For example bulk gold is yellow in colour while nanoparticles of gold have red colour. Similarly bulk silicon is of grey colour but at nanoscale, its colour is red. The melting point of bulk gold is 1064°C but that of nanoscale gold is $\approx$ 300°C.

Nanoparticles can be synthesized by several methods. Solid powder of material is heated upto 10,000 K using thermal plasma. This results in evaporation of solid powder. When these vapours are exiting the plasma region then these cool down as nanoparticles.

By improving material properties, these can be used in many applications like electronics, sensors, magnetics, advanced ceramics, memory storage devices, biotechnology, medical instrumentation etc.

(*d*) **Nanoshells.** "A nanoshell is a special type of spherical nanoparticle having a dielectric core sorrounded by a metallic layer." In nanoshells electrons oscillate simultaneously with respect to all the ions and this osillation state acts as a quasiparticle called plasmon. The inner shell (electric core) and outer shell of nanoshell hybridize to give a lower or higher energy state. The lower energy state couples strongly with incident light while higher energy state couples weakly to incident light. The extent of hybridisation between inner and outer shells of a nanoshell depends on the thickness of outer shell layer. Strong hybridisation takes place when outer shell has small thickness and vice versa. Thus thickness of shell and overall shell radius determines the suitable wavelength for coupling. The light spectrum of nanoshells covers broad spectrum from near IR region to visible region.

Nanoshells are synthesized by a multistep process. Firstly a suspension of nanoparticles in a solution is obtained. Then small sized seed colloid is attached onto dielectric nanoparticles thus forming a discontinuous shell. At least a continuous shell is grown up by using a chemical reduction of metal attached to dielectric nanoparticles.

Due to highly favourable optical and chemical properties, nanoshells are used for biomedical imaging, therapeutic applications, flourescence enhancement of weak molecular emitters etc. Most important application of nanoshells is in the treatment of cancer. Gold nanoshells are introduced into the cancer tumour and then radiations are made incident on these nanoshells. The nanoshells absorb these radiation and their temperature increases to above 30°C. The high temperature causes death of tumor cell.

(6) PROPERTIES OF NANOPARTICLES

The properties of a substance are usually measured by taking large sample ($\approx 10^{23}$ atoms/molecules) volume. However when these properties were checked for same material at nanoscale level then large differences were observed in many physical properties. This means at nanoscale level, physical properties become size dependent. Some of the physical properties of nanoparticles are discussed below :

(*a*) **Optical Properties.** Optical properties such as colour and transparency are observed to change at nanoscale level. For example bulk gold appears yellow in colour while nanosized gold appears red in colour. Similarly bulk silicon appears grey in colour while nanosized silicon appears red in colour. Another example is of zinc oxide, which at bulk scale blocks ultraviolet light and scatters visible light and gives white appearence. While nanoscale zinc oxide is very small in particle size compared with wavelength of visible light and it does not scatters it. Thus it appears transparent.

The main reason for change in optical properties at nanoscale level is that nanoparticles are so small that electrons in them are not as much free to move as in case of bulk material. Because of this restricted movement of electrons, nanoparticles react differently with light as compared to bulk material.

(*b*) **Electrical Properties.** Electrical properties like conductivity/resistivity are also observed to change at nanoscale level. For example conductivity of a bulk material is independent of dimensions like diameter or area of cross section and twist in the conducting wire etc. However it is found that in case of carbon nanotubes conductivity changes with change in diameter/area of cross section. It also changes when some shear force (twist) is given to nanotube. Further conductivity of a multiwalled carbon nanotube is different than that of single nanotube of same dimensions. These carbon nanotubes can be conducting or semiconducting in behaviour while bulk carbon (graphite) is good conductor of electricity.

(*c*) **Mechanical Properties.** It is observed that physical properties like strength, melting point etc. also shows drastic change at nanoscale level. For example on bulk level steel is highly stronger than carbon (graphite). However at nanoscale level cylinders of carbon are 100 times stronger than steel and very flexible.

"The melting point (microscopic definition) of a substance is defined as the temperature at which molecules in it posses just enough energy to overcome intermolecular forces that hold them in a fixed position in a solid." Atoms on the surface of a substance require less energy to move because these are in contact with lesser number of atoms of substance. While atoms inside the bulk of sample are sourrounded by large number of atoms and require more energy to move. Thus at macroscale level if size of sample is changed then percentage change in the number of atoms in surface is negligible and as a result of this melting point does not change with change in size at macroscopic level. However at nanoscale level if size of object is changed then percentage change in number of atoms on the surface is very large. Due to this melting point starts depending on the size of object and goes on decreasing with decrease in size.

(*d*) **Chemical Properties.** Since the percentage of surface atoms in nanoparticles is large compared with bulk objects, thus reactivities of nanomaterials are more than bulk materials.

(*e*) **Magnetic Properties.** Magnetic nanoparticles show a variety of unusual magnetic behaviour when compared to the bulk materials, mostly due to surface/interface effects, including symmetry breaking, electronic environment/charge transfer and magnetic intreractions. Magnetic nanoparticles are those which can be manipulated using magnetic field. These particles usually contain magnetic elements like iron, nickel, cobalt etc. The physical and chemical properties of magnetic nanoparticles largely depend upon the chemical structure and method of synthesis. For example nanosized particles of magnetite show superparamagnetism at a transition temperature, which is smaller than the transition temperature of bulk material. Nanocomposite magnets consisting of uniform mixture of magnetically hard and soft phases have been extensively investigated in recent years due to their useful hard magnetic properties. High energy products and relatively high coercivities can be developed in these nanocomposite magnets. Among the advantages of these magnets are high value of remanence and low cost. In the past few years, magnetic studies in nanostructured materials have focussed on the interaction between electron charges and magnetic spins. These studies have led to discoveries of new and unique phenomena that are neither observable in traditional bulk materials, nor explainable using classical theories. Some examples are : Giant Magnetoresistance (GMR) in multilayers and metallic granular solids, spin valves, spin injection etc. Magnetostrictive materials are of great scientific importance to us. Magnetostrictive phenomena refer to deformation in a material on account of magnetic field. Magnetostrictive films (nanosized) can allow such functions, which cannot be done using existing integrated circuits. For example these constitute driving elements of micro robots, pumps, motors etc. These can also be used for magnetic control of elastic properties or dependance of stress/strain on magnetic permeability to develop various electronic devices like a resonator with magnetically adjustable frequency and stress controlled inductance.

(*f*) **Quantum Confinement or Electron Confinement.** "Quantum confinement is the change of electronic and optical properties when the sample material is of sufficiently small size (typically less than 10 nm)". The bandgap is found to increase as the size of nanostructure decreases. Specifically this phenomenon results from electrons and holes being confined into a dimensions that approaches a critical quantum measurement called Bohr Radius. The first experimental evidence of quantum confinement effects in clusters came from crystalline CuCl clusters grown in silicate glasses. Spectroscopic studies of these clusters clearly indicated upto 0.1eV blueshift of the absorption spectrum compared with bulk sample of same material. A recent study of X-ray absorption spectra in nanodiamond thin films with grain size in the range 3.5 μm- 5.0 μm showed that C-1*s* exciton state and conduction band edge are shifted to higher energies with decrease in grain size especially when the crystallite radius is less than 1.8 nm. Note that in case of silicon and germanium, quantum confinement persists upto 6nm-7nm. Whereas in diamond there is no detectable quantum confinement for sizes larger than 1nm-1.2 nm.

(7) SURFACE AREA TO VOLUME RATIO

When a body of given volume is cut into a number of smaller pieces, then its surface area increases. Thus surface area to volume ratio is also increased. For example consider a cube of each side equal to 10cm. Then its surface area will be

$$S = 6\,(10 \times 10) = 600 \text{ cm}^2$$

while its volume will be

$$V = 10 \times 10 \times 10 = 1000 \text{ cm}^3$$

Thus surface area to volume ratio of the cube is

$$R = \frac{S}{V} = \frac{600 \text{ cm}^2}{1000 \text{ cm}^2} = 0.6 \text{ cm}^{-1} \qquad \text{...(1)}$$

Now suppose that this cube is cut into 1000 identical cubes each of side equal to 1cm. Thus surface area of one smaller cube is $6\,(1 \times 1) = 6 \text{ cm}^2$ and that of all the thousand cubes will be

$$S' = 1000 \times 6 = 6000 \text{ cm}^2$$

On the other hand volume of one small cube will be $1 \times 1 \times 1 = 1\text{cm}^2$ and that of all the cubes will be $V' = 1000 \times 1 = 1000 \text{ cm}^2$. Thus new value of surface area to volume ratio is given by

$$R' = \frac{S'}{V'} = \frac{6000 \text{ cm}^2}{1000 \text{ cm}^2} = 6 \text{ cm}^{-1}$$

Thus
$$\frac{R'}{R} = \frac{6 \text{ cm}^{-1}}{0.6 \text{ cm}^{-1}} = 10$$

This tells that surface area to volume ratio has become 10 times for the example considered above. In general whenever a body is cut into large number of smaller pieces then surface area to volume ratio is increased. Similarly when we go to nano scale, then there is manifold increase in surface area to volume ratio of the material.

It is important to note that all reactions take place at the surface of the material. Thus for a given volume, if the surface area is increased then reactivity of material also increases. Since surface area to volume ratio of nanoparticles is very large, this means that reactivity of a material at nanoscale is much larger than at macroscale. Thus chemical and physical properties of nanoparticles are different from their bulk counterparts and this is attributed to increase in surface area to volume ratio of nanoparticles. An interesting example is that of gold. At the macroscale, gold is an inert element *i.e.* it does not react with many chemicals. However at nanoscales gold particles become extremely reactive and can be used as catalysts to speed up reactions. Another example of increased reactivity due to surface area to volume ratio is that of body's digestive system. In the small intestine of our body, there are millions of folds and sibfolds that increase the surface area to volume ratio of the inner lining of the digestive treat. These folds allow more nutrients and chemicals to be absorbed at the same time. This greatly increases the efficiency of our body and the rate at which we digest food.

(8) CLASSIFICATION OF NANOMATERIALS

Nanomaterials are normally classified into four types :

(*a*) Carbon based nanomaterials

(*b*) Metal based nanomaterials

(*c*) Dendrimers

(*d*) Nanocomposites.

(*a*) **Carbon based nanomaterials.** These nanomaterials are mostly composed of carbon having the usual shapes like spherical, ellipsoidal or tubes. Spherical and ellipsoidal carbon nanomaterials are called Fullerenes while cylindrical shaped nanomaterials are called carbon nanotubes (CNT).

(*b*) **Metal based nanomaterials.** These nanomaterials include quantum dots, nanogold, nanosilver and metal oxides such as titanium oxides.

(*c*) **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. Also because three dimensional dondrimers contain interior cavities into which other molecules could be placed, these are thus useful for drug delivery.

(*d*) **Nanocompositles.** Nanocomposite is a multiphase solid material in which one type of nanoparticles are combined with other type of nanoparticles or nanoparticles are combined with other larger bulk type matterials. Nanocomposites such as nanosized clays are already being added to products ranging from autoparts to packaging materials, to enhance mechanical, thermal and flame retardant properties. These are further classified as metallic nanocomposites and polymer nanocomposites.

(9) FULLERENES

The spherical or ellipsoidal shaped nanomaterials are called fullereness. These are a type of carbon based nanomaterials. Spherical fullerenes are also called bucky balls. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings. However these may also contain pentagonal or sometimes heptagonal rings. The first fullerence discovered was C_{60} and it was named as Buckminster fullerene.

Fig. 4

The basic structure of C_{60} fullerenene is shown in figure (4). It consist of 20 hexagonal and 12 pentagonal rings as the basis of an icosohedral symmetry closed cage structure. Each carbon atom is bonded to three other carbon atoms and is sp^2 hybridised. The C_{60} molecule has two bond lengths-the 6 : 6 ring bonds can be considered as double bonds and are shorter than 6 : 5 bonds. C_{60} is not superaromatic as it tends to avoid double bonds in pentagon rings, resulting in poor electron delocalisation. As a result C_{60} behaves like an electron deficient alkene and reacts readily with electron rich species. C_{60} has only four IR active vibrational bands. Its density is 1.65 g cm^{-3} and its appearence is black and it is odourless. It is soluble in common solvents like benzene, toluene etc. C_{60} fullerenes are useful for secural biological applications because these are not toxic to cells. It is powerful antioxidant and reacts readily with free radicals which are usually responsible for death or damage of a cell. Major pharmaceutical companies are exploring the use of fullerenes in controlling neurological damage of diseases such as Alzheimeri's disease which result due to a radical damage. C_{60} fullerene can be used as organic photovoltaic cell. Fullereness are chemically reactive and can be added to polymer structures to create new co-polymers with specific physical and mechanical properties. These can also be used to make nanocomposites.

(10) CARBON NANOTUBES (CNT)

These are also known as bucky tubes. CNTs are a class of carbon based nanomaterials. "Carbon nanotubes are defined as allotropes of carbon having cylindrical nanostructure". The length to diameter ratio (called aspect ratio) can be as high as 10^8, which is significantly larger than any other material. CNTs exhibit extraordinary strength and Unique electrical and thermal properties. The diameter of a CNT is in the nanoscale range (1 nm). Thus the length of a CNT can be as high as $10^8 \times 1\ nm = 10^{-1}\ m = 10\ cm$. CNTs are catagorized as single walled nanotubes (SWNT) and multiwalled nanotubes (MWNT). The C – C bonds are sp^2 hybridised. This bonding structure is stronger than sp^3 bonds and found in diamond. Due to this CNT have extra strength. In case of SWNT, diameter of tube is ≈ 1 nm and length can be million times the diameter. The structure of SWNT can be obtained by wrapping one atom thick layer of graphite (called graphene) into a seamless cylinder. SWNTs are an important variety of nanotubes. Their bandgap can vary from 0-2eV and their electrical conductivity can show conducting or semiconducting behavior. MWNTs contain multiple rolled layers of Co-axial tubes of graphite. A double walled nanotube (DWNT) is simplest type of MWNTs. The properties and morphology of DWNTs is similar to SWNTs but these are more resistant to chemicals than SWNTs. CNTs are strongest and stiffest nanomaterials yet discovered in terms of tensile strength and modulus of elasticity respectively. In case of MWNTs, it is possible that an inner nanotube core may slide almost without friction, within its outer nanotube shell and thus producing an atomically perfect linear or rotational bearing. This property of CNTs has been used to create world's smallest rotational motor. All CNTs are very good conductors of heat along their length. This property is called "Ballistic conduction". However their thermal conductivity in lateral direction is very small (these behave like thermal insulators in lateral direction). Thus plastics can be loaded up with conductive fillers of CNTs and then these plastics can act as conductive plastics. Note that just like thermal conductivity, the electrical conductivity of CNTs is also very large along the length and very small in lateral direction because electron motion in CNTs is restricted only along the length. Thus conductive plastics can be used in the electrical conductor also.

(11) NANOCOMPOSITES

As already defined, "These are the materials, in which nanoparticles are dispersed in a continuous matrix." Matrices for nano particles can be ceramic, metallic and organic materials. Matrices play the role of structural stability, passivation and supporting substrates. Some nanophase and matrix systems include mechanically hard crystallites of SiC in high strength ceramic materials, magnetic phases of Fe & Co in magnetic materials. Some important types of nano composities are discussed below :

(*a*) **Ceramic Matrix Nano composites.** These are the composites that contain ceramic nanophases either comprising over half of the total volume fraction or with an interconnective relationship. These compositics exhibit great improvements in mechanical properties such as strength, toughness and hardness and abrasion by refining particle size. They have enhanced ductility, toughness, formability and superplasticity by nanophases. Due to disordered grain boundary interface, the electrical and magnetic properties are greatly changed compared with bulk material.

(*b*) **Metallic Nanocomposites.** "It is a kind of nanocomposite obtained by combining metal oxides and nanoscale aluminium powder in a silica base." These have improved properties compared with other nanocomposites. A few properties are listed below :

(*i*) Increased hardness, strength and super plasticity.

(*ii*) Lowered melting point.

(*iii*) increased electrical resistivity due to increased disordered grain surfaces.

(*iv*) increased miscibility of the non-equilibrium components in alloying and solid solution.

(*v*) Improved magnetic properties such as coercivity superparamagnetisation, saturation magnetisation and magnetsatic properties.

The most attractive challanges of metallic nanocomposites are their unique magnetic properties. When sizes of the magnetic particles are small enough to approximate the size of a single magnetic domain, then their spins are all aligned in one direction to give net magnetic dipole moment and the domain walls can be moved easily (by applying small external magnetic field) and the exchange coupling is substantially exhanced in magnetic field. This results in better magnetic properties. It should be noted that high density recording materials require high coercivity and high magnetisation. It is a known fact that maximum value of coercivity exists in nanocomposites containing magnetic (metallic) crystallites of an optimum size comparable with size of magnetic domain. For example Iron powder with a crystallite size of 13 μm exhibits 900 Gauss coercivity compared with bulk iron (10 Gauss). Giant magnetoresistance (GMR) is another attractive property of metallic (magnetic) nanocomposite. GMR is the phenomenon of a large decrease in electrical resistivity of certain materials, when exposed to external magnetic field. This effect is mostly exhibited by multilayered nanocomposites (such as Fe/Cr multilayered nanocomposites). It is known that a smaller particle size results in larger GMR effect. This property can be used for making magnetic sensors and new storage devices from metallic nanocomposites. These materials are used in making power transformers, magnetic recording heads and microwave applications.

(*c*) **Polymer nanocomposites.** "These are polymer matrices reinforced with nanoscale fillers". These nanocomposites have the advantages of common polymeric materials including high toughness, good transparence, easy formability, light weight and low cost. Their matrices may be epoxies, polypropylene, polyesters, clay filters, magnetic (or conducting) metals and oxide ceramics. The improvements of nanoparticles in polymeric matrices are expected to be in structural, mechanical properties, flame retardant, thermal and barrier properties without significant loss of clarity, toughness or impact strength compared with common organic composites. The important properties of polymer nanocomposites are listed below :

(i) These have increased properties such as abrasion, heat retardation & modulus of elasticity due to use of fine fillers in them.

(ii) By adding impurities like TiO_2, Cr_2O_3, Fe_2O_3, ZnC instead of carbon black, their electrostatic properties can be decreased.

(iii) These materials provide magnetic fluid by adding magnetic nanoparticles in fluid polymers.

(iv) These have increased absorption for ultraviolet wavelengths.

(v) Clay is a catagory of fine layer of aluminosilicate mineral and is ofter used as filler in the plastics. It can absorb water and other polar ions between the layers & swell the interlayer distance may times. Many metallic hydroxides and polymers are easy to insert into layers to form intercalation. Intercalation is an important technique to modify layer materials. Normal intercalation will increase the distance between aluminosilicate layers to a certain degree, but the polymer intercalated into the layers can separate the layers into nanoplatelets. These nano platelets greatly improve hardness, modulus of elasticity of strength without loss of toughness & formability.

Polymer nanocomposites are used in barrier packages, food packages, fire retardant pouches, high speed printing film, gasoline tanks, fuel line tubes and shock absorbers. Commercial nylon-clay hybrid with 2% clay can be used as a gas and UV barrier as well as for high heat resistance. These are also used in sensing devices. Polymer nanocomposites can also be used as light emitting diodes (LED).

(12) SYNTHESIS OF NANO MATERIALS

There are a number of methods used for synthesis of nano materials. A few of these are described briefly as under :

(a) Ball Milling (Or Attrition). It is a process used for mechanical deformation and grinding of materials to obtain fine powders in which grain size is in the nanoscale range. It is an example of 'Top Down' technology in which a bulk material is crushed into fine particles. Such nanoparticles are formed in a mechanical device called 'mill', in which energy is imported to a coarse-grained material, which results in reduction of particle size. Many of the materials milled in mechanical attrition devices are highly crystalline, in which crystallite (grain) size after milling lies between 1nm to 10nm in diameter. Such materials are termed as 'nanocrystalline'. The fundamental principle of size reduction in mechanical attrition lies in the energy imparted to the sample during impacts between the milling media as shown in Figure (5). The figure shows that moment of collision, during which particles are trapped between two colliding balls within a space occupied by a dense cloud, dispersion or mass of powder particles. Compaction begins with a powder mass, that is characterized by large spaces between particles as compared to particle size. First stage of compaction starts with rearrangement and restacking of particles. Particles slide past ore another with minimum deformation and fracture producing some fine and irregularly shaped particles. The second stage of compaction involves elastic and plastic deformation of particles. Cold welding may occur between the particles during this stage in case the sample powder is metallic in nature. The final and third stage involving particle fracture

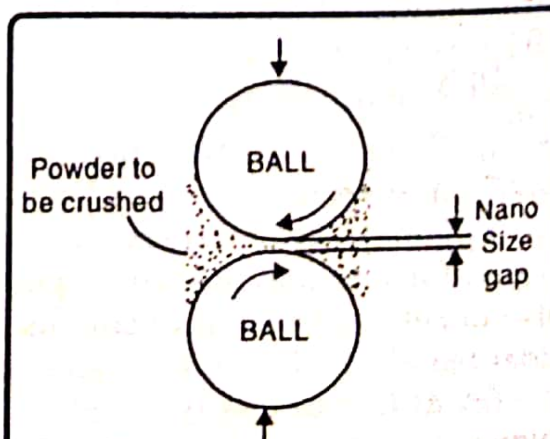


Fig. 5

results in further deformation and/or fragmentation of the particles. Different types of milling equipments are available for mechanical alloying and nano particle formation. These differ from each other in their capacity, efficiency of milling and additional arrangements for heat transfer and particle removal. Some of these one : (1) SPEX Shaker Mills (2) Planetary Ball Mills (3) Attritor Mills. In type (1), the mill has one vial containing the sample and grinding media, which is secured in the clamp and energetically moved back and forth several thousand times per minute. This back and forth motion is combined with lateral movements of the ends of the vial. The ball velocities are high ($\approx$ 5 ms^{-1}) due to which the force of ball's impact is usually very large. This mill can mill about 10-20g powder at a time. In type (2) (also called Pulverisette Mill), a few hundred gram of powder can be milled at a time. This mill owes its name due to planet like movement of the vials. These vials are arranged on a rotating support disk and a special drive mechanism causes them to rotate about their own axes. In case of type (3), there is a rotating horizontal drum half filled with steel balls whose diameter ranges from 0.318 cm to 0.635 cm. As the drum rotates, the balls drop on the metal powder resulting in the grinding. The rate of grinding increases with increase in speed of rotation of drum. However, if speed is too high, then due to stronger centrifugal force the steel balls are pinned with walls of container and hence grinding stops.

Ball milling technique has been used for generation of magnetic, catalytic and structural nano particles. However there are large chances of contamination of the sample during the ball milling processes. The level of contamination can be controlled now a days with the availability of tungsten carbide components and the use of inert atmosphere and/or establishing high vacuum. Other common drawbacks of the technique include low surface area, highly polydisperse (irregular) size of nanoparticles and partially amorphous state of the prepared powders.

(b) Sol-Gel Process. This method is a wet-chemical technique used for preparing mainly metal oxides. A chemical solution (or sol) acts as a precursor for an integrated gel like diphasic system containing both liquid and solid phase whose morphologies range from discrete particles to continuous polymer networks. The solutions of precursors of silica, titanica, zirconia and other oxides are reacted to form irreversible gels that dry and shrink to from rigid oxides. The sol-gel processing is very much like the processing of a nano strcuture. Because the process starts with a nanosized molecular unit which is made to undergo certain chemical reactions at nanoscale range. These chemical reactions turn a homogeneous solution of reactants into an infinite molecular weight oxide polymer'. This polymeric unit is a three dimensional structure skeleton, which is surrounded by inter connected pores. This polymeric unit is isotropic, homogeneous and uniform at nanoscale range. It can exactly replicate its mould and miniaturization of all the features is possible without distortion.

One of the most common homogeneous solution arting as precursor is Tetraorthosilicate" (TEOS), alcohol and water. This solution can react to an extent, where molecular structure can no longer be reversed. This state is known as sol gel transition point. In the whole structure constitution, gel is an elastic solid filling the same volume as the solution. There are two types of chemical processes involved in sot-gel technique.

(i) Non-Aqueous Process. The reaction takes place in three steps. The first step is the hydrolysis of alkonides to make the solution active. The second step involves condensation-polymerisation. In the third step there is further hydrolysis of the solution. The rate of chemical reaction depends on nature of solution, its concentration and pH. Normally a suitable catalyst is used to start the reaction and control the pH of the solution. In these reactions, the molecular weight of the oxide polymer is increased resulting in the formation of mono hydroxide [Me (OH)] or trihydroxide [Me(OH)$_3$] (where Me is metal phase). The majority of transition metal oxides have been prepared by non aqueous sol-gel methods.

(ii) Aqueous Process. This method involves the use of aqueous colloidal solutions which contain nanometer sized particles. The mechanism for attaining sol-gel transition is quite different. The aggregation of sol-particles is normally obtained by changing the pH or the concentration in the sols. Then these sols undergo gelation process in which oxide skeleton structure is in the form of continuous linkages of the sol particles.

The complete sol-gel process in general involves five steps namely Mixing, Gelling, Shape Forming, Drying and Densification. First of all the formation of homogeneous solution is done. This process is called mixing. Then in the gelling process, a suitable gel is formed using appropriate chemical reactions. Then in the shape forming step, we can form bulk materials by casting and moulding of sol-gel. After obtaining suitable geometry or shape these gels must be dried. Thin films and fibres can be dried quickly in air due to their smaller dimensions. However thicker gels (monolithic gels) can be dried in an autoclave by hypercritical technique. Finally in densification, the material is made highly dense or pore free using various routes of sintering.

(13) SYNTHESIS OF CARBON NANOTUBES (CNTs)

There are various mathods for making CNTs. Some of these are discussed briefly below:

(a) Carbon Arc or Arc Discharge Method. In this method we take graphite anode and cathode in close proximity of each other in a close chamber having an inert gas (Argon or neon) at a pressure of approximately 500 torr, as shown in figure (6). The anode is usually doped with a metal catalyst like Nickel or cobalt. A when a potential difference of approximately 20-40V is applied between anode and cathode, then anode is vapourized while cathode evaporates. As a result of this carbon nanotubes are formed on the cathode walls.

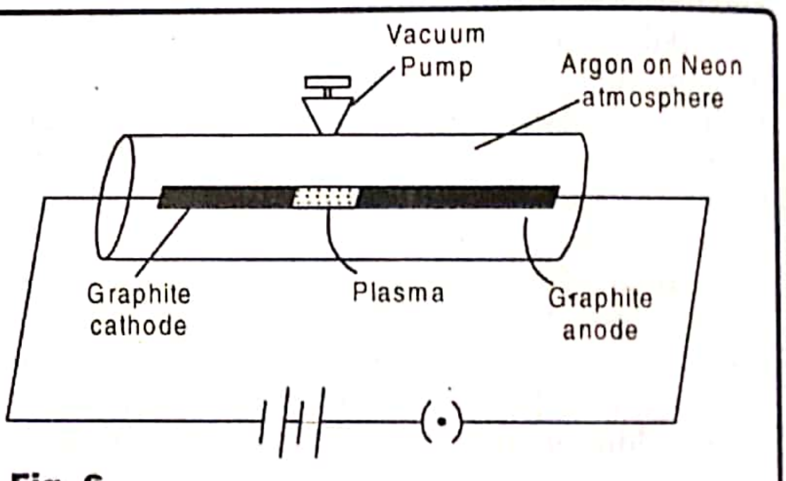


Fig. 6

***(b)* Laser Ablation.** In this method dual pulsed laser is used for synthesising CNTs. Graphite rods doped with Nickel or Cobalt in the ratio 1:1 are vapourised at 1200°C in an atmosphere of argon, followed by heat treatment in vacuum at 1000°C so that C_{60} and other fullerenes can be removed. The initial laser vapourisation is now followed by a second laser pulse in which material is further vapourized in more uniform manner. The second laser pulse breakes up large particles ablated by first pulse and feeds them on growing nanotube structure. With this method CNTs of 10-20nm in diameter and $\approx$ 100 μm length have been prepared.

***(c)* Chemical Vapour Deposition.** Both Laser ablation and carbon arc method discussed above have the limitation that CNTs formed are contaminated with unwanted materials. Further the CNTs formed are highly tangled which makes it extremely difficult to purify and assemble them.

In chemical vapour deposition technique, single wall CNTs can be prepared in gas phase by catalytic disproportionation of carbon monoxide on iron particles. Iron is in the form of iron pentacarbonyl. The addition of 25% hydrogen is found to increase the single walled CNTs yield. This method is carried out at 1100°C and at atmospheric pressure.

However for synthesizing multiwalled CNTs, the catalytic metal particles are supported on a substrate (Sillicon wafer). Iron is deposited from iron pentacarbonyl or by electron beam sputtering. The nanotube growth is achieved by catalytic chemical vapour deposition from hydrocarbon molecules (acetylene, methane) or fullerenes in the temperature range of 750°C – 1100°C.

(14) 1D, 2D AND 3D NANOMATERIALS.

One dimensional nanomaterials are those which have only one dimension in the nanoscale range and other two dimensions are much longer than nanometer. Nanotextured surfaces, quantum dots and nanoring are examples of one dimensional nanomaterials.

Two dimensional nanomaterials are those which have two dimensions in the nanoscale range and third dimension is much larger than nanometer. Carbon nanotubes and nanowires (used in chip technology) are examples of two dimensional nanomaterials.

Three dimensional nanomaterials are those, which have all three dimensions in the nanoscale range. Nano particles like fullerenes and nanoshells are examples of three dimensional nanomaterials.

(15) APPLICATIONS OF NANOTECHNOLOGY

1. Cloth manufactureres are embedding fine spun fibers into fabric to confer stain resistance clothes. These nanowhispers act like peach fuzz & create a cushion of air around the fabric so that liquids bead up and roll off. To attach these whispers to cotton, the cotton is immersed in a tank of water full of billions of nanowhiskers. Then fabric is heated so that water evaporates and these nano whispers form a chemical bond with cotton fibers and attack themselves permanently.
2. Nanopaints are ceramic based coatings that make paint a lot more durable and resistant to rock chips and scratches. In addition to holding up better to weathering, nanopaints have richer and brighter colours than traditional pigments.
3. Scientists have announced that they have invented nanotech based coating material that acts as a permanent air purifier. In near future such paint will be gradually used on buildings to improve air quality. The core of such paints is titanium oxide based compound developed using advanced nanotechnology. Exposed under sunlight, the substance can automatically decompose ingredients like formaldehyde that causes air pollution.
4. Nanotechnology is being used to produce a photovoltaic material, that can be spread like a plastic wrap or paint. These nanocells can be integrated with other building materials & offer the promise of cheap electric power generation, that could finally make solar power a widely used electricity alternative.
5. Nanodevices are used for data storage. These contain a silicon surface formed by depositing small amount of gold on it. The device looks like CD media except that its length is in nanometers. Thus corresponding storage density is million times higher than conventional storage devices.
6. A technique called nanolithography lets us create much smaller devices than current approaches. Atomic force microscope is key device to this technology. With this We can reduce the size of various electronic devices and chips.
7. Researchers are studying electrical interfacing of semiconductors with living cells (in particular neurons) to build hybrid neuro-electronic networks. Cellular processes are coupled to microelectronic devices through direct contact of cell membranes and

semiconductor chips. This research explores the new world at the interface of the electronics in inorganic solids and ionics in living cells providing the basis for future applications in medical prosthetics, brain research and neurocomputation.

8. Quantum dots are small devices that contain a tiny droplet of free electrons and emit photons when submitted to UV light. Quantum dots are considered to have greater flexibility than other flourescent materials, which makes them suited for use in building nanoscale applications where light is used to process information. These quantum dots are sealed in a polymer capsule so that body is protected from cadmium which is hazardous. These polymer capsules were injected into live mice that had human prostate cancers. The dots collected in tumors in large numbers and are visible in UV light under a microscope. Thus these help in defecting the disease at early stage.
9. Using nanotechnology it will be possible in near future to grow cardiac muscle tissue artificially. This will allow us to repair and restore a damaged human heart.
10. If we could cover the proteins that exist on influenza virus, then we could prevent the virus from recognizing and binding to our body cells. A protein recognition system has already been developed, thus nanotechnology can help from protecting individuals from viral diseases.

SHORT ANSWER TYPE QUESTIONS

Q. 1. What are excitons ?

Ans. An exciton is a quasiparticle consisting of a bound state electron hole pair having a definite half life during which it migrates through the crystal and releases its eventual recombination energy in the form of photon.

Q. 2. Define superparamagnetism.

Ans. It is a form of magnetism which appears in small ferromagnetic or ferrimagnetic nanoparticles. In small enough nanoparticles, magnetisation can randomly change direction due to change in temperature. The average time between two successive flips in the direction of magnetisation is called Neel's relaxation time. In the absence of external magnetic field if the average magnetisation of nanoparticles is measured over a time much larger than Neel relaxation time, then it comes out to be zero due to a large number of flips occuring in the time of measurement. Such a state of naoparticles is called superparamagnetic state. If an external magnetic field is applied to nanoparticles in this state then magnetisation of nanoparticles become non zero just like paramagnetic materials. However the magnetic susceptibility of these nano particles is very large compared with paramagnetic materials. Due to this reason the process of magnetising nano particles by applying extrenal magnetic field is called super paramagnetism.

Q. 3. What do you mean by Quantum dot ?

Ans. Quantum dots are semiconductor materials having size in the nanoscale range (2nm-10nm). One quantum dot contains approximately 10-50 atoms. Due to small size materials behave differently than bulk semiconductors and individual semiconductor molecules *i.e.* their properties are intermediate between discrete molecules and bulk matter.

Q. 4. What are possible causes of change in properties of a substance at nanoscale level ?

Ans. (*a*) In case of nanoscale objects gravitational forces are small due to small macro compared to bulk objects. On the other hand electromagnetic force is a function of charge and distance but independent of mass. Thus these forces can be very strong even at nanoscale level. These different forces dominate at nanoscale level.

(*b*) At bulk level classical models apply but at nanoscale level quantum models apply because dual nature of matter dominates.

(*c*) At nanoscale level the ratio of surface area to volume of substance is very large compared with bulk matter.

(*d*) Random molecular motion at nanoscale level becomes significant and cannot be ignored. This random motion of individual molecules can be ignored at macroscale.

Q. 5. Describe some potential risks of nanotechnology.

Ans. (*i*) Nanotechnology's potential is encouraging, but health and safety risks of nanoparticles have not been fully explored. For example substances that are harmless at bulk level can become hazardous at nanoscale level because at nanoscale the reactivities increase.

(*ii*) A growing number of persons are exposed to nanoparticles at workplace and there is danger that the growth of nanotechnology could outplace the development of appropriate safety precautions.

(*iii*) Under some conditions, nanotubes can cross membrane barriers, which suggests that if raw materials reach the organs, these can induce harmful effects such as inflammatory and fibrotic reactions.

Q. 6. Define Nanoscience and nanotechnology.

Ans. *Nanoscience*, in its simplest, means the study of the fundamental principles of molecules and structures, sized between 1 to 100 nanometre at least in one dimension. These structures are known as *nanostructures*. *Nanotechnology*, in short "nanotech", is the study of the controlling matters in its atomic and molecular scale and *application* of these nanostructures into useful 'nanoscale' devices. Nanoscience and nanotechnology are concerned with all properties of structures on the nano-scale whether they are chemical, physical, quantum or mechanical.

Q. 7. What are nanomaterials? How are these classified?

Ans. *Nano materials are those which have structured components with at least one dimension is less than 100nm.* Materials that have one dimension in the nano-scale (and are extended in the other two dimensions) are layers, such as a thin film or surface coatings. Materials that are nano-scale in two dimensions (and extended in one dimension) include nano wires and nano tubes. Quantum dots which are tiny particles of semiconductor materials, colloids, nano particles made up of nanometre sized grains are materials with nano-scale in three dimensions.

Q. 8. Discuss production of nanomaterials in brief.

Ans. Nano materials can be synthesized using a number of methods. These methods are generally classified into two categories

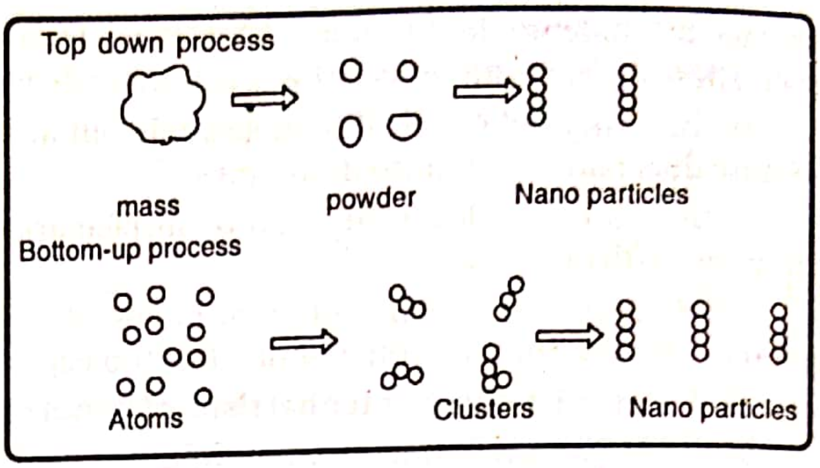
1. Top-down process
2. Bottom-up process

1. Top-down process or physical method. To synthesise a nano material if a mass material was used as a initial material, then the method is known as top-down process. In the top-down process, a bulk material is crushed into fine particles using processes like mechanical alloying, laser ablation etc. The examples of the top-down process are

1. Ball milling
2. Laser ablation

2. Bottom up process of chemical methods. In some methods, the nano-materials are prepared by arranging atom by atom, Due to the nucleation and growth, bigger size grains or a cluster of atoms having a size less than 100 nm are produced. The examples are

1. Chemical vapour deposition
2. Sol-gel method



The schematic representation of these two processes is illustrated in figure

Q. 9. Explain briefly Ball milling and chemical vapour deposition techniques for fabrication of nano materials.

Ans. 1. Ball milling. Ball milling is a mechanical deformation and grinding process of producing fine powders. The grain size of the nano powders depends on the amount of energy input during the milling, milling time, temperature, and atmosphere.

2. Chemical Vapour Deposition (CVD). Two or more vapours flow through a chamber containing a heated wafer. Chemical reaction takes place on hot water surface with the vapour phase gas molecules; the product is deposited on the water itself. A non-reactive carrier gas may be introduced to limit the rate of diffusion of reactant vapours into the water surface.

Q. 10. Write some important properties of nano particles.

Ans. *Nano particles can be made to emit or absorb specific wavelengths (colours), merely by controlling their size.* If semiconductor particles are made small enough, quantum effects come into play, which limit the energies at which electrons and holes can exist in the particles. As energy is related to the wavelength, the optical properties of particles can be finely tuned by changing the size. For example, Gold nano spheres of 100nm appears orange in colour while that of 50nm appears as green.

The electronic bands in metals become narrower due to quantum confinement. For smaller sizes, the 'ionization potential' are larger than that for the bulk. In nano-ceramics and magnetic nano-composites electrical conductivity increases with reduction in particle size, whereas in metals the electrical conductivity decreases.

"Small particles are more magnetic than the bulk materials since the coercivity and the saturation magnetisation values increases with decrease in grain size and increase in surface area per unit volume. So nano particles of even non magnetic solids are found to be magnetic.

As the size decreases, the surface pressure and hence the inter-atomic spacing decreases. SO the "melting point decreases with size" Since the nano phase materials are free from dislocation, they have high strength and superhardness.

Q.11. Write some important applications of nano materials.

Ans. By August 2008, the Project on Emerging Nanotechnologies estimates that over 800 manufacturer-identified nanotech products are publicly available, with new ones hitting the market at a pace of *3-4* per week. Most applications are limited to the use of "first generation" passive nanomaterials which includes titanium dioxide in sunscreen, cosmetics and some food products; Carbon allotrope's used to produce gecko tape; silver in food packaging, clothing, disinfectants and household appliances; zinc oxide in sunscreens and cosmetics, surface coatings, paints and outdoor furniture varnishes; and cerium oxide as a fuel catalyst.

1. Yttrium-samarium-cobalt nanocrystals can be used for making of magnets and these will have unusual magnetic properties because of their extremely large interface area.

Due to high coercivity they can be used in motors, analytical instruments like magnetic resonance imaging.

2. CNT's possess exceptional mechanical properties, like they have high tensile strength and at the same time light weight and can have innumerable applications in the field of transportation.
3. Nanospheres of inorganic materials can act as nanosized "ball bearings" and could be used as lubricants. This controlled shape is can make them to more durable lubricants than conventional ones made of solid lubricants and wear additives.
4. It is practicable to produce non-conventional extraordinary colour paints using nanopartcles as nanopartcles exhibit entirely different optical properties.
5. Fabricated magnetic nanoscale materials have application in the storage of data. If the area needed to record/preserve and retrieve dependably can shrunk to nanoscale, the storage capacity of a disk can be improved dramatically.

   The production of displays with low energy consumption could be accomplished using carbon nanotubes (CNT). Carbon nanotubes are electrically conductive and due to their small diameter of several nanometres, they can be used as field emitters with extremely high efficiency for field emission displays (FED). The principle of operation resembles that of the cathode ray tube, but on a much smaller length scale, their strength sharpness conductivity and inertness make it possible for very efficient and long lasting emitters.
6. Addition of nanoparticulate cerium oxide as a fuel catalyst to diesel fuel improves fuel economy.
7. In nanoscience the term "small material" refers to any material engineered at nanoscale to perform a specific task. 'Photorefractive polymers' are wonderful form of nanoscale whose storage density can far exceed even the best available magnetic storage structures.

QUESTIONS

1. Define nanotechnology and write the properties that change at nanoscale.
2. What do you mean by nanostructures. Name various types of nanostructures.
3. What are fullernes ? Explain their important types.
4. What are carbon nanotubes ? Give their applications.
5. Explain briefly nanorods, nanorings, nanoshells and nanoparticles.
6. What is quantum confinement ? Explain briefly.
7. What are nanocomposites. Explain their types and uses.
8. Write some applications of nanotechnology.
9. What are harmful effects of nanotechnolgoy ?
10. Give ciassification of nanomerials& explain them briefly.
11. Explain working of AFM & STM.
12. What is the effect of structure area to volume ratio on the properties of a material ?
13. Discuss some techniques for the synthesis of nanomaterials.
14. How are LNTs prepared ? Discussed briefly.
15. Give examples of 1-D, 2-D & 3-D nano materials.