



LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- An overview of nanotechnology, nanoscience and nanochemistry.
- General properties of nanomaterials.
- General methods of synthesis of nanomaterials
 - ▶ Bottom-up approach
 - ▶ Top-down approach
- Characterization of nanomaterials
- Characteristics, classification, formation and mechanism of self-assembly.
- Molecular self-assembly and its differences with materials self-assembly.
- General strategy and the forces involved in two-dimensional assemblies.
- Mesoscale self-assembly and similarity and differences between capillary forces and covalent atomic bonds.
- Coercing colloids and supramolecular structures and their applications.
- Various nanoscale materials and their applications.
- General application of nanomaterials in:
 - ▶ Medicine.
 - ▶ Electronics and communications.
 - ▶ Energy sciences and catalysis.
- Future perspectives of nanochemistry.

Nanotechnology can be defined as the manipulation of atoms and molecules at nano (one billionth) scale (1–100 nm) to produce devices, structures or systems having at least one novel or superior property. The materials having at least one dimension in the nano scale are called **nanomaterials**. The conceptualization of nanotechnology was done by Richard Feynman in 1959. The impact of nanotechnology is quite significant. When the bulk materials are reduced to nanometer size, the properties exhibited by these nanomaterials are of tremendous use. For example, opaque materials become transparent (copper), insoluble substances become soluble (gold), stable materials become combustible (aluminium). In fact, at normal scales, gold is chemically inert but at nanoscales, gold nanoparticles can serve as potent chemical catalysts. The study of these nanomaterials is known as **nanoscience**.

22.1 Properties of Nanomaterials

The physical and chemical properties of nanomaterials are significantly different from those of single atoms/molecules and bulk material of the same chemical composition. These differences are related to the spatial arrangement of molecules or structure, electronic structure, energetics, chemical reactivity, phase change or catalytic activity. When the size or dimension of a material is continuously reduced

from a larger or macroscopic size such as meter or centimeter to micro size, the properties remain same at first, and slowly small changes begin to take place as the particle size is reduced further. The size at which the properties of materials change entirely from those in the bulk material is said to be in the nanoscale range. This is generally observed at size below 100 nm.

The properties of nanomaterials are size-dependent because:

1. The surface area to volume ratio of the nanomaterials is relatively larger than that of bulk materials of the same mass. This increases the chemical reactivity and affects strength and electrical properties of the material.
2. The quantum confinement is observed at nanometer sizes that changes the optical, electronic and magnetic properties of the material. The band gap increases as the size of the material is reduced to nanometer range. This effect is caused by the phenomenon resulting from electrons and electron holes being constricted into a dimension which approaches the critical quantum measurement, known as the exciton Bohr radius.

Nanochemistry involves the study of synthesis and characterization of nanomaterials. Professor Geoffrey Ozin is regarded as the father of nanochemistry. Although nanoscience is an interdisciplinary subject, its origin lies in the principles of chemistry which is carried on for further characterisation and practical application by the scientists.

Nanochemistry has a wide range of applications in both discovering new processes as well as materials for use in a variety of fields from medicine to electronics. Nanochemistry allows synthesis of a variety of nanomaterials whose shape, size, defects, surface characteristics and self-assembly can be manipulated to obtain useful products. The combination of number of possible materials coupled with the concepts of nanochemistry is mind boggling. A few of them are:

1. Nanoparticles of various sizes and shapes such as, gold, silver nanoparticles.
2. Nanooxides such as iron oxide, cadmium oxide
3. Carbon nanotubes and fullerenes
4. Nanopolymers and nanomembranes
5. Nanocatalysts
6. Nanoformulations for cosmetics, example, in sunscreens, anti-aging creams, etc.
7. Nanoceramics

These materials have, in turn, applications in various domains:

1. In semiconductor devices, such as nanocapacitors
2. As therapeutic molecules (nanomedicine) for diseases such as cancer.
3. In targeted drug delivery
4. In agriculture
5. In electronics
6. As taste enhancers (nanofoods) and for packaging in food industry
7. In fuel cells
8. In chemical and biosensors
9. In fabric technology
10. In solar cells
11. Nanooptics
12. For manufacture of self-cleaning surfaces

13. In waste water treatment
14. Green nanotechnology

Size-Dependent Properties

Particle-Size vs. Surface Area

If a macroscopic object is divided into smaller parts, the ratio of surface atoms to interior atoms becomes a significant number of the total fraction of atoms. For example, a cube of iron with side 10 cm long, the percentage of surface atoms is only $10^{-3}\%$. When the same cube is cut into smaller cubes with side length 10 nm, the percentage of surface atoms increases to 10%. When the cube is further cut into cube with side length 1 nm, every atom comes on the surface. This inverse relation between the particle size and surface area is responsible for the remarkable changes in the physical and chemical properties of nanomaterials.

Surface Chemistry of Materials

Due to increased surface area, nanomaterials possess greater surface energy and are thermodynamically less stable. The atoms or molecules that exist on the surface or the interface are somewhat different from atoms/molecules in the bulk/interior of the material. These have enhanced reactivity and greater tendency to agglomerate. These have higher surface energy and are relatively unstable. As a system, the nanomaterials thus strive to attain the lower energy state.

Electronic Properties

Various physical properties such as thermal, optical and magnetic properties are dependent on the electronic state of the material. To understand the electronic properties of nanomaterials, let us first understand the electronic properties of solids. In solids, these are determined by the energy levels, types of bonds between atoms, energy bands, energy gaps and Fermi levels. Some characteristics of electronic structure of solids are:

1. In an isolated solid, the electrons move in quantified energy levels. When the distance between atoms is less, electron orbitals interact with each other, which leads to broadening of energy levels to form energy bands.
2. The inner-shell electrons form narrow bands called internal bands and electrons in external shell form valence bands. The electrons in excited state form conduction band.
3. The difference of energy between valence band and conduction band is called energy gap. In metals (or conductors) this energy gap is zero; it is small in case of semiconductors and large in case of insulators.
4. The maximum energy for electrons at absolute zero (0 K) is called Fermi level or Fermi energy. The physical properties of materials are mainly governed by electrons that have energy larger than Fermi energy.

In nanomaterials, the confinement of valence electrons, which are almost free, in finite volume leads to quantification of their energy, similar to energy of nucleons in the nucleus. The band gap ~~decreases~~ ^{increases} when the particle size is decreased and energy gaps gradually convert into discrete molecular electronic levels. If the particle size is less than the wavelength of the electron, the charge carriers may be treated as "particles in a box". The spatial confinement of electrons within the crystallite boundary is referred to as quantum confinement. Since nanomaterials are closer in size to atoms or molecules, quantum mechanical laws are used to describe their behavior. In nanocrystals, the energy levels are well defined and the

addition and subtraction of one atom or electron to the nanocrystal measurably changes the electronic properties.

When the size or dimension of material is continuously reduced, the size at which the properties completely change is the nanoscale (< 100 nm). If one dimension is changed to nanorange then *quantum wells* are obtained. If two dimensions are reduced, the resulting structure is called *quantum wire*. When all three dimensions are reduced, *quantum dots* are obtained, which are zero-dimensional semiconductor spheres. In quantum dot crystal, the energy gap is tunable and can be altered to produce a range of energies between the valence and conduction bands. It can be considered a semiconductor crystal with a small number of atoms and physical dimensions of the order of 10 nm. Thus, when a semiconductor crystal has discrete states, it can be defined as quantum dot.

Mechanical Properties

Nanocrystalline materials have an average crystallite size in the range 1 to 100 nm and are characterized by numerous grain boundaries due to the small size of the grain. The mechanical properties of nanocrystalline materials are determined by their small grain size and the grain boundary. These properties are enhanced by reducing the grain size, as grains of nano-size have no defects inside, unlike micro-grains of relatively larger size. For example, nanocrystalline copper is found to be three times more resistant to applied stress than normal copper crystals and deformed homogeneously. The crystallinity of the grain structure is maintained right up to the grain boundary. The fraction of atoms out of the total volume present at the grain boundaries is large for small size grains and decreases with increase in their size.

In bulk materials constituted by nanoparticles, large number of grain boundaries allow extended grain boundary sliding leading to high plasticity. In nanometer range, it is generally accepted that grain boundaries act both as sources and sinks for dislocations. So intrinsic plastic deformations arise from the interplay between dislocation and grain boundaries.

In nanostructured materials, the intrinsic elastic modulus is the same as conventional grain size materials. However, when the grain size falls below 5 nm, the number of atoms presents at the grain boundary increases and elastic modulus decreases. This decrease is related to increase in the Poisson's ratio.

The nanocrystalline materials exhibit no significant change in ductility as compared to conventional micro-materials. The reduced ductility of hard nanomaterials results in their low toughness and low fracture toughness, thus limiting their use. Their toughness can be improved by combining with soft metal matrix to form nanocomposites. Nanomaterial may also be combined with amorphous phases (matrix) to restrict grain size above initial crack size; randomize orientation of grains and create large grain boundary volumes. A number of layers of nanomaterial may also be combined to achieve the required toughness. Nanocomposites show enhanced ductility and strength when the particle size matches the width of localization of shear force.

22.2 General Methods of Synthesis

There are two approaches generally adopted for the synthesis of nanomaterials and structures. *Top down* approach refers to successive cutting of a bulk material to get nanoparticles. *Bottom up* approach is the building up of a material from the bottom, that is, atom by atom, molecule by molecule or cluster by cluster. Attrition or milling is a typical *top down* method for making nanoparticles, while colloidal dispersion is an example of *bottom up* approach. The two approaches are schematically depicted in Figure 1.

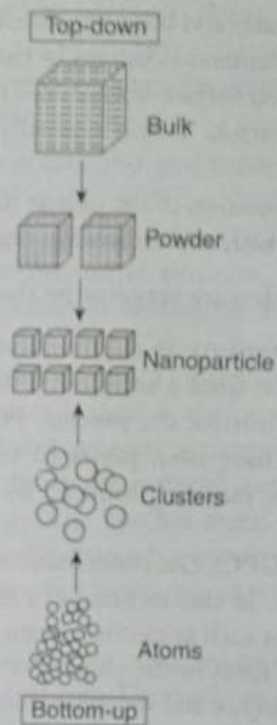
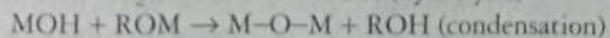


Figure 1 Schematic representation of the building up of nanostructures.

Bottom-Up Approach

1. **Wet chemical synthesis of nanomaterials (sol-gel process):** The sol-gel process is a wet chemical technique (also known as chemical solution deposition) widely used recently in the fields of material science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (*sol*, short for solution) which acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers.

The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides $M(OR)$ can be described as follows:



The sol-gel process can be characterized by a series of distinct steps:

- Step 1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).
- Step 2: Formation of an oxide- or alcohol-bridged network (the gel) by a polycondensation or polyesterification reaction that causes a tremendous increase in the viscosity of the solution.
- Step 3: Aging of the gel during which the polycondensation reactions continue until the gel transforms into a solid mass. This is accompanied by contraction of the gel network and expulsion of solvent from gel pores.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. This process involves fundamental changes in the structure of the gel.

Step 5: Dehydration, during which surface-bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by heating at temperatures up to 800°C.

Step 6: Densification and decomposition of the gels at high temperatures (>800°C). The pores of the gel network are collapsed, and remaining organic species are volatilized.

The production rates of nanopowders are very low by this process.

- Liquid solid reactions(precipitation):** In this method, ultrafine particles of the desired material are produced by precipitation from a solution. The presence of desired nuclei in the solution is a necessary condition to initiate the process. For example, TiO₂ powders with particle sizes in the range 70–300 nm have been prepared from titanium tetraisopropoxide by this method. Similarly, ZnS powders may be produced by reaction of aqueous zinc salt solutions with thioacetamide.
- Gas condensation processing (GPC):** Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as electron beam evaporation devices in an inert gas atmosphere. Clusters of nanoparticles form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase. The cluster or particle size depends critically on (a) the time spent by the particles in the growth phase, (b) gas pressure, (c) the kind of inert gas used and (d) the evaporation rate/vapor pressure of the evaporating material. The size of nanoparticles increases with increase in gas pressure, vapor pressure and mass of the inert gas.

A rotating cylindrical device cooled with liquid nitrogen is employed for the particle collection. The nanoparticles are removed from the surface of the cylinder by means of a scraper. This method is better suited for larger scale synthesis of nanopowders. A major advantage is the improved control over the particle sizes. However, control of the composition of the elements is difficult, reproducibility is poor and the method is extremely slow.

For preparation of nanoparticles from metals with high melting temperatures, sputtering, laser or electron beam evaporation are used. Sputtering is a non-thermal process in which surface atoms are physically ejected by momentum transfer from an energetic bombarding species of atomic/molecular size. Evaporation can also be done from refractory metal crucibles (W, Ta or Mo). Synthesis of alloys or intermetallic compounds can be made by sputtering from an alloy or mixed target. Composite materials such as Cu/Bi or W/Ga have been synthesized by simultaneous evaporation from two separate crucibles onto a rotating collection device.

- Chemical vapor condensation (CVC):** This technique involves pyrolysis of vapors of metal organic precursors in a reduced pressure atmosphere. Nanoparticles of ZrO₂, Y₂O₃ and nano-whiskers have been produced by this method. The evaporative source used in GPC is replaced by a hot wall reactor in the CVC process. Nanosized particles of metals and ceramics can be obtained in good amounts by adjusting the residence time of the precursor molecules; changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber and the temperature of the reactor. The production capabilities in CVC process are much larger than in GPC processing; however, the microstructure of nanoparticles as well as

the properties of materials obtained by CVC are identical to those obtained by GPC prepared powders.

In addition to the formation of nanoparticles of a single precursor, the CVC reactor can also be used for the synthesis of:

- Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor.
 - Coated nanoparticles, that is, ZrO_2 coated with Al_2O_3 or vice versa, by supplying a second precursor at a second stage of the reactor. In this case, nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in the second stage of the reactor.
5. **Laser ablation:** This method is extensively used for the preparation of nanoparticles and particulate films. In this process, a laser beam is used as the primary excitation source for vaporization of metal precursor from the surface and generating clusters directly from a solid sample. A high energy pulsed laser beam hitting the target material generates temperatures (greater than 10^4 K) which vaporizes the substance quickly. The hot metal vapors are directed in a pulsed flow of inert carrier gas (helium) and expanded through a nozzle into a vacuum. The cool, high-density helium flowing over the target serves as a buffer gas in which clusters of the target material are formed.
- The porosity of the clusters formed can be modified by the carrier gas flow rate thus enabling a control of the microstructure of the coatings. The resulting nanoparticulate thick films are suitable candidates for application in membrane technology, catalysis and lithium ion batteries. Synthesis of ZrO_2 and SnO_2 nanoparticulate thick films, lithium manganate, silicon and carbon is also been carried out using this technique.
6. **Hydrothermal synthesis:** This technique is emerging as an important tool for advanced materials processing. It is based on the ability of water and aqueous solutions to dilute the substances at high temperatures and pressures, which are practically insoluble under normal conditions. These include oxides, silicates and sulphides. Autoclaves are used for this purpose because they can withstand high temperature and pressure conditions for a longer period of time. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes the seed to take growth. The possible advantages of the process over the other processes are the ability to create crystalline phases that are not stable at the melting point. Also for synthesis of materials which have high vapor pressure near their melting point.
7. **Thermolysis:** This method involves solvent-less pyrolysis of a suitable precursor material. One of the oldest nanomaterials, activated charcoal, is prepared using this method. Precursor materials such as wood or coal are pyrolyzed at temperatures $600\text{--}900^\circ\text{C}$ in the absence of air to obtain charcoal of specific surface (porous) area up to $2,000\text{ m}^2\text{ g}^{-1}$. In the process, the materials are carbonized in oxidizing atmosphere of CO_2 , O_2 or steam at $600\text{--}1200^\circ\text{C}$ and activation is carried using chemicals such as KOH , NaOH , ZnCl_2 or phosphoric acid.
8. **Solvothermal synthesis:** This is a versatile method for synthesizing nanomaterials at temperatures generally below 200°C . This technique enables synthesis of crystalline products at low temperatures and also helps control the size and morphology of the resultant products.
9. **Electrodeposition:** This technique involves creation of solid materials from electrochemical reactions in liquids. A conducting substrate is placed in liquid containing electrolytes. When a potential is

applied, redox reaction takes place and the material is deposited as thin film at the cathode. Electroless deposition can also be obtained by using complex chemical solutions wherein deposition occurs spontaneously (without applied electric potential) and sometimes auto-catalytically on surfaces. Nanorods and nanoparticles can be fabricated by both the methods using templates. For example, semiconductor ZnO nanotube arrays are synthesized by direct electrochemical deposition from aqueous solutions into the pore channels of anodically-formed alumina.

Top-Down Approach

High-energy ball milling is the milling process commonly used in ceramic processing and powder metallurgy, and involves particle size reduction, solid-state alloying, mixing or blending, and particle shape changes. The process is used only for hard, brittle materials which fracture, deform and cold weld during the milling operation. The technique has been extended to produce a variety of nanocrystalline, amorphous and quasicrystalline materials. A variety of ball mills such as tumbler mills, attrition mills, shaker mills, vibratory mills, planetary mills, etc., are used.

In this process, powders with particle diameters of about 50 μm are placed together with a number of hardened steel or tungsten carbide coated balls in a sealed container which is rigorously agitated. The most effective ratio for the ball to powder masses is 5–10. High-energy milling forces can be obtained using high frequencies and small amplitudes of vibration. The balls are made up of dense material to ensure sufficiently high kinetic energy, which is a function of mass and velocity. The temperature rise during milling is modest and is estimated to be less than or equal to 100–200°C. The process offers the advantage of high production rates of nanopowders.

Some disadvantages associated with the process are:

1. All particles of the precursor may not break down to the required particle size.
2. The nanocrystalline materials prepared by this process may be contaminated by milling tools and atmosphere. This can be reduced by minimizing the milling time, using pure and ductile metal powders which can coat the milling tools and seal the container to prevent exposure to atmospheric gases.

22.3 Characterization of Nanomaterials

Characterization of nanoparticles is important to understand and control their synthesis and applications. However, the main challenge faced currently in characterization of these materials is the inability and lack of instruments to observe, measure and manipulate the materials at the nanoscale. In the past, the studies have been carried out on the collective behaviors and properties of a large number of nanostructured materials, which are generally group characteristics. There is a pressing need for developing methods and instrumentation techniques to observe measure and manipulate the individual nanomaterials and nanostructures. This requires development of techniques that are extremely sensitive, accurate and offer atomic level resolution.

Presently, characterization of nanomaterials is done by using a variety of techniques, mainly drawn from materials science, to probe into the internal structure and properties of a material. Common techniques are electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), ultraviolet-visible spectroscopy, dual polarization interferometry and nuclear magnetic resonance (NMR).

22.9 Nanoscale Materials

Nanoscale materials are nanostructures with size ranging from 1–100 nm. They can be constructed by bottom up or top down techniques. The various nanoscale materials are discussed as follows:

Nanocrystals and Clusters

The size of nanocrystals ranges between 1 and 100 nm. Nanoclusters are groups of atoms or molecules with an intermediate state of matter between molecules and solids. The diameter of nanoclusters ranges up to about 10 nm. Nanoclusters consist up to a few hundreds of atoms, while larger aggregates containing 10^3 or more atoms are often called nanoparticles. Nanoclusters, have properties and structures which are very sensitive to their composition and size (to the count of every atom) which can lead to new and interesting properties not realised in the corresponding bulk material. Traditional materials in the micrometer size particles replaced by metal and semiconductor clusters seem to hold the promise to future leading to miniaturization of devices and eventually a big jump in the world of novel technologies.

Applications of Nanocrystals and Clusters

1. Many techniques are developed to produce clusters for use in different applications like thin film manufacture for advanced electronic or optical devices, production of nanoporous structures, and fabrication of thin membranes of nanoporous materials.
2. Nanoclusters of technologically important inorganic bulk materials such as SiO_2 , ZnO , CdS , etc., were found to be photoinitiators while their corresponding bulk materials did not exhibit this property. ZnS clusters and its aggregates act as effective photocatalysts in reduction of organic compounds.
3. The nanoclusters of cerium oxide (CeO_{2-x}) materials have been found to possess a significant concentration of Ce^{3+} and oxygen vacancies resulting in excellent poisoning resistance against H_2O and CO_2 and substantial reduction in the temperature of selective SO_2 reduction by CO .

Nanocrystalline Materials

Nanocrystalline materials are nanoscale particles (dimension less than a micron) with a crystalline structure (single crystal or polycrystalline). Crystalline nanoparticles are of interest for many reasons. The reduction in the size of crystals has dramatic effects on the properties of bulk materials since more number of atoms in solid is found on grain boundaries where they behave differently from those that are not. The nanocrystalline materials composed of crystallites in the 1–10 nm size range possess very high surface area to volume ratios due to the fine grain size. Nanocrystalline metals exhibit increased strength, hardness and magnetic properties. Semiconductor nanocrystals in <10 nm size range are often referred to as quantum dots. Ceramic nanocrystalline materials show increase in ductility, improved toughness, reduced brittleness and increased wear resistance.

Applications of Nanocrystalline Materials

1. Crystalline nanoparticles used in a solar panel is claimed to have more efficiency and is more flexible and cheaper than many other panels.
2. Crystalline nanoparticles of zeolite are reportedly used as filter to convert crude oil to diesel fuel by a method cheaper than the conventional way.
3. Nanocrystalline and nanoporous Si exhibit electroluminescence, photoluminescence and refractive index changes that can be controlled.

6. The size control of nanoscale catalyst particles has been achieved in preparation of highly dispersed metal colloids and metal clusters fixed on to substrates by electrochemical reduction of metal salts.
5. Materials with higher hydrogen storage per unit volume and weight and considerably increased rate of hydrogen adsorption, like mixtures of nanoscale particles of Mg and Mg_2Ni with high surface area, have been produced by mechanical means.

Fullerenes

Fullerene is the third allotrope of carbon, apart from crystalline diamond and graphite forms, which was discovered in 1985.

It consists of hexagonal rings (like graphite) and alternating pentagonal rings of carbon closed in the form of hollow spheres (like a football) or ellipsoids or tubes (called nanotubes). The first form is also known *bucky ball* form, while the second form is also known as *nanotube* form (Figure 10). The fullerene with 60 carbon atoms arranged as 12 pentagons and 20 hexagons arranged in the form of sphere is called Buckminster fullerene C_{60} . The name *Buckminster fullerene* comes from the inventor of the geodesic dome, Richard Buckminster Fuller. The dome has a structure similar to that of a fullerene. Other fullerenes with 20, 70, 72, 76, 84 and even 100 carbon atoms have also been prepared. Fullerenes were first isolated from the soot of chimneys and extracted with solvents as red crystals.

The structure of fullerenes is similar to graphite with linked hexagonal layers stacked over each other in form of sheets. The hybridization of the carbon atoms in fullerenes is proposed to be between sp^2 and sp^3 , since the molecule is totally symmetrical with all the bond lengths and bond angles being equal.

The chemical and physical properties of fullerene have been a popular topic of recent research. Physical properties of fullerenes can be explained by considering the structure and bonding. Fullerene (C_{60}) is fine black powder having a density of 1.65 g/cm^3 and sublimates at 800 K. It exists as brittle, soft weak crystals typical of covalent substances. They are electrical insulators as there is no movement of electrons available from one molecule to the next and the individual molecules are only held to each other by weak van der Waals forces. The exception could be the formation of nanotubes that are capable of conducting electricity along their length.

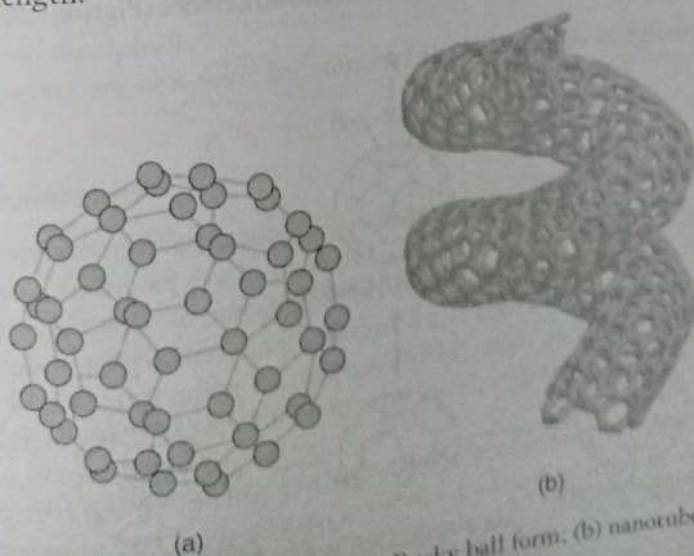


Figure 10. (a) Bucky ball form, (b) nanotube form.

Fullerenes are sparingly soluble in many organic solvents such as benzene, toluene, methyl benzene and carbon disulphide. Different fullerenes give a variety of colored solutions in these solvents, for example, solution of fullerene in toluene is bright red in color. The solubility of fullerenes in water is extremely low.

Types of Fullerenes

1. **Buckyball clusters:** Fullerenes having less than 300 carbon atoms are commonly known as buckyballs. Fullerene with smallest number of carbon atoms known is C_{20} . This is found in nature in soot of coal. The most common and abundant fullerene, C_{60} is called buckminster fullerene.
2. **Nanotubes:** They are hollow cylindrical tubes of carbon which are a few nanometers in diameter and up to several microns in length, with single or multiple walls.
3. **Megatubes:** These are tubes with larger diameter than nanotubes and their walls are made of varying thickness.
4. **Polyfullerenes:** Polymers of fullerenes are made of C_{60} and C_{70} balls linked by covalent bonds in different ways like directly linked, cross-linked, linked through a polymer backbone, through heteroatoms and so on (Figure 11).

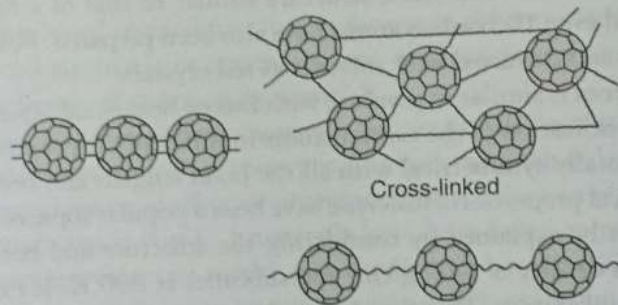


Figure 11 Polyfullerenes.

5. **Endohedral fullerenes:** Fullerene derivatives with various atoms enclosed inside. For example, when metal atoms are enclosed they are called metallo-fullerenes (Figure 12).

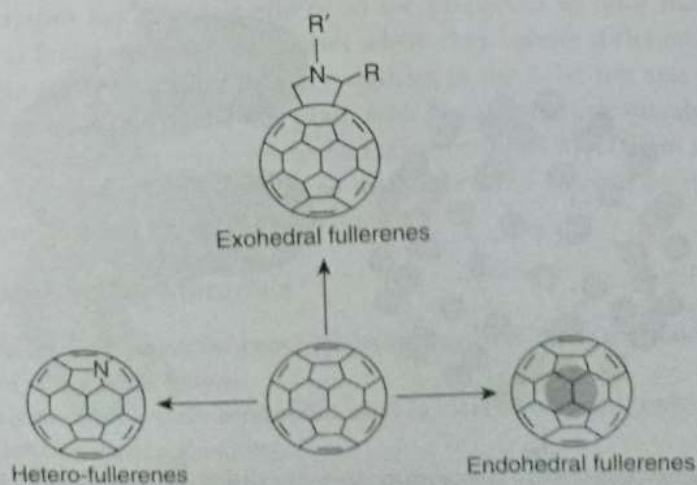


Figure 12 Endohedral fullerenes.

6. **Exohedral fullerenes and heterofullerenes:** Exohedral fullerenes are fullerene derivatives formed by addition or redox reactions on the surface of the fullerene. Hetero-fullerenes are heteroanalogs of C_{60} or higher fullerenes with one or more carbon atoms of the cage replaced with trivalent heteroatoms like nitrogen or boron. For example, $C_{59}N$, $(C_{59}N)_2$.
7. **Nano-onions:** The structures consisting of carbon spheres of increasing diameters layered on top of each other. Due to their layered design these were called nano-onions (Figure 13). These nano-onions have superior lubrication properties compared to other conventional lubricants.

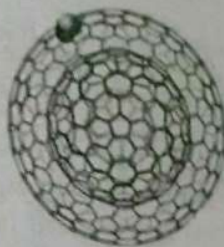


Figure 13 Nano-onions.

8. **Fullerene rings:** Some researchers have succeeded in making a thirteen-membered ring hole in fullerene through which small molecules can pass through or get included.

Characteristics of Fullerenes

1. An important characteristic of C_{60} molecule is its high symmetry with 120 symmetrical operations which map the molecule onto itself. Each carbon atom bonds with three other adjacent atoms using sp^2 hybridization.
2. Chemically fullerenes are stable; breaking the balls requires temperatures over 1000°C . However, fullerenes are not unreactive as they possess π -electrons which are free to localise or delocalise in different chemical situations, reactions such as addition reactions and redox reactions, are possible on their surface. This leads to covalent exohedral adducts and salts.
3. Fullerenes are insoluble in water, sparingly soluble in many other solvents and more soluble in toluene and carbon disulphide.
4. Fullerenes themselves are non-toxic but some of the derivatives of fullerenes could be harmful to the health.

Applications of Fullerenes

1. Oxidation involving free radicals causes cell damage, food spoilage, plastics deterioration, metal corrosion, etc. Therefore, fullerenes due to powerful antioxidant property (they reportedly react readily at a high rate with free radicals), can find application in health and personal care areas.
2. Fullerene nanotubes, which have small diameter and *high aspect ratio*, find use as ideal materials to be used as tips in scanning probe microscopy (SPM), such as scanning tunneling microscopy and atomic force microscopy. The nanotubes attached to the tip enhance SPM resolution to nanoscale as compared to the conventional silicon tip.
3. Fullerene nanotubes are promising as chemical molecular sensors, due to their small size, room temperature operation and high sensitivity. They find application as coating materials on some chemical sensors, such as quartz crystal microbalance and surface acoustic wave sensors (SAW).

4. Field emission displays (FEDs) using carbon nanotubes are being explored by scientists which are expected to be better in terms of power, cost and view angles than the currently available flat panel displays, such as liquid crystal display (LCD) and plasma.
5. Fullerenes blended with polymers are used in organic photovoltaics.
6. Fullerenes can react readily with free radicals, thus preventing cell damage due to oxidation. They can hence be used as antioxidants.
7. Pharmaceutical companies are exploring the use of fullerenes in controlling Alzheimer's and HIV.
8. Fullerenes and its modified forms are capable of targeted and controlled delivery of drugs and genes into cells.
9. Endofullerenes with their protected cage-structure are capable of being applied in MRI, X-ray imaging and radiopharmaceutical diagnostic applications.
10. Other applications of fullerenes like catalysts in certain organic reactions, water purification, fuel cell membrane material are also being explored.

Carbon Nanotubes

Carbon nanotubes (CNTs; also known as buckytubes) are allotropes of carbon with a cylindrical nanostructure (Figure 14). Nanotubes have been synthesized with length-to-diameter ratio of up to 132,000,000:1, which is significantly larger than any other materials known. They possess extraordinary strength and electrical and thermal properties. These novel properties make them useful in many nanoelectronics, optics and other areas of materials science.

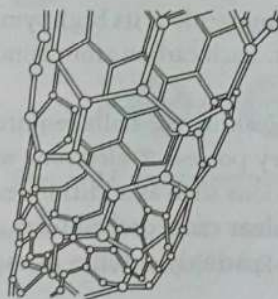


Figure 14 Carbon nanotube.

Types of Carbon Nanotubes

1. **Single-walled nanotubes (SWNTs)** have a diameter of ~ 1 nm, with a tube length many million times longer. The structure of a SWNT can be imagined to be a wrapping of a one-atom-thick layer of graphite (graphene) into a seamless cylinder. The way the graphene sheet is wrapped is denoted by (n, m) called the chiral vector. If $m = 0$, the nanotubes are called *zigzag*. If $n = m$, the nanotubes are called *armchair*.
2. **Multiwalled nanotubes (MWNTs)** consist of multiple rolled layers or otherwise concentric tubes of graphite. There are two models that describe the structures of multiwalled nanotubes. In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, that is, single-walled nanotube within a larger single-walled nanotube. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a rolled newspaper. The interlayer distance in multiwalled nanotubes is approximately equal to the distance between graphene layers in graphite which is 3.4 \AA .

The morphology and properties of double-walled carbon nanotubes (DWNT) are similar to SWNTs but their resistance to chemicals is extremely good. This chemical resistant property is very important when new chemical properties are to be added to the CNTs (called functionalization). In the case of SWNTs, covalent functionalization will break C=C double bonds, leaving "holes" in the structure of the nanotube, hence modifying its mechanical and electrical properties. However in the case of DWNTs, only the outer wall gets modified.

Characteristics of Carbon Nanotubes

1. **Strength:** These are the strongest and stiffest materials known. This strength results from the covalent sp^2 bonds formed between the carbon atoms. In 2000, a multiwalled carbon nanotube was tested to have a tensile strength of 63 GPa and this is equivalent to the ability to withstand tension due to 6422 kg on a cable with cross-section of 1 mm^2 . Its specific strength of up to 48,000 kN·m/kg is the best of materials known when compared to high-carbon steel's value which is 154 kN·m/kg.
2. **Hardness:** A super-hard material has been synthesized by compressing SWNTs to above 24 GPa at room temperature. The hardness of this material was measured to be 52 GPa, whereas the hardness of reference diamond and boron nitride samples is 150 GPa and 62 GPa, respectively. The bulk modulus of compressed SWNTs was 462–546 GPa, a value higher than that of 420 GPa for diamond.
3. **Kinetic:** In multiple concentric nanotubes, an inner nanotube core may slide within its outer nanotube shell almost without friction, hence creating an atomically perfect linear or rotational bearing. This is one of the first valuable examples of molecular nanotechnology.
4. **Thermal:** All nanotubes exhibit good thermal conducting properties along the tube, but they are good insulators laterally to the tube axis. Measurements show that a SWNTs have a room temperature thermal conductivity along its axis of about 3500 W/mK (compared to copper, which has $385 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and thermal conductivity across the axis of about 1.52 W/mK (comparable to that of sand).

Applications of Carbon Nanotubes

1. Carbon nanotubes find application in nanoelectronics. The nanotube integrated memory circuit was first made in 2004. CNT-based transistors can operate at room temperature and are capable of digital switching using a single electron. Depending on the surface features, a carbon nanotube may act as a conductor or as a semiconductor. Structures of carbon nanotubes can be used for thermal management of electronic circuits. An approximately 1 mm thick carbon nanotube layer was used to fabricate coolers.
2. A paper battery is made up of a paper-thin sheet of cellulose infused with aligned carbon nanotubes. The nanotubes act as electrodes to conduct electricity. These batteries provide a long and steady power output comparable to a conventional battery (lithium battery), as well as quick release of high energy (as a supercapacitor). A conventional battery contains a number of components while the paper battery integrates all the components in a single structure, making it more energy efficient.
3. The solar cells have been developed at the New Jersey Institute of Technology using a carbon nanotube complex, formed by a mixture of carbon nanotubes and carbon buckyballs (fullerenes) to form snake-like structures. Carbon buckyballs trap electrons, but they cannot facilitate electron flow. Sunlight excites the polymers while the buckyballs capture electrons. Nanotubes, thus act as a pathway for the electrons or current flow.

3. The other future applications, owing to the possibility of building ordered arrays of nanoparticles in the polymer matrix, are in the manufacture of nanocomposite circuit boards, in neural networks applications, optoelectronics and optical computing and magneto-optical storage media manufacturing.

Biological Nanomaterials

Biological nanomaterials are biological systems which are inherently nano in size. They serve as models and help in understanding the behavior of nanomaterials in general and lead us to approaches like biomimicking. There are many nanophase materials in biological systems. For example, living systems produce mineral material of the bone with particle size in the nanometer scale. These biological nanomaterials could even be used as direct source of novel materials or modified through *in vivo* procedures and in *in vitro* manipulations. Some examples of biological nanomaterials are ferritins and related iron-storage proteins (for probing the magnetic properties of nanoscale materials and also to investigate iron metabolism in living organisms), nanoparticles found in magnetotactic bacteria (use earth's magnetic lines to orient themselves and move in the direction of nutritional or chemical gradients), etc. The field of biological nanomaterials is still in its initial stages and is likely to find many exciting possibilities in the future.

22.10 General Applications of Nanomaterials

The impact of nanotechnology and use of nano-materials extends from healthcare, medicine, energy, agriculture, food to fields such as electronics, communication, optics, chemistry and computing. We will now discuss some important applications of nanomaterials in these areas.

In Medicine

The size of nanomaterials is very similar to that of biological molecules and structures; therefore, these find extensive use in both *in vivo* and *in vitro* biomedical applications. The integration of nanomaterials with biology has led to development of various diagnostic devices, contrast agents, analytical tools, physical therapy applications and drug delivery vehicles.

1. **Diagnostics:** Magnetic nanoparticles, bound to a suitable antibody, are used to label molecules, structures or microorganisms. Gold nanoparticles tagged with short segments of DNA are used for the detection of genetic sequence. Multicolor optical coding for biological assays has been achieved by embedding different-sized quantum dots into polymeric microbeads. Nanopore technology for the analysis of nucleic acids can convert strings of nucleotides directly into electronic signatures.
2. **Drug delivery:** Drug consumption and side-effects can be reduced considerably by depositing the active agent in the diseased regions and inappropriate dose. Nanoporous materials can be used to hold small drug molecules and to transport them to the desired location. Applications include cancer treatment with iron nanoparticles or gold shells.
3. **Tissue repair:** Nanotechnology can help to regenerate or to repair damaged tissues and the technique is called tissue engineering. This uses artificially stimulated cell proliferation through suitable nanomaterial-based scaffolds and growth factors. Tissue engineering might replace today's conventional treatments like organ transplants or artificial implants surgeries.
4. **Transdermal drug delivery:** It involves nanosized protrusions on the underside of patches that would be fixed to the skin like a plaster. The protrusions carrying doses of the drug act as tiny needles, discharging the drug, which can then reach the other parts of the body through tissue fluids.

In Electronics and Communication

• 1027

Nanotechnology has brought revolution in telecommunication, computing and networking industries. The principle aim of nanotechnology is to produce three dimensional confined quantum structured electronic devices such as quantum wires and quantum dot devices. Some successful devices are:

- Quantum well lasers for telecommunication.
- High electron mobility transistors (HEMT) with low noise.
- High gain microwave application and vertical cavity surface emitting lasers for data communication and sensor coding.

The devices made from nanomaterials are light in weight, easy to carry or move and have reduced power requirement. Some consumer products using nanomaterials are:

- Computer hardware.
- Display devices.
- Mobile and communication products.
- Audio products.
- Cameras and films, etc.

Nanomaterials are used to develop semiconductors with much advanced properties. These include:

- Transistors from carbon nanotubes with nanometer dimensions.
- Memory chips with density of one tetrabyte per square inch.
- Very high speed transistors from single atom thick graphene film.
- Lightweight nanoemissive display panel using carbon nanotubes.
- Nomfet (nanoparticle organic memory field-effect transistor) obtained by combining gold nanoparticles with organic molecules.

Machines fabricated with nanomaterials when used can perform multiple functions and do parallel processing.

In Energy Science

Nanomaterials, particularly nanocomposites, are increasingly being used to replace conventional materials for conversion of energy. Some examples of their use are:

1. Non-porous crystalline solids called zeolites are used for refining of oil. Zeolites have well defined molecular structure and called molecular sieves. Their use helps in increasing the yield of petrol by selective removal of impurities.
2. Quantum dots can be used as sources of light emissions. Since the crystals are smaller than the wavelength of light, they do not scatter light and can thereby enhance optical efficiency by up to 50 %. These find applications in ink meant for printing currency notes whereby by shining with a light of specific wavelength, counterfeit currency can be identified.
3. Electrode materials can be changed by nano-structuring, that is, can be imparted nano-texture to improve electrical performance of batteries. Nanoscale particles boost energy storage and power delivery by reducing the distance that the ions have to travel during diffusion. The electrode in the form of nanorods provides an increased surface area compared to conventional micron-size particles. This enhances ionic diffusion, leading to an increase in the speed of the working electrode.
4. Energy production can be brought about using nanomaterials as clean and high efficiency energy sources. For example, white light emitting diodes (LEDs) reduce total electricity consumption and help keep the environment clean.

5. Solar cells can be integrated from nanoscale crystals of semiconductors coated with light-absorbing dye-emitting electrons and from nanostructured diamond thermal cells that capture heat and light from the lattice and emit high-energy electrons. Solar cells built with nanostructures such as terapods (light-absorbing material) have much higher efficiency than plastic solar cells because they always point in the right direction.
6. Ultraporous nanomaterials are being explored for storing hydrogen at high-densities for fuel-cell powered cars. Because of their porous structure, the surface area available for absorption of sunlight is more than in bulk semiconductor material.

In Catalysis

Heterogeneous catalysts used in industry today, consist of small particles (1-10 nm) of catalytically active material attached to porous support. Nanoparticles of metals, semiconductors, oxides, and other compounds are widely used for important chemical reactions.

The use of nanosize particles of catalysts provides large surface area to volume ratio. The increase in contact area between the reactants ensures effective use of catalyst. Studies with gold particles have shown that catalytic properties of materials undergo major modification with change in particle size. Gold is a noble metal with low or negligible chemical reactivity, however, the nanosize gold particles (about 5 nm or less) are effective catalysts in a number of chemical reactions. They also lower the reaction temperature, thus making reactions more energy efficient.

Nanoparticles made of transition element oxides exhibit catalytic properties and these may be enhanced or made more specific by treatment with gold or platinum clusters. There are four main categories of nano-catalysts based on the composition. These include:

- Gold-based (e.g., Au/TiO₂, Au/MgO)
- Other metal based (e.g., Cu, Rh)
- Platinum or palladium based (e.g., Pt/Ru/Ni)
- Nanosize metal particles dispersed in polymers (e.g., Cu/polyaniline, Pt/polypyrrole)

The use of nanomaterials as catalyst is limited by their low thermal stability at the critical sizes required for reactivity. So the key objective of nanocatalysis research is to produce catalysts that show high but selective activity, have low energy consumption, and long lifetime. The research is now focused on controlling the composition and atomic-scale structure of individual nanocomponents to derive best catalytic activity from nanoscale materials.

Miscellaneous Applications

Applications of nanomaterials in other fields are as follows:

1. Nano zinc oxide and titanium oxide are used in sunscreen creams, lotions and other cosmetics. These nanoparticles become transparent and retain their ability to absorb UV radiation.
2. Nanoparticles of tungsten-carbide-cobalt provide a hard coating. This results in a greater resistance to wear in applications such as drill bits, cutting tools and jet engine parts.
3. Nano coating over glass produces self-cleaning glass, which becomes transparent or opaque according to the current applied.
4. Nanotechnology finds applications in the production, processing, safety and packaging of food stuffs.

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|--------------------------------------|------------------------------------|---------------------------------|
| Interfacial or surface self-assembly | Nanoclusters Buckyball clusters | Single-walled nanotubes (SWNTs) |
| Two-dimensional self-Assembly | Polyfullerenes | Multiwalled nanotubes (MWNTs) |
| Langmuir monolayers | Endohedral fullerenes | Dendrimers |
| Mesoscale self-assembly | Chemical vapor deposition | Nanocomposites |
| Supramolecular structures | Arc discharge method | Biological nanomaterials |
| Host-guest complexation | Laser ablation | Nanowires |
| Coercing colloids | Carbon nanotubes (CNT) | |
| Crystal lattice self-assembly | | |

Review Questions

1. What is meant by nanotechnology? How is it significant?
2. What properties of nanoscale materials make them unique and widely useful?
3. What is nanochemistry? What are its applications?
4. What do you understand by self-assembly materials? Explain.
5. Explain the mechanism of self-assembly of materials.
6. Compare molecular and materials self-assembly.
7. What do you understand by two-dimensional assemblies?
8. What is mesoscale self-assembly? How is it similar or different from molecular self-assembly? How and where are they useful?
9. Explain 'coercing colloids' and their applications.
10. What are nanoclusters and nanocrystalline materials? Where do they find application?
11. Discuss supramolecular structures.
12. What are different types of fullerenes? Give their properties and list some of their applications.
13. What are dendrimers? How are they different from regular polymers? Give a few examples to show their application in various fields.
14. Explain the characteristics and applications of carbon nanotubes.
15. What are nanocomposites? List a few of their applications.
16. What are biological nanomaterials? How are they potentially useful?
17. What are nanowires? List some examples and their applications.
18. What in your opinion are the future perspectives of nanochemistry?
19. What are nanomaterials?
20. Discuss nanocrystals.
21. What are the techniques adopted for characterization of nanoparticles?
22. Comment on the electronic and mechanical properties of nanomaterials.
23. Compare top-down and bottom-up processes for synthesis of nanoparticles.
24. What are the applications of carbon nanotubes in the field of catalysis and medicine?
25. What are SWNT and MWNT?