Chapter 2

Concept of Nanotechnology

2.0. Basic concept of Nanotechnology

The nanomaterials are cornerstones of nanoscience and nanotechnology. The nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed.

![Evolution of science and technology and the future](image)

**Fig. 2.1: Evolution of science and technology and the future**

It is already having a significant commercial impact, which will assuredly increase in the future (Fig.2.1). Imagine being able to observe the motion of red blood cell as it moves through our vain, or being able to watch as a type of white blood cell...
(Called A “T-cell”) destroys an invading microbe by engulfing it. What would it be like to observe the vibration of molecules as the temperature rises in a pan of water? To observe sodium and chlorine atoms as they get close enough to actually transfer electrons and form a salt crystal? New scientific look developed and improved over the last few decades, make such observations increasingly feasible. These are example of the effort to view measure and even manipulate materials at the molecular or atomic scale- the major focus of nanotechnology [1].

Thenanotechnology is defined as study and use of structure between 1 nanometer and 100 naometers in size. Thenanotechnology is concerned with materials and systems whose structure component exhibit novel and significantly improved physical, chemical, and biological properties, phenomena and process because of their nanoscale size. The structural features in the range of $\sim 10^{-9}$ to $10^{-7}$ m i.e. 1 to 100 nanometer determine important changes as compared to the behavior of isolated molecules (1 nanometer) or of bulk materials. More generally nanotechnology can be defined as any technique able to work at a submicron scale [2]. It is an interdisciplinary science involving physics, chemistry, biology, engineering materials science, computer science etc.

The past few years, a little word with big potential has been rapidly putting itself into the world’s consciousness. That word is “Nano”. It has conjured up speculation about a seismic shift in almost every aspect of science and engineering with implications for ethics, economics, international relations, day to day life, and even humanity’s conception of its place in the universe. Alarmists see it as the next step in biological and chemical warfare or in extreme cases, as the opportunity for people to create the species that will ultimately replace humanity. Nano is big business. The National science foundation predicts that nano-related goods and services could be a
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$ trillion market by 2015, marking it not only one of the fastest-growing industries in history but also larger than the combined telecommunications and information technology industries at the beginning of the technology companies like HP, NEC and IBM all of whom have developed massive research capabilities for studying and developing nano devices. Despite this impressive lineup, well-recognized abbreviations are not the only organizations that can play. A host of start-ups and smaller concerns are jumping into the nano game as well. Specialty venture capital funds, trade shows, and periodicals are emerging to support them. There is even a stock index of public companies working on nano.

2.1. Nanomaterials

The nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. The nanomaterials are of interest because at this scale they possess unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Some nanomaterials occur naturally but for particular interest those are Engineered Nanomaterials (EN), which are designed for and being used in many commercial products and processes. They can be found in things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items and are used in medicine for purposes of diagnosis, imaging, and drug delivery. Engineered nanomaterials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. The nanomaterials have a much
greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical, and magnetic behaviors.

The nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints, and varnishes. The nanocoatings and nanocomposites are used in diverse consumer products, such as windows, sports equipment, bicycles, and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl rubber/nano-clay composites. Nanoscale titanium dioxide is used in cosmetics, sunscreen creams, and self-cleaning windows and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

2.2 Nanotechnology in Nature

There are lots of nano materials in nature. Nature processes such as sea spray and erosion can also create nanoparticles. Nature is expert in fabricating organic structures at the nano scale. Best and most known example of a self-cleaning surface is the so-called lotus effect. Lotus leaves in particular have the unique ability to hydrophobic particles. When water contacts these particles it does not wet the leaves. Instead it simply rolls off, taking with it any dirt in its path. The human body uses natural nanoscale materials such as proteins and other molecules to control the body’s many systems and processes. For hemoglobin which carries oxygen through the bloodstream is 5nm in diameter (4).
2.3. Significant impact: Nanoscience and Nanotechnology

The nanotechnology literally means any technology performed on a nanoscale that has applications in the real world. The nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions as well as the integration of the resulting nanostructures into larger systems. The nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, comparable to that of semiconductor technology, information technology or cellular and molecular biology. Science and technology research in nanotechnology promises breakthroughs in such areas as materials and manufacturing, medicine and healthcare, energy, biotechnology, information technology and national security. It is widely felt that nanotechnology will be the next industrial revolution.

Nanometer-scale features are mainly built up from their elemental constituents. Chemical synthesis – the spontaneous self-assembly of molecular clusters (molecular self-assembly) from simple reagents in solution or biological molecules (e.g., DNA) are used as building blocks for the production of three-dimensional nanostructures, including quantum dots (nanocrystals) of arbitrary diameter (about 10 to 105 atoms). A variety of vacuum deposition and nonequilibrium plasma chemistry techniques are used to produce layered nanocomposites and nanotubes. Atomically controlled structures are produced using molecular beam epitaxy and organo-metallic vapor phase epitaxy. Micro and nanosystem components are fabricated using top-down lithographic and nonlithographic fabrication techniques and range in size from micro to nanometers. Continued improvements in lithography for use in the production of nanocomponents have resulted in line widths as small as
10 nanometers in experimental prototypes. The nanotechnology field, in addition to the fabrication of nanosystems provides the impetus to development of experimental and computational tools. The micro and nanosystems include micro/nano electromechanical systems (MEMS/NEMS) (e.g., sensors, actuators, and miniaturized systems comprising sensing, processing and/or actuating functions), micromechatronics, optoelectronics, microfluidics and systems integration. These systems can sense, control and activate on the micro/nanoscale and function individually or in arrays to generate effects on the macroscale. Due to the enabling nature of these systems and because of the significant impact they can have on the commercial and defense applications, venture capitalists, industry, as well as the federal government have taken a special interest in nurturing growth in this field. Micro and nanosystems are likely to be the next logical step in the “silicon revolution.” [10-19]

Science and technology continue to move forward in making the fabrication of micro/nanodevices and systems possible for a variety of industrial, consumer, and biomedical applications. A range of MEMS devices have been produced, some of which are commercially used [12-20]. A variety of sensors are used in industrial, consumer, and biomedical applications. Various microstructures or micro components are used in micro instruments and other industrial applications such as micro mirror arrays. The largest “killer” industrial applications are accelerometers (about 85 million units in 2002) and digital micro mirror devices (about $ 400 million in sales in 2001). Integrated capacitive type, silicon accelerometers have been used in airbag deployment in automobiles since 1991 [21- 25]. Other major industrial applications include pressure sensors, inkjet printer heads, and optical switches. Silicon-based piezoresistive pressure sensors for manifold absolute
pressure sensing for engines were launched in 1991 by Nova-Sensor and their annual sales were about 25 million units in 2002. Annual sales of inkjet printer heads with microscale functional components were about 400 million units in 2002. Capacitive pressure sensors for tire pressure measurements were launched by Motorola. Other applications of MEMS devices include chemical sensors, gas sensors, infrared detectors, and focal plane arrays for earth observations, space science and missile defense applications, pico-satellites for space applications, and many hydraulic, pneumatic, and other consumer products. MEMS devices are also being pursued in magnetic storage systems [25], where they are being developed for super-compact and ultrahigh recording-density magnetic disk drives. Several integrated head/suspension micro devices have been fabricated for contact recording applications [28-19]. High-bandwidth, servo-controlled micro actuators have been fabricated for ultrahigh track-density applications which serve as the fine-position control element of a two-stage, coarse/fine servo system coupled with a conventional actuator [30–31]. Millimeter-sized wobble motors and actuators for tip based recording schemes have also been fabricated [32].

BIOMEMS are increasingly used in commercial and defense applications.[33–37]. Other BIOMEMS applications include minimal invasive surgery such as endoscopic surgery, laser angioplasty and microscopic surgery. Implantable artificial organs can also be produced Micro-instruments and micro-manipulators are used to move, position, probe, pattern and characterize nanoscale objects and nanoscale features. Miniaturized analytical equipment includes gas chromatography and mass spectrometry. Other instruments include micro-STM, where STM stands for scanning tunneling microscope. Examples of NEMS include nanocomponents, nanodevices, nanosystems and nanomaterials, such as micro cantilever with
integrated sharp nanotips for STM and atomic force microscopy (AFM), AFM array data storage, AFM tips for nanolithography, dip-pen nanolithography for printing molecules, biological (DNA) motors, molecular gears, molecularly thick films (e.g., in giant magneto-resistive or GMR heads and magnetic media), nanoparticles, (e.g., nanomagnetic particles in magnetic media), nanowires, carbon nanotubes, quantum wires (QWRs), quantum boxes (QB) and quantum transistors [38-42]. BIONEMS include nanobiosensors a microarray of silicon nanowires, roughly a few nm in size, to selectively bind and detect even a single biological molecule, such as DNA or protein, by using nanoelectronics to detect the slight electrical charge caused by such binding or a microarray of carbon nanotubes to electrically detect glucose, implantable drug-delivery devices e.g., micro/nanoparticles with drug molecules encapsulated in functionized shells for a site-specific targeting application and a silicon capsule with a nanoporous membrane filled with drugs for long term delivery, nanodevices for sequencing single molecules of DNA in the human genome project, cellular growth using carbon nanotubes for spinal cord repair, nanotubes for nanostructured materials for various applications, such as spinal fusion devices, organ growth and growth of artificial tissues using nanofibers. The nanoelectronics can be used to build computer memory, using individual molecules or nanotubes to store bits of information, as well as molecular switches, molecular or nanotube transistors, nanotube flat-panel displays, nanotube integrated circuits, fast logic gates, switches, nanoscopic lasers and nanotubes as electrodes in fuel cells.

2.4. Classification of Nanomaterials

The nanomaterials have extremely small size which having at least one dimension 100 nm or less. The nanomaterials can be nanoscale in one dimension (eg. surface films), twodimensions (eg. strands or fibers), or three dimensions (eg.
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Synthesis and Characterization of Nonlinear Optical Nanoparticles and their application ...

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Particles. They can exist in single, fused, aggregated, or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots, and fullerenes (Fig. 2.2). Nanomaterials have applications in the field of nanotechnology and display different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photo catalyst, carbon nano, silica). According to Siegel nanostructured materials are classified as zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

![Classification of Nanomaterials](image)

Fig. 2.2: *Classification of Nanomaterials* (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

The nanomaterials are materials which are characterized by an ultrafine grain size (< 50 nm) or by a dimensionality limited to 50 nm. The nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayers), two (ultrafine-grained over layers or buried layers), and three (nanophase materials consisting of equaled nanometer sized grains) as shown in the above figure 2.2.

There are a large number of techniques available to synthesize different types of films etc. Some of the already existing conventional techniques to synthesize
different types of materials are optimized to get novel nanomaterials and some new techniques are developed. Nanotechnology is an interdisciplinary subject. There are therefore various physical, chemical, biological and hybrid techniques available to synthesis nanomaterials. It can be seen in Fig. 2.3: Synthesis Techniques of Nanomaterial.

**Fig. 2.3: Synthesis Techniques of Nanomaterials**

### 2.5. Importance of Nanomaterials

These materials have created a high interest in recent years by virtue of their unusual below:

1) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.
2) Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

3) Nanosized metallic powders have been used for the production of gas tight materials, dense parts, and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

4) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states which give rise to special properties in addition to the superparamagnetism behavior. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

5) Nanostructured metal clusters and colloids of mono or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity, and lifetime in chemical transformations and electro catalysis (fuel cells).

6) Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NOx, CO, CO2, CH4, and aromatic
hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO$_2$) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

7) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

2.6. Synthesis Methods

The synthesis of nanomaterials can perform by physical methods and Chemical methods.

2.6.1. Physical methods

1. High Energy Ball Milling
2. Melt Mixing

2.6.2. Physical methods based on evaporation

1. Physical vapor deposition with consolidation
2. Ionized cluster beam deposition
3. Laser vaporization
4. Laser pyrolysis

2.6.3. Sputter Deposition

1. DC sputtering
2. RF sputtering
3. Magnetron sputtering
4. ECR plasma deposition
2.6.4. Chemical Vapor deposition

1. Electric arc deposition
2. Ion beam techniques
3. Molecular beam epitaxy

2.7. Chemical methods

Advantages of Chemical Synthesis

1. Simple techniques
2. Inexpensive, less instrumentation compared to any physical methods
3. Low temperature (<350 degree C) synthesis
4. Doping of foreign atoms possible during synthesis
5. Large quantities of the materials can be contained
6. Variety of sizes and shapes are possible
7. Materials are obtained in the form of liquid but can be converted into dry powder of thin films quite easily
8. Self assembly or patterning is possible.

In some cases nanomaterials are obtained as colloidal particles in solutions which can filtered and dried to obtained powder. In some methods we can obtain thin films or nanoporous materials by electrode position, etching etc., as in many cases nanoparticles synthesized by chemical method form colloids.

2.7.1. Colloids and Colloids in solution

The colloids are known since very long time. A class of materials in which two or more phases (Solid, liquid or gas) of same or different materials co-exist with at least one dimension less than a micrometer is known as colloids. Colloids may be particles plates or fibers. Different types of colloids, spherical, lamellar, fibers etc.
Nanomaterials are a subclass of colloids in which one of the dimensions of colloids is in about 1 to 100 nanometer range. There are several examples around us having different combinations of phases in the form of colloids like liquid in gas (fog), liquid in liquid (fat droplets in milk), solid in liquid (tooth paste), solid in solid (tinted glass), gas in liquid (foam) etc. There can be multiple exiting colloids like water and oil bubbles in porous mineral rocks. Organic and inorganic materials can be dispersed in into each other to form colloids. Several examples exist even of bio-colloids. Blood and bones are good examples of bio-colloids. Blood has corpuscles dispersed in serum and bone has colloids of calcium phosphate embedded in collagen. Colloids may even form networks. For examples aero gel is network of colloids particles, pores of which are filled with air.

### 2.7.2. Interactions of Colloids and Medium

The colloids are particles with large surface to volume ratio. Correspondingly there are a large number of atoms/molecules on the surface of a colloidal particle, which do not have as many neighbors as those for an atom/ molecule inside the interior.

![Brownian motion of colloidal particles](image)
Therefore atoms on the surface are in a highly reactive state which easily interacts to form bigger particles are tend to coagulate. It is thus necessary to understand the stability of collides i.e. how collides dispersed in a medium can remain as separated particles.

In general there are number of interactions involved. For the sake of understanding these interactions we consider the inorganic spherical colloids of equal size, dispersed in a liquid medium. When fine particles are dispersed in a liquid medium it is known that they undergo what is known as Brownian motion. If we are able to tag a particle in the liquid as depicted Fig 2.4

It would appear as if it is making a random motion. All other particles also execute random motion, hitting each other and changing their direction of motion in the liquid. Distance travelled between successive collisions is random too. An average distance travelled by a colloidal particle can be found as

$$\Delta R^2 = \left( \frac{kT}{3\pi n r} \right) \Delta t \quad (2.1)$$

Where $\Delta R^2$ - distance travelled by a particle from its original position in time $\Delta t$, $k$ – Boltzamn constant, $T$- Temperature of liquid, $r$- particle radius and $n$ – Viscosity of the liquid.

Interactions of such constantly and randomly moving particles with each other and with liquid in general would be quite complex. Consider for example the Vander Waal’s interaction between two atoms or molecules. There are two parts in the interaction viz. attractive and repulsive parts given by equation 2.2 irrespective of whether there exist permanent dipoles or not. The interaction is given as

$$dG_1 = \left( \frac{A}{R^{12}} \right) - \left( \frac{B}{R^6} \right) \quad (2.2)$$

Where $dG_1$ interaction energy, $A$, $B$ constants and $R$ distance between two particles. Here the first term is repulsive interaction i.e. born repulsive
interaction effective only at short and second term represents long range attractive interaction i.e. Van der Waals attraction. \( dG_1 \) is the interaction energy, A and B are constants and R is distance between electron clouds in each atom and attractive part is due to interaction between fluctuating or permanent dipoles of atoms molecules.

![Fig. 2.5: Van der Walls interaction](image)

2.7.3. Colloids in Vacuum

Lennard –Jones equation 2.2 is sufficient to describe an interaction between two atoms or molecules. When we consider colloids with large number of atoms in them, we need to take into account all the atoms and their interactions with each other. This is quite a complex situation as shown in Fig. 2.6
Interaction even between two spherical particles of same material and same size is complex due to presence of large number of atoms in each particle.

To describe the interaction between colloidal particles, Deraguin, Landau, Verwey and Overbeck proposed a theory known as DLVO theory. In order to reduce the complexity of the problem, they assumed two interacting spherical particles of equal size. Let the radius of each particle be \( r \) and let two particles be separated by a distance \( R \).

### 2.7.4. Colloids in a Medium

So far we considered the colloids just in vacuum. Consider now a situation in which inorganic spherical colloids are immersed in a liquid. The attractive interactions between the colloids get modified through the change of Hamaker constant as \( A_H \), which can be written now as

\[
A_H = \left( \sqrt{A_{1V}} - \sqrt{A_{2V}} \right)^2
\]

where \( A_{1V} \) is the Hamaker constant for particle of inorganic solid under consideration in vacuum and \( A_{2V} \) is Hamaker constant of colloid of medium in vacuum. It can be seen from above equation of colloid particle. Hence the attractive force between colloid particles will in general reduce.

### 2.7.5. Stearic Repulsion

The stability of colloids can be increased by creating what is known as stearic hindrance or repulsion. By adsorbing some layer of a different material on colloidal
particles e.g. polymer or organic molecules on inorganic colloidal particles, it is possible to reduce the attractive forces between them. With addition of adsorbed layers, the effective size of the particles changes, this helps them to stay at a longer distance by reducing the attractive interaction. However in case where the coating material is similar in properties to that of the solvent the effect of coating would be negligible. By anchoring long chain molecules on the particles, it is possible to keep them apart with negligible interaction. This idea is the basis of capped nanoparticles. Thus the colloids interact with each other dynamically and are affected by Van der Waals forces, colloids-colloid interaction medicated through dispersing medium, electric double layer and stearic interactions. All the interactions may not be set in for every case. In general contributions of these various attractive and repulsive interactions, also dictated by temperature, concentration of colloids and dispersing medium are additive and can written as follows.

\[
\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 + \Delta G_5 \quad \text{-------------------(2.4)}
\]

Where \( \Delta G_1 \) is attractive and repulsive, \( \Delta G_2 \) is colloid-colloid attractive, and \( \Delta G_3 \) is electrostatic repulsion, \( \Delta G_4 \) is stearic repulsion and any other.

2.7.6. Synthesis of Colloids

The colloids are thus phase separated submicrometre particles in the form of spherical particles or particles of various shapes and sizes like rods, tubes, plates etc. They are the particles suspended in some host matrix. Metal, alloy, semiconductor, and insulator particles of different shape and sized can be synthesized in aqueous or no aqueous media. Colloidal particles in liquids are stabilized as discussed above as by Coulomb repulsion, which arises due to similar charges they may have acquired on their surfaces. In some cases surface passive molecules may be used which provide sufficient stearic hindrance inhibiting coalescence or aggregation.
Nanomaterials are a special class of colloids particles which are few hundreds of nanometer or smaller in size. Synthesis of colloids is very old method. Marking nanoparticles using colloids route goes back to 19th century when Faraday synthesized gold nanoparticles by wet chemistry route. The particles are so stable that even today the colloidal solution made by him can be seen in British Museum in London. Here we shall discuss some commonly used synthesis methods of metal semiconductor and insulator nanoparticles with some examples. Chemical reactions in which colloidal particles are obtained are carried out in some glass reactor of suitable size. Glass reactor usually has a provision to introduce some precursors, gases, as well as measure temperature, $P_{\text{H}}$ etc during the reaction. It is usually possible to remove the products at suitable time intervals reaction is usually carried out under inert atmosphere like argon or nitrogen gas so as to avoid any uncontrolled oxidation of the products. There is also a provision made to stir the reactants during the reaction by using Teflon coated magnetic needle. Fig.2.7: A typical chemical reactor to synthesize nanoparticles.

Fig.2.7: A typical chemical reactor to synthesize nanoparticles.
2.8. Growth of Nanoparticles

A multi-step process are involving the nucleation and formation of metal seeds, growth of seeds to form nanoparticles and control of the growth using a capping agent and/or quenching. Monitoring batch synthesis requires ultrafast spectroscopic and imaging techniques. Although chemical synthesis of nanoparticles may appear as a complex process, by understanding how nucleation and growth of particles takes place, it is possible to control the various steps and try to achieve monodispered nanoparticles. This can be done with help of LaMer diagram shown in Fig 2.8

As we keep on increasing the concentration of the reactants in the solution, at certain concentration, say \( C_0 \) the formation of nuclei begins.

Fig. 2.8: La Mer Diagram Regions I, II and III are for saturation, nucleation, and growth respectively.

There is no precipitate at this concentration. Further increase in concentration increases nuclei formation up to concentration \( C_N \) and \( C_S \). Concentration \( C_N \) denotes the maximum rate of nuclei formation. When nuclei formation reduces, again \( C_0 \) the minimum contraction for nucleation is reached. No new nuclei can be formed and...
crystal growth reduces the concentration. At this concentration $C_S$, equilibrium is obtained. If new nuclei are formed during the growth of particles, particles with large size distribution are obtained. Therefore it is very important that concentration of solute and its diffusion to dissolve specimen be adjusted properly in order that no fresh nuclei are formed once the concentration has reached $C_N$. Particles can grow at the expense of smaller particles. Larger particles are more stable and grow at the expense of smaller particles. This growth mode is known as Ostwald ripening (Fig2.9). The driving force for larger particle is the reduction in surface free energy. Experimentally it is found that there is sometimes aggregation of particles. Aggregation also reduces the energy of the system. Thus Ostwald ripening and aggregation are competing processes and wither of them is responsible to reduce the surface free energy.

Fig.2.9: Growth and aggregation of colloids.
2.9. Synthesis of Semiconductor nanoparticles by colloidal route

The compound semiconductor nanoparticles can be synthesized by wet chemical route using appropriate salts. Here we shall discuss some methods to obtain semiconductor nanoparticles. Sulfide semiconductors like CdS and ZnS can be synthesized easily by co-precipitation. For example to obtain ZnS nanoparticles any zinc salt like zinc sulphate (ZnSO₄), zinc chloride (ZnCl₂), Zinc nitrate(ZnNO₃) or zinc acetate (Zn(CH₃COO)₂) can be dissolved in aqueous liquid and Na₂S is added to the solution.

Following simple reaction

\[ \text{ZnCl}_2 + \text{Na}_2\text{S} \rightarrow \text{ZnS} + 2\text{NaCl} \]

Results to give particles of ZnS.

To obtain zinc oxide particles one can use following reactions.

\[ \text{ZnCl}_2 + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2\text{NaCl} \]

\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \]

However all these nanoparticles need to be surface passivated as colloids formed in liquids have a tendency to coagulate or ripen due to attractive forces existing between them. The electrostatic and other repulsive forces may not be sufficient to keep them apart. However as it was also discussed earlier, stearic hindrance can be created by appropriately coating the particles to keep them a part. This is often known as chemical capping and has become a widely used method in the synthesis of nanoparticles. Advantage with this chemical route is that, one can get stable particle of variety of materials not only in the solution, but even after drying off the liquid. One can even make thin films of the capped particles by spin coating or dip coating techniques. The coating however has to stable and non-interactive with the particle itself except at the surface. Coatings may be a part of post treatment or a part
of the synthesis reaction to obtain nanoparticles. If it is a part of the synthesis reaction the concentration of capping molecules can be used in two ways to control the size as well as to protect the particles from coagulation.

Chemical capping can be carried out as high or low temperature depending on the reactants. In high temperature reactions, cold organometallic reactants are injected in some solvent like Triocylphosphineoxide (TYOPO) held at temperature >300 °C. For example when Dimehtyl Cadmium and Se powder were injected in TOPO, CdSe nanoparticles capped with PO₄ groups were obtained. There are however other chemical also which can be used as precursors to obtain high quality particles. It is possible to remove the particles of different sizes. The particles with high quality and as narrow size distribution as < 5% have been achieved by this method. Although this is a very good route of synthesizing the nanoparticles, most of the organo-metallic compounds are prohibitively expensive, besides they are also toxic and difficult to handle. Such synthesis should therefore be carried out only under the expert guidance.

2.10. **Chemical capping of Nanoparticles**

A variety of molecules can be used to cape the nanoparticlees. For example capping of metal sulphide nanoparticles by Thiophenol and Mercaptoethanol. In another variation of chemical capping method, reactions of inexpensive and nontoxic chemicals like metal chlorides, nitrates, acetates, inorganic salts are performed at moderate temperatures like 80 to 120. In some cases, it is even possible to synthesize nanoparticles at room temperature. However the initial size distribution can be quite broad. The size distribution can be narrowed down by a method known as size selective precipitation. For this one needs to use a proper pair are Pyridine-Hexane, Chloroform-Methanol, Dimethyl Sulphoxide – Diethyl Ether etc. The
nucleation is then added so that flocculation occurs. Supernatant and flocclulate are separated by centrifugation. Precipitate has larger particles and can be separated; bigger particles therefore pair of solvent-nonsolvent liquids. Some of the solvent nonsolvent pairs are Pyridine – Hexane, Chloroform - Methanol, Dimethyl Sulphoxide - Diethyl Ether etc. The nanoparticles are dispersed in a solvent so as to get an optically clear solution. Nonsolvent solution is then added so that flocculation occurs. Supernatant and flocculate are separated by centrifugation. Precipitate has larger particles and can be separated. Bigger particles there are first separated from smaller particles and redispersed in the solvent solution. The process is continued until no change in the size distribution is observed by repeating the procedure. Advantage of chemical capping method is mainly that nanoparticles are chemically stable over a long time. The thermal stability depends upon the capping molecules used. In most cases, where organic molecules are used particles are stable up to about 200-250 and may find considerable range of applications. Another advantage with both the methods is that while synthesizing the nanoparticles they can be doped with some metal ions so as to get fluorescent particles at relatively low temperature. A wide range of semiconductor nanoparticles can be synthesized by this way and are found to be useful in any applications.

A wide range of metal oxides and other insulators with the wide band gap can be synthesized by chemical precipitation method along with suitable surface passivant, if necessary. Some of the oxides and insulators may be stable and may not agglomerate or coalesce easily.
2.11. Methods for creating nanostructures

There are many different ways of creating nanostructures of course macromolecules or nanoparticles or buckyballs or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (sometimes also called bio-mimetic processes). Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application.

2.11.1. Mechanical grinding

The mechanical attrition is a typical example of ‘top down’ method of synthesis of nanomaterials, where the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials. The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications. Similarly, the serious problems that are usually cited are:

1. Contamination from milling media and/or atmosphere and
2. To consolidate the powder product without coarsening the nanocrystalline microstructure. In fact, the contamination problem is often given as a reason to dismiss the method, at least for some materials. Here we will review the mechanisms presently believed responsible for formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders, and mechanical crystallisation of amorphous materials. The two important
problems of contamination and powder consolidation will be briefly considered. Mechanical milling is typically achieved using high energy shaker, planetary ball, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size, and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere.

Then nanoparticles are produced by the shear action during grinding. Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles be handled in an appropriate vacuum system or glove box. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a

Fig.2.10: Schematic representation of the principle of mechanical milling
homogeneous alloy can be formed. Based on the energy of the milling process and thermodynamic properties of the constituents the alloy can be rendered amorphous by this processing.

2.11.2. Wet Chemical Synthesis of Nanomaterials

The wet chemical synthesis of nanomaterials can be classified into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials. For example, the synthesis of porous silicon by electrochemical etching.

2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

2.11.2.1. Sol-gel process

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive legends. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcinations of the gel produce the oxide. Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as Si (OEt)₄ Tetraethyl Orthosilicate (TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides

\[ \text{M(OR)}_2 \rightarrow \text{MOR} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{ROH} \text{ (hydrolysis)} \]
MOH + ROM → M-O-M + ROH (condensation)

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.

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

3. Aging of the gel (Synthesis) during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of...
the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with synthesis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps:

i. the constant rate period,

ii. the critical point,

iii. the falling rate period,

iv. the second falling rate period.

If isolated by thermal evaporation, the resulting monolith is termed a xerogel. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an aerogel.

4. Dehydration, during which surface-bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 8000°C.

5. Densification and decomposition of the gels at high temperatures (T>8000°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 the Fig.2.12. The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics. The major difficulties to overcome in
developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process. Also production rates of nano powders are very low by this process. The main advantage is one can get monosized nano particles by any bottom up approach.

2.12. Gas phase synthesis of nanomaterials

The gas-phase synthesis methods are increasing interest because they allow an elegant way to control process parameters in order to be able to produce size, shape and chemical composition controlled nanostructures. Before we discuss a few selected pathways for gas-phase formation of nanomaterials, some general aspects of gas-phase synthesis needs to be discussed. In conventional chemical vapor deposition (CVD) synthesis, gaseous products either are allowed to react homogeneously or heterogeneously depending on a particular application.

1. In homogeneous CVD, particles form in the gas phase and diffuse towards a cold surface due to thermophoretic forces and can either be scrapped off from the cold surface to give nano-powders or deposited onto a substrate to yield what is called ‘particulate films’.

2. In heterogeneous CVD the solid is formed on the substrate surface, which catalyses the reaction and a dense film is formed. In order to form nanomaterials several modified CVD methods have been developed. Gas phase processes have inherent advantages, some of which are noted here:

- An excellent control of size, shape, crystallinity and chemical composition
Highly pure materials can be obtained

Multicomponent systems are relatively easy to form

Easy control of the reaction mechanisms

Most of the synthesis routes are based on the production of small clusters that can aggregate to form nanoparticles (condensation). Condensation occurs only when the vapor is supersaturated and in these processes homogeneous nucleation in the gas phase is utilized to form particles. This can be achieved both by physical and chemical methods.

2.12.1. Furnace

The simplest fashion to produce nanoparticles is by heating the desired material in a heatresistant crucible containing the desired material. This method is appropriate only for materials that have a high vapor pressure at the heated temperatures that can be as high as 2000°C. Energy is normally introduced into the precursor by arc heating, electron beam heating or Joule heating. The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound).

To carry out reactive synthesis, materials with very low vapor pressure have to be fed into the furnace in the form of a suitable precursor such as organo metallic, which decompose in the furnace to produce a condensable material. The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. In case a compound is being synthesized, these precursors react in the gas phase and form a compound with the material that is separately injected in the reaction chamber. The clusters would continue to grow if they remain in the supersaturated region. To control their size, they need to be rapidly removed from the supersaturated
environment by a carrier gas. The cluster size and its distribution are controlled by only three parameters:

1) the rate of evaporation (energy input),

2) the rate of condensation (energy removal) and

3) the rate of gas flow (cluster removal).

Because of its inherent simplicity, it is possible to scale up this process from laboratory (mg/day) to industrial scales (tons/day).

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**Fig. 2.13: Schematic representation of gas phase process of synthesis of single phase**

2.12.2. Gas Condensation Processing (GPC)

This technique includes, a metallic or inorganic material, e.g. a suboxide, is vaporized using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr). Cluster 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 the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar or Kr, and on the evaporation rate/vapor pressure of the evaporating material. With increasing gas pressure, vapor pressure and mass of the inert gas used the average particle size of the nanoparticles increases.

![Figure 2.14: Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media](image)

Lognormal size distributions have been found experimentally and have been explained theoretically by the growth mechanisms of the particles. Even in more complex processes such as the low pressure combustion flame synthesis where a number of chemical reactions are involved the size distributions are determined to be lognormal. Originally, a rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no
agglomeration. Subsequently, the nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate. In addition to this cold finger device several techniques known from aerosol science have now been implemented for the use in gas condensation systems such as corona discharge, etc. These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders. However, these methods can only be used in a system designed for gas flow, i.e. a dynamic vacuum is generated by means of both continuous pumping and gas inlet via mass flow controller. A major advantage over convectional gas flow is the improved control of the particle sizes. It has been found that the particle size distributions in gas flow systems, which are also lognormal, are shifted towards smaller average values with an appreciable reduction of the standard deviation of the distribution. Depending on the flow rate of the He-gas, particle sizes are reduced by 80% and standard deviations by 18%. The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo). If metals with high melting points or metals which react with the crucibles, are to be prepared, sputtering, i.e. for W and Zr, or laser or electron beam evaporation has to be used. Synthesis of alloys or intermetallic compounds by thermal evaporation can only be done in the exceptional cases that the vapor pressures of the elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed. Composite materials such as Cu/Bi or W/Ga have been synthesized by simultaneous evaporation from two separate crucibles onto a rotating collection device. It has been found that excellent intermixing on the scale of the particle size can be obtained. However, control of the composition of the elements has been difficult and reproducibility is poor. Nanocrystalline oxide powders are formed by controlled post
oxidation of primary nanoparticles of a pure metal (e.g. Ti to TiO2) or a sub oxide (e.g. ZrO to ZrO2). Although the gas condensation method including the variations have been widely employed to prepare a variety of metallic and ceramic materials, quantities have so far been limited to a laboratory scale. The quantities of metals are below 1 g/day, while quantities of oxides can be as high as 20 g/day for simple oxides such as CeO2 or ZrO2. These quantities are sufficient for materials testing but not for industrial production. However, it should be mentioned that the scale-up of the gas condensation method for industrial production of nanocrystalline oxides by a company called nanophase technologies has been successful.

2.12.3. Chemical Vapor Condensation (CVC)

The evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapor Condensation or the CVC process as shown schematically in Figure 2.15. Depending on the processing parameters nucleation of nanoparticles is observed during chemical vapor deposition (CVD) of thin films and poses a major problem in obtaining good film qualities. The original idea of the novel CVC process which is schematically shown below where, it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained. Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form a metal organic precursor is introduced
into the hot zone of the reactor using mass flow controller. Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesized. Additionally, more complex oxides such as BaTiO₃ or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature. The extension to production of nanoparticles requires the determination of a modified parameter field in order to promote particle formation instead of film formation. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and Coated nanoparticles, i.e., n-ZrO₂ coated with n-Al₂O₃ 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 a second stage of the reactor. Because CVC processing is continuous, the production capabilities are much larger than in GPC processing.

Fig. 2.15: A schematic of a typical CVC reactor
Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

2.13. Properties of Nanomaterials

The nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials. Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelectronics. High density information storage using quantum dot devices
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is also a fast developing area. Reduced imperfections are also important factor in determination of the properties of the nanomaterials. Nanosturctures and Nanomaterials favors of a self purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known. Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photo catalysis, photo electrochemistry, and biomedicine. The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise,

Fig.2.16: Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles.
shape can have dramatic influence on optical properties of metal nanostructures. With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres in fig. 2.16. However, when anisotropy is added to the nanoparticle, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.

2.13.1. Electrical properties

The electrical Properties of Nanoparticles discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of nanocomposites. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps. In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface of the mercury droplet and contribute to the electrical current transport.
2.13.2. Mechanical properties

“Mechanical Properties of Nanoparticles” deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, super plasticity, filled polymer composites, particle-filled polymers, and polymer-based nanocomposites filled with platelets, carbon nanotube-based composites. The discussion of mechanical properties of nanomaterials is in some extent only of quite basic interest the reason being that it is problematic to produce macroscopic bodies with a high density and a grain size in the range of less than 100 nm. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance. These materials are polymers which contain nanoparticles or nanotubes to improve their mechanical behaviors and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter are generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly defined grain sizes and porosities. Therefore, model calculations and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes respectively, leads to
significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a nanoparticulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles, or platelets and on the degree of agglomeration. In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer are the properties obtained. Although, potentially, the best composites are those filled with nanofibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture. Among the most exciting nanocomposites are the polymer-ceramic nanocomposites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

2.13.3. Magnetic properties

Bulk gold and Pt are non-magnetic, but at the nano size they are magnetic. Surface atoms are not only different to bulk atoms but they can also be modified by interaction with other chemical species, i.e. by capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be
possible that non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in nano range. One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects.

However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior. Surface and the core of Au nanoparticles with 2 nm in diameter show ferromagnetic and paramagnetic character, respectively. The large spin-orbit coupling of these noble metals can yield to a large anisotropy and therefore exhibit high ordering temperatures. More surprisingly, permanent magnetism was observed up to room temperature for thiol-capped Au nanoparticles. For nanoparticles with sizes below 2 nm the localized carriers are in the 5d band. Bulk Au has an extremely low density of states and becomes diamagnetic, as is also the case for bare Au nanoparticles. This observation suggested that modification of the d band structure by chemical bonding can induce ferromagnetic like character in metallic clusters.

2.14. Selected applications of nanomaterials

The nanomaterials having wide range of applications in the field of electronics, fuel cells, batteries, agriculture, food industry, and medicines, etc... It is evident that nanomaterials split their conventional counterparts because of their superior chemical, physical, and mechanical properties and of their exceptional formability.

2.14.1. Fuel cells

A fuel cell is an electrochemical energy conversion device that converts the chemical energy from fuel (on the anode side) and oxidant (on the cathode side)
directly into electricity. The heart of fuel cell is the electrodes. The performance of a fuel cell electrode can be optimized in two ways; by improving the physical structure and by using more active electro catalyst. A good structure of electrode must provide sample surface area, provide maximum contact of catalyst, reactant gas, and electrolyte, facilitate gas transport, and provide good electronic conductance. In this fashion the structure should be able to minimize losses.

2.14.2. Carbon nanotubes - Microbial fuel cell

Microbial fuel cell is a device in which bacteria consume water-soluble waste such as sugar, starch, and alcohols and produces electricity plus clean water. This technology will make it possible to generate electricity while treating domestic or industrial wastewater. Microbial fuel cell can turn different carbohydrates and complex substrates present in wastewaters into a source of electricity. The efficient electron transfer between the microorganism and the anode of the microbial fuel cell plays a major role in the performance of the fuel cell. The organic molecules present in the wastewater posses a certain amount of chemical energy, which is released when converting them to simpler molecules like CO\(_2\). The microbial fuel cell is thus a device that converts the chemical energy present in water-soluble waste into electrical energy by the catalytic reaction of microorganisms. Carbon nanotubes (CNTs) have chemical stability, good mechanical properties, and high surface area, making them ideal for the design of sensors and provide very high surface area due to its structural network. Since carbon nanotubes are also suitable supports for cell growth, electrodes of microbial fuel cells can be built using of CNT. Due to three-dimensional architectures and enlarged electrode surface area for the entry of growth medium, bacteria can grow and proliferate and get immobilized. Multi walled CNT scaffolds could offer self-supported structure with large surface area through which
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hydrogen producing bacteria (e.g., E. coli) can eventually grow and proliferate. Also CNTs and MWCNTs have been reported to be biocompatible for different eukaryotic cells. The efficient proliferation of hydrogen producing bacteria throughout an electron conducting scaffold of CNT can form the basis for the potential application as electrodes in MFCs leading to efficient performance.

2.14.3. Catalysis

Higher surface area available with the nanomaterial counterparts, nano-catalysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that it is utilized as a solid-fuel in rocket propulsion, whereas the bulk aluminum is widely used in utensils. Nano-aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activity, and can very well be utilized in manipulating the rate-controlling step.

2.14.4. Phosphors for High-Definition TV

The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render high definition televisions (HDTVs) and personal computers affordable to be purchase.
2.14.5. Next-Generation Computer Chips

The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. By achieving a significant reduction in their size, the microprocessors, which contain these components, can run much faster, thereby enabling computations at far greater speeds. However, there are several technological impediments to these advancements, including lack of the ultrafine precursors to manufacture these components; poor dissipation of tremendous amount of heat generated by these microprocessors due to faster speeds; short mean time to failures (poor reliability), etc. Nanomaterials help the industry break these barriers down by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity, and longer-lasting, durable interconnections (connections between various components in the microprocessors).

Example: Nanowires for junction less transistors

Transistors are made so tiny to reduce the size of sub assemblies of electronic systems and make smaller and smaller devices, but it is difficult to create high-quality junctions. In particular, it is very difficult to change the doping concentration of a material over distances shorter than about 10 nm. Researchers have succeeded in making the junction less transistor having nearly ideal electrical properties. It could potentially operate faster and use less power than any conventional transistor on the market today. The device consists of a silicon nanowire in which current flow is perfectly controlled by a silicon gate that is separated from the nanowire by a thin insulating layer. The entire silicon nanowire is heavily n-doped, making it an excellent conductor. However, the gate is p-doped and its presence has the effect of depleting the number of electrons in the region of the nanowire under the gate. The
device also has near-ideal electrical properties and behaves like the most perfect of transistors without suffering from current leakage like conventional devices and operates faster and using less energy.

![Fig. 2.18: Silicon nanowires in junction less transistors](image)

2.14.6. Elimination of Pollutants

The nanomaterials possess extremely large grain boundaries relative to their grain as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

2.14.7. Sun-screen lotion

Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nanoTiO$_2$ provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO$_2$) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV
radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

2.14.8. Sensors

The sensors rely on the highly active surface to initiate a response with minute change in the concentration of the species to be detected. Engineered monolayers (few Angstroms thick) on the sensor surface are exposed to the environment and the peculiar functionality (such as change in potential as the CO/anthrax level is detected) is utilized in sensing.

2.15. Disadvantages of Nanomaterials

1) Instability of the particles - Retaining the active metal nanoparticles is highly challenging, as the kinetics associated with nanomaterials is rapid. In order to retain nanosize of particles they are encapsulated in some other matrix. Nanomaterials are thermodynamically metastable and lie in the region of high-energy local minima. Hence they are prone to attack and undergo transformation. These include poor corrosion resistance, high solubility, and phase change of nanomaterials. This leads to deterioration in properties and retaining the structure becomes challenging.

2) Fine metal particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

3) Impurity - Because nanoparticles are highly reactive they inherently interact with impurities as well. In addition, encapsulation of nanoparticles becomes necessary when they are synthesized in a solution (chemical route). The stabilization of nanoparticles occurs because of a non-reactive species engulfing the reactive nano-entities. Thereby these secondary impurities become a part of the
synthesized nanoparticles and synthesis of pure nanoparticles becomes highly
difficult. Formation of oxides, nitrides etc. can also get aggravated from the
impure environment/ surrounding while synthesizing nanoparticles. Hence
retaining high purity in nanoparticles can become a challenge hard to overcome.

4) Biologically harmful - Nanomaterials are usually considered harmful as they
become transparent to the cell-dermis. Toxicity of nanomaterials also appears
predominant owing to their high surface area and enhanced surface activity.
Nanomaterials have shown to cause irritation and have indicated to be
carcinogenic. If inhaled their low mass entraps them inside lungs and in no way
they can be expelled out of body. Their interaction with liver/blood could also
prove to be harmful (though this aspect is still being debated on).

5) Difficulty in synthesis, isolation, and application: It is extremely hard to retain
the size of nanoparticles once they are synthesized in a solution. Hence, the
nanomaterials have to be encapsulated in a bigger and stable molecule/material.
Hence free nanoparticles are hard to be utilized in isolation, and they have to be
interacted for intended use via secondary means of exposure. Grain growth is
inherently present in nanomaterials during their processing. The finer grains tend
to merge and become bigger and stable grains at high temperatures and times of
processing.

6) Recycling and disposal - There are no hard-and-fast safe disposal policies
evolved for nanomaterials. Issues of their toxicity are still under question, and
results of exposure experiments are not available. Hence the uncertainty
associated with affects of nanomaterials is yet to be assessed in order to develop
their disposal policies.
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