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MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI- 627 012

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

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M. Sc. Chemistry Course material

Elective - I

Nanomaterials and Nanotechnology

Course Code SCHE11

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Semester - I

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NANOMATERIALS AND NANO TECHNOLOGY

UNIT-I: Introduction of nanomaterials and nanotechnologies, Introduction-role of size, classification-0D, 1D, 2D, 3D. Synthesis-Bottom –Up, Top–Down, consolidation of Nano powders. Features of nanostructures, Background of nanostructures. Techniques of synthesis of nanomaterials, Tools of the nanoscience. Applications of nanomaterials and technologies.

UNIT-II: Bonding and structure of the nanomaterials, Predicting the Type of Bonding in a Substance crystal structure. Metallic nanoparticles, Surfaces of Materials, Nanoparticle Size and Properties. Synthesis- Physical and chemical methods - inert gas condensation, arc discharge, laser ablation, sol-gel, solvothermal and hydrothermal-CVD-types, metallo organic, plasma enhanced, and low-pressure CVD. Microwave assisted and electrochemical synthesis.

UNIT-III: Mechanical properties of materials, theories relevant to mechanical properties. Techniques to study mechanical properties of nanomaterials, adhesion and friction, thermal properties of nanomaterials Nanoparticles: gold and silver, metal oxides: silica, iron oxide and alumina - synthesis and properties.

UNIT-IV: Electrical properties, Conductivity and Resistivity, Classification of Materials based on Conductivity, magnetic properties, electronic properties of materials. Classification of magnetic phenomena. Semiconductor materials – classification-Ge, Si, GaAs, SiC, GaN, GaP, CdS,PbS. Identification of materials as p and n –type semiconductor-Hall effect - quantum and anomalous, Hall voltage - interpretation of charge carrier density. Applications of semiconductors: p-n junction as transistors and rectifiers, photovoltaic and photogalvanic cell.

UNIT-V: Nano thin films, nanocomposites. Application of nanoparticles in different fields. Core-shell nanoparticles - types, synthesis, and properties. Nanocomposites - metal-, ceramic- and polymer-matrix composites-applications. Characterization – SEM, TEM and AFM - principle, instrumentation and applications.

Recommended Text

1. S.Mohan and V. Arjunan, Principles of Materials Science, MJP Publishers, 2016.
2. Arumugam, Materials Science, Anuradha Publications,2007.
3. Giacavazzo et. al., Fundamentals of Crystallography, International Union of Crystallography. Oxford Science Publications, 2010
4. Woolfson, An Introduction to Crystallography, Cambridge University Press, 2012.
5. James F. Shackelford and Madanapalli K. Muralidhara, Introduction to Materials Science for Engineers. 6th ed., PEARSON Press, 2007.

Unit 1

Introduction to nanomaterials

A key driver in the development of new and improved materials, from the steels of the 19th century to the advanced materials of today, has been the ability to control their structure at smaller and smaller scales. The overall properties of materials as diverse as paints and silicon chips are determined by their structure at the micro- and nanoscales. As our understanding of materials at the nanoscale and our ability to control their structure improves, there will be great potential to create a range of materials with novel characteristics, functions and applications. Although a broad definition, we categorise nanomaterials as those which have structured components with at least one dimension less than 100nm.

Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are layers, such as a thin films or surface coatings. Some of the features on computer chips come in this category. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. 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. Some of these materials have been available for some time; others are genuinely new. The aim of this chapter is to give an overview of the properties, and the significant foreseeable applications of some key nanomaterials. 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 properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, 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 unit mass compared with larger particles. 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 tandem with surface-area effects, quantum effects can begin to dominate the properties of matter as size is reduced to the nanoscale. 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.

Materials that exploit these effects include quantum dots, and quantum well lasers for optoelectronics. For other materials such as crystalline solids, as the size of their structural components decreases, there is much greater interface area within the material; this can greatly affect both mechanical and electrical properties. For example, 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 can be made very small, or even nanoscale in size, the interface area within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel. Understanding surfaces and interfaces is a key challenge for those working on nanomaterials, and one where new imaging and analysis instruments are vital.

Nanomaterials are not simply another step in the miniaturization of materials. They often require very different production approaches., classified as ‘top-down’ and ‘bottom-up’. Although many nanomaterials are currently at the laboratory stage of manufacture, a few of them are being commercialised.

Nanoscience

Below we outline some examples of nanomaterials and the range of nanoscience that is aimed at understanding their properties. As will be seen, the behaviour of some nanomaterials is well understood, whereas others present greater challenges. a) Nanoscale in one dimension Thin films, layers and surfaces

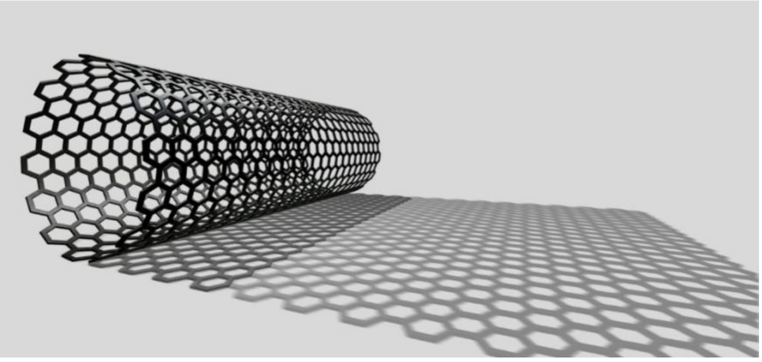
a) One-dimensional nanomaterials

One dimensional such as thin films and engineered surfaces, have been developed and used for decades in fields such as electronic device manufacture, chemistry and engineering. In the silicon integrated-circuit industry, for example, many devices rely on thin films for their operation, and control of film thicknesses approaching the atomic level is routine. Monolayers (layers that are one atom or molecule deep) are also routinely made and used in chemistry. The formation and properties of these layers are reasonably well understood from the atomic level upwards, even in quite complex layers (such as lubricants). Advances are being made in the control of the composition and smoothness of surfaces, and the growth of films. Engineered surfaces with tailored properties such as large surface area or specific reactivity are used routinely in a range of applications such as in fuel cells and catalysts . The large surface area provided by nanoparticles, together with their ability to self assemble on a support surface, could be of use in all of these applications.

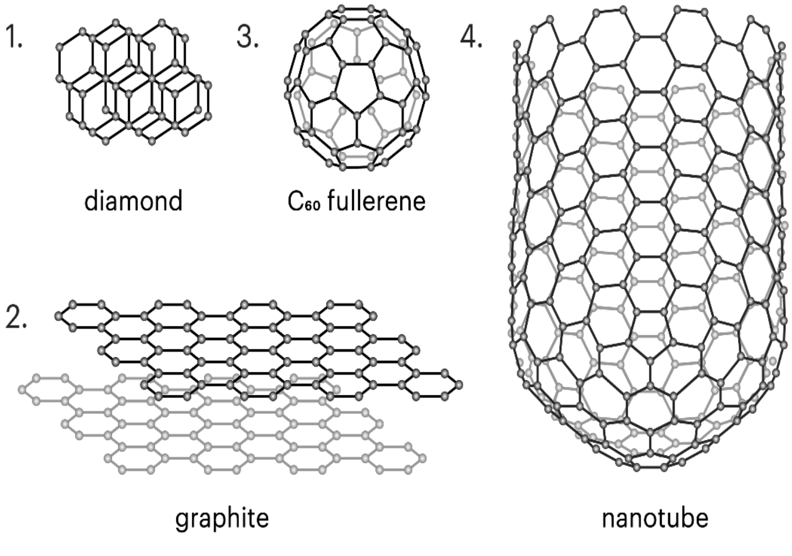
Although they represent incremental developments, surfaces with enhanced properties should find applications throughout the chemicals and energy sectors. The benefits could surpass the obvious economic and resource savings achieved by higher activity and greater selectivity in reactors and separation processes, to enabling small-scale distributed processing (making chemicals as close as possible to the point of use). There is already a move in the chemical industry towards this. Another use could be the small-scale, on-site production of high value chemicals such as pharmaceuticals.

b) Nanoscale in two dimensions

Two dimensional nanomaterials such as tubes and wires have generated considerable interest among the scientific community in recent years. In particular, their novel electrical and mechanical properties are the subject of intense research. Carbon nanotubes 16 Carbon nanotubes (CNTs) were first observed by Sumio Iijima in 1991 (Iijima 1991). CNTs are extended tubes of rolled graphene sheets. There are two types of CNT: single-walled (one tube) or multi-walled (several concentric tubes) (Figure 3.1). Both of these are typically a few nanometres in diameter and several micrometres (10-6m) to centimetres long. CNTs have assumed an important role in the context of nanomaterials, 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 graphene 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.



Schematic of a single-walled carbon nanotube (SWNT)



Schematic of a multi-walled carbon nanotube (MWNT)

C) **Nanoscale in three dimensions** Nanoparticles 21 Nanoparticles are often defined as particles of less than 100nm in diameter. In line with our definitions of nanoscience and nanotechnologies (see Box 2.1), we classify nanoparticles to be particles less than 100nm in diameter that exhibit new or enhanced size-dependent properties compared with larger particles of the same material. Nanoparticles exist widely in the natural world: for example as the products of photochemical and volcanic activity, and created by plants and algae. They have also been created for thousands of years as products of combustion and food cooking, and more recently from vehicle exhausts. Deliberately manufactured nanoparticles, such as metal oxides, are by comparison in the minority. In this report we will refer to these as natural, pollutant and manufactured nanoparticles, respectively.

Fullerenes (carbon 60)

In the mid-1980s a new class of carbon material was discovered called carbon 60 (C60). These are spherical molecules about 1nm in diameter, comprising 60 carbon atoms arranged as 20 hexagons and 12 pentagons: the configuration of a football. The C60 species was named 'Buckminsterfullerene' in recognition of the architect Buckminster Fuller, who was well-known for building geodesic domes, and the term fullerenes was then given to any closed carbon cage. In 1990, a technique to produce larger quantities of C60 was developed by resistively heating graphite rods in a helium atmosphere . Several applications are envisaged for fullerenes, such as miniature 'ball bearings' to lubricate surfaces, drug delivery vehicles and in electronic circuits.

Dendrimers

Dendrimers are spherical polymeric molecules, formed through a nanoscale hierarchical self-assembly process. There are many types of dendrimer; the smallest is several nanometres in size. Dendrimers are used in conventional applications such as coatings and inks, but they also have a range of interesting properties which could lead to useful applications. For example, dendrimers can act as nanoscale carrier molecules and as such could be used in drug delivery. Environmental clean-up could be assisted by dendrimers as they can trap metal ions, which could then be filtered out of water with ultra-filtration techniques**.**

Quantum dots

Nanoparticles of semiconductors (quantum dots) were theorized in the 1970s and initially created in the early 1980s. If semiconductor particles are made small enough, quantum effects come into play, which limit the energies at which electrons and holes (the absence of an electron) 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. Recently, quantum dots have found applications in composites, solar cells (Gratzel cells) and fluorescent biological labels (for example to trace a biological molecule) which use both the small particle size and tuneable energy levels. Recent advances in chemistry have resulted in the preparation of monolayer-protected, high-quality, monodispersed, crystalline quantum dots as small as 2nm in diameter, which can be conveniently treated and processed as a typical chemical reagent.

Bottom-up manufacturing

It involves the building of structures, atom-by-atom or molecule-by-molecule. The wide variety of approaches towards achieving this goal can be split into three categories: chemical synthesis, self-assembly, and positional assembly. As discussed below, positional assembly (with its many practical drawbacks as a manufacturing tool) is the only technique in which single atoms or molecules can be placed deliberately one-by-one. More typically, large numbers of atoms, molecules or particles are used or created by chemical synthesis, and then arranged through naturally occurring processes into a desired structure.

Chemical synthesis is a method of producing raw materials, such as molecules or particles, which can then be used either directly in products in their bulk disordered form, or as the building blocks of more advanced ordered materials, produced using the techniques. The precursor phase is the starting point, and the material can be in any physical state (or multiphase) or spatial arrangement to other components. The first step is the creation of a new phase or state where the nanoparticles either form or can be formed by a chemical step. In other words, the phase change itself could bring about nanoparticle formation (rare but possible) although generally the circumstances are created whereby nanoparticles can be made, for example vaporisation of a precursor mixture. Once in a state where nanoparticles can be made, usually a chemical reaction of some description is performed to generate the desired material. A further phase transformation or even solid-state reaction may be necessary to produce the final product. Potential exposure of the workforce to nanoparticles is likely to be greatest when these materials are processed in a gaseous environment; in such cases worker exposure will need to be monitored closely.

However, nanoparticles have a tendency to agglomerate, and are therefore often manufactured from a liquid phase as this enables surface energies to be better controlled, reducing agglomeration. This also reduces the potential exposure level of workers. Processing and handling ability is very important for nanomaterials: mixing nanoscale particles together before agglomerating and (for example) sintering can generate wholly new complex nanophase materials which could not be made by any other method. Most genuinely nanoscale and nanostructured materials, however, are still at the laboratory scale of synthesis (kilograms per day scale of operation or even less). It gives our estimates of current and future production of nanomaterials. Metal oxides, such as titanium dioxide, zinc oxide, silicon dioxide, aluminium oxide, zirconia and iron oxide, are currently the most commercially important nanoparticles.

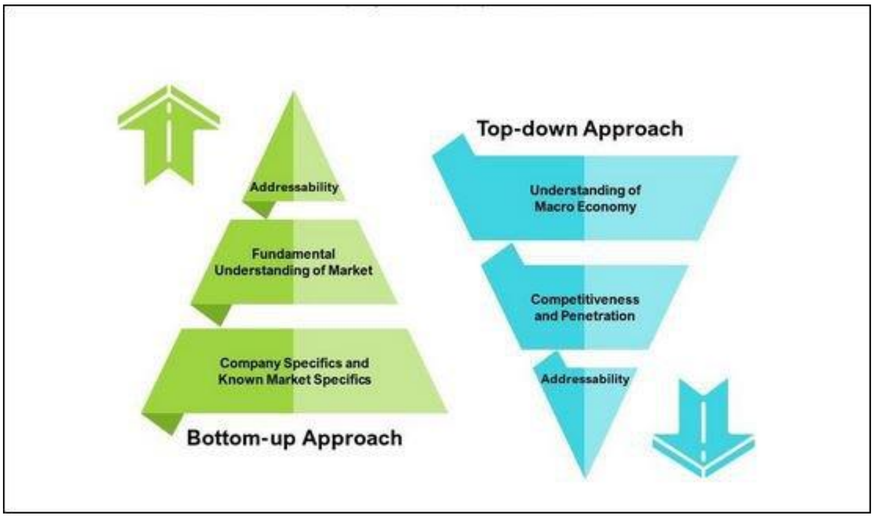
They are available as dry powders or liquid suspensions. The quantities currently used in the skincare market sectors (titanium dioxide etc.) amount to 1,000–2,000 tonnes per annum worldwide, with the nanoscalar component materials worth approximately $10 to $100,000 per tonne. Although the world market for nanoparticles is expected to increase during the next few years, to provide perspective, it is worth noting that the global production rate of all chemicals is around 400M tonnes per annum (European Commission 2001), and so chemicals in nanoparticulate form account for only a tiny fraction of the total (around 0.01%) currently produced. Nanoscalar inorganic, metallic or semiconductor material often will have multifunctionality, which enables it to be used across many industry sectors. Zinc oxide, for example, will have more commercial use as an optoelectronic material (for displays or advanced solar and photovoltaic cells) where it will be fixed in the final product, than as an ingredient for skincare products, where particles will be free.

Top-down manufacturing

Top-down manufacturing involves starting with a larger piece of material and etching, milling or machining a nanostructure from it by removing material (as, for example, in circuits on microchips). This can be done by using techniques such as precision engineering and lithography, and has been developed and refined by the semiconductor industry over the past 30years. Top-down methods offer reliability and device complexity, although they are generally higher in energy usage, and produce more waste than bottom-up methods. The production of computer chips, for example, is not yet possible through bottom-up methods; however, techniques using bottom-up (or hybrid top-down/bottom-up) methods are under exploration.

The top-down approach is essentially the breaking down of bulk material to get nano-sized particles. This can be achieved by using advanced techniques such as precision engineering and lithography which have been developed and optimized by industry during recent decades. Precision engineering supports the majority of the micro-electronics industry during the entire production process, and the high performance can be achieved through the use of a combination of improvements.

These include the use of advanced nanostructure based on diamond or cubic boron nitride and sensors for size control, combined with numerical control and advanced servo-drive technologies. Lithography involves the patterning of a surface through exposure to light, ions or electrons, and the deposition of material on to that surface to produce the desired material.



a) **Precision engineering** .In general, ultra-precision engineering and manufacture underpin much of the micro-electronics industry in everything from the production of the flat low-damage semiconductor wafers used as substrates for computer chips, to the mechanical stages used to position the wafers, to the manufacture of the precision optics used to print the patterns on the wafers. In addition, the techniques of ultra-precision engineering are used in a variety of consumer products such as computer hard disks, CD and DVD players.

b) **Lithography** manufacturing in the ICT sector predominantly involves lithographic processes that pattern a semiconductor wafer in a sequence of fabrication steps. Lithography involves the patterning of a surface through exposure to light, ions or electrons, and then subsequent etching and/or deposition of material on to that surface to produce the desired device. The ability to pattern features in the nanometre range is fundamental to the success of the IT industry and the ITRS roadmap. The main lithographic tools can be conveniently separated into methods that use a focused beam of electrons or ions to write patterns, and those that rely on the projection of light through a mask to define a pattern over a complete semiconductor wafer. Electron- and ion-based methods are both capable of making sub-10nm structures (with electron beam lithography having the greatest routine resolution), but they are too slow to be used directly in production. Optical lithography is used for production of semiconductor devices. Although it does not have the resolution of the beam-based techniques, it provides rapid throughput and cost-effective manufacture. Electron beam lithography is primarily used to fabricate the masks used for optical lithography, and ion beam techniques are mostly used to repair masks and for specialist device applications.

Techniques developed in the microelectronics industry have also enabled the miniaturisation of small mechanical moving devices (MEMS), which in turn have lead to research into NEMS. MEMS technology seeks to exploit and extend the capabilities that have been provided by silicon integrated circuit manufacturing from one of making chips for electronic signal processing to the provision of on-chip sensing and/or actuation through the use of moving mechanical parts. Some MEMS technologies are starting to attain maturity in manufacture (for example, MEMS accelerometers are used widely in air-bag sensors). However, there are currently difficulties in the reproducible large-scale manufacture of more complex MEMS systems. Although not strictly a 'nanotechnology' as defined in this report, MEMS, NEMS and the technologies used to make them are used extensively in techniques that can access and exploit the nanoscale (such as SPMs or lab-on-a-chip and biosensing). The reducing dimensional tolerances (less than 100nm) being provided by modern lithographic patterning techniques are now enabling the production of structures of such small dimensions that they are becoming a legitimate part of nanotechnologies in their own right.

Applications

Below we list some key current and potential shortand long-term applications of nanomaterials. Most current applications represent evolutionary developments of existing technologies: for example, the reduction in size of electronics devices.

a) **Current**

Sunscreens and cosmetics Nanosized titanium dioxide and zinc oxide are currently used in some sunscreens, as they absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light and so are more appealing to the consumer. Nanosized iron oxide is present in some lipsticks as a pigment but it is our understanding that it is not used by the European cosmetics sector. The use of nanoparticles in cosmetics has raised a number of concerns about consumer safety.

b) **Composites**

An important use of nanoparticles and nanotubes is in composites, materials that combine one or more separate components and which are designed to exhibit overall the best properties of each component. This multi-functionality applies not only to mechanical properties, but extends to optical, electrical and magnetic ones. Currently, carbon fibres and bundles of multi-walled CNTs are used in polymers to control or enhance conductivity, with applications such as packaging. A particular type of nanocomposite is where nanoparticles act as fillers in a matrix; for example, carbon black used as a filler to reinforce car tyres. However, particles of carbon black can range from tens to hundreds of nanometres in size, so not all carbon black falls within our definition of nanoparticles.

c) Clays

Clays containing naturally occurring nanoparticles have long been important as construction materials and are undergoing continuous improvement. Clay particle based composites – containing plastics and nano-sized flakes of clay – are also finding applications such as use in car bumpers.

d) Coatings and surfaces

Coatings with thickness controlled at the nano- or atomic scale have been in routine production for some time, for example in MBE or metal oxide CVD for optoelectonic devices, or in catalytically active and chemically functionalized surfaces. Recently developed applications include the self-cleaning window, which is coated in highly activated titanium dioxide, engineered to be highly hydrophobic (water repellent) and antibacterial, and coatings based on nanoparticulate oxides that catalytically destroy chemical agents . Wear and scratch-resistant hard coatings are significantly improved by nanoscale intermediate layers (or multilayers) between the hard outer layer and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion. A range of enhanced textiles, such as breathable, waterproof and stainresistant fabrics, have been enabled by the improved control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganics.

c) Paints

Incorporating nanoparticles in paints could improve their performance, for example by making them lighter and giving them different properties. Thinner paint coatings (‘lightweighting’), used for example on aircraft, would reduce their weight, which could be beneficial to the environment. However, the whole life cycle of the aircraft needs to be considered before overall benefits can be claimed (see section 4.5). It may also be possible to substantially reduce solvent content of paints, with resulting environmental benefits. New types of foulingresistant marine paint could be developed and are urgently needed as alternatives to tributyl tin (TBT), now that the ecological impacts of TBT have been recognised. Anti-fouling surface treatment is also valuable in process applications such as heat exchange, where it could lead to energy savings. If they can be produced at sufficiently low cost, fouling-resistant coatings could be used in routine duties such as piping for domestic and industrial water systems. It remains speculation whether very effective anti-fouling coatings could reduce the use of biocides, including chlorine. Other novel, and more long-term, applications for nanoparticles might 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.

F) Fuel Cells

Engineered surfaces are essential in fuel cells, where the external surface properties and the pore structure affect performance. The hydrogen used as the immediate fuel in fuel cells may be generated from hydrocarbons by catalytic reforming, usually in a reactor module associated directly with the fuel cell. The potential use of nano-engineered membranes to intensify catalytic processes could enable higher-efficiency, small-scale fuel cells. These could act as distributed sources of electrical power. It may eventually be possible to produce hydrogen locally from sources other than hydrocarbons, which are the feedstocks of current attention.

G) Displays

The huge market for large area, high brightness, flat-panel displays, as used in television screens and computer monitors, is driving the development of some nanomaterials. Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol–gel techniques (a process for making ceramic and glass materials, involving the transition from a liquid ‘sol’ phase to a solid ‘gel’ phase) are candidates for the next generation of light-emitting phosphors. 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.

H) Batteries

The growth in portable electronic equipment (mobile phones, navigation devices, laptop computers, remote sensors), there is great demand for lightweight, high-energy density batteries. 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 are envisioned to require less frequent recharging and to last longer because of their large grain boundary (surface) area.

I) Fuel additives

Research is underway into the addition of nanoparticulate ceria (cerium oxide) to diesel fuel to improve fuel economy by reducing the degradation of fuel consumption over time .

J) Catalysts

In general, nanoparticles have a high surface area, and hence provide higher catalytic activity. Nanotechnologies are enabling changes in the degree of control in the production of nanoparticles, and the support structure on which they reside. It is possible to synthesise metal nanoparticles in solution in the presence of a surfactant to form highly ordered monodisperse films of the catalyst nanoparticles on a surface.

Unit -2

Unique Properties of Nanomaterials

Nanomaterials are of interest because of its scale and unique optical, magnetic, electrical, and other properties emerge. They are a link between bulk materials and atomic or molecular structures. While bulk materials have constant physical properties regardless of its size, among nanoparticles the size often dictates the physical and chemical properties. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials, those larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects.

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 behaviours**.**

Physical properties of nanoparticles

Nanoparticles are unique because of their large surface area and this dominates the contributions made by the small bulk of the material. For example, zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions.

Other examples of the physical properties of nanoparticles:

- Coloured nanoparticles of yellow gold and gray silicon are red in color

- Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C)

- Absorption of solar radiation in photovoltaic cells is much higher in nanoparticles than it is in thin films of continuous sheets of bulk material (since the particles are smaller), they absorb greater amount of solar radiation .

Optical properties of nanoparticles are unique : Nanoparticles also often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. One example of this is that gold nanoparticles appear deep red to black in solution.

Formation of suspensions: An important physical property of nanoparticles is their ability to form suspensions. This is possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences. In bulk materials this interactions usually result in a material either sinking or floating in a liquid.

Magnetization and other properties of nanoparticles :Other properties unique among nanoparticles are quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super-paramagnetism in magnetic materials. For example, ferroelectric materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage. Thus this property is not always desired in nanoparticles.

Diffusion properties of nanoparticles: At elevated temperatures especially, nanoparticles possess the property of diffusion. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. Although this does not affect the density of the final product but there is a chance of agglomeration.

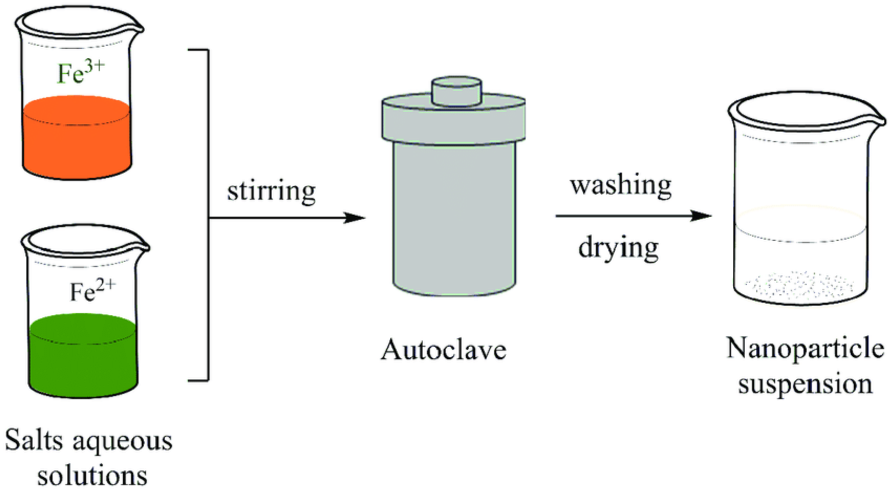
Hardness of nanoparticles:Clay nanoparticles, when incorporated into polymer matrices, increase reinforcement, leading to stronger plastics. These nanoparticles are hard, and impart their properties to the polymer (plastic). Nanoparticles have also been attached to textile fibers in order to create smart and functional clothing.

Nanomaterial - Synthesis and Processing

There are many different ways of creating nanostructures. Macromolecules or nanoparticles or bucky balls or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or nearequilibrium 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.

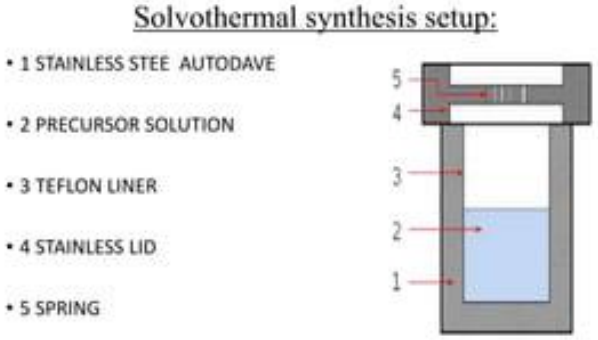
Hydrothermal synthesis

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal. Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large goodquality crystals while maintaining control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows. Uses: A large numbers of compounds belonging to practically all classes have been synthesized under hydrothermal conditions, elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals that have been efficiently grown are emeralds, rubies, quartz, alexandrite and others. The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multi-component systems at elevated temperatures and pressures.



Solvothermal synthesis

Solvothermal synthesis is a method of producing chemical compounds. It is very similar to the hydrothermal route (where the synthesis is conducted in a stainless steel autoclave), the only difference being that the precursor solution is usually not aqueous (however, this is not always the case in all literature uses of the expression (Figure 3). Using the solvothermal route gains one the benefits of both the sol-gel and hydrothermal routes. Thus solvothermal synthesis allows for the precise control over the size, shape distribution, and crystallinity of metaloxide nanoparticles or nanostructures. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type, and precursor type. Solvo-thermal synthesis has been used in laboratory to make nano structured titanium dioxide, graphene,carbon and other materials.



STRUCTURE AND BONDING OF NANOMATERIALS

A nanostructure is a structure of intermediate size between microscopic and molecular structures. Nanostructural detail is microstructure at nanoscale.

Nanostructured film

Synthesis and characterization

Nanostructured films are commonly created using magnetron sputtering from an appropriate target material.Films can be elemental in nature, formed by sputtering from a pure metal target such as copper, or composed of compound materials. Varying parameters such as the sputtering rate, substrate temperature, and sputtering interrupts allow the creation of films with a variety of different nanostructured elements. Control over nano-twinning, tailoring of specific types of grain boundaries, and restricting the movement and propagation of dislocations have been demonstrated using films produced via magnetron sputtering.Methods used to characterize nanostructured films include transmission electron microscopy, scanning electron microscopy, electron backscatter diffraction, focused ion beam milling, and nanoindentation. These techniques are used as they allow imaging of nanoscale structures, including dislocations, twinning, grain boundaries, film morphology, and atomic structure.

Nanostructured films with superior mechanical properties allow previously unusable materials to be utilized in new applications, enabling advances fields where coatings are heavily utilized, such as aerospace, energy, and other engineering fields.Production scalability of nanostructured films has already been demonstrated, and the ubiquity of sputtering techniques in industry is predicted to facilitate the incorporation of nanostructured films into existing applications.

Nanofiber

Nanofibers are fibers with diameters in the nanometer range (typically, between 1 nm and 1 µm). Nanofibers can be generated from different polymers and hence have different physical properties and application potentials. Examples of natural polymers include collagen, cellulose, silk fibroin, keratin, gelatin and polysaccharides such as chitosan and alginate. Examples of synthetic polymers include poly(lactic acid)(PLA), polycaprolactone (PCL), polyurethane (PU), poly(lactic-co-glycolic acid) (PLGA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(ethylene-co-vinylacetate) (PEVA). Polymer chains are connected via covalent bonds.The diameters of nanofibers depend on the type of polymer used and the method of production. All polymer nanofibers are unique for their large surface area-to-volume ratio, high porosity, appreciable mechanical strength, and flexibility in functionalization compared to their micro fiber counterparts.

Nanofibers have many possible technological and commercial applications. They are used in tissue engineering, drug delivery,seed coating material,cancer diagnosis,lithium-air battery,optical sensors, air filtration,redox-flow batteries and composite materials.

Nanowires

A nanowire is a nanostructure in the form of a wire with the diameter of the order of a nanometre (10^{-9}metres). More generally, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length. At these scales, quantum mechanical effects are important—which coined the term "quantum wires".

Synthesis

There are two basic approaches to synthesizing nanowires: top-down and bottom-up. A top-down approach reduces a large piece of material to small pieces, by various means such as lithography,milling or thermal oxidation. A bottom-up approach synthesizes the nanowire by combining constituent adatoms. Most synthesis techniques use a bottom-up approach. Initial synthesis via either method may often be followed by a nanowire thermal treatment step, often involving a form of self-limiting oxidation, to fine tune the size and aspect ratio of the structures.After the bottom-up synthesis, nanowires can be integrated using pick-and-place techniques. Nanowire production uses several common laboratory techniques, including suspension, electrochemical deposition, vapor deposition, and VLS growth. Ion track technology enables growing homogeneous and segmented nanowires down to 8 nm diameter. As nanowire oxidation rate is controlled by diameter, thermal oxidation steps are often applied to tune their morphology.

Predicting the type of bonding in a substance crystal structure

Crystal structure prediction (CSP) is the calculation of the crystal structures of solids from first principles. Reliable methods of predicting the crystal structure of a compound, based only on its composition, has been a goal of the physical sciences since the 1950s. Computational methods employed include simulated annealing, evolutionary algorithms, distributed multipole analysis, random sampling, basin-hopping, data mining, density functional theory and molecular mechanics.

Molecular crystals

Predicting organic crystal structures is important in academic and industrial science, particularly for pharmaceuticals and pigments, where understanding polymorphism is beneficial. The crystal structures of molecular substances, particularly organic compounds, are very hard to predict and rank in order of stability. Intermolecular interactions are relatively weak and non-directional and long range. This results in typical lattice and free energy differences between polymorphs that are often only a few kJ/mol, very rarely exceeding 10 kJ/mol. Crystal structure prediction methods often locate many possible structures within this small energy range. These small energy differences are challenging to predict reliably without excessive computational effort.

Since 2007, significant progress has been made in the CSP of small organic molecules, with several different methods proving effective. The most widely discussed method first ranks the energies of all possible crystal structures using a customised MM force field, and finishes by using a dispersion-corrected DFT step to estimate the lattice energy and stability of each short-listed candidate structure.More recent efforts to predict crystal structures have focused on estimating crystal free energy by including the effects of temperature and entropy in organic crystals using vibrational analysis or molecular dynamics.

Crystal structure prediction software

The following codes can predict stable and metastable structures given chemical composition and external conditions (pressure, temperature):

AIRSS - Ab Initio Random Structure Searching based on stochastic sampling of configuration space and with the possibility to use symmetry, chemical, and physical constraints. Has been used to study bulk crystals, low-dimensional materials, clusters, point defects, and interfaces. Released under the GPL2 licence. Regularly updated.

CALYPSO - The Crystal structure AnaLYsis by Particle Swarm Optimization, implementing the particle swarm optimization (PSO) algorithm to identify/determine the crystal structure. As with other codes, knowledge of the structure can be used to design multi-functional materials (e.g.,superconductive, thermoelectric, superhard, and energetic materials). Free for academic researchers. Regularly updated.

GASP - predicts the structure and composition of stable and metastable phases of crystals, molecules, atomic clusters and defects from first-principles. Can be interfaced to other energy codes including: VASP, LAMMPS, MOPAC, Gulp, JDFTx etc. Free to use and regularly updated.

GRACE - for predicting molecular crystal structures, especially for the pharmaceutical industry. Based on dispersion-corrected density functional theory. Commercial software under active development.

GULP - Monte Carlo and genetic algorithms for atomic crystals. GULP is based on classical force fields and works with many types of force fields. Free for academic researchers. Regularly updated.

USPEX - multi-method software that includes evolutionary algorithms and other methods (random sampling, evolutionary metadynamics, improved PSO, variable-cell NEB method and transition path sampling method for phase transition mechanisms). Can be used for atomic and molecular crystals; bulk crystals, nanoparticles, polymers, surface reconstructions, interfaces; can optimize the energy or other physical properties. In addition to finding the structure for a given composition, can identify all stable compositions in a multicomponent variable-composition system and perform simultaneous optimisation of several properties. Free for academic researchers. Used by >4500 researchers. Regularly updated.

XtalOpt - open source code implementing an evolutionary algorithm.

Bimetallic nanoparticle

A bimetallic nanoparticle is a combination of two different metals that exhibit several new and improved properties.Bimetallic nano materials can be in the form of alloys, core-shell, or contact aggregate. Due to their novel properties, they have gained a lot of attention among the scientific and industrial communities. When used as catalysts, they show improved activity as compared to their monometallic counterparts. They are cost-effective, stable alternatives that exhibit high activity and selectivity. Hence a lot of effort has been put into the advancement of these catalysts. The combination or the type of metals present, how they are combined, and their size determines their properties.

The synthesis of bimetallic nanoparticles can be done using co-reduction, successive reduction, reduction of complexes containing both the metals and electrochemical methods. Co-reduction and successive reduction methods are the most popular preparative techniques.

Methods of synthesis

Co-reduction method

The co-reduction method is similar to that of the reduction method used in the synthesis of monometallic nanoparticles. The difference is that for bimetallic nanoparticle synthesis two metal precursors will be used instead of one. The two precursors along with the stabilizing agent are completely dissolved in a suitable solvent. The metals will be present in their ionic states. To convert them into their zerovalent states a reducing agent is added. The light transition metals have lower reduction potential which means that they are rarer to undergo reduction. These light transition metals when present in their zerovalent states tend to undergo oxidation very quickly and therefore are unstable. Since these metals are very important in the field of catalysis, several methods to stabilize them are sought after.

Successive reduction method

In the successive reduction method, the two precursors are added one after the other. This method generally leads to the formation of core-shell bimetallic nanoparticles. The precursor of the metal that has to form the core is added along with the stabilizing agent first. This is followed by the reducing agent. Once the complete reduction of the first metal is ensured, the second metal precursor is added. The second metal ion gets adsorbed on the nanoparticle surface and gets reduced. This results in the core-shell structure of the bimetallic nanoparticle.

Reduction of bimetallic complexes

A complex containing both the metals to be present in the bimetallic nanoparticle is taken as the precursor. The aqueous solution of these complexes in different concentrations is taken in a quartz vessel and reduced using a photoreactor. Polyvinylpyrrolidone can be used as a stabilizer. The size and composition of the nanoparticles vary with the concentration of the aqueous solution. The composition of the nanoparticles can be analyzed using EDX studies.

Electrochemical method

In chemical methods, the metal ions are reduced to their zerovalent states using a reducing agent. In the electrochemical process, bulk metal is converted into metal atoms. The size of the particle synthesized using this method can be controlled by manipulating the current density. There are two anodes made up of the constituent bulk metal and a platinum metal plate is used as the cathode. The stabilizing agent is mixed with the electrolyte. When current is passed ions of the metals are formed at the anode and are reduced by the electrons generated in the platinum electrode. The major attractions of this method are its cost-effectiveness, high yield, ease of isolation, and the ability to control the composition of metal simply through variation of current density.

Properties os nanomaterials

Nanoparticles have different analytical requirements than conventional chemicals, for which chemical composition and concentration are sufficient metrics. Nanoparticles have other physical properties that must be measured for a complete description, such as size, shape, surface properties, crystallinity, and dispersion state. The bulk properties of nanoparticles are sensitive to small variations in these properties, which has implications for process control in their industrial use. These properties also influence the health effects of exposure to nanoparticles of a given composition.

Surface area

Surface area is an important metric for engineered nanoparticles because it influences reactivity and surface interactions with ligands. Specific surface area refers to the surface area of a powder normalized to mass or volume. Different methods measure different aspects of surface area.

Direct measurement of nanoparticle surface area utilizes adsorption of an inert gas such as nitrogen or krypton under varying conditions of pressure to form a monolayer of gas coverage. The number of gas molecules needed to form a monolayer and the cross-sectional area of the adsorbate gas molecule are related to the "total surface area" of the particle, including internal pores and crevices, using the Brunauer–Emmett–Teller equation.Organic molecules can be used in place of gasses, such as ethylene glycol monoethyl ether.

There are several indirect measurement techniques for airborne nanoparticles, which do not account for porosity and other surface irregularities and therefore may be inaccurate. Real-time diffusion chargers measure the "active surface area", the area of the particle that interacts with the surrounding gas or ions and is accessible only from the outside. Electrical mobility analyzers calculate the spherical equivalent diameter, which can be converted using geometric relationships. These methods cannot discriminate a nanoparticle of interest from incidental nanoparticles that may occur in complex environments such as workplace atmospheres. Nanoparticles can be collected onto a substrate and their external dimensions can be measured using electron microscopy, then converted to surface area using geometric relations.

SHAPE

Morphology refers to the physical shape of a particle, as well as its surface topography, for example, the presence of cracks, ridges, or pores. Morphology influences dispersion, functionality, and toxicity, and has similar considerations as size measurements. Evaluation of morphology requires direct visualization of the particles through techniques like scanning electron microscopy, transmission electron microscopy, and atomic force microscopy.Several metrics can be used, such as sphericity or circularity, aspect ratio, elongation, convexity, and fractal dimension.[5] Because microscopy involves measurements of single particles, a large sample size is necessary to ensure a representative sample, and orientation and sample preparation effects must be accounted for.

INERT GAS CONDENSATION

Inert Gas Condensation for Nanoparticle Synthesis

As a class of bottom-up viewpoint in nanoparticle synthesis, inert gas condensation is a perfectly developed and popular nanoparticle synthesis technique owing to its capability and flexibility to control the synthesis process. Briefly, the material is evaporated under the pure helium atmosphere with the helium atoms serving as a cooling agent condensing the atoms to finalize the formation of nanoscale particles.

Principles of Inert-Gas Condensation

As it was mentioned earlier, inert gas condensate is a bottom up technique to obtain nanostructured materials based on two major preliminary steps. The first step involves the evaporation of the material to be obtained in nanoscale range and the second is the rapid condensation of the evaporate material to favor the particle size and morphology. The inert gas condensation devices are generally made of a chamber whose pressure is evacuated to fall down to 2 × 10-6 Torr using a diffusion pump. Another part is a crucible where the material in heated gradually via irradiation from graphite as the predetermined temperature source. After the evacuation is done, inert gases like He, Xe, or Ar are leaked into the chamber with lower pressures of about 0.5 to 4 with the subsequent fast heating of chamber at constant temperature and inert gas pressure. At this point, the particles with ultrafine sizes in the inert gas phase are collected in a surface that is cooled by water. The Collection process is carried out via a carbon coated electron microscope being attached to the core of the water cooled surface to give a simultaneous observation of the particle size by transmission electron microscope. It is also possible to obtain the sample as a monolayer on the grid.

Morphology and Crystal Structure of Particles

In inert gas condensation method the size and crystal and properties of nanoparticles depend on the pressure, species that are present in the atmosphere and the particle growth region above the surface of the evaporation chamber. The time the nuclei spend in the growth region and the amount of pressure critically determine the size and morphology of the particles. However, a high pressure in the growth region could lead to a large particle size because of the consecutive agglomeration and less sintering. Therefore, in order to obtain particles in smaller and finer sizes, the pressure has to be kept low. More importantly, the size and morphology of the particles differ depending on three zones with different temperatures and metal vapor concentration, where the collection of operation is carried out 1.

Advantages of Inert Gas Condensation Method

Inert gas condensate has emerged as a technique with a lot of advantages in fabrication and synthesis of nanomaterials. In fact, an extensive range of materials such as intermetallic compounds, ceramics metals, alloys, semiconductors and composites can be synthesized via inert gas condensation technique. Specifically, it is possible to generate nanoscale particles from just about any material that can be vaporized. Inert gas condensation is a very flexible one in terms of cluster sizes to be made, controlling the size and the size distribution of the particles over a broad range through the process and parameter alteration such as temperature and pressure. Particle surface cleanliness and ultrafine sizes of the particles make it possible to overcome the conventional restrictions of kinetics and phase equilibria through the combination of high driving forces, diffusion distances and more importantly, uncontaminated surfaces. So far, inert gas condensation has been employed to synthesize metallic nanoparticles like manganese (Mn) nanoparticles, Nickel (Ni) nanoparticles, iron and iron oxide nanoparticles and size-controlled gold/palladium nanoparticles (Au/Pd NPs) 1.

Synthesis of carbon nanotubes

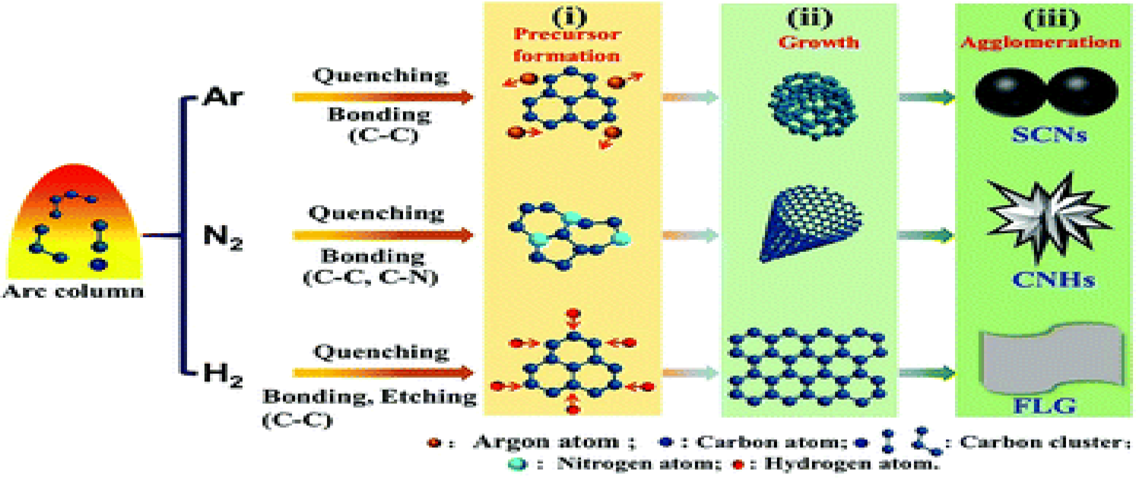
Techniques have been developed to produce carbon nanotubes in sizable quantities, including arc discharge, laser ablation, high-pressure carbon monoxide disproportionation, and chemical vapor deposition (CVD). Most of these processes take place in a vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth are making CNTs more commercially viable.

Types

Arc discharge

The arc discharge method is useful for the generation of various nanostructured materials. It is more known for producing carbon-based materials, such as fullerenes, carbon nanohorns (CNHs), carbon nanotubes, few-layer graphene (FLG), and amorphous spherical carbon nanoparticles. The arc discharge method has great significance in the generation of fullerene nanomaterials. In the formation process, two graphite rods are adjusted in a chamber in which a certain helium pressure is maintained. Filling the chamber with pure helium is important as the presence of moisture or oxygen inhibits fullerene formation. Carbon rod vaporization is driven by arc discharge between the ends of the graphite rods.

The conditions under which arc discharge takes place play a significant role in achieving new forms of nanomaterials. The conditions under which different carbon-based nanomaterials are formed via the arc discharge method are explained in Fig. 6. Various carbon-based nanomaterials are collected from different positions during the arc discharge method, as their growth mechanisms differ. MWCNTs, high-purity polyhedral graphite particles, pyrolytic graphite, and nano-graphite particles can be collected from either anode or cathode deposits or deposits at both electrodes. Apart from the electrodes, carbon-based nanomaterials can also be collected from the inner chamber. Different morphologies of single-wall carbon nanohorns (SWCNHs) can be obtained under different atmospheres. For example, ‘dahlia-like’ SWCNHs are produced under an ambient atmosphere, whereas ‘bud-like’ SWCNHs are generated under CO and CO2 atmospheres.The arc discharge method can be used to efficiently achieve graphene nanostructures. The conditions present during the synthesis of graphene can affect its properties. Graphene sheets prepared via a hydrogen arc discharge exfoliation method are found to be superior in terms of electrical conductivity and have good thermal stability compared to those obtained via argon arc discharge.



Laser ablation

Laser ablation synthesis involves nanoparticle generation using a powerful laser beam that hits the target material. During the laser ablation process, the source material or precursor vaporizes due to the high energy of the laser irradiation, resulting in nanoparticle formation. Utilizing laser ablation for the generation of noble metal nanoparticles can be considered as a green technique, as there is no need for stabilizing agents or other chemicals. A wide range of nanomaterials can be produced through this technique, such as metal nanoparticles, carbon nanomaterials, oxide composites, and ceramics. Pulsed laser ablation in liquids is an exciting approach for producing monodisperse colloidal nanoparticle solutions without using surfactants or ligands. The nanoparticle properties, such as average size and distribution, can be tuned via adjusting the fluence, wavelength, and laser salt addition.

Plasma torch

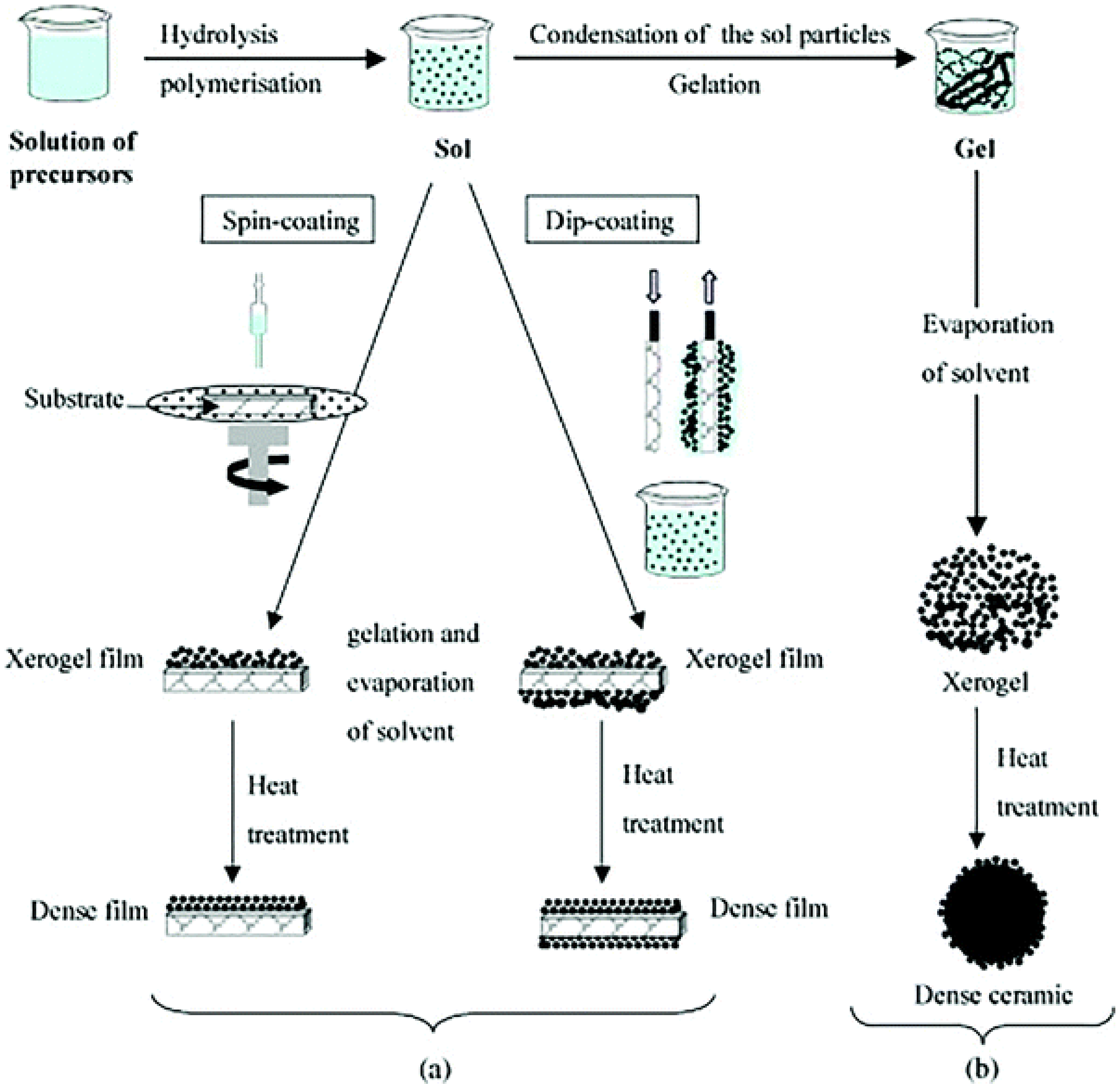
Single-walled carbon nanotubes can also be synthesized by a thermal plasma method, first invented in 2000 at INRS (Institut national de la recherche scientifique) in Varennes, Canada, by Olivier Smiljanic. In this method, the aim is to reproduce the conditions prevailing in the arc discharge and laser ablation approaches, but a carbon-containing gas is used instead of graphite vapors to supply the necessary carbon. Doing so, the growth of SWNT is more efficient (decomposing the gas can be 10 times less energy-consuming than graphite vaporization). The process is also continuous and low cost. A gaseous mixture of argon, ethylene and ferrocene is introduced into a microwave plasma torch, where it is atomized by the atmospheric pressure plasma, which has the form of an intense 'flame'. The fumes created by the flame contain SWNT, metallic and carbon nanoparticles and amorphous carbon.

Another way to produce single-walled carbon nanotubes with a plasma torch is to use the induction thermal plasma method, implemented in 2005 by groups from the University of Sherbrooke and the National Research Council of Canada.The method is similar to arc discharge in that both use ionized gas to reach the high temperature necessary to vaporize carbon-containing substances and the metal catalysts necessary for the ensuing nanotube growth. The thermal plasma is induced by high-frequency oscillating currents in a coil, and is maintained in flowing inert gas. Typically, a feedstock of carbon black and metal catalyst particles is fed into the plasma, and then cooled down to form single-walled carbon nanotubes. Different single-wall carbon nanotube diameter distributions can be synthesized.

The induction thermal plasma method can produce up to 2 grams of nanotube material per minute, which is higher than the arc discharge or the laser ablation methods.

The sol–gel method

The sol–gel method is a wet-chemical technique that is extensively used for the development of nanomaterials. This method is used for the development of various kinds of high-quality metal-oxide-based nanomaterials. This method is called a sol–gel method as during the synthesis of the metal-oxide nanoparticles, the liquid precursor is transformed to a sol, and the sol is ultimately converted into a network structure that is called a gel. Conventional precursors for the generation of nanomaterials using the sol–gel method are metal alkoxides. The synthesis process of nanoparticles via the sol–gel method can be completed in several steps. In the first step, the hydrolysis of the metal oxide takes place in water or with the assistance of alcohol to form a sol. In the next step, condensation takes place, resulting in an increase in the solvent viscosity to form porous structures that are left to age. During the condensation or polycondensation process, hydroxo- (M–OH–M) or oxo- (M–O–M) bridges form, resulting in metal–hydroxo- or metal–oxo-polymer formation in solution. During the aging process, polycondensation continues, with changes to the structure, properties, and porosity. During aging, the porosity decreases, and the distance between the colloidal particles increases. After the aging process, drying takes place, in which water and organic solvents are removed from the gel. Lastly, calcination is performed to achieve nanoparticles.Fig. 9 shows film and powder formation using the sol–gel method. The factors that affect the final product obtained viathe sol–gel method are the precursor nature, hydrolysis rate, aging time, pH, and molar ratio between H2O and the precursor. The sol–gel method is economically friendly and has many other advantages, such as the produced material being homogeneous in nature, the processing temperature being low, and the method being a facile way to produce composites and complex nanostructures.



Chemical vapor deposition (CVD)

Nanotubes being grown by plasma enhanced chemical vapor depositionAnimated pent-first nucleation. The catalytic vapor phase deposition of carbon was reported in 1952 and 1959, but it was not until 1993 that carbon nanotubes were formed by this process. In 2007, researchers at the University of Cincinnati (UC) developed a process to grow aligned carbon nanotube arrays of length 18 mm on a FirstNano ET3000 carbon nanotube growth system.

During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination. The metal nanoparticles can also be produced by other ways, including reduction of oxides or oxides solid solutions. The diameters of the nanotubes that are to be grown are related to the size of the metal particles. This can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer. The substrate is heated to approximately 700 °C. To initiate the growth of nanotubes, two gases are bled into the reactor: a process gas (such as ammonia, nitrogen or hydrogen) and a carbon-containing gas (such as acetylene, ethylene, ethanol or methane). Nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. This mechanism is still being studied.The catalyst particles can stay at the tips of the growing nanotube during growth, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate. Thermal catalytic decomposition of hydrocarbon has become an active area of research and can be a promising route for the bulk production of CNTs. Fluidised bed reactor is the most widely used reactor for CNT preparation. Scale-up of the reactor is the major challenge.

CVD is the most widely used method for the production of carbon nanotubes. For this purpose, the metal nanoparticles are mixed with a catalyst support such as MgO or Al2O3 to increase the surface area for higher yield of the catalytic reaction of the carbon feedstock with the metal particles. One issue in this synthesis route is the removal of the catalyst support via an acid treatment, which sometimes could destroy the original structure of the carbon nanotubes. However, alternative catalyst supports that are soluble in water have proven effective for nanotube growth.

If a plasma is generated by the application of a strong electric field during growth (plasma-enhanced chemical vapor deposition), then the nanotube growth will follow the direction of the electric field. By adjusting the geometry of the reactor it is possible to synthesize vertically aligned carbon nanotubes (i.e., perpendicular to the substrate), a morphology that has been of interest to researchers interested in electron emission from nanotubes. Without the plasma, the resulting nanotubes are often randomly oriented. Under certain reaction conditions, even in the absence of a plasma, closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a carpet or forest.

TYPES

CVD is practiced in a variety of formats. These processes generally differ in the means by which chemical reactions are initiated.

Classified by operating conditions:

Atmospheric pressure CVD (APCVD) – CVD at atmospheric pressure.

Low-pressure CVD (LPCVD) – CVD at sub-atmospheric pressures.Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.

Ultrahigh vacuum CVD (UHVCVD) – CVD at very low pressure, typically below 10−6 Pa (≈ 10−8 torr). Note that in other fields, a lower division between high and ultra-high vacuum is common, often 10−7 Pa.

Sub-atmospheric CVD (SACVD) – CVD at sub-atmospheric pressures. Uses tetraethyl orthosilicate(TEOS) and ozone to fill high aspect ratio Si structures with silicon dioxide (SiO_2).

Most modern CVD is either LPCVD or UHVCVD.

Microwave plasma-assisted CVD (MPCVD)

Plasma-enhanced CVD (PECVD) – CVD that utilizes plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors. The lower temperatures also allow for the deposition of organic coatings, such as plasma polymers, that have been used for nanoparticle surface functionalization.

Remote plasma-enhanced CVD (RPECVD) – Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.

Low-energy plasma-enhanced chemical vapor deposition (LEPECVD) - CVD employing a high density, low energy plasma to obtain epitaxial deposition of semiconductor materials at high rates and low temperatures.

Atomic-layer CVD (ALCVD) – Deposits successive layers of different substances to produce layered, crystalline films. See Atomic layer epitaxy.

Combustion chemical vapor deposition (CCVD) – Combustion Chemical Vapor Deposition or flame pyrolysis is an open-atmosphere, flame-based technique for depositing high-quality thin films and nanomaterials.

Hot filament CVD (HFCVD) – also known as catalytic CVD (Cat-CVD) or more commonly, initiated CVD, this process uses a hot filament to chemically decompose the source gases.The filament temperature and substrate temperature thus are independently controlled, allowing colder temperatures for better absorption rates at the substrate and higher temperatures necessary for decomposition of precursors to free radicals at the filament.

Hybrid physical-chemical vapor deposition (HPCVD) – This process involves both chemical decomposition of precursor gas and vaporization of a solid source.

Metalorganic chemical vapor deposition (MOCVD) – This CVD process is based on metalorganic precursors.

Rapid thermal CVD (RTCVD) – This CVD process uses heating lamps or other methods to rapidly heat the wafer substrate. Heating only the substrate rather than the gas or chamber walls helps reduce unwanted gas-phase reactions that can lead to particle formation.

Vapor-phase epitaxy (VPE)

Photo-initiated CVD (PICVD) – This process uses UV light to stimulate chemical reactions. It is similar to plasma processing, given that plasmas are strong emitters of UV radiation. Under certain conditions, PICVD can be operated at or near atmospheric pressure.

Laser chemical vapor deposition (LCVD) - This CVD process uses lasers to heat spots or lines on a substrate in semiconductor applications. In MEMS and in fiber production the lasers are used rapidly to break down the precursor gas—process temperature can exceed 2000 °C—to build up a solid structure in much the same way as laser sintering based 3-D printers build up solids from powders.

Solvothermal synthesis is a method of producing chemical compounds, in which a solvent containing reagents is put under high pressure and temperature in an autoclave. Many substances dissolve better in the same solvent in such conditions than at standard conditions, enabling reactions that would not otherwise occur and leading to new compounds or polymorphs. Solvothermal synthesis is very similar to the hydrothermal route; both are typically conducted in a stainless steel autoclave. The only difference being that the precursor solution is usually non-aqueous.

Solvothermal synthesis has been used prepare MOFs, titanium dioxide, and graphene, carbon spheres, chalcogenides and other materials.

Solvents

Besides water (hydrothermal synthesis), solvothermal syntheses make use of a large range of solvents, including ammonia, carbon dioxide, dimethylformamide, and various alcohols such as methanol, or glycols such as hexane-1,6-diol.

Formic acid as reaction medium

Formic acid decomposes at high temperatures to carbon dioxide and hydrogen or carbon monoxide and water. This property allows formic acid to be used as a reducing and carbon dioxide-rich reaction medium in which it is possible to form various oxides and carbonates.

Ammonia as reaction medium

The critical temperature and pressure of ammonia are 132.2 °C and 111 bar. In these conditions, it is possible to obtain a range of amides, imides, and nitrides. Although its dielectric constant is lower than that of water, ammonia behaves as a polar solvent especially at high pressures.

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows if a steel tube is used.There are autoclaves made out of thick walled glass, which can be used up to 300 °C and 10 bar.

Uses

A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals that have been efficiently grown are emeralds, rubies, quartz, alexandrite and others. The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multicomponent systems at elevated temperatures and pressures.

Methods

Temperature-difference method

This is the most extensively used method in hydrothermal synthesis and crystal growing. Supersaturation is achieved by reducing the temperature in the crystal growth zone. The nutrient is placed in the lower part of the autoclave filled with a specific amount of solvent. The autoclave is heated in order to create a temperature gradient. The nutrient dissolves in the hotter zone and the saturated aqueous solution in the lower part is transported to the upper part by convective motion of the solution. The cooler and denser solution in the upper part of the autoclave descends while the counterflow of solution ascends. The solution becomes supersaturated in the upper part as the result of the reduction in temperature and crystallization sets in.

Temperature-reduction technique

In this technique, crystallization takes place without a temperature gradient between the growth and dissolution zones. The supersaturation is achieved by a gradual reduction in temperature of the solution in the autoclave. The disadvantage of this technique is the difficulty in controlling the growth process and introducing seed crystals. For these reasons, this technique is very seldom used.

MICROSCOPE ASSISTED ELECTROCHEMICAL SYNTHESIS

This technique is based on the difference in solubility between the phase to be grown and that serving as the starting material. The nutrient consists of compounds that are thermodynamically unstable under the growth conditions. The solubility of the metastable phase exceeds that of the stable phase, and the latter crystallize due to the dissolution of the metastable phase. This technique is usually combined with one of the other two techniques above.

UNIT - 3

Mechanical properties of common nanomaterials classes:

Crystalline metal nanomaterials: Dislocations are one of the major contributors toward elastic properties within nanomaterials similar to bulk crystalline materials. Despite the traditional view of there being no dislocations in nanomaterials. Ramos, experimental work has shown that the hardness of gold nanoparticles is much higher than their bulk counterparts, as there are stacking faults and dislocations forming that activate multiple strengthening mechanisms in the material. Through these experiments, more research has shown that via nanoindentation techniques, material strength; compressive stress, increases under compression with decreasing particle size, because of nucleating dislocations. These dislocations have been observed using TEM techniques, coupled with nanoindentation. Silicon nanoparticles strength and hardness are four times more than the value of the bulk material.The resistance to pressure applied can be attributed to the line defects inside the particles as well as a dislocation that provides strengthening of the mechanical properties of the nanomaterial. Furthermore, the addition of nanoparticles strengthens a matrix because the pinning of particles inhibits grain growth. This refines the grain, and hence improves the mechanical properties. However, not all additions of nanomaterials lead to an increase in properties for example nano-Cu. But this is attributed to the inherent properties of the material being weaker than the matrix.

Nonmetallic nanoparticles and nanomaterials: Size-dependent behavior of mechanical properties is still not clear in the case of polymer nanomaterials however, in one research by Lahouij they found that the compressive moduli of polystyrene nanoparticles were found to be less than that of the bulk counterparts. This can be associated with the functional groups being hydrated. Furthermore, nonmetallic nanomaterials can lead to agglomerates forming inside the matrix they are being added to and hence decrease the mechanical properties by leading to fracture under even low mechanical loads, such as the addition of CNTs. The agglomerates will act as slip planes as well as planes in which cracks can easily propagate. However, most organic nanomaterials are flexible and these and the mechanical properties such as hardness etc. are not dominant.

Nanowires and nanotubes: The elastic moduli of some nanowires namely lead and silver, decrease with increasing diameter. This has been associated with surface stress, oxidation layer, and surface roughness. However, the elastic behavior of ZnO nanowires does not get affected by surface effects but their fracture properties do. So, it is generally dependent on material behavior and their bonding as well.

The reason why mechanical properties of nanomaterials are still a hot topic for research is that measuring the mechanical properties of individual nanoparticles is a complicated method, involving multiple control factors. Nonetheless, Atomic force microscopy has been widely used to measure the mechanical properties of nanomaterials.

Adhesion and friction of nanoparticles

When talking about the application of a material adhesion and friction play a critical role in determining the outcome of the application. Therefore, it is critical to see how these properties also get affected by the size of a material. Again, AFM is a technique most used to measure these properties and to determine the adhesive strength of nanoparticles to any solid surface, along with the colloidal probe technique and other chemical properties. Furthermore, the forces playing a role in providing these adhesive properties to nanomaterials are either the electrostatic forces, VdW, capillary forces, solvation forces, structure force, etc. It has been found that the addition of nanomaterials in bulk materials substantially increases their adhesive capabilities by increasing their strength through various bonding mechanisms. Nanomaterials dimension approaches zero, which means that the fraction of the particle's surface to overall atoms increases.

Along with surface effects, the movement of nanoparticles also plays a role in dictating their mechanical properties such as shearing capabilities. The movement of particles can be observed under TEM. For example, the movement behavior of MoS2 nanoparticles dynamic contact was directly observed in situ which led to the conclusion that fullerenes can shear via rolling or sliding. However, observing these properties is again a very complicated process due to multiple contributing factors.

Applications specific to Mechanical Properties:

- Lubrication
- Nano-manufacturing
- Coatings

Thermal Properties

 The melting point of a material directly correlates with the bond strength. In bulk materials, the surface to volume ratio is small and hence the surface effects can be neglected. However, in nanomaterials the melting temperature is size dependent and it decreases with the decrease particle size diameters. The reason is that in nanoscale materials, surface atoms are not bonded in direction normal to the surface plane and hence the surface atoms will have more freedom to move.

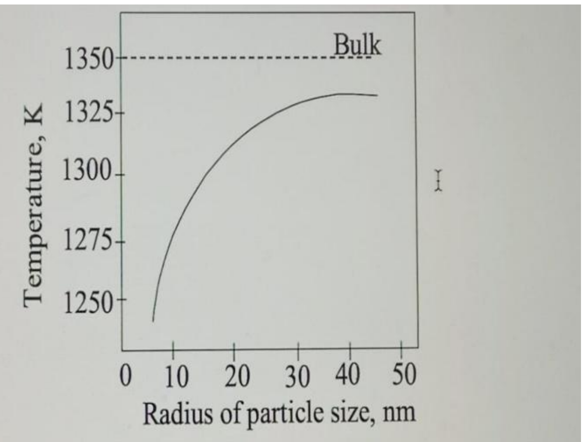


Fig 1.2: Effect of Particle Size on the Melting Point

Silver oxide Nanoparticle

Silver nanoparticles are nanoparticles of silver of between 1 nm and 100 nm in size. While frequently described as being 'silver' some are composed of a large percentage of silver oxide due to their large ratio of surface to bulk silver atoms. Numerous shapes of nanoparticles can be constructed depending on the application at hand. Commonly used silver nanoparticles are spherical, but diamond, octagonal, and thin sheets are also common.

Their extremely large surface area permits the coordination of a vast number of ligands. The properties of silver nanoparticles applicable to human treatments are under investigation in laboratory and animal studies, assessing potential efficacy, biosafety, and biodistribution.

Synthesis methods

Wet chemistry

The most common methods for nanoparticle synthesis fall under the category of wet chemistry, or the nucleation of particles within a solution. This nucleation occurs when a silver ion complex, usually AgNO3 or AgClO4, is reduced to colloidal Ag in the presence of a reducing agent. When the concentration increases enough, dissolved metallic silver ions bind together to form a stable surface. The surface is energetically unfavorable when the cluster is small, because the energy gained by decreasing the concentration of dissolved particles is not as high as the energy lost from creating a new surface. When the cluster reaches a certain size, known as the critical radius, it becomes energetically favorable, and thus stable enough to continue to grow. This nucleus then remains in the system and grows as more silver atoms diffuse through the solution and attach to the surface When the dissolved concentration of atomic silver decreases enough, it is no longer possible for enough atoms to bind together to form a stable nucleus. At this nucleation threshold, new nanoparticles stop being formed, and the remaining dissolved silver is absorbed by diffusion into the growing nanoparticles in the solution.

As the particles grow, other molecules in the solution diffuse and attach to the surface. This process stabilizes the surface energy of the particle and blocks new silver ions from reaching the surface. The attachment of these capping/stabilizing agents slows and eventually stops the growth of the particle. The most common capping ligands are trisodium citrate and polyvinylpyrrolidone (PVP), but many others are also used in varying conditions to synthesize particles with particular sizes, shapes, and surface properties.

Monosaccharide reduction

There are many ways silver nanoparticles can be synthesized; one method is through monosaccharides. This includes glucose, fructose, maltose, maltodextrin, etc., but not sucrose. It is also a simple method to reduce silver ions back to silver nanoparticles as it usually involves a one-step process. There have been methods that indicated that these reducing sugars are essential to the formation of silver nanoparticles. Many studies indicated that this method of green synthesis, specifically using Cacumen platycladi extract, enabled the reduction of silver. Additionally, the size of the nanoparticle could be controlled depending on the concentration of the extract. The studies indicate that the higher concentrations correlated to an increased number of nanoparticles. Smaller nanoparticles were formed at high pH levels due to the concentration of the monosaccharides.

Another method of silver nanoparticle synthesis includes the use of reducing sugars with alkali starch and silver nitrate. The reducing sugars have free aldehyde and ketone groups, which enable them to be oxidized into gluconate. The monosaccharide must have a free ketone group because in order to act as a reducing agent it first undergoes tautomerization. In addition, if the aldehydes are bound, it will be stuck in cyclic form and cannot act as a reducing agent. For example, glucose has an aldehyde functional group that is able to reduce silver cations to silver atoms and is then oxidized to gluconic acid. The reaction for the sugars to be oxidized occurs in aqueous solutions. The capping agent is also not present when heated.

Citrate reduction

An early, and very common, method for synthesizing silver nanoparticles is citrate reduction. This method was first recorded by M. C. Lea, who successfully produced a citrate-stabilized silver colloid in 1889. Citrate reduction involves the reduction of a silver source particle, usually AgNO3 or AgClO4, to colloidal silver using trisodium citrate, Na3C6H5O7. The synthesis is usually performed at an elevated temperature (~100 °C) to maximize the monodispersity (uniformity in both size and shape) of the particle. In this method, the citrate ion traditionally acts as both the reducing agent and the capping ligand, making it a useful process for AgNP production due to its relative ease and short reaction time. However, the silver particles formed may exhibit broad size distributions and form several different particle geometries simultaneously. The addition of stronger reducing agents to the reaction is often used to synthesize particles of a more uniform size and shape.

Light-mediated growth

Light-mediated syntheses have also been explored where light can promote formation of various silver nanoparticle morphologies.

Silver mirror reaction

The silver mirror reaction involves the conversion of silver nitrate to Ag(NH3)OH. Ag(NH3)OH is subsequently reduced into colloidal silver using an aldehyde containing molecule such as a sugar. The silver mirror reaction is as follows:

2(Ag(NH3)2)+ + RCHO + 2OH− → RCOOH + 2Ag + 4NH3.

The size and shape of the nanoparticles produced are difficult to control and often have wide distributions. However, this method is often used to apply thin coatings of silver particles onto surfaces and further study into producing more uniformly sized nanoparticles is being done.

Properties

Catalysis

Using silver nanoparticles for catalysis has been gaining attention in recent years. Although the most common applications are for medicinal or antibacterial purposes, silver nanoparticles have been demonstrated to show catalytic redox properties for dyes, benzene, and carbon monoxide. Other untested compounds may use silver nanoparticles for catalysis, but the field is not fully explored.

Supported on silica spheres – reduction of dyes

Silver nanoparticles have been synthesized on a support of inert silica spheres. The support plays virtually no role in the catalytic ability and serves as a method of preventing coalescence of the silver nanoparticles in colloidal solution. Thus, the silver nanoparticles were stabilized and it was possible to demonstrate the ability of them to serve as an electron relay for the reduction of dyes by sodium borohydride.Without the silver nanoparticle catalyst, virtually no reaction occurs between sodium borohydride and the various dyes: methylene blue, eosin, and rose bengal.

Mesoporous aerogel – selective oxidation of benzene

Silver nanoparticles supported on aerogel are advantageous due to the higher number of active sites. The highest selectivity for oxidation of benzeneto phenol was observed at low weight percent of silver in the aerogel matrix (1% Ag). This better selectivity is believed to be a result of the higher monodispersity within the aerogel matrix of the 1% Ag sample. Each weight percent solution formed different sized particles with a different width of size range.

Biological research

Researchers have explored the use of silver nanoparticles as carriers for delivering various payloads such as small drug molecules or large biomolecules to specific targets. Once the AgNP has had sufficient time to reach its target, release of the payload could potentially be triggered by an internal or external stimulus. The targeting and accumulation of nanoparticles may provide high payload concentrations at specific target sites and could minimize side effects.

Gold Nanoparticles:

Gold nanoparticles (AuNPs) are extremely promising objects for solving a wide range of biomedical problems. The gold nanoparticles production by biological method (“green synthesis”) is eco-friendly and allows minimization of the amount of harmful chemical and toxic byproducts. This review is devoted to the AuNPs biosynthesis peculiarities using various living organisms (bacteria, fungi, algae, and plants). The participation of various biomolecules in the AuNPs synthesis and the influence of size, shapes, and capping agents on the functionalities are described. The proposed action mechanisms on target cells are highlighted. The biological activities of “green” AuNPs (antimicrobial, anticancer, antiviral, etc.) and the possibilities of their further biomedical application are also discussed.

Properties of Gold Nanoparticles

Au NPs Biosynthesis

Chemical and physical methods were traditionally applied for the synthesis of gold nanoparticles. However, their use is accompanied by several drawbacks. For the chemical methods, the main disadvantages (for example, using Citrate reduction, 1-amino-2-naphthol-4-sulfonic acid (ANSA)) are supposed to use highly toxic reagents, environmental pollution, carcinogenic solvents, contamination of precursor. On the other hand, physical methods (for example, a laser irradiation method) require expensive equipment and high energy consumption. In addition, the low stability of AuNPs, difficulties in controlling crystal growth, and particle aggregation make the above methods less advantageous. Currently, the "green" method of AuNPs synthesis is attracting more attention due to the expansion of nanotechnology capabilities. The use of non-toxic agents without additional stabilizers and reducing agents, renewable materials, low energy expenditure, and ecological safety are the key factors of biological synthesis popularity. The living organisms' great diversity allows the production of specific, practice-oriented gold nanoparticles. Moreover, the biomolecules involved in the biosynthesis by bacteria, fungi, algae, and plants have a positive effect both on the synthesis process and on the resulting AuNPs.

The biosynthesis mechanism. The production of gold nanoparticles is a sufficiently simple process that does not require an increase in temperature and pressure. The general scheme assumes the following: the biological extract (bacterial, fungal, plant, etc.) is added dropwise to the HAuCI4 salt solution and mixed well to initiate the AuNPs synthesis process. The color change of the resulting solution indicates the nanoparticles production. Notwithstanding that many publications are illustrating the AuNPs synthesis using different organisms (bacteria, algae, fungi, plants), the mechanism of the biogenic process is not fully understood. The biosynthesis takes place in two steps: at the first, Au3+ is reduced to Au0, and at the second, agglomeration and stabilization result in the AuNPs formation (Figure 1). Interestingly, a wide variety of bio-compounds (enzymes, phenols, sugars, etc.) can participate both in the gold reduction and in the stabilization and capping of nanoparticles.

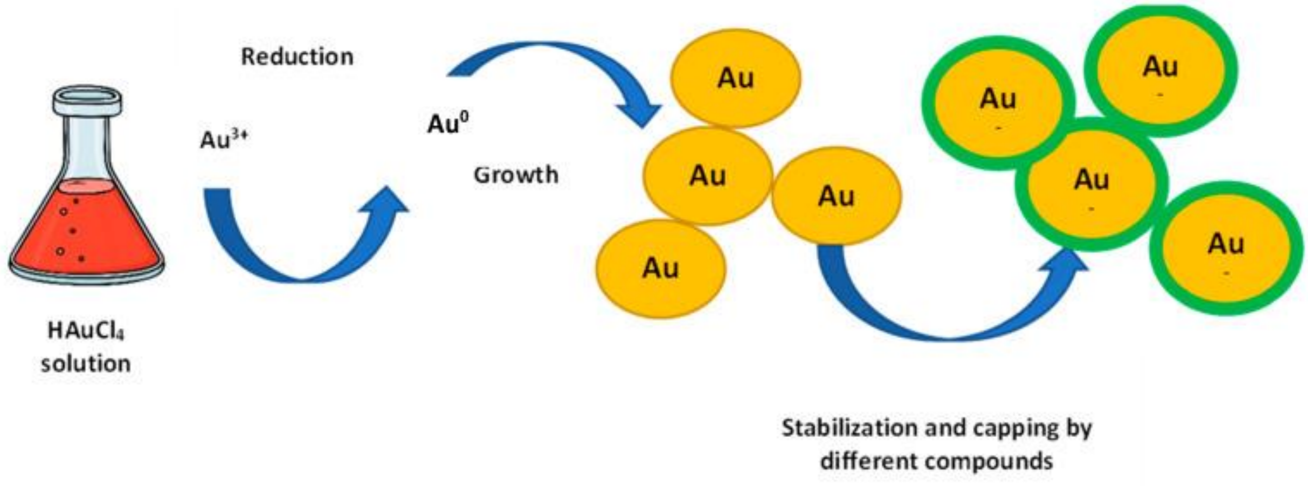
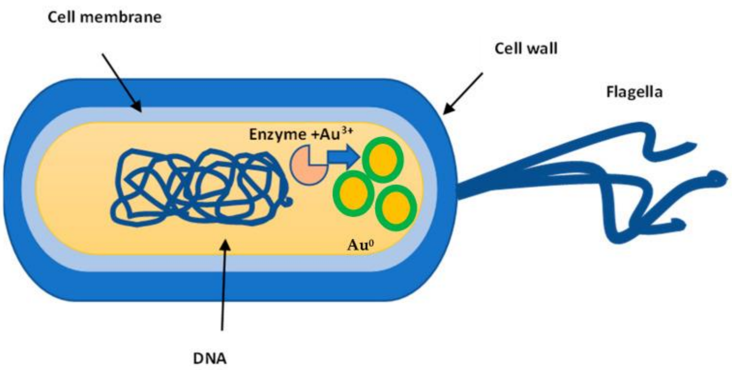


Figure 1

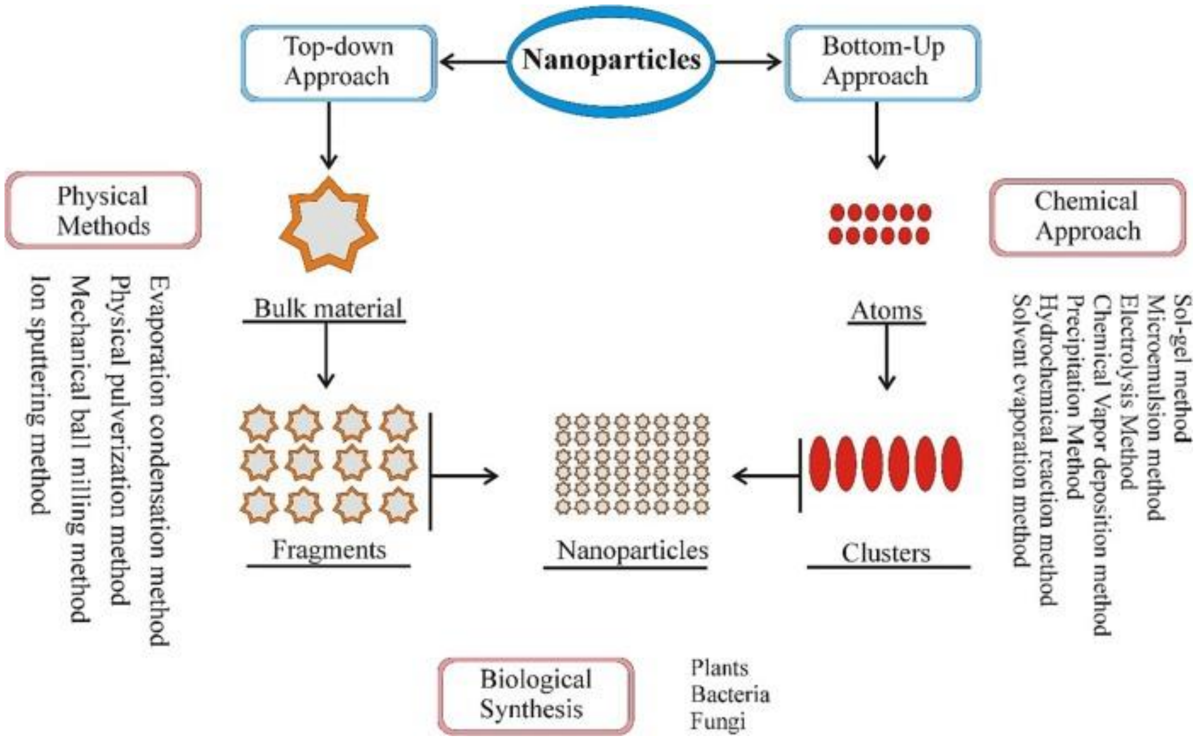
Mechanism of biosynthesis of Au NPs .

Biosynthesis by bacteria. Microorganisms can act as a potential "factory" for gold nanoparticles production. The biosynthesis mechanism was found to be both extracellular and intracellular for bacteria according to the location of AuNPs production (Figure 2) .



Synthesis of silica nanoparticles

A growing number of researchers are working on the synthesis of nanoscale metals using chemical, physical, and green synthesis methods. Synthesis techniques play a key role in controlling nanoparticle characteristics such as morphology, size, structure, and performance. Silica nanoparticles' electrochemical and physiochemical properties, as well as their optical and electrical properties, are also affected. The features of silica nanoparticles are sometimes retained after they precipitate out of suspensions when they are coated. As illustrated in Fig. 1, the different methodologies used to synthesize silica particles can be divided into two categories: top-down and bottom-up. The preparation methods of silica nanoparticles can be divided into physical methods and chemical methods and green synthetic methods.



Synthesis of silica nanoparticles by different approaches.

Physical methods

Synthesis of silica nanoparticles by physical methods involves applying external forces, such as heat or mechanical energy, to facilitate the formation of the particles. These methods include evaporation condensation method, physical pulverization method, mechanical ball milling method and ion sputtering method.

Evaporation and condensation method

The evaporative condensation method, which has a wide range of applications, involves heating the original material, evaporating it, and then condensing it with the addition of inert gas to achieve silica nanoparticles. The procedure is relatively simple, but the yield is very low, the equipment requirements are high, and the collection of silica nanoparticles during the actual operation process is also more complicated and challenging.

Physical crushing method

Using mechanical tension from outside the object being crushed, solid material particles are first deformed and then crushed to the desired size. This method will result in less pure and irregularly distributed silica nanoparticles when used in industrial production, thus it is important to consider the risk that the raw material may be accompanied by fire and explosion during the crushing process.

Mechanical ball milling method

This technique uses balls to crush reactants into the desired size using mechanical force. It is frequently used to reduce bulky solids into tiny particles. Continuous production can be done reasonably easily in industry, but typically the ball milling method requires a lot of time, making it unsuitable for laboratory research involving the creation of silica nanoparticles.

Ion sputtering technique

In this technique, an applied electric field is used to ionize argon or other inert gases, creating the glow discharge phenomena. The particles produced by the ionization then assault the target, sputtering out and depositing on it. The capacity to individually regulate ion energy, flux, species, and angle of incidence across a broad range is provided by ion beam sputtering.

Chemical methods

Chemical reactions are employed to synthesize silica nanoparticles using chemical methods. These methods include sol–gel method, microemulsion method, electrolysis method, chemical vapor deposition method, precipitation method, hydrothermal reaction method, solvent evaporation method and so on.

Sol-gel method

This method is the so-called “bottom-up” nanoparticle preparation method, that is, the process of preparing solid silica nanoparticles from small molecules. The process involves converting the monomer into a colloidal solution (Sol), which acts as a precursor to discrete particles or network polymers (or gels), typically precursors of metalloalkalks.. This method can produce silica nanoparticles with uniform particle size and high purity of the product.

Microemulsion method

this method is a simple and widely used controllable nanoparticle synthesis method developed in recent years, generally used to prepare silica nanoparticles is generally W/O type microemulsion (reversed-phase microemulsion), the “water core” as a reaction site for the generation of silica nanoparticles (often called “micro-reactor”), the product can only grow in a limited space because of the surfactant and cosurfactant bound so that the nanoparticle size can be controlled, the particle size of the silica nanoparticles prepared by this method is small, The distribution is uniform, and the product is easy to achieve high purification, and the obtained product monodispersity is good.

Electrolysis method

The electrolysis method usually includes two methods: aqueous solution and molten salt electrolysis. Electrolysis is a technique that uses direct current to drive non-spontaneous chemical reactions that separate elements from natural sources such as ores. This method can prepare many high-purity metal ultrafine particles that cannot be prepared or are difficult to prepare by other general methods.

Chemical vapor deposition

This method refers to the process of generating silica nanoparticles through chemical reactions on the substrate under heating conditions. This method is widely used in the preparation of silica nanoparticles, and in theory it is simple to operate, easy to obtain products, and its particle size distribution is narrow.

Precipitation method

In aqueous solution, precipitation is the process of converting dissolved raw materials from supersaturated solution into insoluble solids, and the solids formed are called precipitates, and then silica nanoparticles are obtained after a series of post-treatment. It can be divided into direct precipitation method, co-precipitation method and uniform precipitation method.

Hydrothermal reaction method

hydrothermal reaction method is a method of synthesizing silica nanoparticles by using the interaction between raw materials in aqueous solution under high temperature and high-pressure conditions, and the advantages of this method are good product dispersion, easy size control and high purity.

Solvent evaporation method

solvent evaporation method is a crystal growth method that carries out high-temperature evaporation treatment of the solvent to make the raw material in a supersaturated state, so as to provide sufficient driving force in the growth process of silica nanoparticles, and the silica nanoparticles prepared by solution evaporation are small in size and good in dispersion, but the operation of the synthesis process is very difficult.

Iron oxide nanoparticle

Iron oxide nanoparticles are iron oxide particles with diameters between about 1 and 100 nanometers. The two main forms are composed of magnetite (Fe3O4) and its oxidized form maghemite (γ-Fe2O3). They have attracted extensive interest due to their superparamagnetic properties and their potential applications in many fields (although cobalt and nickel are also highly magnetic materials, they are toxic and easily oxidized) including molecular imaging.

Structure

Magnetite has an inverse spinel structure with oxygen forming a face-centered cubic crystal system. In magnetite, all tetrahedral sites are occupied by Fe^{3+} and octahedral sites are occupied by both $Fe^{3+}$and Fe^{2+}. Maghemite differs from magnetite in that all or most of the iron is in the trivalent state (Fe^{3+}) and by the presence of cation vacancies in the octahedral sites. Maghemite has a cubic unit cell in which each cell contains 32 oxygen ions, $21^{1/3}$ Fe^{3+}ions and 2⅔ vacancies. The cations are distributed randomly over the 8 tetrahedral and 16 octahedral sites.

Synthesis

The preparation method has a large effect on shape, size distribution, and surface chemistry of the particles. It also determines to a great extent the distribution and type of structural defects or impurities in the particles. All these factors affect magnetic behavior. Recently, many attempts have been made to develop processes and techniques that would yield "monodisperse colloids" consisting of nanoparticles uniform in size and shape.

Coprecipitation

By far the most employed method is coprecipitation. This method can be further divided into two types. In the first, ferrous hydroxide suspensions are partially oxidized with different oxidizing agents. For example, spherical magnetite particles of narrow size distribution with mean diameters between 30 and 100 nm can be obtained from a Fe(II) salt, a base and a mild oxidant (nitrate ions).The other method consists in ageing stoichiometric mixtures of ferrous and ferric hydroxides in aqueous media, yielding spherical magnetite particles homogeneous in size.[10] In the second type, the following chemical reaction occurs:

$$2\ Fe^{3+} + Fe^{2+} + 8\ OH^- \rightarrow Fe_3O_4\downarrow + 4\ H_2O$$

Optimum conditions for this reaction are pH between 8 and 14, Fe^{3+}/Fe^{2+} ratio of 2:1 and a non-oxidizing environment. Being highly susceptibile to oxidation, magnetite (Fe_3O_4) is transformed to maghemite (γFe_2O_3) in the presence of oxygen:

$$2\ Fe_3O_4 + O_2 \rightarrow 2\ \gamma Fe_2O_3$$

The size and shape of the nanoparticles can be controlled by adjusting pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), or the Fe(II)/Fe(III) concentration ratio.

Microemulsions

A microemulsion is a stable isotropic dispersion of 2 immiscible liquids consisting of nanosized domains of one or both liquids in the other stabilized by an interfacial film of surface-active molecules. Microemulsions may be categorized further as oil-in-water (o/w) or water-in-oil (w/o), depending on the dispersed and continuous phases. Water-in-oil is more popular for synthesizing many kinds of nanoparticles. The water and oil are mixed with an amphiphillic surfactant. The surfactant lowers the surface tension between water and oil, making the solution transparent. The water nanodroplets act as nanoreactors for synthesizing nanoparticles. The shape of the water pool is spherical. The size of the nanoparticles will depend on size of the water pool to a great extent. Thus, the size of the spherical nanoparticles can be tailored and tuned by changing the size of the water pool.

Aluminium oxide nanoparticle

Nanosized aluminium oxide (nanosized alumina) occurs in the form of spherical or nearly spherical nanoparticles, and in the form of oriented or undirected fibers.

Properties

Properties, of the final material, defined as the set of properties of the solid Aluminium oxide and specific properties of nanostructures.

Properties of nanoscale colloidal alumina particles:

Small diameter of the particles/fibers (2–10 nm)

High specific surface area (>100 m2/g)

High defectiveness of the material surface and specific structure of the nanoparticles (the volume and size of pores, degree of crystallinity, phase composition, structure, and composition of the surface — modification possibility)

Properties of the nanoscale fibers of aluminium oxide:

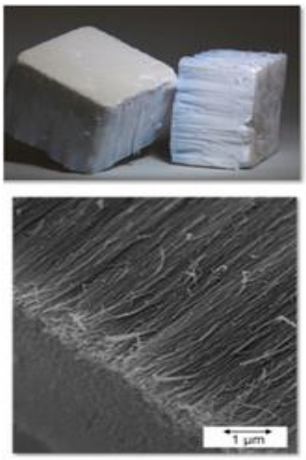
The ratio of length-diameter about 20,000,000:1

A high degree of orientation of the fibers

The weak interaction of the fibers among themselves

Absence of surface pores

High surface concentration of hydroxyl groups



Methods of obtaining powders of aluminium oxide nanometer scale

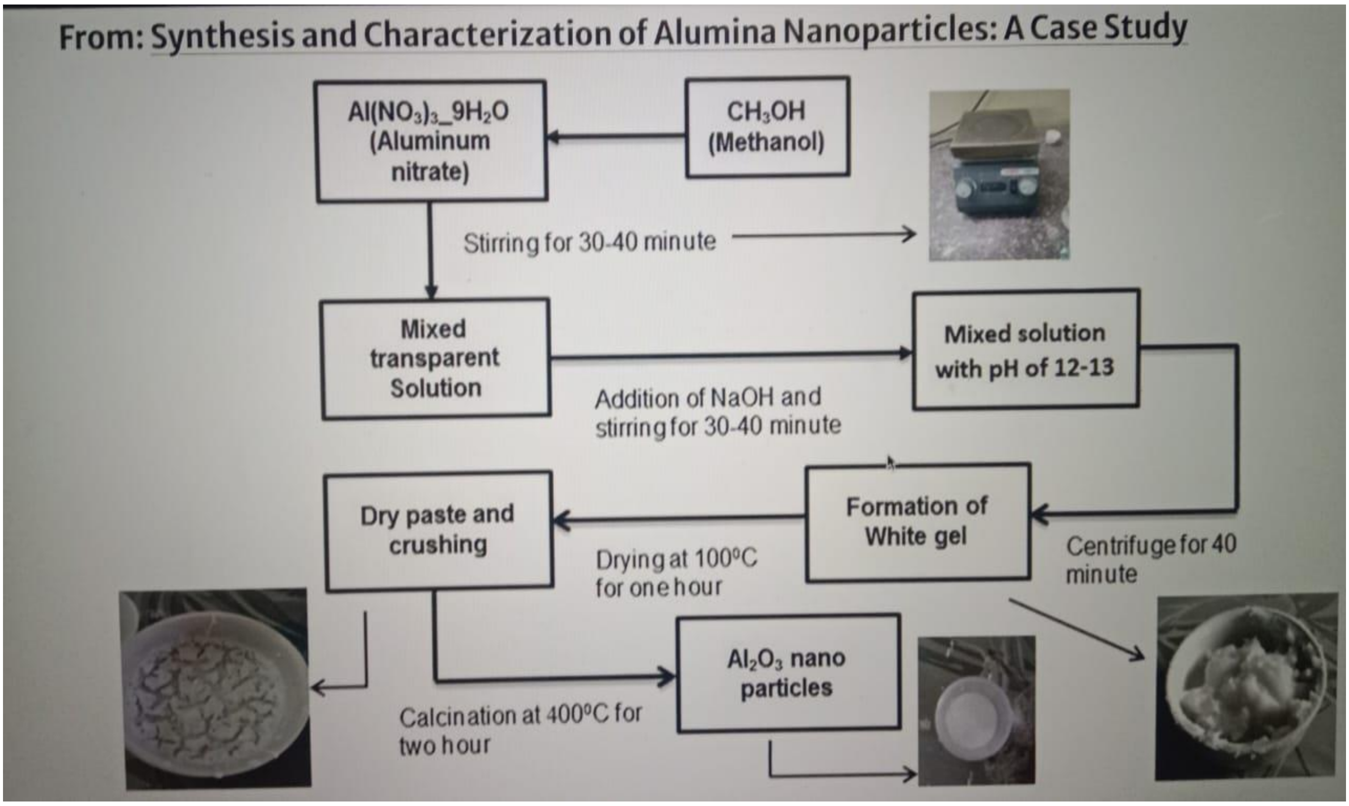
Industrially obtained alumina nano fibers of Nafen brand

1. Grinding powder alumina particles of a nanometer level (for example, 10-50 nm). For example, using a planetary mill using grinding bodies of size less than 0.1 µm.
2. The decomposition of fresh chemically-synthesized AlOOH or Al(OH)3 to aluminium oxide in the rapid achievement of the temperature of decomposition 175 °C and use for it the pressure of 5 bars within thirty minutes. The sooner of the temperature of decomposition of the hydroxo-compounds of aluminium is achieved, the smaller the resulting particles nano oxide in size.

Synthesis of Al_2O_3 NPs

Synthesis of aluminum nitrate (Al (NO3)3_9H2O), methanol (CH3OH), and sodium hydroxide (NaOH) was done in a magnetic stirrer (make: REMI 2 MLH) and centrifuge setup (Made: REMI R-303) with a maximum speed of 3800 rpm. Phase identification of the formed particles was performed using X-ray diffraction (XRD) analysis (make: Bruker, Model No.: D2 Phaser 2nd Gen). The microstructural analysis of the developed sample was performed with the scanning electron microscope (SEM) (make: FEG quanta 250). The Zetasizer ZS90 (Malvern Instruments Ltd.) was applied for the measurement of hydrodynamic particle size of the developed nanoparticles. The Zetasizer works on the principle of dynamic light scattering to measure the particles suspended under different suspension medium. Here, distilled water (DI water) was used for the dissolution medium for the alumina nanoparticles. The mechanical-type ball milling was employed for the removal of particle agglomeration after the synthesis process. The milling was performed for 2 h with ball-to-powder ratio 2:1 with a speed of 100 rpm at normal atmospheric medium in room temperature.

In the beginning, the aluminum nitrate ($Al\ (NO_3)_3\_9H_2O$) of purity (assay > 99%) 25 grams and methanol (CH_3OH) were mixed properly with magnetic stirrer to get a transparent solution. The premixed sodium hydroxide (NaOH) solution is then mixed slowly to obtain a pH in the range of 10–11. The pH of 10–11 indicates the formation of aluminum hydroxide mixture. For the proper distribution of sodium hydroxide and premixed solution is stirrer for 1 h. While stirring the solution, the aluminum hydroxide particles settled down at the bottom of the jar. The obtained mixture is then centrifuged for 30 to 40 min to get white colloidal suspension of alumina solution. Before the calcination process, the obtained colloidal suspension is heated in the furnace at a temperature of 250 °C for 1 h for the drying purpose and the final calcinations are done at a temperature of 400 and 600 °C with a heating rate of 5 °C per minute for 2 h and then being cooled slowly up to room temperature. The schematic representation of the generation of the alumina nanoparticles is shown in Fig. 1.



UNIT - 4

Electrical Properties of nanomaterials

The properties like conductivity or resistivity are come under category of electrical properties. These properties are observed to change at nanoscale level like optical properties. The examples of the change in electrical properties in nanomaterials are:

1) Conductivity of a bulk or large material does not depend upon dimensions like diameter or area of cross section and twist in the conducting wire etc. However it is found that in case of carbon nanotubes conductivity changes with change in area of cross section.

2) It is also observed that conductivity also changes when some shear force (in simple terms twist) is given to nanotube.

3) Conductivity of a multiwalled carbon nanotube is different than that of single nanotube of same dimensions.

4) The carbon nanotubes can act as conductor or semiconductor in behaviour but we all know that large carbon (graphite) is good conductor of electricity.

These are the important electrical properties of nanomaterials with their examples.

Electrical resistivity and conductivity

Electrical resistivity (also called volume resistivity or specific electrical resistance) is a fundamental specific property of a material that measures its electrical resistance or how strongly it resists electric current. A low resistivity indicates a material that readily allows electric current. Resistivity is commonly represented by the Greek letter ρ (rho). The SI unit of electrical resistivity is the ohm-metre (Ωm). For example, if a 1 m^3 solid cube of material has sheet contacts on two opposite faces, and the resistancebetween these contacts is 1 Ω, then the resistivity of the material is 1 Ωm..

Electrical conductivity (or specific conductance) is the reciprocal of electrical resistivity. It represents a material's ability to conduct electric current. It is commonly signified by the Greek letter σ (sigma), but κ (kappa) (especially in electrical engineering) and γ (gamma) are sometimes used. The SI unit of electrical conductivity is siemens per metre (S/m). Resistivity and conductivity are intensive properties of materials, giving the opposition of a standard cube of material to current. Electrical resistance and conductance are corresponding extensive properties that give the opposition of a specific object to electric current.

Causes of conductivity

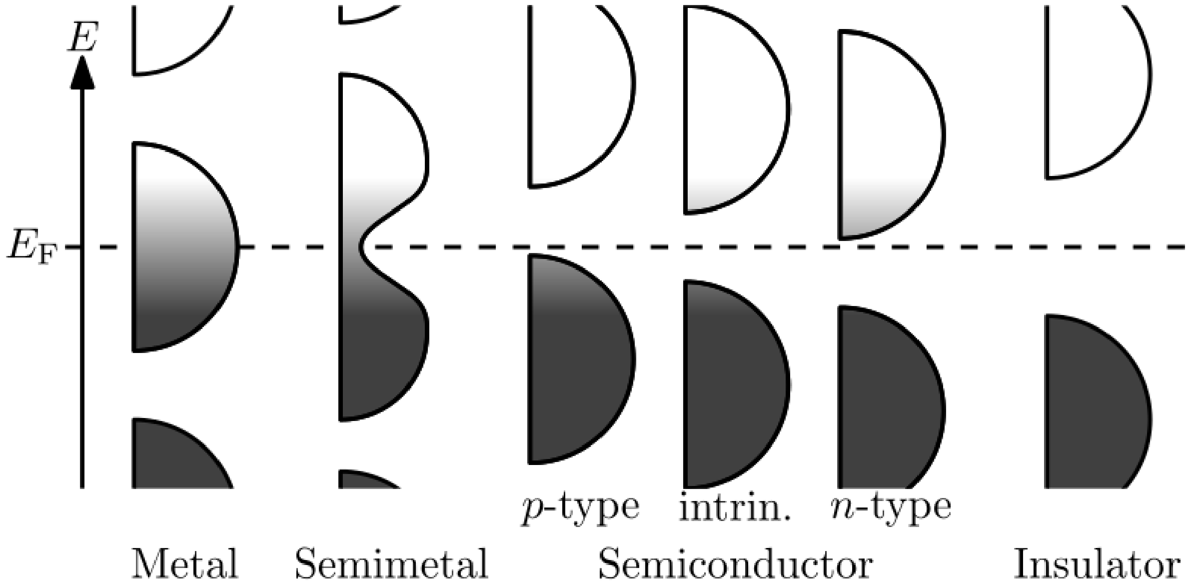
Band theory simplified

According to elementary quantum mechanics, an electron in an atom or crystal can only have certain precise energy levels; energies between these levels are impossible. When a large number of such allowed levels have close-spaced energy values – i.e. have energies that differ only minutely – those close energy levels in combination are called an "energy band". There can be many such energy bands in a material, depending on the atomic number of the constituent atoms and their distribution within the crystal.

The material's electrons seek to minimize the total energy in the material by settling into low energy states; however, the Pauli exclusion principle means that only one can exist in each such state. So the electrons "fill up" the band structure starting from the bottom. The characteristic energy level up to which the electrons have filled is called the Fermi level. The position of the Fermi level with respect to the band structure is very important for electrical conduction: Only electrons in energy levels near or above the Fermi level are free to move within the broader material structure, since the electrons can easily jump among the partially occupied states in that region. In contrast, the low energy states are completely filled with a fixed limit on the number of electrons at all times, and the high energy states are empty of electrons at all times.

Electric current consists of a flow of electrons. In metals there are many electron energy levels near the Fermi level, so there are many electrons available to move. This is what causes the high electronic conductivity of metals.

An important part of band theory is that there may be forbidden bands of energy: energy intervals that contain no energy levels. In insulators and semiconductors, the number of electrons is just the right amount to fill a certain integer number of low energy bands, exactly to the boundary. In this case, the Fermi level falls within a band gap. Since there are no available states near the Fermi level, and the electrons are not freely movable, the electronic conductivity is very low.



Resistivity and conductivity of various materials

- A conductor such as a metal has high conductivity and a low resistivity.
- An insulator like glass has low conductivity and a high resistivity.
- The conductivity of a semiconductor is generally intermediate, but varies widely under different conditions, such as exposure of the material to electric fields or specific frequencies of light, and, most important, with temperature and composition of the semiconductor material.

In semiconductors and insulators

Main articles: Semiconductor, Insulator (electricity), and Charge carrier density

In metals, the Fermi level lies in the conduction band (see Band Theory, above) giving rise to free conduction electrons. However, in semiconductors the position of the Fermi level is within the band gap, about halfway between the conduction band minimum (the bottom of the first band of unfilled electron energy levels) and the valence band maximum (the top of the band below the conduction band, of filled electron energy levels). That applies for intrinsic (undoped) semiconductors. This means that at absolute zero temperature, there would be no free conduction electrons, and the resistance is infinite. However, the resistance decreases as the charge carrier density (i.e., without introducing further complications, the density of electrons) in the conduction band increases. In extrinsic (doped) semiconductors, dopant atoms increase the majority charge carrier concentration by donating electrons to the conduction band or producing holes in the valence band. (A "hole" is a position where an electron is missing; such holes can behave in a similar way to electrons.) For both types of donor or acceptor atoms, increasing dopant density reduces resistance. Hence, highly doped semiconductors behave metallically. At very high temperatures, the contribution of thermally generated carriers dominates over the contribution from dopant atoms, and the resistance decreases exponentially with temperature.

Superconductivity

The electrical resistivity of a metallic conductor decreases gradually as temperature is lowered. In normal (that is, non-superconducting) conductors, such as copper or silver, this decrease is limited by impurities and other defects. Even near absolute zero, a real sample of a normal conductor shows some resistance. In a superconductor, the resistance drops abruptly to zero when the material is cooled below its critical temperature. In a normal conductor, the current is driven by a voltage gradient, whereas in a superconductor, there is no voltage gradient and the current is instead related to the phase gradient of the superconducting order parameter. A consequence of this is that an electric current flowing in a loop of superconducting wire can persist indefinitely with no power source.

- In a class of superconductors known as type II superconductors, including all known high-temperature superconductors, an extremely low but nonzero resistivity appears at temperatures not too far below the nominal superconducting transition when an electric current is applied in conjunction with a strong magnetic field, which may be caused by the electric current. This is due to the motion of magnetic vortices in the electronic superfluid, which dissipates some of the energy carried by the current. The resistance due to this effect is tiny compared with that of non-superconducting materials, but must be taken into account in sensitive experiments. However, as the temperature decreases far enough below the nominal superconducting transition, these vortices can become frozen so that the resistance of the material becomes truly zero.

classification of materials based on conductivity

Nanomaterials can be classified in various ways.

On the basis of electrical properties, they can be classified as

Conducting (metallic)
Superconductivity (semiconductor)
Non-conducting (insulators)

On the basis of magnetic properties, they can be classified as:

Magnetic nanomaterials
Non-magnetic nanomaterials

The most commonly adopted method of classification is based on their dimension. On the basis of dimensions, they are classified as:

Zero-dimensional nanomaterials:

Such materials have all three length scales Lx (length along X-axis), Ly (length along Y-axis, and Lz (length along Z-axis) in the nanoscopic range. Examples: Quantum dots, metallic nanoclusters, nanosphere, nanorods, nanocubes, etc.

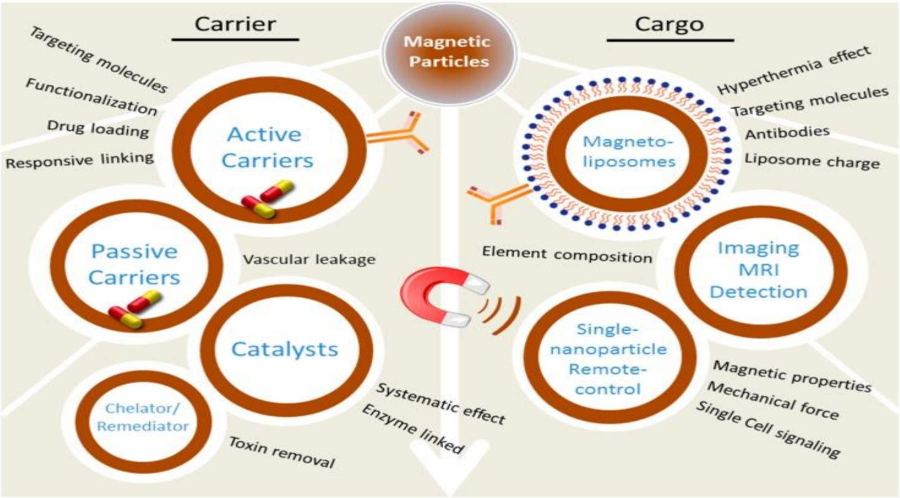
One-dimensional nanomaterials: In such materials, one of the dimensions is out of the nanoscopic range. Nanowires, nanotubes, etc. are some examples of one-dimensional nanomaterials.

Two-dimensional nanomaterials: In these materials, any two dimensions are out of the nanoscopic range. Examples: Nanofilms, nanosheets, nano-coatings, and so on.

Three-dimensional nanomaterials: In these materials, all three dimensions are out of the nanoscopic range.

Classification of Materials based on Magnetic Nanoparticles:

Magnetic Nanoparticles Design



From Physics and Chemistry to Nanomedicine

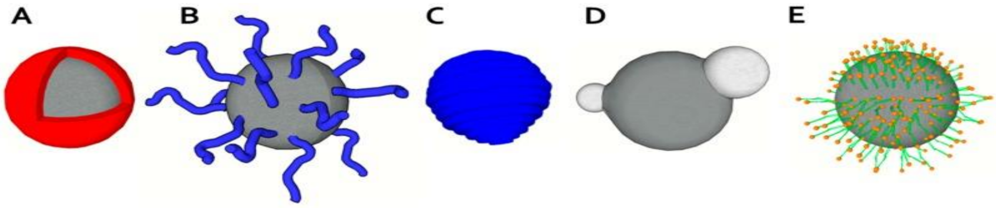
The design of magnetic nanoparticles for applications in nanomedicine is not easily implemented. There are many factors that should be taken into consideration at each step of the synthesis. These factors can dramatically change the expected outcome, yet they can be optimized in the early design steps. Both physical and chemical properties of particles can be controlled to fit various applications. Generally, magnetic nanoparticles are applied in nanomedicine and particularly in the field of cancer treatment. Magnetic nanoparticle devices or magnetic composites are attractive for drug delivery due to their ability to respond to exogenous stimuli via a magnetic field. This allows controlling drug release in spatial, temporal, and dosage controlled fashions. Nanocarriers can reach the tumor environment either passively through the leaky vasculature environment or actively using selective ligands. Magnetic nanoparticles were used as a drug carrier for doxorubicin (an anthracycline antibiotic with antineoplastic activity) encapsulated into the apoferritin for targeted cancer therapy. An MRI-based method was employed to control doxorubicin delivery via magnetic particles targeted using integrin ligands. MRI applications also include MRI-guided cell replacement therapy and MRI-based imaging of cancer-specific gene delivery. A liposome-based nanodevice used magnetic particles as carriers for DNA and drugs. Paramagnetic nano- and microparticles were used for diagnostic detection of cancer biomarkers, viruses, and bacteria.

Physical Design

Magnetic properties are important for nanoparticles employed in externally controlled hyperthermia or heat induced by generated magnetic fields. The magnetic force can be utilized for movement and transportation of biological objects. The ability to drive a mechanical force within the cells is demonstrated to be useful for molecular level cell-signaling and controlling of cell fate. These capabilities have been used in applications of drug release, disease treatment and remote-control of single cell functions. The size of magnetic nanoparticles is one of the major physical properties that can be utilized to tailor other properties such as magnetism and surface area. Controlled size synthesis of iron oxide nanoparticles has been explored by many researchers. For example, organic-phase synthesis has been used to produce particles smaller than 20 nanometers. A later size increase was controlled by a seed mediated growth. The major factors affecting particle size in the first step include the boiling point of solvent and reaction time. Researchers coat particles to produce a stable system. The surface charge plays a role in maintaining repulsion between particles; however, it is important to optimize the ratio of inert to reactive compounds on the surface to ensure colloidal stability of the nanoparticles. several elements that can be fabricated with iron oxide to achieve new physical and chemical characteristics. For instance, gold-fabricated magnetic nanoparticles show desired magnetic as well as optical (from gold) characteristics. Metallic iron and cobalt-fabricated magnetic nanoparticles allow higher magnetization, yet the former requires coating to protect it from oxidation. Platinum-fabricated magnetic nanoparticles show great potential as contrast agents for both MRI and X-ray computed tomography (CT). On the other hand, porous magnetic nanoparticles have the same characteristics of solid nanoparticles yet they offer the additional opportunity to store and release drugs.

Magnetic Nanoparticles Synthesis

From the chemical point of view, materials commonly used for manufacturing magnetic portion can be divided into materials based on compounds (usually oxides) of iron, cobalt, nickel and some other elements usually combining several metals. These combined materials usually include materials based on copper, zinc, strontium, and barium. Magnetic nanoparticles also include the group of metallic nanoparticles and nanoalloys. Naturally, surface coatings of nanoparticles are an integral part of their synthesis. Finally, the choice of core nature and surface modification is managed with regard to the intended use of the particles . The use of bifunctional linkers (like avidin-biotin technique) is useful for attaching functional ligands with desired properties (“click” chemistry) and for further improving magnetic nanoparticle features. Other examples of targeted surface modification of magnetic nanoparticles are those with the intended application potential for DNA detection or imaging techniques, typically X-ray Computed Tomography or MRI. For surface modification of such nanoparticles several concepts using different metals such gadolinium or hybrid materials were used. Moreover, magnetic nanoparticles with magnetic coating were described. Several basic concepts of coating and functionalization of surface exist, including polymeric coating, liposomes and micelles utilization, and core-shell structures (Figure 2).



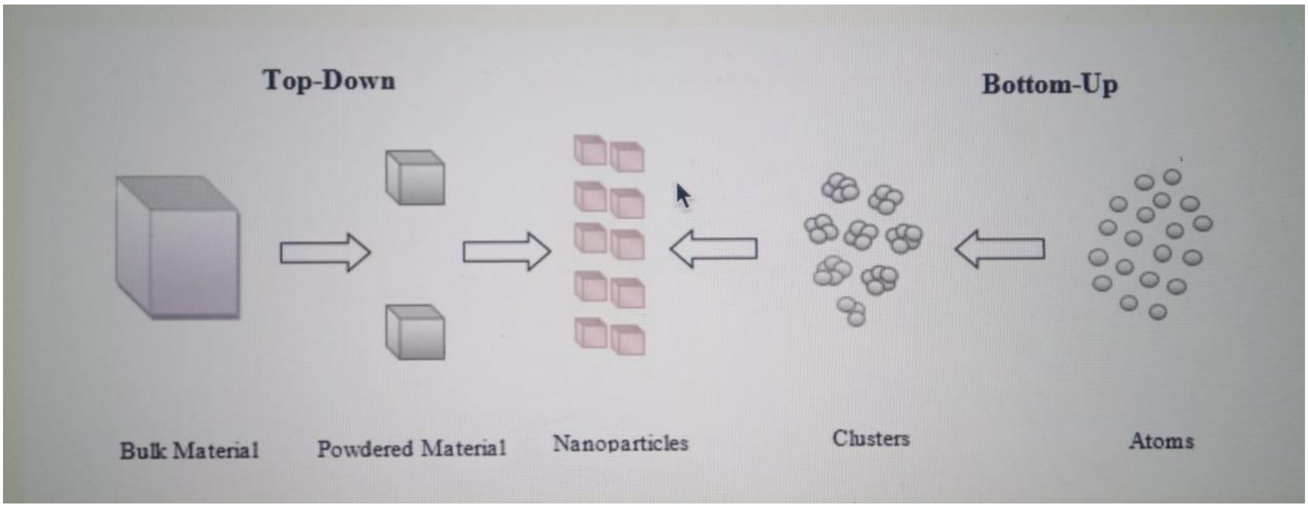
Classification of Materials based on Electronic Nanoparticles:

Nanotechnology approaches for nanoelectronics

There are mainly two types of approaches for the synthesis of nanomaterials used in nanoelectronics:

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

Top-down approach discusses about the slicing or successive cutting of a bulk material in order to get nano-dimensional particles. Bottom-up approach refers to the stockpile of a material from the bottom: atom by atom, molecule by molecule, or cluster by cluster. Attrition or milling is a characteristic top-down method in the production of nanoparticles, while the colloidal dispersion is a good illustration of bottom-up approach in the synthesis of nanoparticles. The major difficulty with top-down approach is the defectiveness of surface structure and significant crystallographic impairment of the processed patterns. These deficiencies lead to extra challenges in the device design and construction. But this approach leads to the bulk fabrication of nanomaterial. Regardless of the flaws produced by top-down approach, they will continue to play an imperative role in the production of nanostructures. When structures plunge into a nanometer scale, there is a minute chance for top-down approach. All the tools we have possessed are too large to deal with such miniature subjects. Bottom-up approach also assures a better chance to attain nanostructures with less defects and more consistent chemical composition. On the contrary, top-down approach presumably introduces internal stress, additionally to surface defects and contaminations.



Classification of magnetic phenomena

(mention same in magnetic properties)

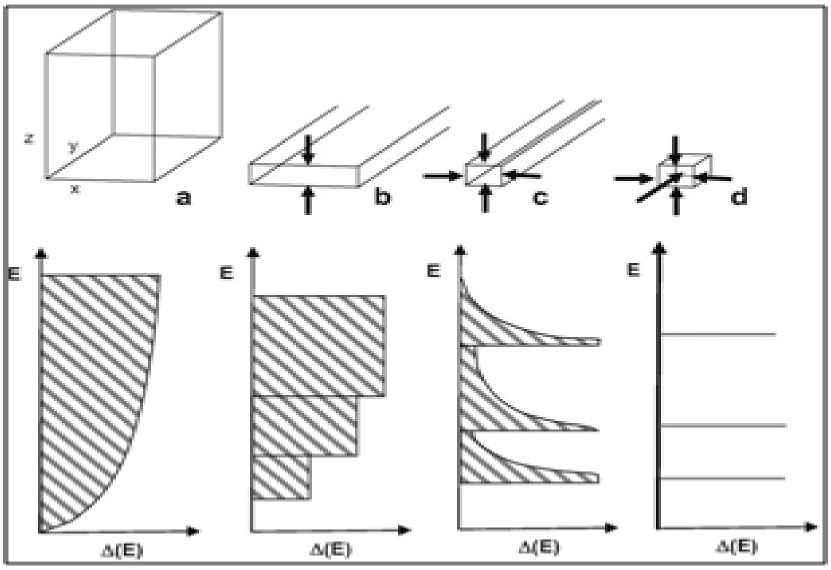
Semiconductor Nanomaterials, Methods and Applications:

Semiconductor Nanoparticles

Semiconductor nanocrystals (NCs) are made from a variety of different compounds. They are referred to as II-VI, III-V or IV-VI semiconductor nanocrystals, based on the periodic table groups into which these elements are formed. For example, silicon and germanium are group IV, GaN, GaP, GaAs, InP and InAs are III-V, while those of ZnO, ZnS, CdS, CdSe and CdTe are II-VI semiconductors.

Classifications of Semiconductor Nanostructures

In nanocrystalline materials, the electrons are confined to regions having one, two or three dimensions (Figure 1) when the relative dimension is comparable with the de Broglie wavelength. For a semiconductor like CdSe, the de Broglie wavelength of free electron is around 10 nm. The nanostructures of semiconductor crystals having the zdirection below this critical value (thin film, layer structure, quantum well) are defined as 2D nanostructures. When the dimension both in the x and z direction is below this critical value (linear chain structure, quantum wire) the nanostructures are defined as 1D and when the y direction is also below this threshold (cluster, colloid, nanocrystal, quantum dot) it is referred to as 0D.



Zero Dimensional (0D) Nanostructures

In the early stages of research on nano-building block synthesis, zero dimensional shapes were regarded as the most basic and symmetric, including spheres and cubes. Several semiconductor nanocrystals have been grown from the ageing processes of ionic precursors inside organic micelles. However, nanocrystals obtained by this method have relatively poor crystallinity or polydispersity in their size. As an alternative way to solve these problems, a thermal decomposition method of organometallic precursors under hot organic solution was adopted. At first, Chestnoy et al (1986) synthesized various II–VI semiconductor nanospheres with high colloidal stability, using coordinating solvents (e.g., 4-Ethylpyridine), but the size tunability and monodispersity of the nanocrystals obtained, were still poor. Murray et al (1993) successfully developed a more advanced methodology to prepare CdSe nanocrystals of varied sizes via the method of injecting a precursor solution containing dimethylcadmium and trioctylphosphine selenide into a hot trioctylphosphine oxide (TOPO) solution. The size of nanocrystals varied from 1.2 to 12 nm with high monodispersity and crystallinity; the nanocrystals obtained were highly soluble in various organic solvents. Optical spectra clearly exhibited size dependent quantum confinement effects, indicating the high monodispersity and high crystallinity of nanocrystals.

Quasi One Dimensional (1D) Nanostructures

The term quasi one dimensional nanostructures is used, because the dimensions are often larger than the indicated threshold, although elongation along one main axis still exists. When the diameter of the nanorod, nanowire or nanotube becomes smaller, there is often a significant change in the properties with respect to crystalline solids or even two dimensional systems. A bismuth nanowire is an excellent example, which transforms into a semiconductor, as the wire diameter becomes smaller. By controlling the growth variables such as temperature, the choice of capping molecules, precursor concentrations, crystalline phases of the nuclei and the choice of the regime between kinetically controlled and thermodynamically controlled growth, various nano-building blocks with multi-dimensionalities have been produced. To generate one dimensional nanocrystals, researchers have explored the ‘one step in situ synthesis’ of 1D nanorods, utilizing methods similar to those for the well studied spherical nanocrystals. For example, the use of binary capping molecules such as TOPO and hexylphosphonic acid (HPA) was effective for the generation of shape anisotropy in CdSe along with the intrinsic hexagonal structure nature.

The non-hydrolytic high temperature injection method can be effectively utilized, for high quality nanorods synthesis. III–V Semiconductor one-dimensional nanocrystals including InP, GaAs and InAs can also be synthesized via solution–liquid–solid (SLS) processes. In the case of group IV semiconductor systems, it is extremely difficult to obtain nanorods by typical solution based precursor injection methods, due to their highly covalent character. In contrast, Morales and Lieber (1998) used gas phase synthesis such as chemical vapor deposition, where one-dimensional silicon & germanium wires can be easily obtained on a substrate, using vapour–liquid–solid (VLS) growth mechanisms.

Transition metal oxides consist of an important group of materials used in white pigment, electronic ceramics, cosmetics, support in catalysis, and as photocatalysts. Nanostructured titania are of particular interest, with potential applications as solar cell materials. Chemseddine and Moritz (1999) demonstrated elongated TiO_2 nanocrystals synthesized by hydrolysis and polycondensation of titanium alkoxide[Ti(OR)4], in the presence of tetramethyl ammonium hydroxide, as a stabilizer and reaction catalyst. Penn and Banfield (1999) also reported naturally aligned titania nanocrystals under hydrothermal conditions, by adopting an oriented attachment mechanism into the nanocrystal development. The hydrothermal treatment of titanium alkoxide precursors produces diamond shaped anatase titania nanocrystals.

Two Dimensional (2D) Nanostructures

The family of 2D nanosystems encompasses all those systems that exhibit two dimensions exceeding the third one. However, the number and variety of inorganic nano objects belonging to this family is far lower. with respect to 0D and 1D nanosystems. Indeed, nature tends to organize materials in a three dimensional way. 2D assemblies usually do not grow except under special and controlled experimental conditions. The main synthesis methodologies of 2D nanostructures can be summarized as follows: (i) anisotropic crystal growth, (ii) surfactant-assisted synthesis and (iii) the assembly of simpler 0D or 1D nanosystems.

All 2D flat nanocrystals possess an overall size in the order of 10 nm. Such a size limitation is pursued, in order to prevent the growth along only one specific direction, leading to a 1D system. The synthesis of two dimensional nanocrystals is achieved by the self-assembly of solutions and the constituting elements of these systems are usually metals. Discoidal nanocrystals are typical flat building blocks. They are typically obtained by surfactant assisted synthesis, or anisotropic crystal growth passing through colloidal systems.

2D prismatic shapes can be prepared by photoinduced shape changes. Silver nanoprisms are synthesized by the irradiation of Ag nanospheres with visible light together with an unexpected colour change (from yellow, which is a characteristic surface plasmon band of the spherical particle, to green and finally blue), and a marked change in shape, from nanospheres into nanoprisms. Nanosized prisms from transition metals, such as Pd or Ni or from semiconductors, such as CdS, were also reported. The triangular nanocrystals of CdS turned out to be flat and the crystalline phase was proved to be a hexagonal wurtzite structure.

Three Dimensional (3D) Nanosystems

Objects having either an overall size in the non-nanometric range (mainly in micrometer or millimeter range), but displaying nanometric features (such as nanosized confinement spaces) or resulting from the periodic arrangement and assembly of nanosized building blocks, can be classified as ‘3D nanosystems’. They exhibit different molecular and bulk properties. In particular, 3D nanocrystals superstructures are prepared by assembling basic nanosized building blocks such as; 0D spheres 1D rods and 2D plates, to have bigger sized structures of innovative shapes. On the contrary, nanoporous materials are made with a ‘complementary’ approach, since a system of nanosized void pores is obtained within a continuous bulk material. Simpler nanosystems can otherwise be used as ‘artificial atoms’ to build three-dimensional superstructures, such as superlattices in which a given nanoparticle is in a predictable and periodic lattice point. For this purpose, 0D nanosystems (and mainly nanoparticles) are the best choice, since they can easily lead to the highly ordered 3D closely packed patterns, kept together by chemical interparticle interactions. Superlattices of CdSe nanocrystals can be obtained, using a selective evaporation technique from a solution of octane & octanol containing spherical CdSe nanocrystals. Such superstructures display a face centered cubic packing of CdSe nanocrystals. They exhibit novel optical properties which are different from those of diluted CdSe nanospheres in solution.

n-type and p-type Semiconductor – Definition

In general, there are two types of dopant atoms resulting in two types of extrinsic semiconductors. These dopants that produce the desired controlled changes are classified as either electron acceptors or donors and the corresponding doped semiconductors are known as:

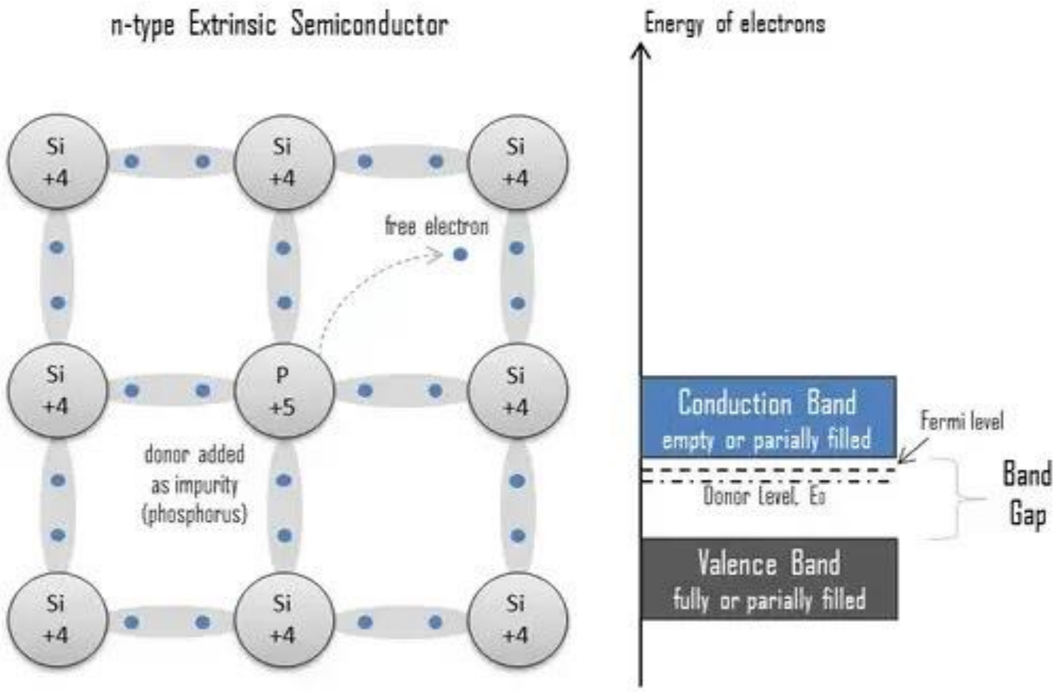
n-type Semiconductors.

p-type Semiconductors.

Extrinsic semiconductors are components of many common electrical devices, as well of many detectors of ionizing radiation. For these purpose, a semiconductor diode (devices that allow current in only one direction) usually consists of p-type and n-type semiconductors placed in junction with one another.

n-type Semiconductors

An extrinsic semiconductor which has been doped with electron donor atoms is called an n-type semiconductor, because the majority of charge carriers in the crystal are negative electrons. Since silicon is a tetravalent element, the normal crystal structure contains 4 covalent bonds from four valence electrons. In silicon, the most common dopants are group III and group V elements. Group V elements (pentavalent) have five valence electrons, which allows them to act as a donor. That means, the addition of these pentavalent impurities such as arsenic, antimony or phosphorus contributes free electrons, greatly increasing the conductivity of the intrinsic semiconductor. For example, a silicon crystal doped with boron (group III) creates a p-type semiconductor whereas a crystal doped with phosphorus (group V) results in an n-type semiconductor.



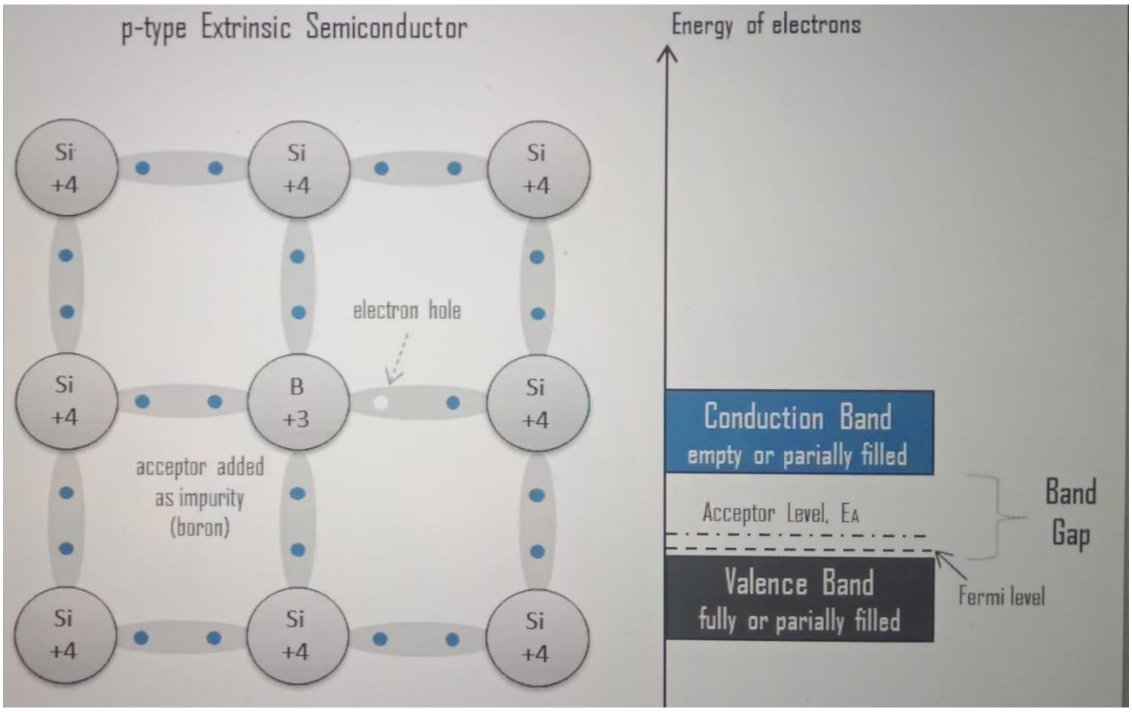
The conduction electrons are completely dominated by the number of donor electrons. Therefore:

The total number of conduction electrons is approximately equal to the number of donor sites, n≈ND.

Charge neutrality of semiconductor material is maintained because excited donor sites balance the conduction electrons. The net result is that the number of conduction electrons is increased, while the number of holes is reduced. The imbalance of the carrier concentration in the respective bands is expressed by the different absolute number of electrons and holes. Electrons are majority carriers, while holes are minority carriers in n-type material.

p-type Semiconductors

An extrinsic semiconductor which has been doped with electron acceptor atoms is called a p-type semiconductor, because the majority of charge carriers in the crystal are electron holes (positive charge carriers). The pure semiconductor silicon is a tetravalent element, the normal crystal structure contains 4 covalent bonds from four valence electrons. In silicon, the most common dopants are group III and group V elements. Group III elements (trivalent) all contain three valence electrons, causing them to function as acceptors when used to dope silicon. When an acceptor atom replaces a tetravalent silicon atom in the crystal, a vacant state (an electron hole) is created. An electron hole (often simply called a hole) is the lack of an electron at a position where one could exist in an atom or atomic lattice. It is one of the two types of charge carriers that are responsible for creating electric current in semiconducting materials. These positively charged holes can move from atom to atom in semiconducting materials as electrons leave their positions. The addition of trivalent impurities such as boron, aluminum or gallium to an intrinsic semiconductor creates these positive electron holes in the structure. For example, a silicon crystal doped with boron (group III) creates a p-type semiconductor whereas a crystal doped with phosphorus (group V) results in an n-type semiconductor.



The number of electron holes are completely dominated by the number of acceptor sites. Therefore:

The total number of holes is approximately equal to the number of donor sites, p ≈ NA.

Charge neutrality of this semiconductor material is also maintained. The net result is that the number of electron holes is increased, while the number of conduction electrons is reduced. The imbalance of the carrier concentration in the respective bands is expressed by the different absolute number of electrons and holes. Electron holes are majority carriers, while electrons are minority carriers in p-type material.

Hall Effects

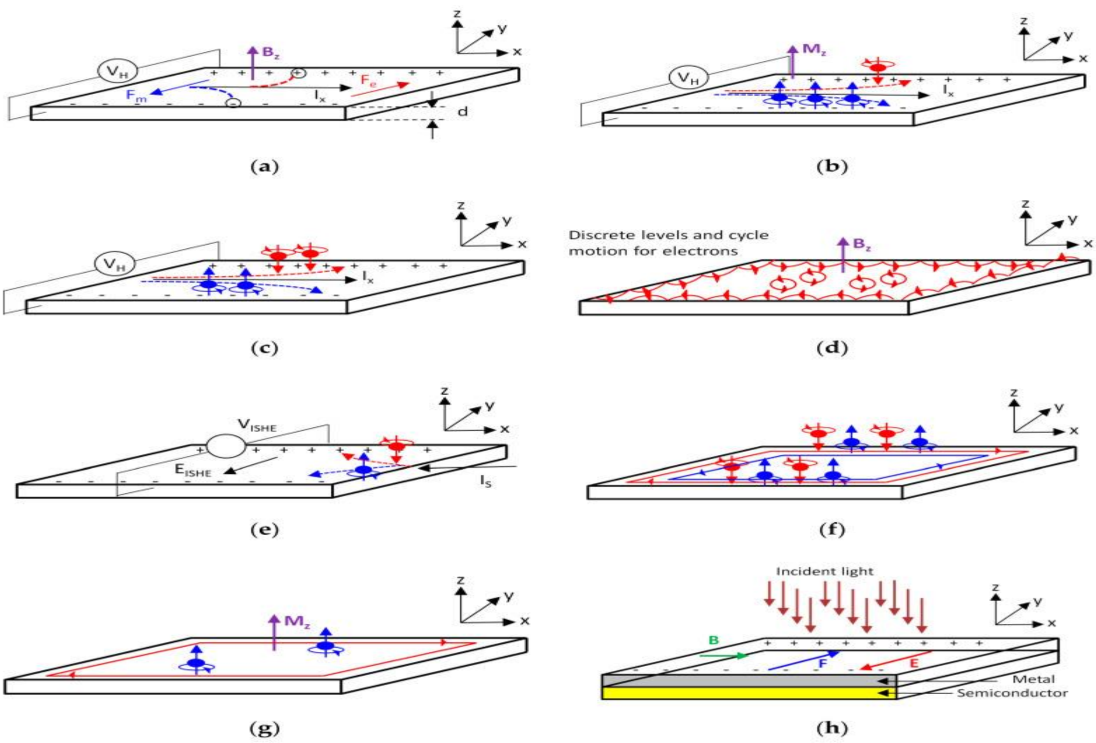
The Hall Effect, also called Original or Ordinary Hall Effect (OHE), can be used to distinguish currents that are composed of positively charged particles from those that are composed of negatively charged particles, as emphasized by Lorentz. If these effects were primarily discovered and applied at the macroscale level, other Hall related effects appeared at the microscale level over the years.

AHE—Anomalous Hall Effect, 1881

In 1881, two years after he discovered the OHE, Hall reported that the effect was ten times larger in ferromagnetic conductors than in non-magnetic conductors. This new effect, entitled “Anomalous” Hall Effect (AHE), is presented in Figure 3b. As per Nagaosa et al., both discoveries were remarkable, given the limited knowledge at that time on how free carriers’ move through conductors. The first discovery, OHE, provided an elegant tool to measure carriers' concentration more accurately in non-magnetic conductors, and introduced the semiconductor physics and solid-state electronics in the late 1940s. For a long period, AHE remained an enigmatic problem to explain since it involves topology and geometry concepts, which have been formulated only in the last decades. Only after the Berry phase approach was adopted, it was possible to link between the topological nature of the Hall currents and the AHE itself. In nanoscale systems, where a priori direct measurements are not straight forward and sometimes not possible, the AHE can serve as a useful probe of electron spin polarization.

IQHE—Integer Quantum Hall Effect, 1980

In regard to the Quantum Hall Effect, presented in Figure 3d, it would be wiser to refer to the two parts separately: The Integer Quantum Hall Effect (IQHE) and the Fractional Quantum Hall Effect (FQHE). Discovered approximately 100 years after Hall's initial work, and first published in 1980, by Von Klitzing, the IQHE effect was observed in a 2D electron system, located at Si/SiO2 interface or a Field Effect Transistor (MOS-FET). The device, sharing a Hall bar geometry, is placed into a strong magnetic field of about 15 T and at liquid helium temperature. This important research discovery granted Von Klitzing the 1985 Nobel Prize in Physics and led to the adoption of internationally accepted rules for resistance calibration. The IQHE is obtained by varying the gate voltage in such a way that the Hall resistance varies stepwise by values of h/ie2 (i is an integer) while h is the Planck constant and e the electron charge. The i step indicates the filling of a Landau level corresponding to a quantized cyclotron orbit of the electron in a magnetic field. As explained explicitly by Prof. D. Tong in his recent lectures at Cambridge University , the origin of these plateaux is related to impurities, creating "disorder" and causing a split that degenerates eigenstates of the electron wave functions. In fact, such quantum phenomenon can be explained without considering the interactions between electrons, assuming that there are quantum states for a single particle in a magnetic field. More recently, in 2007, the integer quantum Hall Effect was reported in graphene at room temperature .



FQHE—Fractional Quantum Hall Effect, 1982

The Fractional Quantum Hall Effect (FQHE) was observed for the first time, and reported in 1982, by Tsui in a 2D high electron mobility GaAlAs heterostructure at liquid helium temperature. When compared to the Integer Quantum Hall Effect, the Fractional Quantum Hall Effect (FQHE) presents, additional plateaux of Hall resistance at fractional values of i = 1/3, 2/3, and 3/2 in the h/ie2 expression. A decade later, in 1998, Tsui was the recipient of the Physics Nobel Prize along with Laughlin and Stromer, for “Their discovery of a new form of quantum fluid with fractionally charged excitations”. Indeed, in the FQHE, electrons are expected to bind together with magnetic flux lines and make new quasiparticles, also called “composite fermions”, paving the way to a new quantum state of matter as described in more detail by D. Tong in his lectures.

QAHE—Quantum Anomalous Hall Effect, 2013

In the case of the Quantum Anomalous Hall Effect (QAHE), presented in Figure 3g, the phenomenon is running in a system without any external applied magnetic field, as described clearly only recently by Liu. Defined as a quantized Hall Effect, it represents a new appearance of topological structure in many-electrons systems, and sharing a high potential of possible applications in electronic devices. More recently, the effect was largely investigated, theoretically modeled, and physically experimented.

HALL VOLTAGE

Applications of semiconductors p-n junction as transistors and rectifiers

The p-n junction

If an abrupt change in impurity type from acceptors (p-type) to donors (n-type) occurs within a single crystal structure, a p-n junction is formed. On the p side, the holes constitute the dominant carriers and so are called majority carriers. A few thermally generated electrons will also exist in the p side; these are termed minority carriers. On the n side the electrons are the majority carriers, while the holes are the minority carriers. Near the junction is a region having no free-charge carriers. This region, called the depletion layer, behaves as an insulator.

The most important characteristic of p-n junctions is that they rectify; that is to say, they allow current to flow easily in only one direction. the current-voltage characteristics of a typical silicon p-n junction. When a forward bias is applied to the p-n junction (i.e., a positive voltage applied to the p-side with respect to the n-side), the majority charge carriers move across the junction so that a large current can flow. However, when a reverse bias is applied, the charge carriers introduced by the impurities move in opposite directions away from the junction, and only a small leakage current flows initially. As the reverse bias is increased, the current remains very small until a critical voltage is reached, at which point the current suddenly increases. This sudden increase in current is referred to as the junction breakdown, usually a nondestructive phenomenon if the resulting power dissipation is limited to a safe value. The applied forward voltage is usually less than one volt, but the reverse critical voltage, called the breakdown voltage, can vary from less than one volt to many thousands of volts, depending on the impurity concentration of the junction and other device parameters.

Two-terminal junction devices

A p-n junction diode is a solid-state device that has two terminals. Depending on impurity distribution, device geometry, and biasing condition, a junction diode can perform various functions. There are more than 50,000 types of diodes with voltage ratings from less than 1 volt to more than 2,000 volts and current ratings from less than 1 milliampere to more than 5,000 amperes. A p-n junction also can generate and detect light and convert optical radiation into electrical energy.

Rectifier

This type of p-n junction diode is specifically designed to rectify an alternating current—i.e., to give a low resistance to current flow in one direction and a very high resistance in the other direction. Such diodes are generally designed for use as power-rectifying devices that operate at frequencies from 50 hertz to 50 kilohertz. The majority of rectifiers have power-dissipation capabilities from 0.1 to 10 watts and a reverse breakdown voltage from 50 to more than 5,000 volts. (A high-voltage rectifier is made from two or more p-n junctions connected in series.)

Zener diode

This voltage regulator is a p-n junction diode that has a precisely tailored impurity distribution to provide a well-defined breakdown voltage. It can be designed to have a breakdown voltage over a wide range from 0.1 volt to thousands of volts. The Zener diode is operated in the reverse direction to serve as a constant voltage source, as a reference voltage for a regulated power supply, and as a protective device against voltage and current transients.

Varactor diode

The varactor (variable reactor) is a device whose reactance can be varied in a controlled manner with a bias voltage. It is a p-n junction with a special impurity profile, and its capacitance variation is very sensitive to reverse-biased voltage. Varactors are widely used in parametric amplification, harmonic generation, mixing, detection, and voltage-variable tuning applications.

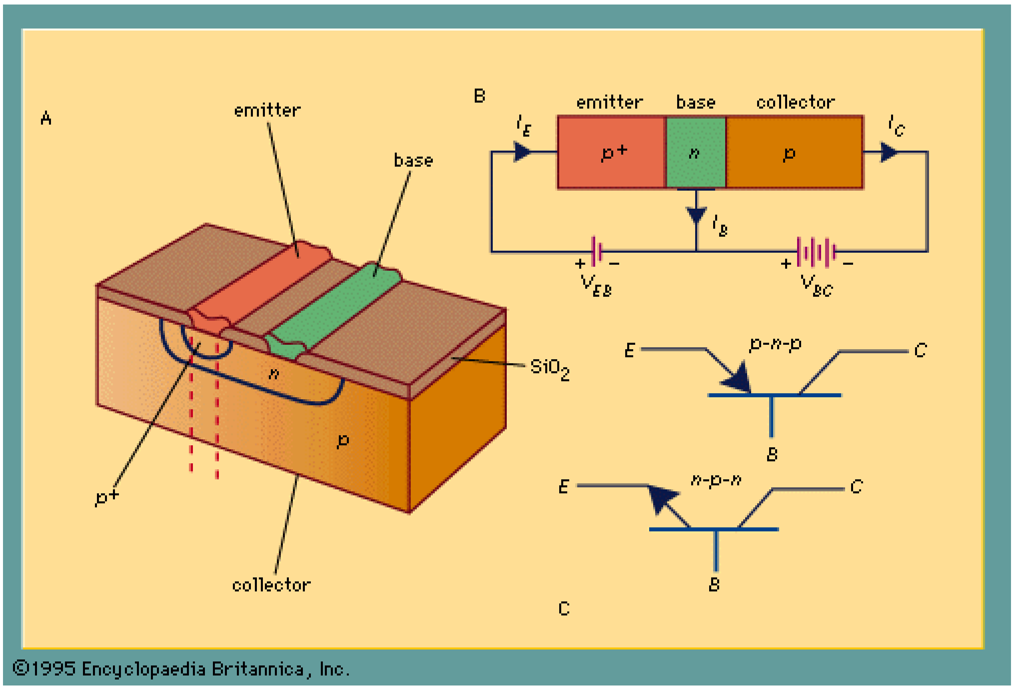
Tunnel diode

A tunnel diode consists of a single p-n junction in which both the p and n sides are heavily doped with impurities. The depletion layer is very narrow (about 100 angstroms). Under forward biases, the electrons can tunnel or pass directly through the junction, producing a negative resistance effect (i.e., the current decreases with increasing voltage). Because of its short tunneling time across the junction and its inherent low noise (random fluctuations either of current passing through a device or of voltage developed across it), the tunnel diode is used in special low-power microwave applications, such as a local oscillator and a frequency-locking circuit.

The p-i-n diode

A p-i-n diode is a p-n junction with an impurity profile tailored so that an intrinsic layer, the “i region,” is sandwiched between a p layer and an n layer. The p-i-n diode has found wide application in microwave circuits. It can be used as a microwave switch with essentially constant depletion-layer capacitance (equal to that of a parallel-plate capacitorhaving a distance between the plates equal to the i-region thickness) and high power-handling capability.

Bipolar transistors

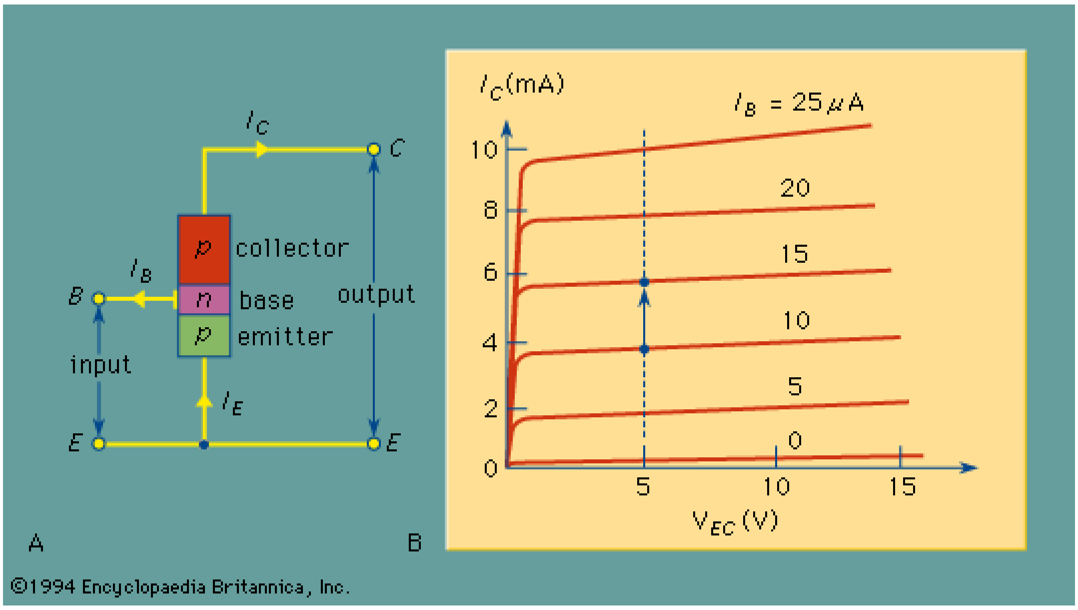


This type of transistor is one of the most important of the semiconductor devices. It is a bipolar device in that both electrons and holes are involved in the conduction process. The bipolar transistor delivers a change in output current in response to a change in input voltage at the base. The ratio of these two changes has resistance dimensions and is a “transfer” property (input-to-output), hence the name transistor.

A perspective view of a silicon p-n-p bipolar transistor is shown in Figure 4A. Basically the bipolar transistor is fabricated by first forming an n-type region in the p-type substrate; subsequently a p+ region (very heavily doped p-type) is formed in the n region. Ohmic contacts are made to the top p+ and n regions through the windows opened in the oxide layer (an insulator) and to the pregion at the bottom.

An idealized, one-dimensional structure of the bipolar transistor, shown in Figure 4B, can be considered as a section of the device along the dashed lines in Figure 4A. The heavily doped p+ region is called the emitter, the narrow central n region is the base, and the p region is the collector. The circuit arrangement in Figure 4B is known as a common-base configuration. The arrows indicate the directions of current flow under normal operating conditions—namely, the emitter-base junction is forward-biased and the base-collector junction is reverse-biased. The complementary structure of the p-n-p bipolar transistor is the n-p-n bipolar transistor, which is obtained by interchanging p for n and n for p . The current flow and voltage polarity are all reversed. The circuit symbols for p-n-p and n-p-n transistors are given in Figure 4C.

The bipolar transistor is composed of two closely coupled p-n junctions. The emitter-base p+-n junction is forward-biased and has low resistance. The majority carriers (holes) in the p+-emitter are injected (or emitted) into the base region. The base-collector n-p junction is reverse-biased. It has high resistance, and only a small leakage current will flow across the junction. If the base width is sufficiently narrow, however, most of the holes injected from the emitter can flow through the base and reach the collector. This transport mechanism gives rise to the prevailing nomenclature: emitter, which emits or injects carriers, and collector, which collects these carriers injected



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The current gain for the common-base configuration is defined as the change in collector current divided by the change in emitter current when the base-to-collector voltage is constant. Typical common-base current gain in a well-designed bipolar transistor is very close to unity. The most useful amplifiercircuit is the common-emitter configuration, as shown in Figure 5A, in which a small change in the input current to the base requires little power but can result in much greater current in the output circuit. A typical output current-voltage characteristic for the common-emitter configuration is shown in Figure 5B, where the collector current IC is plotted against the emitter-collector voltage VEC for various base currents. A numerical example is provided using Figure 5B. If VEC is fixed at five volts and the base current IB is varied from 10 to 15 microamperes (μA; 1 μA = 10−6 A), the collector current IC will change from about four to six milliamperes (mA; 1 mA = 10−3 A), as can be read from the left axis. Therefore, an increment of 5 μA in the input-base current gives rise to an increment of 2 mA in the output circuit—an increase of 400 times, with the input signal thus being substantially amplified. In addition to their use as amplifiers, bipolar transistors are key components for oscillators and pulse and analog circuits, as well as for high-speed integratedcircuits. There are more than 45,000 types of bipolar transistors for low-frequency operation, with power outputs up to 3,000 watts and a current rating of more than 1,000 amperes. At microwave frequencies, bipolar transistors have power outputs of more than 200 watts at 1 gigahertz and about 10 watts at 10 gigahertz.

Photovaltic and Photogalvanic cell in nanotechnology

Photogalvanic Cells

Classification of solar cell

Since, solar energy is completely natural, it is considered a clean energy source. It does not disrupt the environment or create any threat to eco-systems like oil and some other energy sources might be. It does not cause green house effect, air or water pollution. Along with these merits solar energy has two major drawbacks: it is intermittent (requires some form of a storage system so that the energy can be made available when it is needed) and diffuse (requires large areas of collectors).

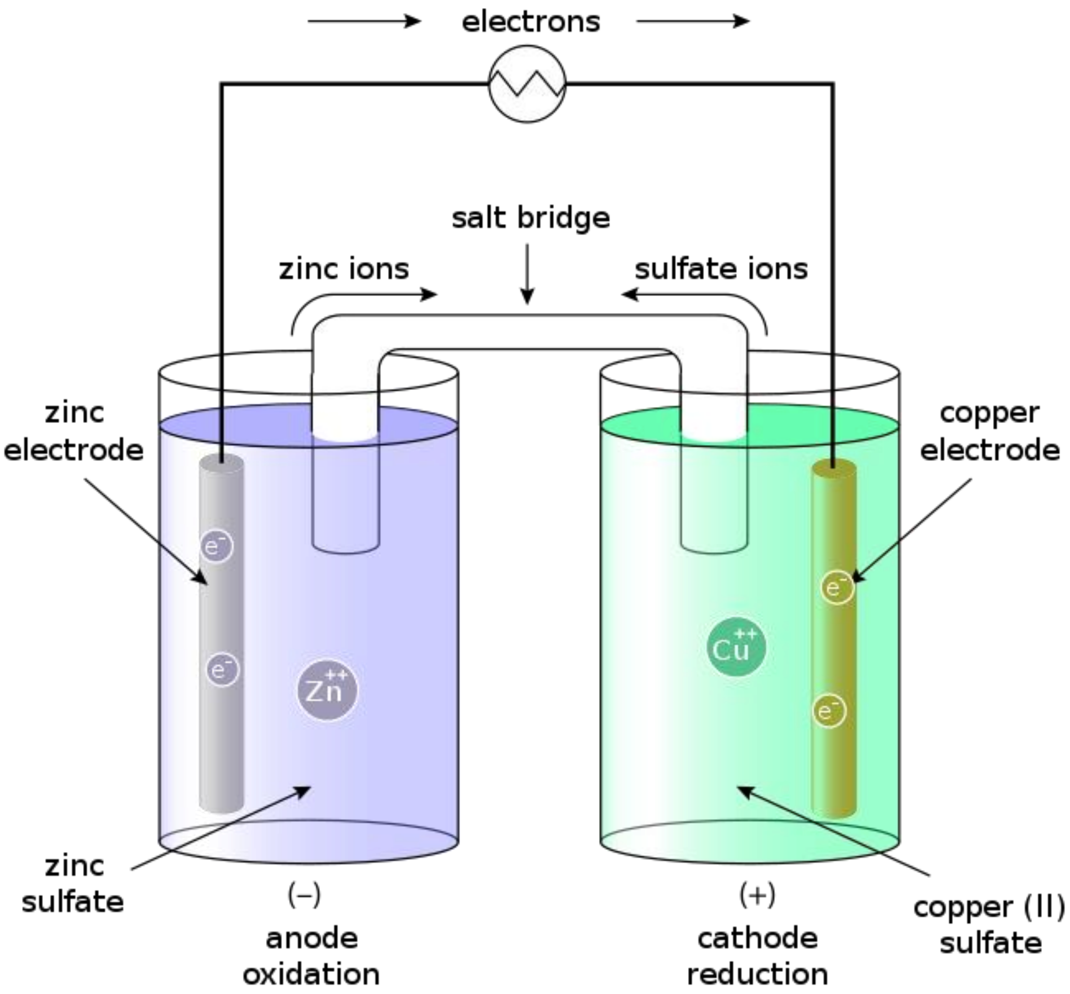
Photogalvanic effect and its type

When one of the two electrodes immerged in an electrolyte, is illuminated a potential difference arises between the electrodes. This effect is Becquerel effect, so called photogalvanic effect [168]. The effect was first observed by French physicist A. E. Becquerel in 1839, and explained his discovery in ‘Les Comptes Rendus de l’Academie des Sciences’, the production of an electric current when two plates of platinum or gold dipped in an acid, neutral or alkaline solution are exposed.

Chronological development of photogalvanic cell

To quote Prof. N. Lichtin in the preface to the proceedings of workshop (IPS-0 [177]) that, “the possibility of utilizing the sun light which reaches the earth’s surface each day as a practical source of energy is a major challenge to modern science and technology”. Photochemistry is a highly dynamic area of both basic and applied research, offers an obvious potential route to practical use of solar energy”.

Principles



Galvanic cells are extensions of spontaneous redox reactions, but have been merely designed to harness the energy produced from said reaction. For example, when one immerses a strip of zinc metal (Zn) in an aqueous solution of copper sulfate ($CuSO_4$), dark-colored solid deposits will collect on the surface of the zinc metal and the blue color characteristic of the Cu^{2+} ion disappears from the solution. The depositions on the surface of the zinc metal consist of copper metal, and the solution now contains zinc ions. This reaction is represented by

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$$

In this redox reaction, Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu. When electrons are transferred directly from Zn to Cu^{2+} , the enthalpy of reaction is lost to the surroundings as heat. However, the same reaction can be carried out in a galvanic cell, allowing some of the chemical energy released to be converted into electrical energy. In its simplest form, a half-cell consists of a solid metal (called an electrode) that is submerged in a solution; the solution contains cations (+) of the electrode metal and anions (−) to balance the charge of the cations.The full cell consists of two half-cells, usually connected by a semi-permeable membrane or by a salt bridge that prevents the ions of the more noble metal from plating out at the other electrode.

A specific example is the Daniell cell (see figure), with a zinc (Zn) half-cell containing a solution of $ZnSO_4$ (zinc sulfate) and a copper (Cu) half-cell containing a solution of $CuSO_4$ (copper sulfate). A salt bridge is used here to complete the electric circuit.

If an external electrical conductor connects the copper and zinc electrodes, zinc from the zinc electrode dissolves into the solution as Zn^{2+} ions (oxidation), releasing electrons that enter the external conductor. To compensate for the increased zinc ion concentration, via the salt bridge zinc ions leave and anions enter the zinc half-cell. In the copper half-cell, the copper ions plate onto the copper electrode (reduction), taking up electrons that leave the external conductor. Since the Cu^{2+} ions (cations) plate onto the copper electrode, the latter is called the cathode. Correspondingly the zinc electrode is the anode.

Galvanic corrosion

Galvanic corrosion is the electrochemical erosion of metals. Corrosion occurs when two dissimilar metals are in contact with each other in the presence of an electrolyte, such as salt water. This forms a galvanic cell, with hydrogen gas forming on the more noble (less active) metal. The resulting electrochemical potential then develops an electric current that electrolytically dissolves the less noble material. A concentration cell can be formed if the same metal is exposed to two different concentrations of electrolyte.

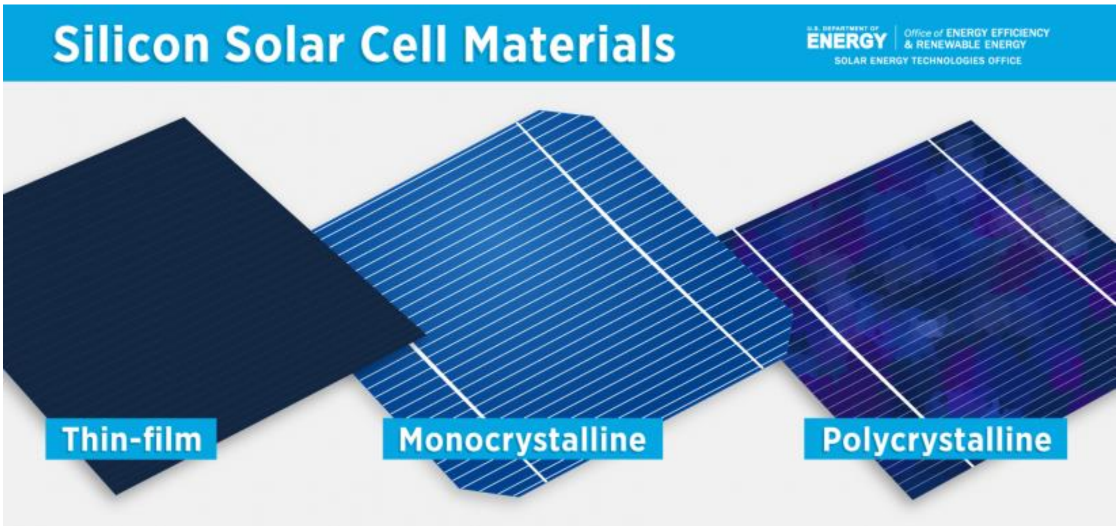
Solar photovoltic cell

When light shines on a photovoltaic (PV) cell – also called a solar cell – that light may be reflected, absorbed, or pass right through the cell. The PV cell is composed of semiconductor material; the "semi" means that it can conduct electricity better than an insulator but not as well as a good conductor like a metal. There are several different semiconductor materials used in PV cells.

When the semiconductor is exposed to light, it absorbs the light's energy and transfers it to negatively charged particles in the material called electrons. This extra energy allows the electrons to flow through the material as an electrical current. This current is extracted through conductive metal contacts – the grid-like lines on a solar cells – and can then be used to power your home and the rest of the electric grid.

The efficiency of a PV cell is simply the amount of electrical power coming out of the cell compared to the energy from the light shining on it, which indicates how effective the cell is at converting energy from one form to the other. The amount of electricity produced from PV cells depends on the characteristics (such as intensity and wavelengths) of the light available and multiple performance attributes of the cell.

An important property of PV semiconductors is the bandgap, which indicates what wavelengths of light the material can absorb and convert to electrical energy. If the semiconductor's bandgap matches the wavelengths of light shining on the PV cell, then that cell can efficiently make use of all the available energy.



SILICON

Silicon is, by far, the most common semiconductor material used in solar cells, representing approximately 95% of the modules sold today. It is also the second most abundant material on Earth (after oxygen) and the most common semiconductor used in computer chips. Crystalline silicon cells are made of silicon atoms connected to one another to form a crystal lattice. This lattice provides an organized structure that makes conversion of light into electricity more efficient.

Solar cells made out of silicon currently provide a combination of high efficiency, low cost, and long lifetime. Modules are expected to last for 25 years or more, still producing more than 80% of their original power after this time.

THIN-FILM PHOTOVOLTAICS

A thin-film solar cell is made by depositing one or more thin layers of PV material on a supporting material such as glass, plastic, or metal. There are two main types of thin-film PV semiconductors on the market today: cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS). Both materials can be deposited directly onto either the front or back of the module surface.

CdTe is the second-most common PV material after silicon, and CdTe cells can be made using low-cost manufacturing processes. While this makes them a cost-effective alternative, their efficiencies still aren't quite as high as silicon. CIGS cells have optimal properties for a PV material and high efficiencies in the lab, but the complexity involved in combining four elements makes the transition from lab to manufacturing more challenging. Both CdTe and CIGS require more protection than silicon to enable long-lasting operation outdoors.

PEROVSKITE PHOTOVOLTAICS

Perovskite solar cells are a type of thin-film cell and are named after their characteristic crystal structure. Perovskite cells are built with layers of materials that are printed, coated, or vacuum-deposited onto an underlying support layer, known as the substrate. They are typically easy to assemble and can reach efficiencies similar to crystalline silicon. In the lab, perovskite solar cell efficiencies have improved faster than any other PV material, from 3% in 2009 to over 25% in 2020. To be commercially viable, perovskite PV cells have to become stable enough to survive 20 years outdoors, so researchers are working on making them more durable and developing large-scale, low-cost manufacturing techniques.

ORGANIC PHOTOVOLTAICS

Organic PV, or OPV, cells are composed of carbon-rich (organic) compounds and can be tailored to enhance a specific function of the PV cell, such as bandgap, transparency, or color. OPV cells are currently only about half as efficient as crystalline silicon cells and have shorter operating lifetimes, but could be less expensive to manufacture in high volumes. They can also be applied to a variety of supporting materials, such as flexible plastic, making OPV able to serve a wide variety of uses.PV

QUANTUM DOTS

Quantum dot solar cells conduct electricity through tiny particles of different semiconductor materials just a few nanometers wide, called quantum dots. Quantum dots provide a new way to process semiconductor materials, but it is difficult to create an electrical connection between them, so they’re currently not very efficient. However, they are easy to make into solar cells. They can be deposited onto a substrate using a spin-coat method, a spray, or roll-to-roll printers like the ones used to print newspapers.

Quantum dots come in various sizes and their bandgap is customizable, enabling them to collect light that’s difficult to capture and to be paired with other semiconductors, like perovskites, to optimize the performance of a multijunction solar cell.

MULTIJUNCTION PHOTOVOLTAICS

Another strategy to improve PV cell efficiency is layering multiple semiconductors to make multijunction solar cells. These cells are essentially stacks of different semiconductor materials, as opposed to single-junction cells, which have only one semiconductor. Each layer has a different bandgap, so they each absorb a different part of the solar spectrum, making greater use of sunlight than single-junction cells. Multijunction solar cells can reach record efficiency levels because the light that doesn’t get absorbed by the first semiconductor layer is captured by a layer beneath it.

While all solar cells with more than one bandgap are multijunction solar cells, a solar cell with exactly two bandgaps is called a tandem solar cell. Multijunction solar cells that combine semiconductors from columns III and V in the periodic table are called multijunction III-V solar cells.

Multijunction solar cells have demonstrated efficiencies higher than 45%, but they’re costly and difficult to manufacture, so they’re reserved for space exploration. The military is using III-V solar cells in drones, and researchers are exploring other uses for them where high efficiency is key.

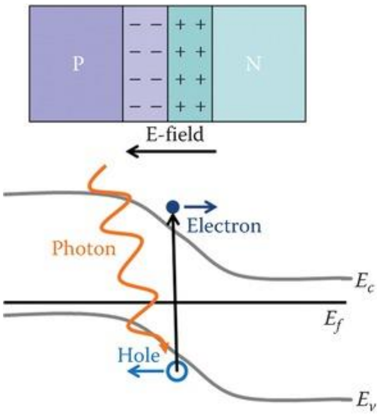
CONCENTRATION PHOTOVOLTAICS

Concentration PV, also known as CPV, focuses sunlight onto a solar cell by using a mirror or lens. By focusing sunlight onto a small area, less PV material is required. PV materials become more efficient as the light becomes more concentrated, so the highest overall efficiencies are obtained with CPV cells and modules. However, more expensive materials, manufacturing techniques, and ability to track the movement of the sun are required, so demonstrating the necessary cost advantage over today's high-volume silicon modules has become challenging.

Photovoltaic (PV) Cell Basics

A PV cell is essentially a large-area p–n semiconductor junction that captures the energy from photons to create electrical energy.

At the semiconductor level, the p–n junction creates a depletion region with an electric field in one direction. When a photon with sufficient energy hits the material in the depletion region, the energy from the photon excites a valence electron into the conduction band, leaving a hole in the valence band. Due to the electric field in the depletion region, the electron and hole will travel in opposite directions and generate a net current.



There are two basic types of crystalline silicon cells: mono-crystalline (m-c) and poly-crystalline (p-c).

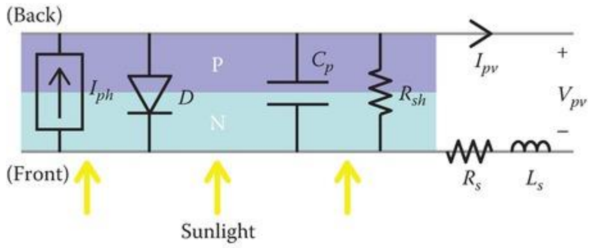
The m-c cells have one uniform lattice through the entire cell and allow electronics to flow easily through the materials, while p-c cells have multiple crystalline structures, or grains, which can impede electron flow. Thus, p-c cells tend to have lower conversion efficiency than m-c cells, but they are slightly cheaper to manufacture. Both m-c and p-c cells are widely used in PV panels and in PV systems today.

Photovoltaic (PV) Cell Components

The basic structure of a PV cell can be broken down and modeled as basic electrical components. Figure 4 shows the semiconductor p–n junction and the various components that make up a PV cell.

The photon-to-electron flow process explained previously can be modeled as a current source, Iph, where the generated current depends on the intensity of the light hitting the cell. The p–n semiconductor junction is modeled as a diode, D, with the direction as shown in Figure 4.

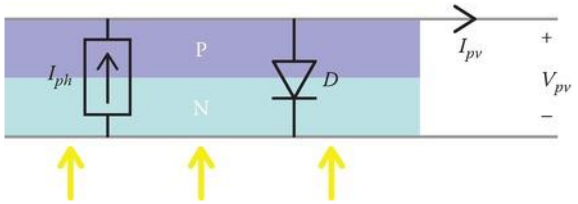
The current source and diode make up the ideal model of a PV cell, but in real life, there are additional parasitic components. The p–n junction will have associated parallel capacitance, Cp, and parallel resistance (also called shunt resistance), Rsh, while the wire leads attached to the PV cell will have associated series resistance, Rs, and series inductance, Ls. These parasitic components are often ignored when only a simple representation of a PV cell or panel is needed, but they should be taken into consideration when more accurate modeling is required.



PV cell basic structure electrical model components with parasitic

PV Operating Characteristics

While there are many environmental factors that affect the operating characteristics of a PV cell and its power generation, the two main factors are solar irradiance G, measured in W/m^2, and temperature T, measured in degree Celsius (°C). The relation between these two factors and the PV operating characteristics can be modeled mathematically. First, we examine the ideal model that consists of just the photocurrent source Iph and a diode,



Ideal PV model with a current source and diode.

The photocurrent Iph depends on both the irradiance and temperature according to

$Iph(G,T)=[Iscn+Ki(T-Tn)]GGn(1)$

where

Iscn is the nominal short-circuit current

Ki is the current temperature coefficient

Gn is the nominal solar irradiance, which is typically 1000 W/m2

Tn is the nominal cell temperature, which is typically 25 °C

These values can be determined from the ratings listed for commercial PV cells or panels. Also, the current Id and voltage Vd of the diode are expressed by an exponential relation, and they are represented as

$Id(T,Vd)=Is(T)[exp(Vd/\alpha Vt(T))]$ - 2

where

Is is the diode saturation current

a is the diode ideality constant

Vd is the diode voltage

Vt is the thermal voltage of the semiconductor junction

The diode saturation current depends on temperature and can be defined as

$$I_s(T) = \frac{I_{scn}+K_i(T-T_n)}{\exp\left(\frac{V_{ocn}+K_v(T-T_n)}{\alpha V_t(T)}\right)} \qquad (3)$$

where

Iscn is the nominal short-circuit current

Ki is the current temperature coefficient

Tn is the nominal cell temperature

Vocn is the nominal open-circuit voltage

Kv is the voltage temperature coefficient

a is the diode ideality factor

Vt is the thermal voltage

Note that the diode voltage Vd is the same as the PV voltage Vpv for the ideal model. Also, the thermal voltage Vt depends on temperature T and is defined by

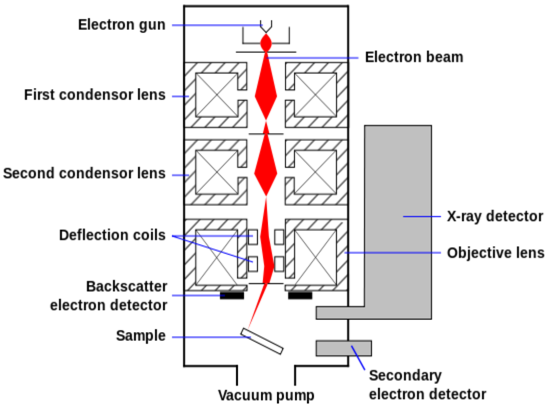
$$Vt(T)=kT/qNs \text{-}(4)$$

Given the solar irradiance and temperature, this explicit equation in (4) can be used to determine the PV current for a given voltage. These equations can also be rearranged using basic algebra to determine the PV voltage based on a given current.

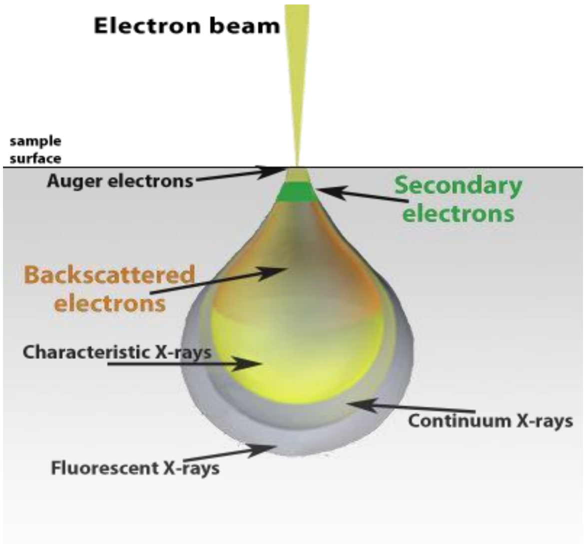
Unit-5

Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scanpattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer.



In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and FEG, which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide. The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current.Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube). Each pixel of computer videomemory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to a computer data storage. Sample-Electron Interaction The scanning electron microscope (SEM) produces images by scanning the sample with a highenergy beam of electrons. As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by one or more detectors to form images which are then displayed on the computer screen. When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Many signals, like secondary electrons and X-rays, are produced as a result of this interaction inside the sample.



The maximum resolution obtained in an SEM depends on multiple factors, like the electron spot size and interaction volume of the electron beam with the sample. While it cannot provide atomic resolution, some SEMs can achieve resolution below 1 nm. Typically, modern full-sized SEMs provide resolution between 1-20 nm whereas desktop systems can provide a resolution of 20 nm or more.

Transmission Electron Microscope

(TEM) The transmission electron microscope is a very powerful tool for material science. A high energy beam of electrons is shone through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. Chemical analysis can also be performed. TEM can be used to study the growth of layers, their composition and defects in semiconductors. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots. The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms.

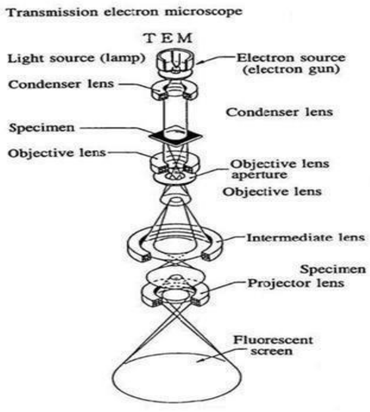


Fig 1

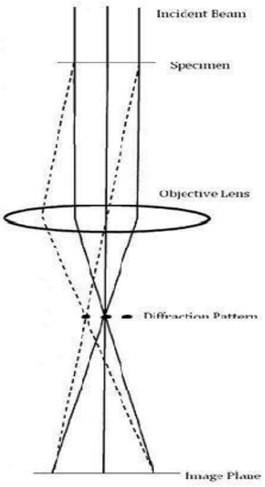


Fig 2

Imaging

The beam of electrons from the electron gun is focused into a small, thin, coherent beam by the use of the condenser lens. This beam is restricted by the condenser aperture, which excludes high angle electrons. The beam then strikes the specimen and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion is focused by the objective lens into an image on phosphor screen or charge coupled device (CCD) camera. Optional objective apertures can be used to enhance the contrast by blocking out high-angle diffracted electrons. The image then passed down the column through the intermediate and projector lenses, is enlarged all the way.
The image strikes the phosphor screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons are transmitted through while the lighter areas of the image represent those areas of the sample that more electrons were transmitted through.

Diffraction

Fig2. shows a simple sketch of the path of a beam of electrons in a TEM from just above the specimen and down the column to the phosphor screen. As the electrons pass through the sample,they are scattered by the electrostatic potential set up by the constituent elements in the specimen.After passing through the specimen they pass through the electromagnetic objective lens which focuses all the electrons scattered from one point of the specimen into one point in the image plane. Also, shown in fig 2 is a dotted line where the electrons scattered in the same direction by the sample are collected into a single point. This is the back focal plane of the objective lens and is where the diffraction pattern is formed.

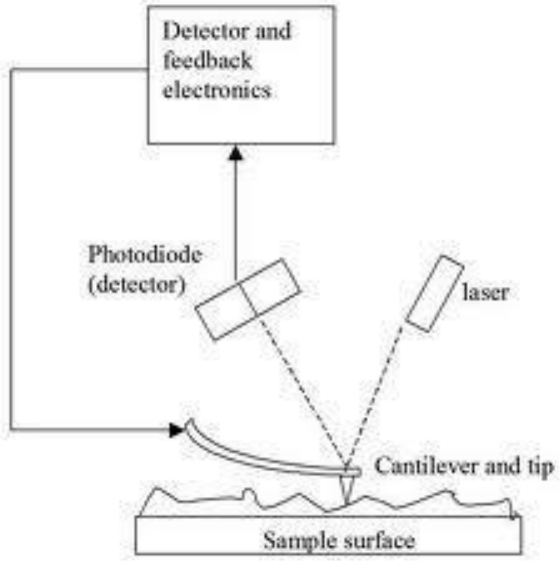
Specimen Preparation

A TEM specimen must be thin enough to transmit sufficient electrons to form an image with minimum energy loss. Therefore specimen preparation is an important aspect of the TEM analysis. For most electronic materials, a common sequence of preparation techniques is ultrasonic disk cutting, dimpling, and ion-milling. ***Dimpling*** is a preparation technique that produces a specimen with a thinned central area and an outer rim of sufficient thickness to permit ease of handling. ***Ion milling*** is traditionally the final form of specimen preparation. In this process, charged argon ions are accelerated to the specimen surface by the application of high voltage. The ion impingement upon the specimen surface removes material as a result of momentum transfer.

Atomic Force Microscopy (AFM)

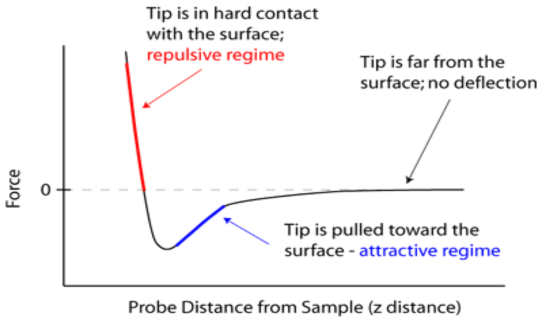
Atomic Force Microscopy (AFM) is a form of scanning probe microscopy (SPM) where a small probe is scanned across the sample to obtain information about the sample's surface. The information gathered from the probe's interaction with the surface can be as simple as physical topography or as diverse as measurements of the material's physical, magnetic, or chemical properties. These data are collected as the probe is scanned in a raster pattern across the sample toform a map of the measured property relative to the X-Y position. Thus, the AFM microscopic image shows the variation in the measured property, e.g,. height or magnetic domains, over the area imaged.

The AFM probe has a very sharp tip, often less than 100Å diameter, at the end of a small cantilever beam. The probe is attached to a piezoelectric scanner tube, which scans the probe across a selected area of the sample surface. Inter atomic forces between the probe tip and the sample surface cause the cantilever to deflect as the sample's surface topography (or other properties) changes. A laser light reflected from the back of the cantilever measures the deflection of the cantilever. This information is fed back to a computer, which generates a map oftopography and/or other properties of interest. Areas as large as about 100 µm square to less than 100 nm square can be imaged.



The Atomic Force Microscope was developed to overcome a basic drawback with STM - that it can only image conducting or semiconducting surfaces. The AFM, however, has the advantage ofimaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples.

Measuring forces Because the atomic force microscope relies on the forces between the tip and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated bymeasuring the deflection of the lever, and knowing the stiffness of the cantilever. Hook's law gives $F = -kz$, where F is the force, k is the stiffness of the lever, and z is the distance the lever is bent.



AFM Modes of operation

Because of AFM's versatility, it has been applied to a large number of research topics. The Atomic Force Microscope has also gone through many modifications for specific application requirements.

Contact Mode - The first and foremost mode of operation, contact mode is widely used. In this mode the AFM probe is scanned at a constant force between the probe and the sample surface to obtain a 3D topographical map. As the tip is raster-scanned across the surface, it is deflected as it moves over the surface corrugation. In constant force mode, the tip is constantly adjusted to maintain a constant deflection, and therefore constant height above the surface. It is this adjustment that is displayed as data. However, the ability to track the surface in this manner is limited by the feedback circuit. Sometimes the tip is allowed to scan without this adjustment, and one measures only the deflection. This is useful for small, high-speed atomic resolution scans,and is known as variable-deflection mode. Lateral resolution of <1 nm and height resolution of
<1 Å can be obtained.

Because the tip is in hard contact with the surface, the stiffness of the lever needs to be less that the effective spring constant holding atoms together, which is on the order of 1 - 10 nN/nm. Most contact mode levers have a spring constant of < 1N/m.

Noncontact mode - Noncontact mode belongs to a family of AC modes, which refers to the use of an oscillating cantilever. A stiff cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but not touching it (hence, "noncontact"). The forces between the tip and sample are quite low, on the order of pN (10^{-12} N). The detection scheme is based on measuring changes to the resonant frequency or amplitude of the cantilever.

The particles which are from 1 to 100 nm in size, are termed as nanoparticles. In nanotechnology, the particle is an object which acts as a complete unit with regard to its properties. Individual molecules are not regarded as nanoparticles, rather these are the particles which demonstrate size dependent properties.

The properties of a nanoparticle substantially differ from those of bulk forms of the same materials. Nanoclusters are the groups of atoms or molecules which have at least one dimension in 1-10 nm range. The size distribution within a nanocluster is very narrow, i.e., almost all the particles present in the cluster are of approximately same size. The agglomerates of ultra fine particles, nanoparticles, or nanoclusters are called nanopowders. Single crystals of nanometer dimensions or single domain ultrafine particles are called nanocyrstals Classification Particles can be further classified into following types, depending upon their diameters: 1. Ultrafine particles are similar to nanoparticles and have dimensions in the range of 1-100 nm. 2. Fine particles with dimensions between 100-2500nm. 3. Coarse particles with dimensions between 2500-10000nm. Nanoparticles are highly significant for scientific research owing to their potential use in medicine, physics, electronics, optoelectronics, etc.

Surface coatings in biological applications

The surface of the nanoparticles should be polar to provide good aqueous solubility and prevent nanoparticle coagulation. Highly charged surfaces lead to non-specific interactions, while the polyethylene glycol terminated cells avoid non-specific bindings. Biomolecules can be attached to the nanoparticles to direct them to specific sites in the body, even specific organelles in a cell, or to monitor individual protein or RNA molecules. Most commonly used tags to mark the nanoparticles include monoclonal antibodies, aptamers, streptavidin or peptides. These tags must be attached with the nanoparticles covalently, and also, their quantity per nanoparticles must be controlled for efficient operation. Multivalent nanoparticles have several tags attached to them which may cause their clustering, thereby activating the cell signaling paths, giving stronger anchoring. On the other hand, monovalent nanoparticles bear single binding sites, thus prevent cluster formation. These nanoparticles are suitable to track the behaviour of individual protein molecules.

Health and Safety There are various speculations both medically as well as environmentally that nanoparticles are hazardous. Owing to their huge surface areas, these particles are highly reactive or catalytic. As they are extremely small, they can pass through the cell membrane and may interact with the cell organelles. Presently, this interaction is not very well understood. Nonetheless, the nanoparticles are unlikely to enter the cell nucleus, Golgi complex, or other cell organelles mainly because of the particle size and intercellular aggregation. These days, a lager variety of cosmetics and sunscreens are produced which contain nanoparticles for effective working. It is still unknown whether the presence of nanoparticles in these products pose any health hazards or not. The investigations on the use of zinc nanoparticles have revealed that they do not get absorbed in the bloodstream in vivo. The following sections discuss the possible health risks posed by various frequently used nanoparticles.

a. **Carbon Nanotubes (CNTs)**: Carbon nanomaterials are widely used in production of composites for vehicles, sports equipments, etc., as well as integrated circuits in electronics industry. The interactions of carbon nanomaterials, e.g., CNTs with natural organic matter greatly affect their coagulations as well as deposition, thereby affecting their transport, transformation, and exposure in aquatic environments. CNTs have shown some toxic impacts in various environments, and a complete understanding of these harmful effects requires intense investigations.

b. Cerium Oxide: Cerium oxide (CeO2) nanoparticles are widely utilised in electronics, biomedical tools, energy, fuel additives, etc. Due to such diverse range of applicants, the nanoparticles of cerium oxide usually disperse in environment, thereby exposing to their risks. CeO2 nanoparticles are being continuously released into the environment due to their use in fuel additives**.**

c. Titanium Dioxide: Titanium dioxide nanoparticles are used in multiple products. Different sized nanoparticles made of titanium dioxide can be found sunscreens, cosmetics, and paints and coatings, etc. Recent application area for these particles is to remove contamination from drinking water.

d.Nano Silver: Silver nanoparticles are used in textiles, food packaging, etc., due to their antibacterial properties. The possibility of these particlesto enter the food chain and thereby their impact needs extensive investigations. e. Iron: Apart from its applications as smart fluids for optics polishing as well as nutrient supplements, nanoscale iron is being investigated for water treatment as well.

F.**Nanomedicine**

Nanomedicine implies the application of nanotechnology for medical uses. It includes medical uses of nanomaterials and biological devices, nanoscaled biosensors, etc. Future generation applications include biological nanoscaled machines. However, the possibilities of toxicity and environment impact of nanomaterials is an important concern. Nanomaterials can be manipulated to perform various specialised functions. This can be achieved by interfacing the nanomaterials with various biomolecules or structures. Since the nanomaterials are similar in size to various biomolecules and structures, they can be used for in vivo as well as in vitro biomedical research and applications. Till now, various diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug delivery vehicles, etc., have been developed by integrating nanomaterials with biology.

Drug Delivery One of the most celebrated application of nanotechnology is in targeted drug delivery to specific cells. Due to the possibility of transport of medicine directly to the affected area, the drug consumption can be minimised. This also lowers the side effects caused by the drugs. Targeted drug delivery is extremely significant in reducing the side effects of the drug as well as decreasing the treatment costs by lowering the drug consumption. Drug delivery focuses to maximise bioavailability at the specific site in the body and also maximises the availability of the drug over a certain period of time. Nano engineered devices can be used to achieve this due to their ability to target individual molecules. Nanoscaled devices offer various advantages such as less invasiveness, fast biochemical reactions, and possibility to implant within the body. These devices are much faster and effective than the conventional drug delivery practices. The efficiency of nanomedicine depends on: (a) efficient drug encapsulation, (b) successful transport of the drug to specific site, and (c) efficient release of drug

NANOPARTICLES

Nanoparticles can be engineered with distinctive compositions, sizes, shapes, and surface chemistries to enable novel techniques in a wide range of biological applications. The unique properties of nanoparticles and their behavior in biological milieu also enable exciting and integrative approaches to studying fundamental biological questions. This review will provide an overview of various types of nanoparticles and concepts of targeting nanoparticles. We will also discuss the advantages and recent applications of using nanoparticles as tools for drug delivery, imaging, sensing, and for the understanding of basic biological processes.

There are many types of NP platforms with differing size, shape, compositions, and functionalities. Furthermore, each type of NPs can potentially be fabricated using different techniques, such as both nanoprecipitation and lithography for polymeric NPs. While it is not within this manuscript’s scope to discuss the differences in NP platforms and their fabrication in detail, we will discuss the major characteristics and functionalities of each NP that are relevant for biomedical research.

Liposomes

The first NP platform was the liposomes. Liposomes were first described in 1965 as a model of cellular membranes.Since then, liposomes have moved from a model in biophysical research to one of the first NP platforms to be applied for gene and drug delivery. Liposomes are spherical vesicles that contain a single or multiple bilayered structure of lipids that self-assemble in aqueous systems.

Albumin-bound

Albumin-bound NPs (nab) uses the endogenous albumin pathways to carry hydrophobic molecules in the bloodstream. Albumin naturally binds to the hydrophobic molecules with non-covalent reversible binding, avoiding solvent-based toxicities for therapeutics.As a result, this platform has been successfully adapted as drug delivery vehicle. Abraxane, a 130-nm nab paclitaxel was approved by the FDA in 2005 for the treatment of metastatic breast cancer.

Polymeric

Polymeric NPs formed from biocompatible and biodegradable polymers have been extensively investigated as therapeutic carriers. Polymeric NPs are formulated through block-copolymers of different hydrophobicity.These copolymers spontaneously assemble into a core-shell micelle formation in an aqueous environment.Polymeric NPs have been formulated to encapsulate hydrophilic and/or hydrophobic small drug molecules, as well proteins and nucleic acid macromolecules.

Quantum dot

First discovered in 1980, quantum dots (QDs) are semiconductor particles that are less than 10 nm in diameter. QDs display unique size-dependent electronic and optical properties.Most QDs studied consist of a cadmium selenide (CdSe) core and a zinc selenide (ZnS) cap.The absorption spectra of these particles are very broad and emission is confined to a narrow band. QDs can also emit bright colors, have long lifetimes, high efficiencies and are stable against photobleaching. They can be generated to have different biochemical specificities and can be simultaneously excited and detected.

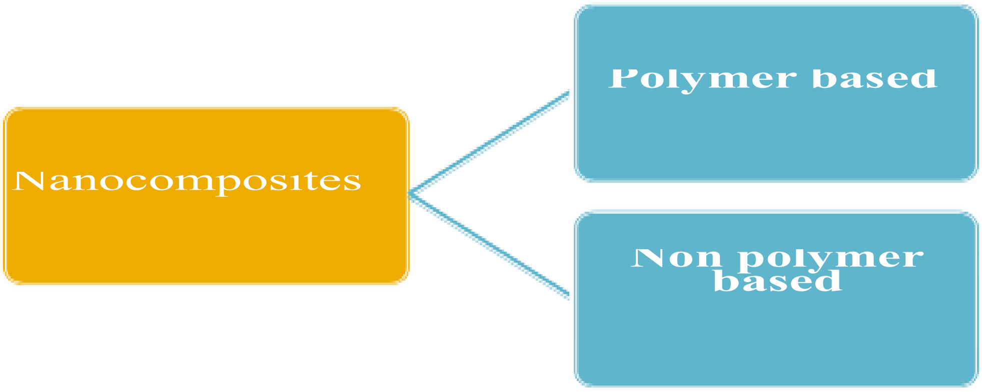
Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometre range (1 nm = 10–9 m) . Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase Mostly composite material consists of one or more discontinuous phases of distributed in one continuous phase. Hybrid components are that which are with several discontinuous phases of different natures. Discontinuous phase is usually harder and with superior mechanical properties than continuous phase. The continuous phase is called “matrix”. The discontinuous phase is called “reinforcement, or reinforcing material. (Jean-Marie Berthelot).Conducting polymer-based composites are novel materials with less than a decade of history. It is believed that the total control of the whole conducting polymer-based composite system and the optimisation of their physical properties (such as electrical conductivity and colloidal stability) are yet to be achieved, while both their commercial availability in the near future and a big leap forward for materials science are expected with their appropriate utilization. In the case of biodegradable polymer-based nanocomposites, recent developments in preparation, characterization and properties, including crystallization behaviour and melt rheology, of both the matrix and the layered (montmorillonite) nanocomposites have been discussed . Similarly, an emphasis on toughness and interfacial bonding between CNTs and polymer matrices is critically discussed to underline the stress transfer from the matrix and the potential of these composites for possible macroscale CNT-polymer production . Here, problems encountered so far are considered, and hints given regarding a critical volume fraction of CNTs to get appropriate strengthening (as observed in microcomposites); possible failure mechanisms in such composites are also presented.

Finally, to the best of our knowledge, and in view of the very limited work on metal-based nanocomposites including the ones with CNT reinforcements, no review is available to-date on this system.

Classification of Nanocomposites:

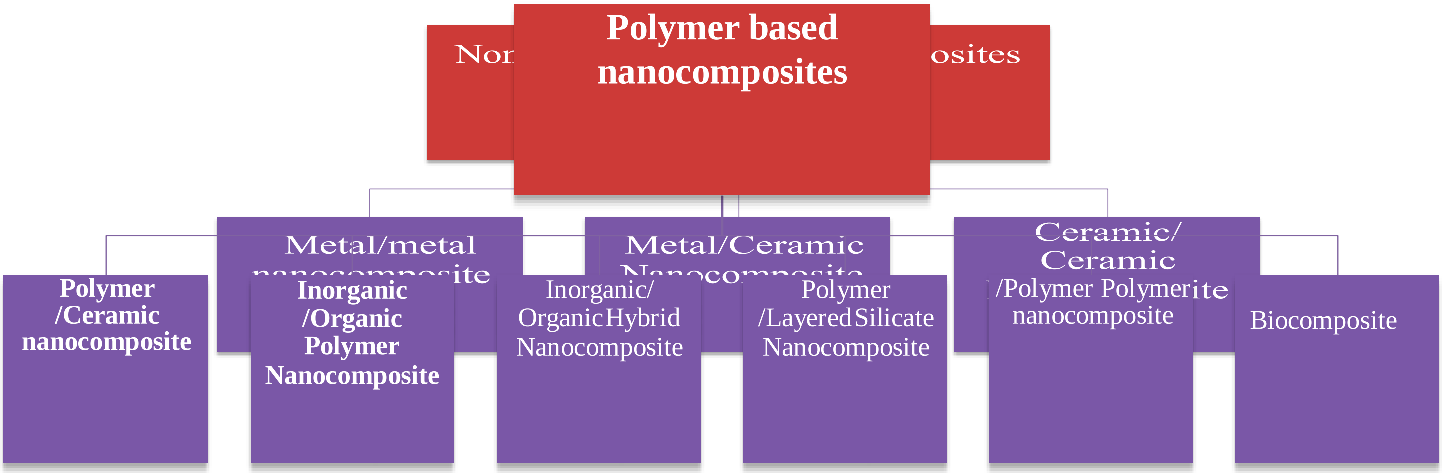
On the bases of their engineering applications, nanocomposites can be classified as;

- Functional materials i.e. based on electrical, megnetical, and/or optical behaviour, example is nanolayered semiconductor (semiconductor superlattice) composed of alternating layer of single crystal GaAs and Ga AlxAs1-x.
- Structural materials i.e. based on their mechanical properties.



Non-Polymer Based Nanocomposites:

Non-polymer based nano composites can further be classified as below:



Polymer Based Nanocomposites:

Depending on the type of filler, i.e., the nanoscale material nanocomposites, for sensing applications they are divided into:

- Metal oxide–metal oxide–based nanocomposites,
- Polymer-based nanocomposites,
- Carbon-based nanocomposites, and Noble-metal–based nanocomposites

Due to their large aspect ratios (i.e., size-to-volume ratios), submicrometer size, and unique properties, nanosensors, nanoprobes, and other nanosystems are revolutionizing the fields of chemical and biological analysis. Catalysis, separation, sorption, and fuel cells are other important fields for nanocomposite applications. Nanocomposites can be considered as solid structures with nanometer-scale dimensional repeat distance between the different phases. Typically, nanocomposites are classified as inorganic matrix (inorganic-inorganic nanocomposites), organic filler in organic (organic-organic nanocomposites), and hybrid materials, i.e., organic in inorganic or inorganic in organic matrix. Non- polymer based nanocomposite materials can be classified as follows:

Metal/Metal Nanocomposites:

Bimetallic nanoparticles either in the form of alloy or core-shell structures or being investigated in some depth because of their improved catalytic properties and changes in the electronic/optical properties related to individual, separate metals. It is postulated their interesting Physico-chemical properties, result from the combination of two kinds of metals and their fine structures.

Metal/Ceramic Nanocomposites:

In these types of composites, the electric, magnetic, chemical, optical and mechanical properties of both phases are combined. Size reduction of the components to the nanoscale causes improvement of theabove mentioned properties and leads to new application. The polymer precursors techniques offers an attractive rough to such composites proving a chemically inert and hard ceramic matrix.

Ceramic/Ceramic Nanocomposites:

Ceramic Nano composites could solve the problem of fracture failures in artificial joint implants; these would extend patient’s mobility and eliminate the high cost of surgery. The use of Zirconia-toughened alumina nanocomposite to form Ceramic/ceramic implants with potential life spends of more than 30 years.

Polymer/ceramic nanocomposites:

Nanocomposites consist of single ceramic layers (1nm thick) homogeneously dispersed in a continuous matrix. the host ceramic layer tend to orient themselves parallel to each other due to dipole-dipole interaction.

Natural Bone is a nanocomposite-bone consisting of approximately 30% matrix (collagen) material and 70% nanosized minerals (hydroxyapatite).

Inorganic/ Organic polymer nanocomposites:

Metal polymer nanocomposites attract attention because of unique properties of metal clusters which are dispersed in polymer matrix. the typical size of such metal cluster is approximately 1- 10 nm. The properties of clusters and nanoparticles (band gap, spectral properties, the transport of electrons are very different from those of bulk materials and from individual atom or molecules.

The size and grains depends on mobility of the metal atoms on the polymer surface. For example, in the case of polymethylmethacrylite (PMMA) polymer the cluster size depends on the amount of the cross linking of the polymer, which obviously changes the mobility of the metal atoms.

Inorganic/Organic hybrid nanocomposite

Hybrid inorganic/organic materials are not simply physical mixtures; they can be broadly defined as nanocomposites with organic and inorganic components intimately mixed. Indeed, hybrids are either homogenous system derived from monomers and miscible organic/inorganic components, or heterogenous systems (nanocomposites) where at least one of the component has the scale of nanometer.

Polymer/ Layered silicate Nanocomposites

Polymer/Layered silicate (PLS) nanocomposites materials are attracting considerable interest in polymer science research. In recent years the PLS nanocomposites have attracted great interest both in industry and academia, because they often exhibits remarkable improvements in materials when compare with virgin polymer and conventional macro and macro composites.

Hactorite and montmorillonite are among the most commonly used smectite-type- layered silicates for the preparation of the nanocomposites.

Polymer/polymer Nanocomposites

Polymers are more than ever under pressure to be chip and offered property profiles. The gap between block co-polymer self assembly and offer nanostructured plastic endowed with still unexplored combinations of properties is getting narrower. Mixtures of different polymers often phase separate,even when their monomer mixed homogenously.

Biocomposites

Metals and metal alloys are used in orthopaedics, dentistry and other load bearing applications. Ceramics are used with emphasis on either their chemically inert nature or high bioactivity; all polymers are used for soft tissue replacements and used for many other non structural application. Naturally occurring composites are within us all. Collagen is highly abundant and varies with more than 14 types discovered. All variations are formed from tropo-collagen molecules, which are inelastic.

Classification of Nanocomposite

Metal Oxide–Based Nanocomposites:

Nanocomposites can be based on a metal oxide matrix in which the filler is also metal oxide nanoparticles, nanowires, etc. As is by now well known, metal oxides are important semiconductors which can be used as sensing materials in chemical sensors. The advantages offered by wide-band-gap semiconductor oxides include their stability in air, relative inexpensiveness, and easy preparation in the ultradispersed state. Since porous metal oxides have attractive properties such as simplicity of preparation, tunable porosity, good chemical stability, low-temperature encapsulation, negligible swelling, mechanical and biodegradable stability, and high sensitivity at lower operating temperatures for detection of reducing and oxidizing gases, they have been used for the fabrication of chemical sensors and biosensors.

Metal oxide- based nanocomposites can be prepared by various methods. There are some methods like mechanical and chemical, which can be used. By using mechanical method which can grind the metal and give very small grain size and also give homogeneous mixture (ball milling) . In this process, alloying occurs as a result of repeated breaking up and joining (welding) of the component particles. The process can prepare highly metastable structures such as amorphous alloys and nanocomposite structures with high flexibility. Materials prepared by this method were used in a gas- sensing application. For example, it was found that sensors based on $Fe2O3$ (Sn, Ti, Zr) nanocomposites prepared this way showed improved sensitivity to ethanol and hydrocarbons. Scaling up of synthesized materials to industrial quantities is easily achieved for this mechanical alloying process, but purity and homogeneity of structures produced remains a challenge. In addition to erosion and agglomeration, high- energy milling can provoke chemical reactions, which can influence the properties of nanocomposites. Metal oxides–based nanocomposites can also be prepared by sol-gel processes. Aerogels, because of their high-porosity structure, are an ideal starting material for use in nanocomposites Aerogel nanocomposites can be fabricated in various ways, depending on when the second phase is introduced into the aerogel material. The second component can be added during the sol-gel processing of the metal oxides (before supercritical drying). It can also be added into the vapour phase (after supercritical drying), or chemical modification of the aerogel particles may be effected through reactive gas treatments. These general approaches can produce many varieties of nanocomposites. Deposition from the aerosol phase and laser ablation or pulsed laser deposition can also be successfully used for deposition of nanocomposites.

Polymer-Based Nanocomposites:

Polymer–nanoparticle composite materials have also attracted the interest of a number of researchers, due to their synergistic and hybrid properties. Ease of processability of organic polymers combined with the better mechanical and optical properties of nanoparticles has led to the fabrication of many devices. These are the nanocomposites based on polymer filler in any matrix, better described as nano filled polymer composites can be prepared using polymers. Polymer/ceramic nanocomposites (polymer matrices filled with ceramic nanopowders) are a promising material for embedded capacitors. They combine the high dielectric constant of ceramic powders and the processability and flexibility of polymers. In addition, advances in nanotechnology may enable polymer/metal nanocomposites (polymer matrices dispersed with metal nanopowders) to compete favourably with more traditional ceramic-filled polymer composites. (Nanocomposites: metal and ceramic filled polymer for Dielectrics, nano Engineered Materials).

The most important step in fabrication of polymer-based nanocomposites is the dispersion of filler in the matrix. Various mechano chemical approaches, including sonication by ultrasound, can be used for this purpose. However, the scope of such approaches for dispersing the nanoparticles is limited by re aggregation of the individual nanoparticles and establishment of an equilibrium state under certain conditions, which determines the size distribution of the agglomerate of the dispersed nanoparticles. Other limitations are related to temperature conditions and the limited stability of some types of inorganic nanoparticles to mechanical impacts .

Particles coated with a polymer shell are considerably more stable against aggregation because of a large decrease of their surface energy in comparison with bare particles. Such a polymer shell can be obtained by first synthesizing the inorganic nanoparticles and then dispersing them in a polymer solution. Finally, the polymer-coated inorganic nanoparticles are precipitated into a nonsolvating phase. This is the so-called ex-situ approach. Such a process of polymer shell formation on preformed inorganic cores can also be realized by polymerization of the desired monomer with organic nanoparticles dispersed in it. Then the nanocomposite material is formed. The ex-situ approach is the most general one because there are no limitations on the kinds of nanoparticles and polymers that can be used . The presence of such a shell increases the compatibility of the particles in the polymer matrix and makes it easier to disperse them.

In some cases, the process of polymer-based nanocomposite formation and nanoparticle preparation can be combined into one process or performed as a series of consecutive processes in one reactor (the in situ approach). In the in situ methods, nanocomposites are generated inside a polymer matrix by precursors, which are transformed into the desired nanoparticles by appropriate reactions. In situ approaches are currently getting much attention because of their obvious technological advantages over ex situ methods . One-step synthesis leads to improved compatibility of the filler and the polymer matrix and enhanced dispersion of the filler.

Up to now, in situ formation of particles in a liquid medium has probably been the most widely used method for the preparation of polymer nanocomposites containing isotropic inorganic particles . Commonly, soluble inorganic or organometallic compounds are converted by chemical reactions to colloids in water or organic solvents. The polymer may be already present during colloid synthesis or may be added afterwards. The particle dispersion can be destabilized or stabilized by the polymer, depending on the system. In the former case, the nanocomposite forms spontaneously by co-precipitation after colloid formation; in the latter case, nanocomposites can be obtained by addition of a solvent that acts as a co-precipitation agent, by casting followed by solvent evaporation, or by spin coating .

Inorganic particles can also be prepared in situ in solid polymer matrices, e.g., by thermal decomposition of incorporated precursors, reaction of incorporated compounds with gaseous species, or when polymer films containing an incorporated precursor are immersed in liquids containing the reactive species required for formation of the desired colloid. If solid reaction by-products arise from the particle synthesis, they can be embedded in the nanocomposites, hence the formation of volatile reaction side products which are able to leave polymer matrices should be preferred if possible .

Several powders of surface-modified colloids have been found to disperse well in liquids. Such dispersions can be mixed with dissolved polymers, and subsequently nanocomposites can readily be obtained by casting followed by solvent evaporation or by spin coating. The preparation of nanocomposites by diffusion of dispersed colloids in polymer films is also possible. This method is suited only for rather insoluble polymers with good swelling behaviour or for very thin films. Some nanoparticles which can be isolated as powders disperse in polymer melts without pronounced agglomeration of the primary particles, especially colloids that are coated with a layer of organic molecules. This affords a simple technique for the preparation of nanocomposites by direct mixing of particles and polymers.

Nano thin flim

There are many ways to deposit a nanosized film, in what is termed ‘bottom-up’ deposition methods. Nanosized films can also be produced by top-down approaches—such as lithography or etching—where larger materials are broken down to create nanosized structures. However, there are limits to how thin top-down approaches can go, so bottom-up methods are required to realize extremely thin films.

There are a number of bottom-up deposition methods that can be used to grow a nanofilm. In all cases, these nanofilms are deposited on to a substrate—because the films are built up and fabricated atom by atom—but can be removed in many cases after the film has been created. The most common bottom-up deposition methods for fabricating nanofilms are chemical vapor deposition (CVD), physical vapor deposition (PVD) and atomic layer deposition (ALD), and these are covered in more detail below. In addition to the methods mentioned here, there are also various nucleation-growth methods that rely on wet chemical methods, but these approaches are often unpredictable and can suffer from grain boundary defects where nano-islands/nano-clusters join together during the film formation process. So, for that reason, this article looks at different high-quality techniques rather than wet chemical methods.

Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is a class of techniques. In recent years, they have become best known for the method which can produce single-layer graphene on different substrates, but it is also a method that can be used with a wide range of materials. It has become a well-established method that is known for creating uniform nanofilms that are of high quality. In many cases, it is a process that is associated with harder materials.

Physical Vapor Deposition (PVD)

Much like CVD, physical vapor deposition (PVD) is another general class of methods that can be used to deposit atoms on to a surface to create a nanosized thin film. PVD is much like CVD in many respects and is also performed in a vacuum environment. Where CVD differs from method to method in the deposition method, PVD does also. However, PVD also varies in the methods used to generate the vaporized atoms that enter the reaction chamber.