

Chapter 15

Nanotechnology

15.1 Introduction

In recent years nanotechnology has become one of the most important and exciting forefront fields in Physics, Chemistry, Biology and Engineering and Technology. It is likely to provide many breakthrough that will change the direction of technological advances. This chapter on Nanomaterials aims at providing a broad coverage and insight into this area.

15.2 Nanoscale

Nano means 10^{-9} . A nanometre (nm) is one thousand millionth of a metre (i.e. 10^{-9} m). Atoms are extremely small and the diameter of a single atom can vary from 0.1 to 0.5 nm depending on the type of the element. For example, one carbon atom is approximately 0.15 nm in diameter and a water molecule is almost 0.3 nm across. To understand how small one nm is let us see few comparisons. A red blood cell is approximately 7,000 nm wide. Quite often people make a comparison with a human hair, which is about 80,000 nm wide. In Fig. 1, nanoscale objects are compared.

15.3 What are Nanomaterials?

All materials are composed of grains, which in turn comprise of many atoms. Depending on the size, these grains may be visible or invisible to the naked eye. Conventional materials have grains of size varying from hundreds of microns to centimeters. Any bulk material we take, its size can be expressed in three dimensions. Any planar material we take, its area can be expressed in two dimensions. Any linear material we take, its length can be expressed in one dimension. *Nanomaterials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.*

- Materials that are nanoscale in one dimension are layers, such as thin films or surface coatings.
- Materials that are nanoscale in two dimensions include nanowires and nanotubes.

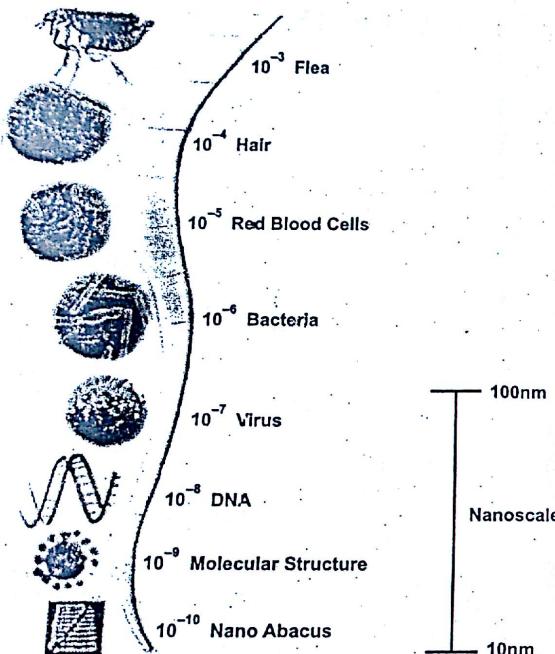


Fig. 1 Nanoscale objects

- Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometre-sized grains, also fall into this category.

15.4 Classification of Nanomaterials

Materials referred to as nanomaterials generally fall into two categories : fullerenes and inorganic nanoparticles.

15.4.1 Fullerene

The fullerene are a class of allotropes of carbon which are graphene sheets rolled into tubes or hollow spheres. Spherical fullerenes are also called *buckyballs*, and

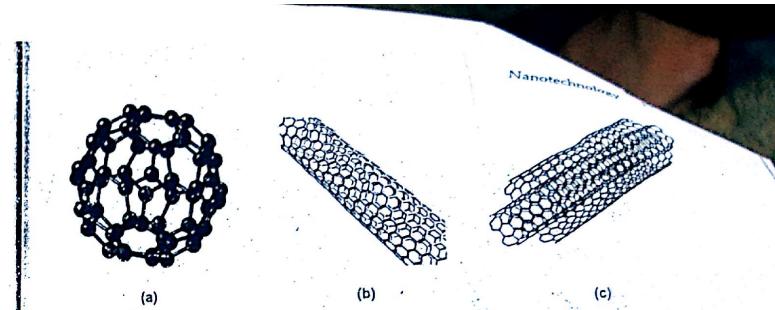


Fig. 2 Fullerene In the form of (a) bucky ball, (b) single walled carbon nanotube and (c) multiwalled carbon nanotubes

cylindrical one are called carbon *nanotubes* or *buckytubes*. Fullerenes are similar in structure to graphite, but they may contain pentagonal rings.

The first fullerene discovered was *buckminsterfullerene C₆₀* in 1985. It was named after Richard Buckminster Fuller, a famous architectural modeler who designed geodesic dome. Since buckminsterfullerenes have a similar shape to that of the dome, they bear this name.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes are members of the fullerene structural family. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). These cylindrical carbon molecules have novel properties. They are potentially useful in many applications in nanotechnology, electronics, optics and materials science. They exhibit extraordinary strength and unique electrical properties. Also they are efficient conductors of heat. Because of its importance, we shall study about CNTs in some more detail later.

15.4.2 Nanoparticles

Nanoparticles sized between 1 and 100 nm are available in different forms such as clusters, metal nanoparticles, colloids, nanocrystals, quantum dots etc.

- Nanoclusters have dimension between 1 and 100 nm and a narrow size distribution.
- Nanopowders are agglomerates of nanoparticles or nanoclusters.
- Nanometer sized single crystals or single domain ultrafine particles are called nanocrystals.
- When nanoparticles are in suspended form in liquid phase, it is called nanocolloids.
- Quantum dots are tiny particles of semiconductor materials.

Because of their small size, nanoparticles have a high surface area/volume ratio resulting in a high reactivity. They exhibit quantum confinement effect also.

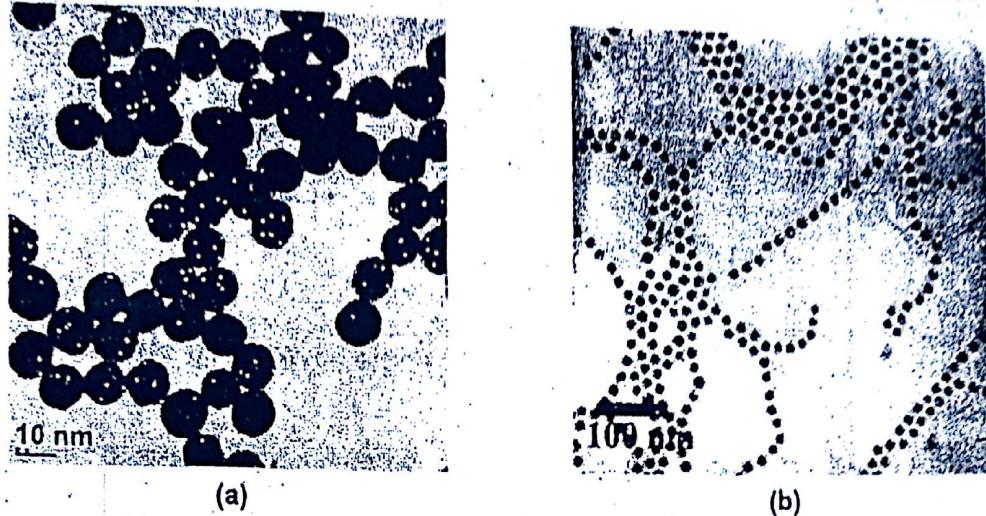


Fig.3 Transmission Electron Microscopic picture of (a) Gold nanoparticles of 10 nm size and (b) Cobalt nanoparticles of 15 nm size

15.5 Why the properties of nanoparticles are different?

We are interested in the nanoscale materials because at this scale the properties of materials are very much different from those at a larger scale. Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance the properties such as reactivity, strength and electrical characteristics.

1. Increase in surface area to volume ratio:

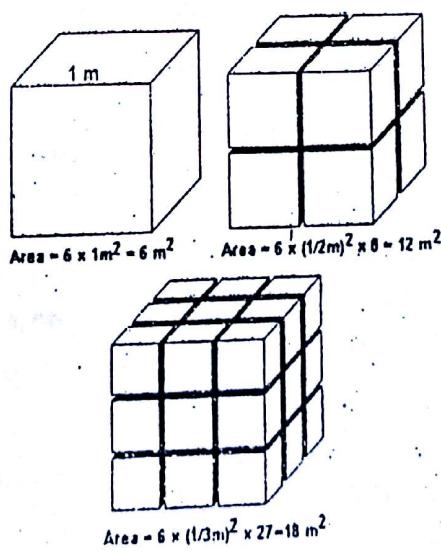


Fig.4 When the given object is divided into smaller pieces, the surface area increases

First, nanomaterials have a relatively larger surface area when compared to the larger form of the material of same volume (or mass). Let us consider a sphere of radius "r",

$$\text{Its surface area} = 4\pi r^2$$

$$\text{Its volume} = \left(\frac{4}{3}\right) \pi r^3$$

$$\text{Surface area to its volume ratio} = \left(\frac{3}{r}\right)$$

Thus when the radius of the sphere decreases, its surface area to volume ratio increases. Let us consider another example. For a one cubic volume shown in Fig. 4, the surface area is 6 m^2 . When it is divided into eight pieces its surface area becomes 12 m^2 . When the same volume is divided into 27 pieces its surface area becomes 18 m^2 . Thus we find that when the given volume is divided into smaller pieces, the surface area increases. Hence as particle size decreases, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per given volume (i.e. for the chosen mass) compared with larger particles. It makes materials more chemically reactive. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles. In some cases materials that are inert in their larger form are reactive when produced in their nanoscale form. This affects their strength or electrical properties.

2. Quantum confinement effects:

When atoms are isolated the energy levels are discrete. When very large number of atoms are closely packed to form a solid, the energy levels split and form bands. Nanomaterials represent intermediate stage.

We have studied the problems of particles in a potential well as well as in a potential box. When the dimensions of such wells or boxes are of the order of de Broglie wavelength of electrons or mean free path of electrons (i.e. within few tens of nanometre), energy levels of electrons change. This effect is called **Quantum confinement**. When the material is in sufficiently small size typically 10 nanometers or less, organization of energy levels into which electrons can climb or fall change. Specifically, the phenomenon results from electrons and "holes" being squeezed into a dimension that approaches a critical quantum measurement, called the "exciton Bohr radius." These can affect the optical, electrical and magnetic behaviour of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale.

15.6 Synthesis of Nanomaterials

Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles).

Nanomaterials can be synthesised by 'top down' techniques, producing very small structures from larger pieces of material. One way of doing this is mechanical crushing of solid into fine nanopowder (ball milling).

Nanomaterials may also be synthesised by 'bottom up' techniques, atom by atom or molecule by molecule. One way of doing this is to allow the atoms or molecules arrange themselves into a structure due to their natural properties e.g. Crystals grown.

Now there are many known methods to produce nanomaterials. Let us study briefly few of these methods.

15.6.1

Plasma arcing

Sputtering ✓

Plasma is an ionized gas. To produce plasma, potential difference is applied between the two electrodes. The gas between the electrodes gets ionized and results in electric discharge. An arc passes from one electrode to the other. The two electrodes must be separated by approximately 1mm in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). Positively charged ions pass to the cathode and get deposited in the form of nanoparticles. The yield rate of nanoparticles depends on the uniformity of the plasma arc and the temperature of the deposit form on the cathode. Plasma arcing is used to produce carbon nanotubes when carbon electrodes are used.

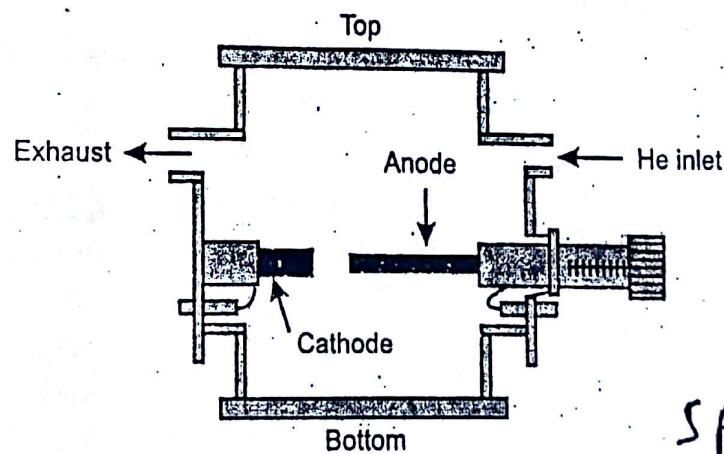


Fig. 5 Plasma arc method of synthesis of nanoparticles

15.6.2 Chemical vapour deposition

In this method nanoparticles are deposited from gas phase. Material is heated to form a gas and then allowed to deposit on a solid surface, usually under high vacuum. In deposition by chemical reaction new product is formed. Nanopowders of oxides and carbides of metals can be formed if vapours of carbon or oxygen are present with the metal.

It involves pyrolysis of vapours of metal organic precursors in a reduced pressure atmosphere. In the simplest form shown in Fig.6, a metal-organic precursor is introduced into the hot zone of the reactor using mass flow controller. The precursor

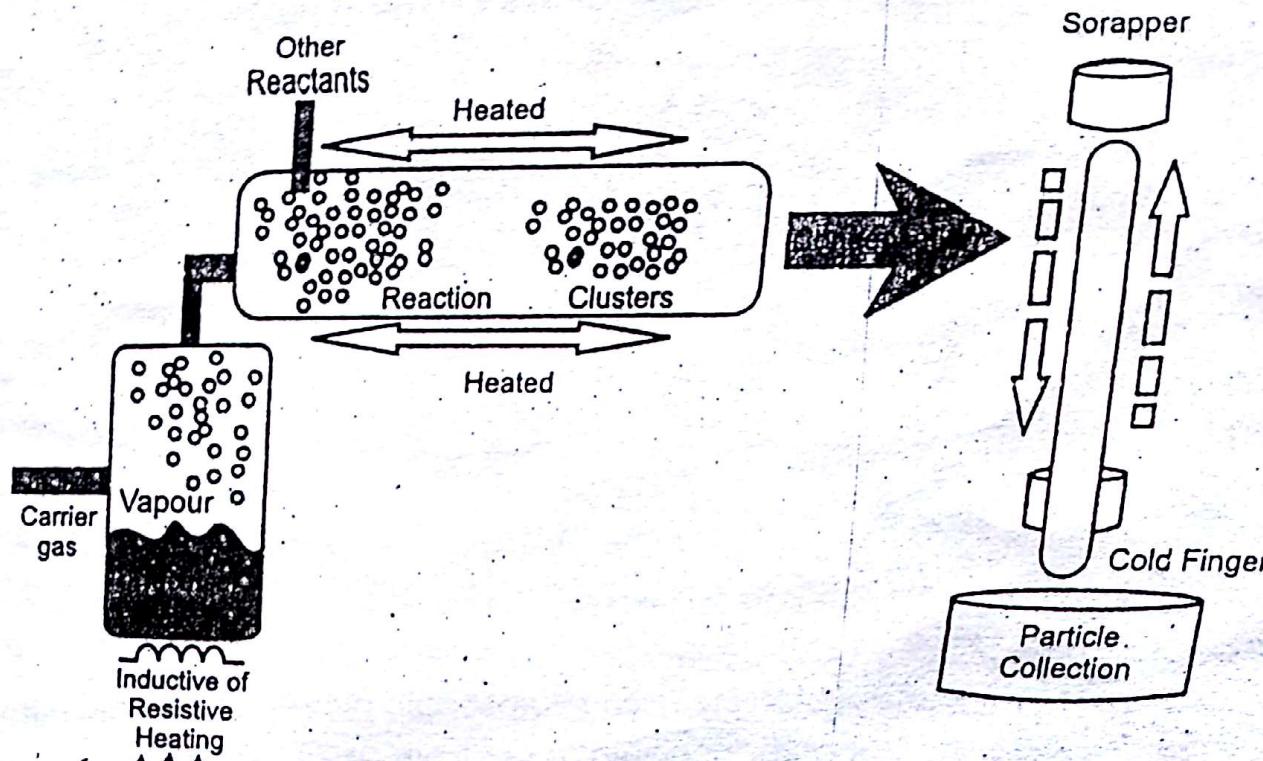


Fig. 6 A schematic of a typical Chemical Vapour Deposition reactor

is vapourised either by resistive or inductive heating. The carrier gas such as Ar or Ne carries the hot atoms to the reaction chamber. The hot atoms collide with cold atoms and undergo condensation through nucleation and form small clusters. In side reaction chamber other reactants are added to control the reaction rate. Then these clusters are allowed to condense on a moving belt arrangement with scrapper to collect the nanoparticles. The particle size could be controlled by rate of evaporation (energy input), rate of cluster formation (energy removal rate) and rate of condensation (cluster removal from the reaction chamber). CVD method of synthesis of nanoparticles has many advantages.

1. the increased yield of nanoparticles
2. a wider range of ceramics including nitrides and carbides can be synthesised.
3. more complex oxides such as BaTiO_3 or composite structures can be formed
4. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of
 - (a) Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and
 - (b) Coated nanoparticles, i.e., n-ZrO_2 coated with $\text{n-Al}_2\text{O}_3$ or vice versa, by supplying a second precursor at a second stage of the reactor.

15.6.3 Sol- Gel method

The solutions in which molecules of nanometer are dispersed appear clear. The colloids in which molecules of size ranging from 20 nm to 100 nm appear milky. A colloid suspended in a liquid is called as *sol*. A suspension that keeps its shape is

called *gel*. Thus *sol-gels* are suspensions of colloids in liquids that keep their shape. Sol-gel formation occurs in different stages.

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: Gelation resulting from the formation of an oxide- or alcohol-bridged network (the *gel*) by a polycondensation or polyesterification reaction. This results in a dramatic increase in the viscosity of the solution.

Step 3: Aging of the gel (Syneresis), 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. If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.

Step 5: Dehydration, during which surface-bound M-OH groups are removed. This is normally achieved by calcining the monolith at temperatures up to 800°C.

Step 6: Densification and decomposition of the gels at high temperatures ($T > 800^\circ\text{C}$). The pores of the gel network are collapsed, and remaining organic species are volatilized.

The typical steps that are involved in sol-gel processing are shown in Fig.7. By different process one can get either nano film coating or nano powder or dense ceramic with nanograins.

This method has the following advantages:

- The possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures.
- One can get monosized nanoparticles.

The disadvantages of this method are:

- Controlling the growth of the particles is difficult.
- Stopping the newly formed particles from agglomeration is also difficult.
- Stoppers prepared by sol-gel method are $\text{Si}(\text{OR})_4$ where R is alkyl groups of various types.

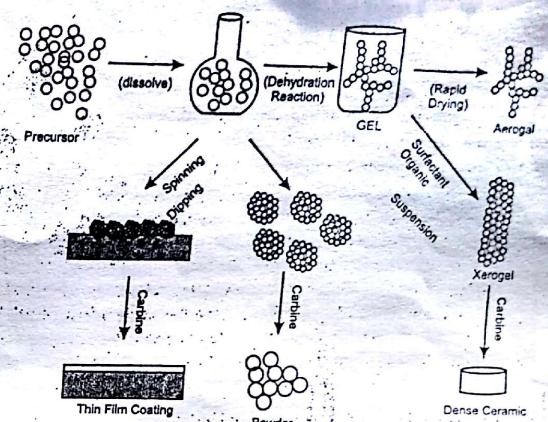


Fig. 7 Schematic representation of sol-gel process of synthesis of nanomaterials

15.6.4 Electrodeposition

Electrodeposition technique is used to electroplate a material. In many liquids called electrolytes (aqueous solutions of salts, acids etc.), when current is passed through two electrodes immersed inside the electrolyte, certain mass of the substance liberated at one electrode gets deposited on the surface of the other. By controlling the current and other parameters, it is possible to deposit even a single layer of atoms. Nanostructured films of copper, platinum, nickel, gold etc. can be produced by electrodeposition. The films thus obtained are mechanically robust, highly flat and uniform. Since these films have larger surface areas, they exhibit quite different and favorable electrical properties. They have very wide range of applications. These include batteries, fuel cells, solar cells, magnetic read heads, etc.

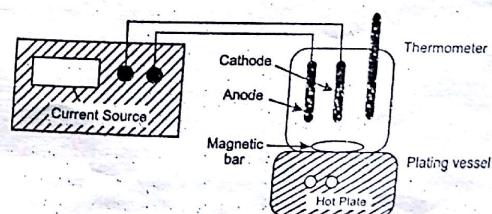


Fig. 8 Schematic representation of electrodeposition method of synthesis of nanostructured films

15.6.5 Ball milling

In ball milling, also called mechanical crushing, small balls are allowed to rotate around the inside of a drum and then fall on a solid with gravity force and crush the solid into nanocrystallites. Ball milling can be used to prepare a wide range of elemental and oxide powders. For example, iron with grain sizes of 10-30 nm can be formed. Other crystallites, such as iron nitriles, can be made using ammonia gas. A variety of intermetallic compounds based on nickel and aluminium can be formed. Ball milling is the preferred method for preparing metal oxides.

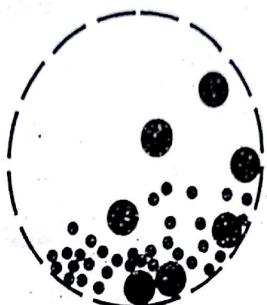


Fig. 9 Ball milling—very heavy small balls inside the rotating drum crush the solid into nanopowder

15.7 Properties of Nanoparticles

The physical, electronic, magnetic, and chemical properties of materials depend sensitively on size. Small particles display behaviours that are different from those of the individual atoms or bulk. Let us see few of them in brief.

15.7.1 Physical properties

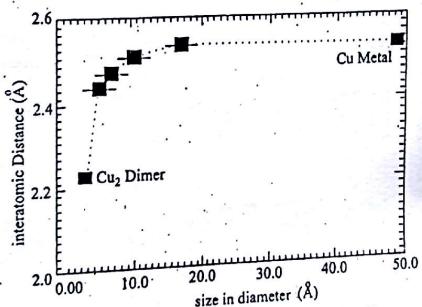


Fig. 10 Interatomic distance in Cu_n as a function of size

How does the geometrical arrangement of atoms and their stability change with size? Starting from the bulk, the first effect of reducing particle size is to increase of surface to volume ratio. This changes the surface pressure and results in a change in the interparticle spacing. This effect is shown in Fig. 10 for the case of Cu_n particles. The interatomic spacing decreases with size.

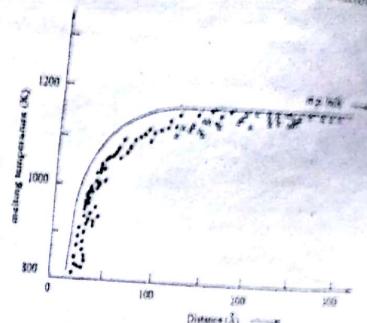


Fig. 11 Melting point of small Au_n particles as a function of size

The change in interparticle spacing and the large surface-to-volume ratio in particles have a combined effect on material properties. Variations in the surface free energy change the chemical potential. This affects, for example, the thermodynamic properties of which the simplest example is the melting point. Fig. 11 shows the melting point of Au_n particles as a function of size. The melting point decreases with size and at very small sizes the decrease is faster.

15.7.2 Chemical properties

The large surface-to-volume ratio, the variations in geometry and the electronic structure have a strong effect on catalytic properties. As an example, the reactivity of small clusters has been found to vary by orders of magnitude when the cluster size is changed by only a few atoms.

Another important possible application is hydrogen storage in metals. Most metals do not absorb hydrogen, only few met also absorb on their surfaces with a hydrogen-to-metal atom ratio of 1. This limit is significantly enhanced in small sizes. It has been shown that small positively charged clusters of Ni, Pd, and Pt containing between 2 and 60 atoms can absorb up to eight hydrogen atoms per metal atom. The number of absorbed atoms decreases with increasing cluster size. This shows that small particles may be very useful in hydrogen storage devices in metals.

15.7.3 Electrical properties

In nanoscale, the electrical properties depend on the size. For example, the resistance of a material is due to the scattering of conduction electrons with vibrating atoms and impurities. The mean distance travelled between two successive collisions is called mean free path or scattering length. When the dimension of the solid becomes comparable to this quantity the scattering probability decreases and hence electrical properties change. When its size is in the order of mean free path or de-Broglie wavelength of electrons or holes which carry current, electronic structure of the system changes completely.

If only one length of the three-dimensional nanostructure is of a nanodimension, then structure is known as a *quantum well*. Instead if two sides are of nanometer scale, then the resulting structure is *quantum wire*. A *quantum dot* has all three dimensions in the nanoscale.

We know the energy of a particle inside a potential box as

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where $n^2 = n_1^2 + n_2^2 + n_3^2$

If we apply the case of electrons in a metal, when $L = 1\text{cm}$, separation between consecutive energy levels can be shown to be of the order 10^{-14}eV . This we can

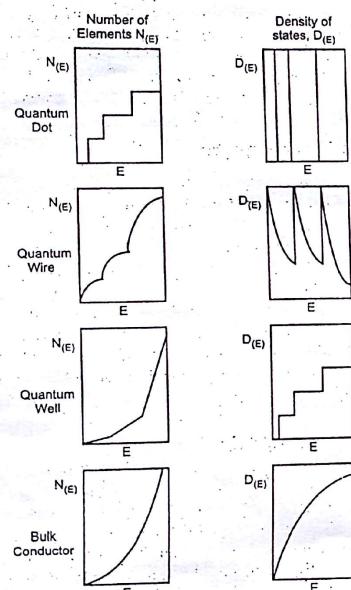


Fig. 12 Number of electrons $N(E)$ (left side) and density of states $D(E)$ (right side) plotted against the energy for four quantum structures

consider to be continuous or quasi-continuous. But when $L = 100\text{nm}$, separation between energy levels works out to be 10^{-4}eV . Thus we find that in nanoscale range, energy levels are discrete.

The density of states $D(E)$ of conduction electrons is strongly affected by the dimensionality of the material.

In Fig.12 number of electrons $N(E)$ and density of states $D(E)$ have been plotted against the energy for four different quantum structures. We find that due to quantum confinement the energy levels narrow down and become discrete when we move from bulk to dot.

The change in electrical properties cannot be generalized. In nanoceramics and magnetic nanocomposites the electrical conductivity increases with reduction in particle size whereas in metals electrical conductivity decreases.

15.7.4 Optical properties

Nanocrystalline systems have novel optical properties. Suppose we have a suspension of nanoparticles in a host. Depending on the particle's size, different colors are seen. Gold nanospheres of 100 nm appear orange in colour while 50 nm nanospheres appear green in colour. 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 wavelength (or colour), this means that the optical properties of the particle can be finely tuned depending on its size. Thus, particles can be made to emit or absorb specific wavelengths (colours) of light, merely by controlling their size. The linear and nonlinear optical properties of such materials can be finely tailored by controlling the crystal dimensions, and the chemistry of their surfaces.

15.7.5 Magnetic properties

The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume) of the grains. Therefore nanomaterials present good properties in this field also.

Table 3 gives a brief summary of the observed magnetic behaviour of very small particles of various metals as well as their behaviour in bulk. In small particles a large fraction of the atoms reside at the surface. These atoms have lower coordination

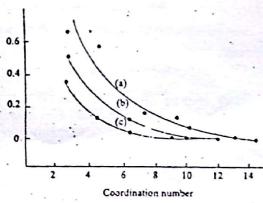


Fig.13 Deviation from the bulk magnetic moment in (a) Fe , (b) Co , and (c) Ni as a function of nearest neighbour coordination (in various structures)

numbers than the interior atoms. Investigation indicate that the local magnetic moment is primarily determined by the local coordination number. Fig.13 shows the calculated dependence of the magnetic moment on the nearest coordination number. It is clear that as the coordination number decreases, the moment increases towards the atomic value. i.e. **small particles are more magnetic than the bulk material.** The magnetic moment of Co_n particles of $\sim 2\text{ nm}$ exhibited 20% higher value than that of the bulk.

Table 1 Magnetism in bulk and in nanoparticles

Metal	Bulk	Cluster
Na, K	Paramagnetic	Ferromagnetic
Fe, Co, Ni	Ferromagnetic	Superparamagnetic
Gd, Tb	Ferromagnetic	Rotors/Superparamagnetic
Cr	Antiferromagnetic	Frustrated paramagnetic
Rh	Paramagnetic	Ferromagnetic

Nanoparticles of **even nonmagnetic solids are found to be magnetic.** It has been found theoretically as well as experimentally that the magnetism is special to small sizes and disappears in clusters containing more than 80 atoms. At small sizes, the clusters become spontaneously magnetic.

In addition to free clusters, clusters of nonmagnetic elements supported on metal substrates have also been proposed to be magnetic. Ferromagnetic and antiferromagnetic multilayers have been found to exhibit **giant magneto-resistance (GMR).**

15.7.6 Mechanical properties

Most metals are made up of small crystalline grains; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving it strength. If these grains are nanoscale in size, the interface area (grain boundary) within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel. Because of the nanosize, many of their mechanical properties such as hardness and elastic modulus, fracture toughness, scratch resistance, fatigue strength, and hardness are modified.

The mechanical behaviour of nanostructured materials prepared by gas condensation method is of great interest. Few observations are:

- 30-50% lower elastic moduli than for conventional grain size materials.
- 2-7 times higher hardness and strength for nano-crystalline pure metals ($\sim 10\text{ nm}$ grain size) than those of large grained ($> 1\mu\text{m}$) metal.
- Decreasing hardness with decreasing grain size in the nanoscale grain size regime (i.e., when grain size is less than 10 nm).

iv) **Superplastic behaviour in brittle ceramics or intermetallics with nanoscale grain sizes at low homologous temperatures.**

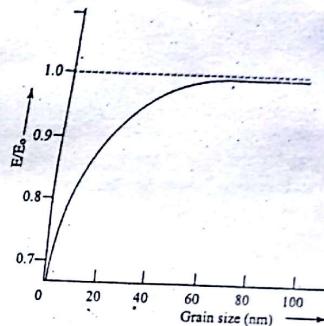


Fig. 14 Ratio of Young's modulus (E) of nanocrystalline materials to (E_0) of conventional grain size materials as a function of grain size

The presence of extrinsic defects such as pores and cracks may be responsible for the low values of E in nanocrystalline materials. The intrinsic elastic moduli of nanostructured materials are essentially the same as those for conventional grain size materials until the grain size becomes very small, e.g. $< 50\text{ nm}$, as shown in Fig.14 for nanocrystalline Fe . At lower grain size the number of atoms associated with the grain boundaries and triple junctions become very large.

The experimental results of hardness measurements show different behaviour namely positive slope, zero slope and negative slope depending on the grain size when it is less than 20 nm . This may be due to changes in structure as densification, stress relief, phase transformations, or grain boundary structure changes with methods employed in synthesis of the sample. Thus, the hardness, strength and deformation behaviour of nanocrystalline materials is unique and not yet well understood.

Superplasticity is the capability of some polycrystalline materials to exhibit very large texture deformations without necking or fracture. Typically, elongation of 100% to $> 1000\%$ are considered to be defining features of this phenomenon. As grain size is decreased it is found that the temperature at which superplasticity occurs is lowered and the strain rate for its occurrence is increased i.e. Superplasticity has been observed at somewhat lower temperatures and at higher strain rates in nanocrystalline materials. Much differing results obtained so far suggest that very different mechanism may be causing superplastic behaviour in nanocrystalline materials.

In Table 2 the properties of nanomaterials are listed.

Table 2 Properties of nanomaterials

Properties	Examples
Catalytic	Better catalytic efficiency through higher surface-to-volume ratio
Electrical	Increased electrical conductivity in ceramics and magnetic nanocomposites, increased electric resistance in metals
Magnetic	Increased magnetic coercivity up to a critical grain size, superparamagnetic behaviour
Mechanical	Improved hardness and toughness of metals and alloys, ductility and superplasticity of ceramic
Optical	Spectral shift of optical absorption and fluorescence properties, increased quantum efficiency of semiconductor crystals
Biological	Increased permeability through biological barriers (membranes, blood-brain barrier, etc.), improved biocompatibility

15.8 Applications of Nanomaterials

Nanoparticles are "the small particles with a big future". Because of their extremely small particle size, they have extremely large specific surface area. Hence they are chemically very active. They are stronger and more ductile. They have electronic states quite different from those of bulk.

In *dispersed state* nanoparticles are used as fillers, paints, magnetic recording media, ferrofluids, drugs, phosphors, rocket propellant, fuel additives etc.

In *consolidated state* nanoparticles are used as catalysts, electrodes of solar cells and fuel cells, sensors, adsorbents, synthetic bone, self-cleaning glass etc.

In *ordered assembly form* nanoparticles are used as quantum electronic devices, photonic crystals, DNA chips, biosensors etc.

In *very dense phase* nanoparticles are used in synthesis of flexible/dense ceramics and insulators, harder metals etc.

In different areas nanoparticles are finding their applications.

i) Materials Technology

- *Cutting tools* made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are *more wear and erosion-resistant*, and *last longer* than their conventional (large-grained) counterparts. They are finding applications in the drills used to bore holes in circuit boards.

- *Wear and scratch-resistant hard coatings* are significantly improved by nanoscale intermediate layers (or multilayers) between hard outer layers and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion.
- It is now possible to *synthesis harder metals* having hardness 5 times higher than normal metals using nanoparticles.
- Ceramics are hard, brittle and difficult to machine. However, with a reduction in grain size to the nanoscale, ceramic ductility can be increased. Zirconia, normally a hard, brittle ceramic, has even been rendered *superplastic* (for example, able to be deformed up to 300% of its original length).
- Nanocrystalline ceramics, such as silicon nitride and silicon carbide, have been used in such *automotive applications as high-strength springs, ball bearings and valve lifters*, because they can be easily formed and machined, as well as exhibiting excellent chemical and high-temperature properties. They are also used as components in high-temperature furnaces.
- A carbon nanoparticles act as fillers in a matrix; for example, they are used as a filler to *reinforce car tyres*.
- Clay particle based composites containing plastics and nano-sized flakes of clay are also finding applications such as use in *car bumpers*.
- Nanocoating of highly activated titanium dioxide is highly hydrophobic (water repellent) and antibacterial. Recently developed applications include the *self-cleaning windows*. Coatings based on nanoparticulate oxides catalytically *destroy chemical agents*.
- Stronger, lighter, wear resistant, tougher and flame retardant polymers are synthesized with nanoparticles as *fillers*. They are used in replacement of body parts and metals.
- Magnets made of nanocrystalline yttrium-samarium-cobalt grains possess unusual magnetic properties due to their extremely large grain interface area. *High coercivity* can be obtained because magnetization flips cannot easily propagate past the grain boundaries. This could lead to applications in *motors*, analytical instruments like *magnetic resonance imaging (MRI)*.
- Useful as *magnetoresistance spin valves*.
- In general, nanoparticles have a high surface area, and hence provide *higher catalytic activity*.
- Smart magnetic fluids are used as,
 - *vacuum seals*

- viscous dampers,
- cooling fluids,
- magnetic separators etc.

- Nano-engineered membranes could potentially lead to more energy-efficient *water purification processes*, notably in desalination by reverse osmosis.
- Nanoparticles react with pollutants in soil and groundwater and transform them into *harmless compounds*. Iron nanoparticles transform chlorinated hydrocarbons (which are carcinogens) into less harmful end products in groundwater.
- Improved control of porosity at the nanoscale has important applications. A range of enhanced textiles, such as *breathable, waterproof and stain resistant fabrics*, have been enabled by this technique in variety of polymers and inorganics.
- Other novel, and more long-term, applications for nanoparticles lie in paints that *change colour in response to change in temperature or chemical environment*, or paints that have *reduced infra-red absorptivity* and so reduce heat loss.
- Nanosized titanium dioxide and zinc oxide are currently used in *sunscreens*. They absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light.
- It is possible to produce *unusual colour paints* using nanoparticles since nanoparticles exhibit entirely different optical properties.
- Nanosized iron oxide is present in some *lipsticks* as a pigment.
- Nanospheres of inorganic materials could be used as *lubricants*, in essence by acting as nanosized 'ball bearings'.

ii) Information Technology

- Nanoscale-fabricated magnetic materials also have applications in *data storage*. If the area required to record one piece of information can be shrunk in the nanoscale (and can be written and read reliably), the storage capacity of the disk can be improved dramatically.
- Coatings with thickness controlled at the nano- or atomic scale have been used in *optoelectronic devices* or in *catalytically active* and chemically functionalized surfaces.
- Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol-gel techniques are candidates for the next generation of *light-emitting phosphors*. They will have huge market for large area, high brightness, flat-panel displays (as used in television screens and computer monitors).

- Nanoparticles are used for *information storage*.
- Quantum electronic devices* have started replacing bulky conventional devices.
- Nano dimensional *photonic crystals* are used in chemical/optical computers.

iii) Biomedicals

- Nanocrystalline zirconium oxide (zirconia) is hard, wear resistant, bio-corrosion resistant and bio-compatible. It therefore presents an attractive alternative *material for implants*. Other nanoceramics can also be made as strong, light aerogels by sol-gel techniques. Nanocrystalline silicon carbide is a candidate material for *artificial heart valves* primarily because of its low weight, high strength and inertness.
- Biosensitive nanoparticles are used for *tagging of DNA and DNA chips*.
- Controlled drug delivery* is possible using nanotechnology. Diffusion of medicine through nanoporous polymer reservoir as per the requirement is very useful in controlling the disease.
- Nanostructured ceramics readily interact with bone cells and hence finds application as an *implant material*.

iv) Energy storage

- Addition of nanoparticulate ceria (cerium oxide) to diesel fuel *improves fuel economy* by reducing the degradation of fuel consumption over time.
- In fuel cells, the external surface properties and the pore structure affect performance. The hydrogen used as the immediate fuel in cells is generated from hydrocarbons by *catalytic reforming*. Nano-engineered membranes intensify catalytic processes and enable higher-efficiency, small-scale fuel cells. Nanocrystalline materials synthesized by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than conventional ones. Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydrides require less frequent recharging and last longer.
- Since the hydrogen absorbing capacity increases with decrease of size of nanoparticles, nanoparticles of *Ni, Pd and Pt* are useful in *hydrogen storage devices*.
- Useful in *magnetic refrigeration*.
- Metal nanoparticles are very useful in *fabrication of ionic batteries*.

In fact, the ability to control properties by changing size, composition, or dimension shows that nanoscale materials will form the basis of a new class of atomically engineered materials with tailored properties.

15.9 Carbon Nanotubes (CNTs)

Carbon nanotubes were first observed by Sumio Iijima in 1991. So far we know only three forms of carbon, namely diamond, graphite, and amorphous carbon. Now we come to know that there is a whole family of other forms of carbon known as Carbon nanotubes, which are related to graphite. The molecular structure of graphite is one-atom-thick a planar network of interconnected hexagonal rings of carbon atoms. Such a graphite sheet is called **graphene**. When graphite sheets are rolled into a cylinder and their edges joined, they form carbon nanotubes. The way they are rolled is represented by a pair of indices (n, m) called the **chiral vector**. The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $n = m$, they are called **zigzag**. If $n = m$, they are called **armchair**. Otherwise they are called **chiral**.

15.9.1 Types of CNTs

A nanotube may consist of one tube of graphite, a one-atom thick single-wall nanotubes (Fig. 15(a)), or a number of concentric tubes called multiwalled nanotubes (Fig. 15(b)). Both of these are typically a few nanometres in diameter. Their length may vary from several micrometres to centimetres.

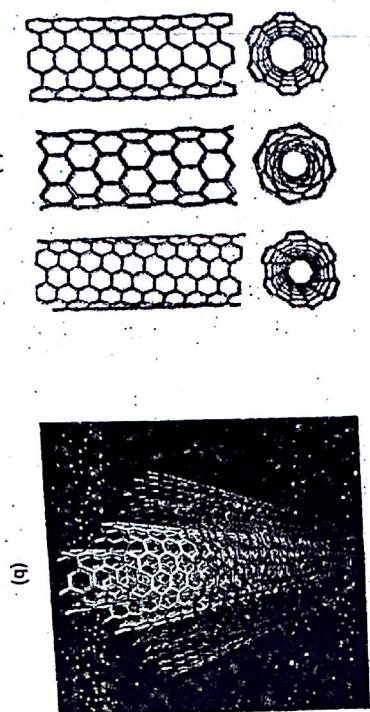


Fig. 15 (a) Different types of single walled nanotubes and (b) Multi walled nanotubes

Multi walled nanotubes can come in an even more complex array of forms. In Russian Doll model each concentric single-walled nanotube can have different structures, and hence there are a variety of sequential arrangements. The simplest sequence is when concentric layers are identical but differ in diameter. In Parchment model, a single sheet of graphite is rolled in around itself like rolling a newspaper. The structure of the nanotube influences its properties - including electrical and thermal conductivity, density, and lattice structure. Both type and diameter are important. The wider the diameter of the nanotube, the more it behaves like graphite. The narrower the diameter of the nanotube, the more its intrinsic properties depends upon its specific type.

Carbon nanotubes have assumed an important role because of their novel chemical and physical properties. They are

- mechanically very strong (their Young's modulus is over 1 terapascal, making CNTs as stiff as diamond),
- flexible (about their axis), and can conduct electricity extremely well.

The helicity of the graphite sheet determines whether the CNT is a semiconductor or metallic. All of these remarkable properties give CNTs a range of potential applications: for example, in reinforced composites, sensors, nanoelectronics and display devices.

CNTs come in a variety of diameters, lengths, and functional group content. They are available for industrial applications in bulk (metric ton). Several CNT manufacturers have > 100 ton per year production capacity for multi walled nanotubes.

15.10 Fabrication of CNTs

Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs. Three distinct methods of synthesis with the arc discharge apparatus are presented here.

15.10.1 Arc method in inert gas atmosphere

This method creates nanotubes through arc-vapourisation of two carbon rods placed end to end, separated by approximately 1 mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). When the anode is doped with Ni or Co single walled nanotubes are produced. Instead if pure graphite electrodes are used multiwalled nanotubes are obtained.

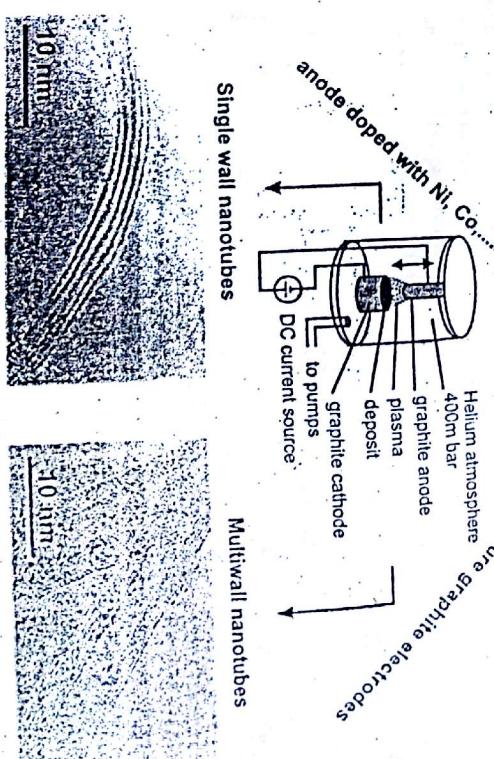


Fig. 16 Experimental setup of an arc discharge apparatus

15.10.2 Arc method in liquid nitrogen

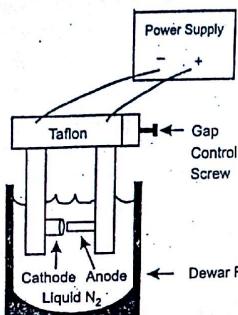


Fig. 17 Arc method of production of nanotubes in liquid nitrogen

Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen. A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vapourises one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode.

15.10.3 Plasma rotating arc discharge method

Plasma rotating arc discharge technique is a economical route to mass production of MWNTs. The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapour perpendicular to the anode. In addition, the rotation distributes the micro discharges uniformly and generates a stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature. At a

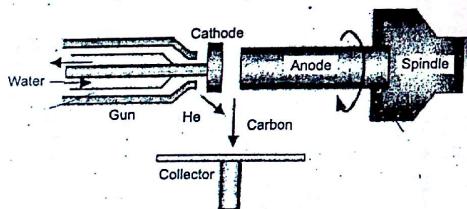


Fig. 18 Schematic diagram of plasma rotating electrode system
rotation speed of 5000 rpm a yield of 60% is found at a formation temperature of 1025°C without the use of a catalyst. The yield increases up to 90% after purification if the rotation speed is increased and the temperature is raised to 1150°C.

15.10.4 Pulsed laser deposition

Pulsed Laser Deposition (PLD) is a thin film deposition technique. A high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited as shown in Fig.19. This material is vaporized from the target. It is then deposited as a thin film on a substrate (such as a silicon wafer facing the target). This process can occur in ultra high vacuum or in the presence of a background gas. Oxygen is commonly used when depositing oxides to fully oxygenate the deposited films.

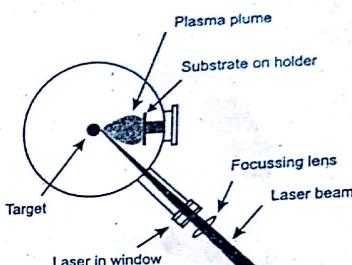


Fig. 19 Pulsed laser deposition method of growing carbon nanotubes

The ablation of the target material upon laser irradiation and the creation of plasma are very complex processes. The removal of atoms from the bulk material is done by vaporization of the bulk at the surface region. When laser pulse of suitable wavelength and sufficient energy falls on the target the surface of the target is then heated up and the material is vaporized. High energy species are emitted from the surface. The sputtered species from the substrate and the particles emitted from the target form a collision region, which serves as a source for condensation of particles. These condensed particles of nanosize get deposited on the film and the film grows on the substrate surface. This also depends on the condition of the surface of the substrate such as temperature, surface nature such as cut, roughness etc.,

The quality of the film grown, the size of the nanoparticles deposited and the rate of deposition depend on various laser parameters such as the laser fluence [Joule/cm^2], laser energy, and pulse duration.

15.10.5 Chemical vapour deposition

Chemical Vapour Deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as a plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The en-

ergy source is used to "crack" the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it binds. Carbon nanotubes are formed if the proper parameters are maintained.

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes grow. Ammonia may be used as the etchant. The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900°C range. These are the basic principles of the CVD process. Two different techniques are explained in more detail.

Plasma enhanced chemical vapour deposition

The plasma enhanced CVD method generates a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. Fig.20 shows a schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure.

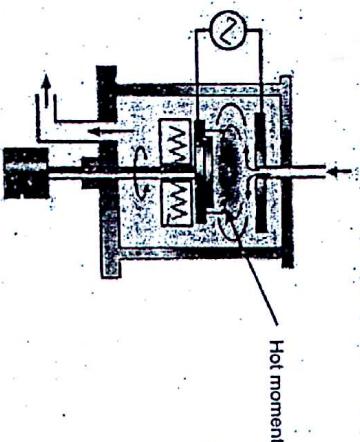


Fig.20 Schematic diagram of plasma CVD apparatus

A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metal, such as Fe, Ni and Co are used on for example a Si, SiO_2 , or glass substrate using thermal CVD or sputtering. After nanoscopic fine metal particles are formed, carbon nanotubes are grown on the metal particles on the substrate by glow discharge generated from high frequency power. A carbon containing reaction gas, such as C_2H_2 , CH_4 , C_2H_4 , C_2H_6 , CO is supplied to the chamber during the discharge.

The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni seems to be the most suitable pure-metal

catalyst for the growth of aligned multi-walled carbon nanotubes (MWNTs). The diameter of the MWNTs is approximately 15 nm. The highest yield of carbon nanotubes achieved was about 50% and was obtained at relatively low temperatures (below 330°C).

Thermal chemical vapour deposition

In this method Fe, Ni, Co or an alloy of the three catalytic metals is initially deposited on a substrate. After the substrate is etched in a diluted HF solution with distilled water, the specimen is placed in a quartz boat. The boat is positioned in a CVD reaction furnace, and nanometre-sized catalytic metal particles are formed after an additional etching of the catalytic metal film using NH_3 gas at a temperature of 750 to 1050°C. As carbon nanotubes are grown on these fine catalytic metal particles in process. Fig.21 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.

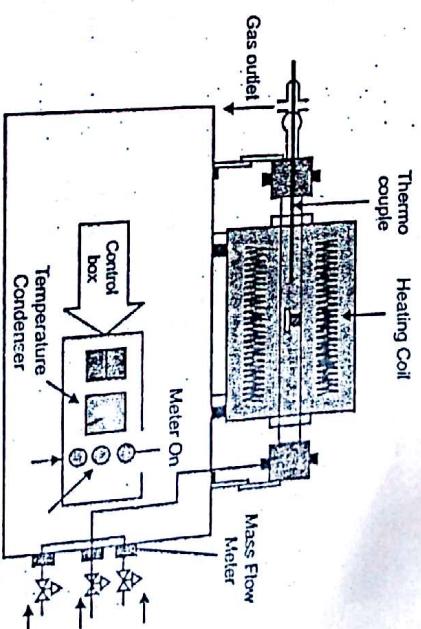


Fig.21 Schematic diagram of thermal CVD apparatus

When growing carbon nanotubes on a Fe catalytic film by thermal CVD, the diameter range of the carbon nanotubes depends on the thickness of the catalytic film. By using a thickness of 13 nm, the diameter distribution lies between 30 and 40 nm. When a thickness of 27 nm is used, the diameter range is between 100 and 200 nm. The carbon nanotubes formed are multiwalled.

Excellent alignment, as well as positional control on nanometre scale, can be achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes.

15.11 Properties of CNTs

Let us see few unique properties of CNTs.

a) Electrical Conductivity

CNTs can be highly conducting, and hence can be said to be metallic. Their conductivity has been shown to be a function of their chirality, the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior. Conductivity in multi walled CNTs is more complex. The conductivity and resistivity of single walled nanotubes has been measured by placing electrodes at different parts of the CNTs. The resistivity of the single walled nanotube was of the order of 10^{-4} ohm-cm at 27°C. This means that single walled nanotubes are the most conductive carbon fibers known. It has been reported that individual single walled nanotubes may contain defects. These defects allow the single walled nanotubes to act as transistors. Likewise, joining CNTs together forms transistor-like devices. A nanotube with a neutral junction (where a straight metallic section is joined to a chiral semiconducting section) behaves as a rectifying diode.

b) Strength and Elasticity

The carbon atoms of a single sheet of graphite form a planar honeycomb lattice, in which each atom is connected via a strong chemical bond to three neighboring atoms. Because of these strong bonds, the basal plane elastic modulus of graphite is one of the largest of any known material. For this reason, CNTs are expected to be the ultimate high-strength fibers. Single walled nanotubes are stiffer than steel, and are very resistant to damage from physical forces. The current Young's modulus value of single walled nanotubes is about 1 TeraPascal.

Table 3 CNT's Mechanical Properties

Material	Young's modulus (GPa)	Tensile Strength (GPa)	Density (g/cm ³)
Single wall nanotube	1054	150	1.4
Multi wall nanotube	1200	150	2.6
Diamond	600	130	3.5
Kevlar	186	3.6	7.8
Steel	208	1.0	7.8
Wood	16	0.008	0.6

c) Thermal Conductivity and Expansion

The strong in-plane graphitic carbon - carbon bonds make them exceptionally strong and stiff against axial strains. The almost zero in-plane thermal expansion but large inter-plane expansion of single walled nanotubes implies strong in-plane coupling and high flexibility against non-axial strains. Preliminary experiments on the thermal properties of CNTs show very high thermal conductivity.

d) Highly Absorbent

The large surface area and high absorbency of CNTs make them ideal candidates for use in air, gas, and water filtration.

15.12 Applications of CNTs

The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures. The highest tensile strength of an individual multi-walled carbon nanotube has been tested to be 63 GPa. Carbon nanotubes were found in *Damascus steel* from the 17th century, possibly helping to account for the legendary strength of the swords made of it.

Structural

- Because of the carbon nanotube's superior mechanical properties, many structures have been proposed ranging from everyday items like clothes and sports gear to combat jackets and space elevators.
- Nanotube reinforcements in polymeric materials may also significantly improve the thermal and thermomechanical properties of the composites.
- A lot of research is being done in replacing activated charcoal with CNTs in certain ultra high purity applications.
- An important use of *nano particles and nanotubes in composites*. Composite materials combine one or more separate components and are designed to exhibit overall the best properties of each component. Currently, carbon fibres and bundles of multi-walled CNTs are used in composites having potential long-term applications.
- CNTs have exceptional mechanical properties, particularly *high tensile strength and light weight*. An obvious area of application would be in *nanotube reinforced composites*, with performance beyond current carbon-fibre composites. Such light, high strength material will have numerous applications in transportation.

In electrical circuits

- The joining of two carbon nanotubes with different electrical properties to form a diode has been proposed.

- Nanotube based transistors have been made that operate at room temperature and that are capable of digital switching using a single electron.

The first nanotube integrated memory circuit was made in 2004. One of the main challenges has been regulating the conductivity of nanotubes. Depending on subtle surface features a nanotube may act as a plain conductor or as a semiconductor.

- Large structures of carbon nanotubes can be used for thermal management of electronic circuits. An approximately 1 mm-thick carbon nanotube layer was used as a special material to fabricate coolers, this material has very low density, 20 times lower weight than a similar copper structure, while the cooling properties are similar for the two materials.
- CNTs are being investigated for **low voltage field-emission displays**; their strength, sharpness, conductivity and inertness make them potentially very efficient and long-lasting emitters.

As paper batteries

- A paper battery is a battery engineered to use a paper-thin sheet of cellulose (which is the major constituent of regular paper, among other things) infused with aligned carbon nanotubes. The nanotubes act as electrodes; allowing the storage devices to conduct electricity. The battery, which functions as both a lithium-ion battery and a supercapacitor, provides a long, steady power output.

As a vessel for drug delivery

- The nanotube's versatile structure can be used for localized drug delivery in and around the body. This is especially useful in treating cancerous cells. Currently chemotherapy often damages healthy as well as cancerous cells due to its poor ability to target specific body parts. Nanotubes can be filled with a drug and delivered to specific areas where a chemical trigger can release the drugs from the nanotube. A test using dye and a polymer cap to seal the nanotubes has been reported in the literature.

Ultracapacitors

- Nanotubes are used to improve ultracapacitors. With a nanotube electrode the spaces may be tailored to size-few too large or too small-and consequently the capacity should be increased considerably.

15.13 Summary of Applications of Nanotechnology

Automotive industry	Chemical industry	Engineering
• Light weight construction	• Fillers for paint systems	• Wear protection for tools and machines (anti blocking coatings, scratch resistant coatings on plastic parts, etc.)
• Painting(fillers, base coat, clear coat)	• Coating systems based on nano composites	• Lubricant-free bearings
• Catalysts	• Impregnation of papers	
• Tires (fillers)	• Switchable adhesives	
• Sensors	• Magnetic fluids	
• Coatings for windscreen and car bodies	• Magnetic fluids	
Electronic industry	Construction	Medicine
• Data memory (MRAM, GMR-HD)	• Construction materials	• Drug delivery systems
• Displays (OLED, FED)	• Thermal insulation	• Active agents
• Laser diodes	• Flame retardants	• Contrast medium
• Glass fibres	• Surface-finishing materials for wood, floors, stone, facades, tiles, roof tiles, etc.	• Medical rapid tests
• Optical switches	• Filter s (IR-blocking)	• Prosthetics and implants
• Conductive, antis-tatic coatings	• Facade coatings	• Antimicrobial agents and coatings
	• Groove mortar	• Agents in cancer therapy
Textile/fabrics/	Energy	
• Non wovens	• Fuel cells	
• Surface processed textiles	• Solar cells	
• Smart clothes	• Batteries	
	• Capacitors	
Food and drinks	Household	sports/outdoor
• Package materials	• Ceramic coatings for irons	• Ski wax
• Storage life sensors	• Odors catalyst	• Antifogging of glasses/goggles
• Additives	• Cleaner for glass, ceramic, floor, windows	• Anti fouling coatings for ships/boats
• Clarification of fruit juices		• Ringforced tennis rackets and balls

15.14 Characterization of Nanoparticles

For characterization of nanoparticles both X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) are the most widely used techniques. In chapter 3 we have studied in detail about XRD. Let us see how it is used to characterize the nanoparticle.

15.14.1 XRD Analysis

Typical XRD pattern of silver particles prepared by the chemical method is shown in the Fig.22.

The XRD study indicates the formation of silver (Ag) nano particles.

From this study, considering the peak of diffraction angle at 45 degrees, average particle size has been estimated by using Debye-Scherrer formula

$$D = \frac{0.9\lambda}{W \cos \theta}$$

where ' λ ' is wavelength of X-Ray (0.1541 nm), 'W' is FWHM (full width at half maximum) (0.011 radian), ' θ ' is the diffraction angle (45°) and 'D' is particle diameter (size). The average particle size is calculated to be around 14 nm. Thus using XRD pattern we are able to calculate the particle size. To 'see' the particle, we have to go for TEM.

15.14.2 Electron Microscope

Immediate application of wave nature of matter is electron microscope. The resolving power of a microscope is inversely dependent on the wavelength of radiation used and hence, shorter the wavelength higher the resolution. One may ask, then why X-rays cannot replace visible light in optical microscopes? Since the refractive index of glass is almost unity at X-ray wavelength, glass lenses cannot produce focusing effect on X-rays. Hence, construction of high-resolution microscope using X-rays is not possible. Since the accelerated electron beam behaves as waves at X-ray wavelength region, one can use electron beam for construction of microscope. In electron microscope, current - carrying coils produce magnetic fields that act as lenses to focus an electron beam on a specimen.

Principle

1. In microscope, shorter the wavelength of radiation higher the resolution. Since accelerated electron beam exhibits wave properties at shorter wavelength region, it is used.

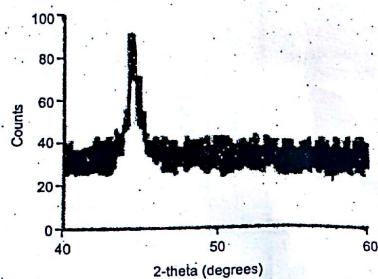


Fig. 22 X-ray diffraction of Ag nano particles

2. Electron beam is focused by suitable electric and magnetic fields in electron microscopes:

Construction

An electron microscope (shown in Fig.23 b) is similar in principle to an optical microscope (shown in Fig.23 a). An electron gun has a filament as a source of electrons. The electrons emitted by the filament are accelerated by a large potential applied to the electrodes in the electron gun. The accelerated electron beam passes through a electromagnet which acts as a condensing lens. Parallel beam of electron from this magnetic condensing lens falls on the object to be magnified. Transparent regions of the object transmits more electrons while denser regions transmit less. Thus the electron beam transmitted by the object carries its image. The next electromagnet called magnetic objective lens forms an enlarged image of the object on its other side. The third electromagnet called magnetic projection lens further magnifies this image on the fluorescent screen, producing a final image. Due to the scintillation action of the fluorescent screen the magnified image can be viewed. One can use suitable photographic plate for a permanent record.

Since electron beam operates in vacuum, the entire apparatus is mounted inside a glass chamber, which is vacuumised. In the electron gun the voltage applied can be as large as 300 kV. Magnifications of over 1,000,000 X have been achieved with electron microscopes. Electron microscopes can resolve up to 0.1 nm.

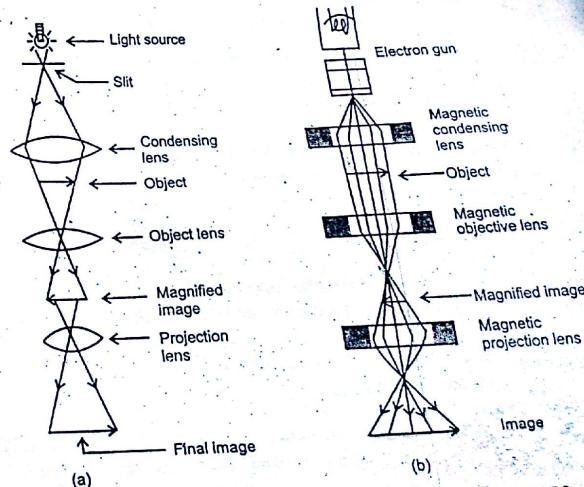


Fig. 23 (a) Optical Microscope (b) Electron Microscope

Uses

Electron microscope is used in many fields.

1. In medicine and biology, it is used to study virus. The bacteria are seen in detail. This helps in preparing medicines for control of diseases.
2. Used in the investigation of atomic structure and also structure of crystals.
3. Used for the study and analysis of small particles forming colloids.
4. Used in industry to study the structure of textile fibers.
5. To study the structure of paints and characterize them.
6. Very useful in surface engineering of metals.

Limitations

1. Cannot be used for study of living organisms since they decompose in vacuum.
2. Takes more time for each study since very high vacuum has to be achieved.

Comparison between optical microscope and electron microscope

	Optical microscope	Electron microscope
Source	optical light	electron gun
Lenses	optical lenses	electromagnetic lenses
for focusing		
Magnification	1000 X	1,000,000 X
Resolution	100nm	0.1nm
Environment	atmosphere	high vacuum

15.14.3 Scanning Electron Microscope (SEM)

The image in *Scanning Electron Microscopy (SEM)* is produced by scanning the sample with a focussed electron beam and detecting the secondary and/or back scattered electrons. Electrons and photons are emitted at each beam location and subsequently detected. When transmitted electrons are utilized for imaging, it results in *Transmission Electron Microscopy (TEM)*.

A schematic representation of a SEM is shown in Fig.24. Each component/part is labelled and their functions are briefed below. Since electrons are used instead of photons, all the lenses are electrostatic/magnetostatic.

1. The electron gun produces a stream of monochromatic electrons.
2. The electron stream is condensed by the first condenser lens. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam.

3. The second condenser lens forms the electrons into a thin, light coherent beam.
4. Objective aperture further eliminates high angle electrons from the beam.
5. A set of coils acting as electrostatic lens scans and sweeps the beam in a grid fashion (as in television). The beam dwells on points for a period of time determined by the scan speed. Dwell time is usually in microsecond range.
6. The objective lens focuses the scanning beam onto the part of the specimen.
7. When the beam strikes the sample interaction occurs. Before the beam moves to the next dwell point, the various instruments housed to measure various interactions count the number of interactions and display a pixel on a CRT. The intensity of display is determined by the interaction number. More interactions give a brighter pixel.
8. This process is repeated until the grid scan is finished and then repeated. The entire pattern can be scanned 30 times per second.

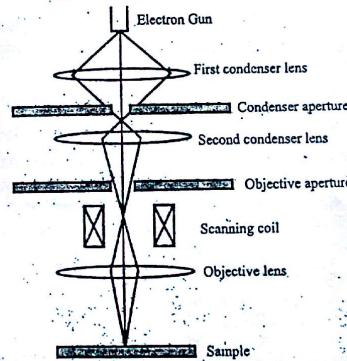


Fig.24 Scanning electron microscope

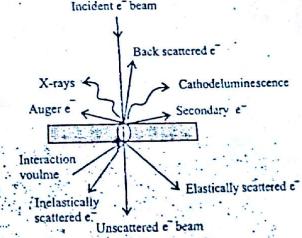


Fig.25 Specimen interactions

Specimen Interaction

Specimen interaction results in salient features of an electron microscope. When the energetic electrons strike the sample, various interactions occur. The interactions occurring on the top side of the thick or bulk sample results in *Scanning Electron Microscope (SEM)* while the interactions occurring on the bottom side of the thin or foil sample result in *Transmission Electron Microscope (TEM)*.

Bulk specimen interactions used in SEM

Backscattered electrons:

When an incident electron collides with an atom in the specimen which is nearly normal to the incident path, we get backscattered electron at nearly 180° . The intensity of backscattered electrons varies with specimen's atomic number. Hence when backscattered electrons are collected and imaged, higher atomic number elements appear brighter than lower atomic number elements. This interaction is therefore utilized to differentiate parts of the specimen that have different average atomic number.

Secondary electrons:

When an incident electron passes very near an atom in the specimen, it may impart some of its energy to the lower energy electron (usually in the K-shell) resulting in ionization of the electron in the specimen atom. This ionized electron leaves the atom with a very small kinetic energy (~ 5 eV) and is called secondary electrons. Each incident electron can produce several secondary electrons that are very near the secondary electrons have low energy, only the secondaries that are very near the surface (< 100 nm) can leave the sample. Any change in the *topography* of the sample changes the yield of the secondary electrons. Hence image formed collecting secondary electrons gives the topography of the sample.

Auger electrons:

During the emission of secondary electron a lower energy electron from the same atom can leave a vacancy into inner shell. A higher energy electron is released by the fall to the lower energy filling the vacancy. The surplus energy is released by the emission of outer-orbit electron. These electrons are called Auger electrons. They have a characteristic energy, unique to each element from which they are emitted.

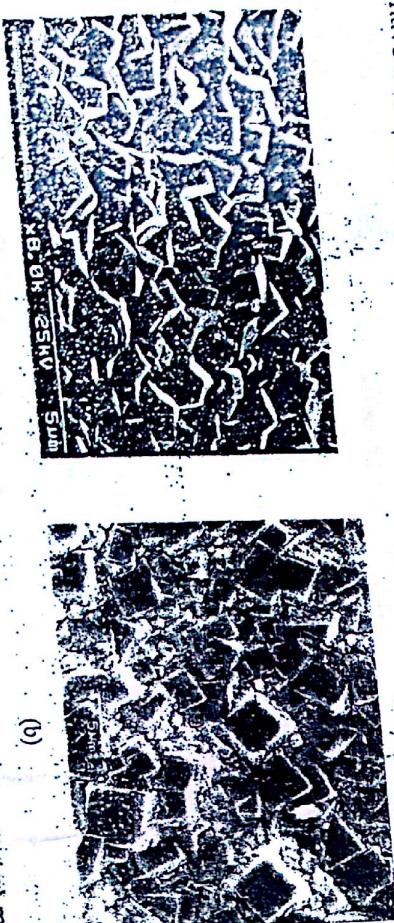


Fig. 26 Scanning Electron microscopic picture of Chemical Vapour Deposited a) microcrystalline diamond and b) a mixture of microcrystalline diamond and nanocrystalline diamond (magnification 8000 \times)

These electrons are collected and sorted according to their energies to give compositional information about the sample.

X-rays:

When the vacancy due to the emission of secondary electron is filled by the fall of an electron from higher orbit to lower orbit, the difference in energy may be released as X-rays. Hence X-rays thus emitted will have a characteristic energy unique to the element from which it originates.

Applications

SEM gives useful information on:

1. Topography:

The surface features of an object or "how it looks", its texture, detectable features limited to a few nanometers.

2. Morphology:

The shape, size and arrangement of particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching, detectable features limited to a few nanometers.

3. Composition:

The elements and compounds the sample is composed of and their relative ratios, in areas ~ 1 micrometer in diameter.

4. Crystallographic information:

The arrangement of atoms in the specimen and their degree of order, only useful on single-crystal particles > 20 micrometers.

The most common use in the area of semi-conductor applications are

1. to view the surface of the device
2. for failure analysis
3. cross-sectional analysis to determine the device dimensions such as MOSFET channel length or junction depth.
4. on-line inspection of wafer processing production
5. inspection of integrated-circuits etc.

15.14.4 Transmission Electron Microscope (TEM)

- A schematic representation of a TEM is shown in Fig. 27. Each component/part labelled and their functions are briefed below.
1. The electron gun produces a stream of monochromatic electrons.

2. This stream is focused to a small coherent beam by the first and second condense lenses.
3. The condenser aperture knocks off high angle electrons.
4. The beam strikes the specimen.
5. The transmitted portion is focused by the objective lens into an image.
6. Objective aperture enhances the contrast by blocking out high-angle diffracted electrons.
7. Selected area aperture enables to examine the periodic diffraction of electrons by an ordered arrangement of atoms in the sample.
8. Intermediate and projector lenses enlarge the image.
9. The beam strikes the phosphor screen and image is formed on the screen. The darker areas of the image represents thicker or denser sample areas since these areas transmit lesser electrons. The brighter areas of the image represents thinner or lesser dense sample areas since these areas transmit more electrons.

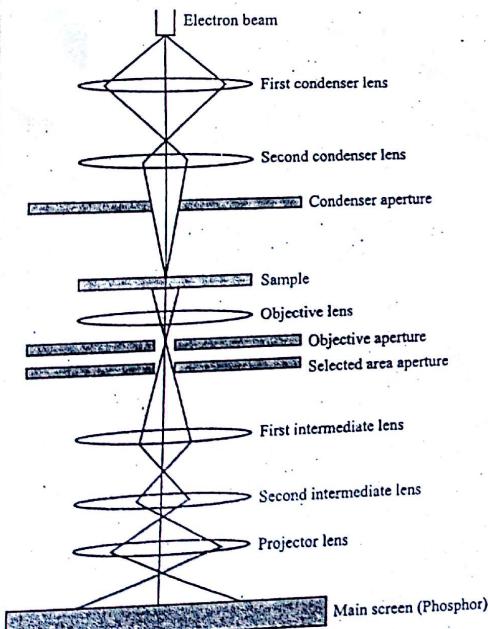


Fig. 27 Transmission electron microscope

Thin specimen interactions used in TEM

Unscattered electron:

These are electrons transmitted through a thin specimen without any interaction occurring inside the specimen. The intensity of transmitted unscattered electrons is inversely proportional to the thickness of the specimen. Hence thicker areas of the specimen appear darker than the thinner areas.

Elastically scattered electrons:

These are electrons that are scattered (deflected from their original path) by atoms in the specimen without loss of energy. These scattered electrons are then transmitted through the remaining portions of the specimen. The scattered electrons follow Bragg's law:

$$2d \sin \theta = n\lambda$$

Hence by collecting the scattered electrons at different angles, one can get information about the orientation, atomic arrangement and phases present.

Inelastically scattered electrons:

These are electrons that interact with specimen atoms in an inelastic manner, losing energy. Then they are transmitted through the remaining portions of the specimen. The inelastic loss of energy is characteristic of the elements that have interacted with. These energies are unique to bonding state of each element. Hence this can be used to extract both compositional and bonding information.

TEM Analysis

A TEM image of the silver nano particles studied using XRD in section 15.14.1 is shown in the Fig.28. The A_g nano particles are spherical in shape with a smooth surface morphology. The diameter of the nano particles is found to be approximately 15 nm. TEM image also shows that the produced nano particles are more or less uniform in size and shape.

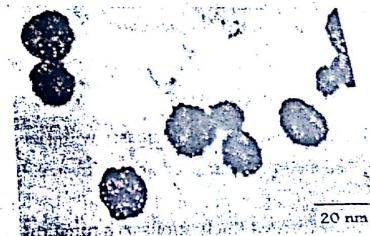


Fig. 28 TEM image of Ag nano particles

Applications

TEM gives the following useful informations:

1. Morphology:

The size, shape and arrangement of particles as well as their relationship to one another on the scale of atomic diameters.

2. Crystallographic information: The arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects a few nanometers in diameter.

3. Compositional information:

The elements and compounds the sample is composed of and their relative ratios.

15.15 Conclusion

Though nanomaterials were existing, only now we have realized that they are very different and hence important. In 20 years or so all devices and computer chips will be nanodevices. Several universities have started courses on nanotechnology.

Summary

1. Nanomaterials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.
2. Nanoscience can be defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.
3. Nanotechnology can be defined as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometre scale.
4. Two principal factors cause the properties of nanomaterials to differ significantly from other materials:
 - i) increased relative surface area and
 - ii) quantum effects
5. Interatomic spacing decreases with size.
6. The melting point decreases with size.
7. The ionization potential at small sizes are higher than that for the bulk and show marked fluctuations as a function of size.
8. Small particles are more magnetic than the bulk materials.
9. Even nonmagnetic solids are found to be magnetic.
10. In nanoparticles many of their mechanical properties such as hardness and elastic modulus, fracture toughness, scratch resistance, fatigue strength and hardness are modified depending on their size.
11. Nanomaterials can be synthesised in many methods.
 - i) Plasma arcing

ii) Chemical vapour deposition

iii) Sol-Gels

iv) Electro deposition and

v) Ball milling

12. Carbon nanotubes (CNTs) are extended tubes of rolled graphite sheets.

13. CNTs are mechanically very strong.

14. CNTs are flexible (about their axis), and can conduct electricity extremely well.

15. Nanomaterials find very wide applications.

i) Materials Technology

- Harder metals
- flexible/dense ceramics and insulators (super plastic)
- fillers in replacement of body parts and metals-car tyres
- unusual colour paints
- smart magnetic fluids
- film precursors
- magneto resistance spin valves
- sunscreens, self cleaning windows
- lipsticks
- improves full economy
- wear and scratch-resistant hard coatings
- lubricants
- high tensile strength and light weight-nanotube reinforced composites.

ii) Information Technology

- Information storage-high density data storage
- quantum electronic devices
- Photonic crystals
- Efficient display devices
- Electron spin operated computer chips.

iii) Biomedical

- Tagging of DNA and RNA chips with biosensitive nanoparticles
- Controlled drug delivery
- Bio-implant materials, artificial heart valves

iv) Energy storage

- Hydrogen storage devices
- improved fuel efficiency
- fabrication of fuel efficiency
- fabrication of ionic batteries
- magnetic refrigeration