Learning Objectives

After studying this chapter, the student will be able to:

- ➡ Get knowledge about nanomaterials and their classification
- ➡ Understand the methods of preparing nanomaterials
- ➡ Discuss the properties in detail
- ➡ Get knowledge about the application of nanomaterilas in various fields.

8.1 INTRODUCTION

Nanomaterials play a vital role in the recently developed science and technology.

What is Nanoscience?

Definition 1 - *Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales; where properties differ significantly from those of larger scale.*

Defintion 2 - *Nanoscience is the study of atoms, molecules and objects whose size is of the nanometer scale (1- 100nm).*

What is Nanotechnology?

Definition 1 - *Nanotechnology is the application of the principles of nanoscience into useful nanodevices and components. By manipulating the concepts of nanoscience, nanotechnology aims at improving the lifestyle of the human race.*

Definition 2 - *Nanotechnology is the technique of design, production of devices and systems by controlling the shape and size at the nanometer scale.*

What is a nanoparticle?

A particle with size in the range of 1-100nm is called a nanoparticle.

Where nanomaterials are found and used?

Nanomaterials are the materials containing nanocrystals, i.e. their grain size is in the 1 to 100 nm range. The nanomaterials may be metals, alloys, intermetallics and ceramics.

Some nanomaterials occur naturally. But of particular ineterest are, engineered nanomaterials which are developed for use in many commercial products. For example, electronic devices, sporting goods, cosmetics, textiles, sunscreens, tyres, paint, varnishes etc. In medical field, they are used for the purpose of imaging, targeted drug delivery, diagnosis etc.

Conventional materials have grain size ranging from few micron to several millimeters and contain several billion atoms each. But, nanomaterials contain only nine hundred atoms each. As the grain size decreases, there is a significant increase in the volume fraction at grain boundaries or interfaces.

In general, the nanomaterials exhibit greatly altered properties such as physical, chemical and mechanical compared to their normal large sized grain counter parts with the same chemical composition. Because of their unique microstructure, the nanomaterials are said to have high strength, hardness, formability, toughness and are more brittle.

8.2 CLASSIFICATION OF NANOSTRUCTURES

There are different classifications of nanostructures in nanotechnology. The most popular mode of nanostructure classification is according to their dimensions on the nanoscale which is of the order of a few nanometers (1-100nm), in at least one dimension (direction).

Nanostructures can be described as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanomaterials. All of the 0D,1D,2D and 3D nanostructures can be nanocrystalline or amorphous.The schematic picture of the four types of nanocrystalline materials are shown in Figure 8.1.

Zero-dimensional (0D) nanostrucures - *In 0D nanostructures, all of the three dimensions (x,y,z) are in the nanometric size range. Electrons confined in three dimensions.*

Example : Nanoparticles or well separated nanopowders and quantum dots.

One-dimensional (1D) nanostructures - *In 1D nanostructures, two dimensions (x,y) are in the nanometric size range and the third dimension (z) remains large. Electrons confined in two dimensions.* These structures have shape like a rod.

Example : Nanotubes, nanorods, nanoneedles and quantum wire.

Two-dimensional (2D) nanostructures - *In 2D nanostructures, one dimension (z) is reduced to the nanometric size range and the other two dimension (x,y) remain large. Electrons confined in one dimension.* These 2D structures display plane like structures.

Example : Nano thin films, nanocoatings and nanolayers.

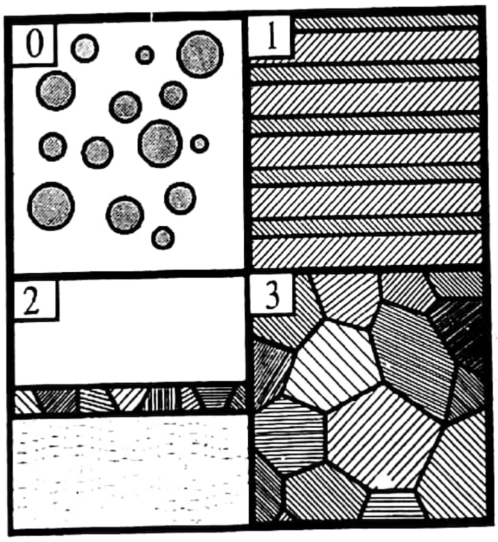

Figure 8.1: Schematic diagram of the four types of nanocrystalline materials

Three-dimensional (3D) nanostructures - *The 3D nanostructures have all the three dimensions (x,y,z) outside of the nanometric size range. A 3D nanostructure can include different distributions of nanoparticles or nanocrystallites, nanocomposite materials, groups of nanowires and nanotubes and also different nanolayers.*

Among the above type nanomaterials, most attention is paid to the synthesis and characterisation of 3D nanostructures. The 3D nanomaterials has wider applications based on their strength, improved formability and soft-magnetic properties. The 2D layered nanostructure's finds application in electronic field. Recently, one-dimensional 1D semiconductor nanostructures (wires, rods, belts, and tubes) have become the focus of intensive research, owing to their unique application in the fabrication of electronic, optoelectronic, and sensor devices on a nanometer scale.

Based on dimensionality of nanocrystalline material, the typical methods of synthesis are shown in Table 8.1.

Table 8.1

Dimension	Terminology	Typical Method of Synthesis
Zero-dimensional (0D)	Clusters	1. Sol-gel method
One- dimensional (1D)	Filamentary (Wire)	1. Chemical Vapour Deposition (CVD) 2. Pulsed laser deposition 3. ElectroDeposition (ED)
Two- dimensional (2D)	Layered or Lamellar	1. Vapour Phase Deposition (VPD) 2. Sputtering 3. Molecular Beam Epitaxy (MBE)
Three-dimensional (3D)	Crystalline	1. Gas condensation 2. Mechanical alloying

Size Dependence And Quantum Effects

When the particles are in nanoscale of about 1-100nm, the materials properties change significantly from those at larger scales. This is the size scale where the so called quantum effects rule the behaviour and properties of particles. In this scale range, the properties of particles are size dependent. Thus when the particle is in nanoscale, the properties such as, melting point, flourescence, electrical conductivity, chemical reactivity, magnetic permeability etc change as a function of the size of the particle.

The unique properties that occur at nanoscale level is illustrated with examples.

We all know, the colour of bulk gold is yellow. But the colour of a nanoscale gold is red or purple. This change in colour (wavelength) at nanoscale level in gold is due to the electron confinement. Because of the electron confinement, nanogold particles react differently when exposed to light compared to bulk gold.

As a second example, if we take bulk copper in the form of wire or ribbon, bending occurs with movement of copper atoms at about 50nm scale. But this behaviour is not seen in nanoscale copper. The nanocopper particles are smaller than 50nm and are said to behave as super hard materials. That is, the nanocopper is observed not to exhibit the malleability and ductitlity properties as that of a bulk copper.

It is not only the nanogold and copper; but as well as of other noblemetals and semiconductors rely on electron confinement. Electron confinement is a very successful model for describing the size dependent electronic structure of nanoscale materials.

When electrons are confined in all three dimensions, the nanomaterials behave completely different in terms of its optical and electronic properties. When the dimension of a material approach the electron wavelength, in one or more dimensions, quantum mechanical characteristics of electrons that are not manifest in the bulk material can start to contribute or even dominate the physical properties of the material.

Basically, there are two types of size dependent effects.

(i) Increase in surface area to volume ratio of materials. This effect can make nanomaterials more chemically reactive and affect their strength, melting point or electrical properties.

(ii) Quantum effects which show discontinuous behaviour due to completion of shells in systems with delocalised electrons. The quantum effect may affect the optical, electrical and magnetic behaviour of materials.

Besides quantum size effect, the nanomaterials behaviour is different due to surface effects which dominate as nanocrystal size decrease.

Surface Area To Volume Ratio In Nanomaterials

The surface area to volume ratio, also called the surface to volume ratio (SA : V) is the amount of surface area per unit volume of an object. Surface area to volume ratio is a great way to measure the efficiency of nanotechnology.

Surface area to volume ratio in nanoparticles have a significant effect on the nanoparticles property(ies). Nanoparticles have a larger surface area compared to the same volume of the bulk material.

Let us assume that, the nanoparticles are spherical in shape. Let us consider the radius of the atom to be 'r'. Then,

the surface area of the spherical atom $= 4\pi r^2$

the volume of the spherical atom $= \frac{4}{3}\pi r^3$.

Therefore, the surface area to the volume ratio is $SA : V = \dfrac{4\pi r^2}{\frac{4}{3}\pi r^3} = \dfrac{3}{r}$

The above value of SA:V ratio shows that, the surface area to volume ratio increases with the decrease in radius of the sphere (i.e.size of the atom) and vice versa. It can also be concluded that, when a given volume is divided into smaller pieces, the surface area increases. Therefore as particle size decreases, a greater portion of the atoms are found at the surface compared to those inside and thus affecting reactivity.

Therefore, smaller grains have more surface area with respect to their volume. More surface area to volume ratios are favourable for chemical reactions.

The increase in surface area to volume ratio is true for any shape.

...ron Confinement (Quantum Confinement)

...ectron confinement or quantum confinement is another process that occur in nanoparticles.

...is Quantum Confinement?

...tum confinement describes how the electronic and optical properties change when the ...rial size is at nanoscale.

One of the most direct effect of reducing the size of materials to nanoscale is the appearance ...quantisation effects due to the confinement of the movement of electrons. This leads to the ...crete energy levels depending on the size of the structure. Control over dimensions as well as ...mposition of structures thus makes it possible to tailor material properties to specific applications. ...antisation effects play a major role in semiconductor electronics and optoelectronic components.

The quantisation confinement can be observed only when the diameter of the material is of the ...me magnitude as the wavelength of the electron wave function.

Quantum confinement effects describe electrons in terms of energy levels, potential well, valence ...nd, conduction band and energy band gap. The electrons in a bulk material can be described by ...ergy bands or electron energy levels. These energy levels are described as continuous, because ...of the difference in energy is negligible. In this case, the electrons behave as if it were free in which ...case the confinement dimensions are large compared to the wavelength of the particle. At this stage, ...the band gap remains at its original energy due to a continuous energy state.

However when the material size is decreased towards nanoscale, the cofinement dimensions ...lso naturally decrease. In other words, the energy spectrum becomes discrete measured as quanta ...ather than continuous as in bulk materials. *This situation of discrete energy levels is called ...uatum confinement.*

Thus to conclude; in nanomaterials, the electrons are cofined in space rather than free to move ...as in the case of bulk materials.

Nanoscale quanutum confinement can be 0D, 1D or 2D.

0D confinement is found in quantum dots. In quantum dots, the electrons have no freedom in ...any dimension and the electrons are said to be localized at a point implying that; a change in any of ...the directions changes the properties.

1D confinement is found in nanowires . Electron confinement in one direction results in a quantum wire, leaving the electrons free to move only along one direction.

2D confinement is found in quantum wells. In quantum well, the electrons are confined within a two dimensional area.

Note:

In 1D and 2D nanomaterials, the electron confinement and delocalisation coexist but in 3D nanomaterials, the electrons are fully delocalised.

Nanomaterials are basically carbon structures. Some of the well known nanomaterials are fullerenes, carbon nanotubes and other nanoparticles.

Fullerenes (C_{60} molecule), C_{70} and C_{78} molecule are better known as nanoparticles.

Using a variety of synthesis method, it is possible to produce nanostructured materials in the form of thin films, coatings, powder and as a bulk material.

The methods used for the synthesis of nanoparticles can be broadly classified into physical, chemical, biological, self assembly and hybrid methods. Irrespective of the method of synthesising, it is very important to consider their stability in terms of their composition as well as their size.

The methods employed to produce nanomaterials are numerous, with each method having its own advantages and disadvantages depending on the desired properties and application. A few commonly used methods are briefly described in this section.

Note:

- **Fullerenes:** A form of carbon that contains molecules with 60 carbon atoms arranged in a structure resembling a geodesic dome.

8.3.1 Classification of Synthesis Methods

The methods for the synthesis of nanomaterials are classified into two processes.

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

The top-down process involves, the breaking down of a large piece of a bulk material to generate the required smaller and smaller nanostructured material through etching or milling from the bulk material. The schematic representation of this process is shown in Figure 8.2.

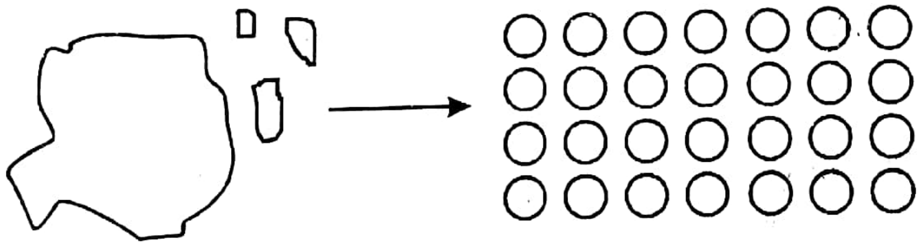

Figure 8.2: Top-down approach

The bottom-up process involves the process of building up of the atom or molecular constituents into a larger nanostructured material. The schematic representation of this process is shown in Figure 8.3. The bottom up approach is a powerful approach of creating identical structures with atomic precision.

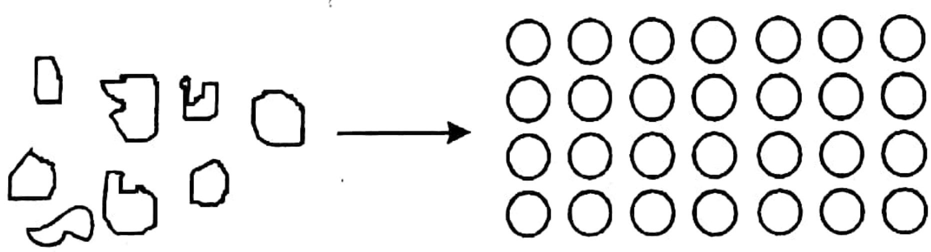

Figure 8.3: Bottom-up approach