Nanomaterials

Introduction

Nanoscience is a phenomena of manipulation of materials at the atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scales.

Nanotechnology is the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale.

Nanomaterials are defined as particles in the form of crystals, rods, or spheres having size between 1 nm and 100 nm at least in one dimension.

A nanometre is one billionth of a meter, or 10^{-9} m. Materials in this range of size exhibit some remarkable specific properties. For example crystals in the nanometre scale have a low melting point and reduced lattice constants.

Nanosystems display electronic, photochemical, electrochemical, optical, magnetic, mechanical or catalytic properties that differ significantly not only from those of molecular units, but also from those of macroscopic systems.

Physical properties that make nanomaterials different from bulk (macroscale) materials

1. Due to smallness of nanomaterials, their mass is extremely small and gravitational forces become negligible, instead electromagnetic forces are dominant in determining the behaviour of atoms and molecules.

2. For objects of very small mass, such as electrons, (wave – particle duality of matter) wave like nature has more pronounced effect. The position of electrons are represented by wave function. Quantum mechanics is used to describe motion and energy instead of classical mechanics.

3. The consequence of this is the tunnelling. It is the penetration of an electron into an energy region that is classically forbidden. For a particle having less energy than the energy required to overcome a potential barrier, there is no probability of finding the particle on the other side of the barrier according to classical theory. But quantum mechanically, there is a finite probability of the particle tunnelling through the barrier. The condition for this to happen is that the thickness (energy potential) of the barrier must be comparable to the wavelength of the particle. This is observed at nanometre scale.

4. Quantum confinement – In a nanomaterial, such as a metal, electrons are confined in space rather than free to move in the bulk of the material.

5. Quantisation of energy – Electrons in a nanomaterial can exist at discrete energy levels.

6. At nanoscale, the random motions are of same scale as the size of the material. This has an influence on how particle behave.

7. Increased surface to volume ratio – One of the distinguishing properties of nanomaterials is that they have increased surface area. This leads to unique properties of materials at nanoscale.

Synthesis of nanomaterials

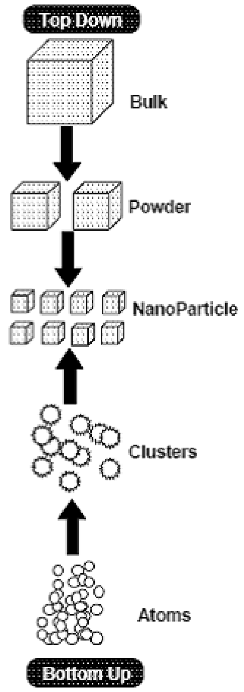
There are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures. They are

(1) top-down method of miniaturizing materials,

(2) bottom-up method of building molecular structures atom by atom or molecule by molecule.

The top-down approach has been advanced by Richard Feynman in 1959 lecture stating that "there is plenty of room at the bottom" and it is ideal for obtaining structures with long-range order and for making connections with macroscopic world.

The bottom-up approach was pioneered by Jean-Marie Lehn (revealing that "there is plenty of room at the top") and it is best suited for assembly and establishing short-range order at the nanoscale.



Top-down approach

This approach use larger (macroscopic) initial structures, which can be externally controlled in the processing of nanostructures.

Typical examples are photolithography, etching through the mask, ball milling and application of severe plastic deformation.

1. Top-Down: lithography - The most used top-down approach is photolithography. It has been used to manufacture computer chips and produce structures smaller than 100 nm. Typically, an oxidized silicon (Si) wafer is coated with a 1µm thick photoresist layer. After exposure to ultraviolet (UV) light, the photoresist undergoes a photochemical reaction, which breaks down the polymer by rupturing the polymer chains. Subsequently, when the wafer is rinsed in a developing solution, the exposed areas are removed leading to nanosize material. The other methods are electron-beam lithography and X – ray lithography.

In a ball milling process a powder mixture placed in the ball mill (a cylinder with steel balls which are rotating at high speeds) is subjected to high-energy collision from the balls. At the initial stage of ball milling, the powder particles are flattened by the compressive forces due to the collision of the balls. Micro-forging leads to changes in the shapes of individual particles, or cluster of particles being impacted repeatedly by the milling balls with high kinetic energy.At the intermediate stage of the mechanical alloying process, the intimate mixture of the powder constituents decreases the diffusion distance to the micrometre range. Fracturing and cold welding are the dominant milling processes at this stage. At the final stage of the mechanical alloying process, considerable refinement and reduction in particle size is achieved.

Bottom-up approach

This approaches include the miniaturization of materials components (up to atomic level) with further self assembly process leading to the formation of nanostructures. During self-assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structures.

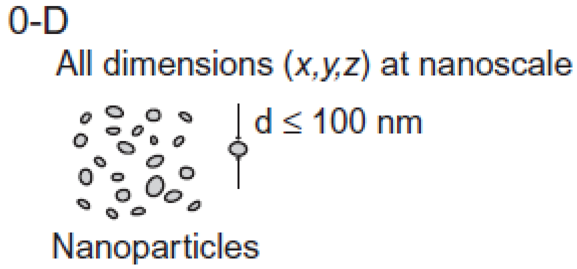
Examples- 1. sol-gel processing, 2. chemical vapour deposition (CVD), 3. plasma or flame spraying synthesis, 4. laser pyrolysis, 5. atomic or molecular condensation – Inert gas condensation.

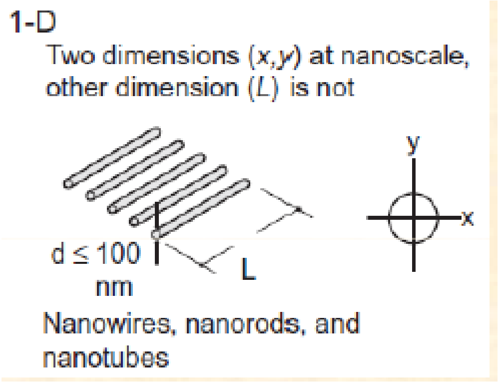
1. The sol-gel technique for synthesis of nanomaterials is a wet- chemical technique. Such techniques are used for the fabrication of materials starting from a chemical solution (sol, short for solution) which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Precursors in the form of acetates or carbonates or nitrates are taken and then dissolved in deionized water. This starting material is used to produce a colloidal suspension known as gel. After that a gelling agent for example, polyvinyl alcohol is added and this will produce a gel. A thin film coating is made on a substrate for example, Ni or Ti sheets and glass. At last the film is annealed at suitable temperature and then characterized.
2. In a chemical vapour deposition process, vapour is formed in a reaction chamber by pyrolysis reduction, oxidation or nitridation, and then deposited on the surface. Areas of growth are controlled by patterning processes like photolithography or photomasking (deposition patterns are etched on to the surface layers of the wafers).
3. The inert gas condensation (IGC) process is one of the most known and simplest technique for production of nanoparticles (in particular, Me nanopowders). An inorganic material is vaporized inside a vacuum chamber into which an inert gas (typically argon or helium) is periodically admitted. Once the atoms boil off, they quickly lose their energy by colliding with the inert gas. The vapour cools rapidly and supersaturates to form nanoparticles with sizes in the range 2–100 nm that collect on a finger cooled by liquid nitrogen.
4. The production route for 1-D rod-like nanomaterials by liquid phase methods is similar to that for the production of nanoparticles. CVD methods have been adapted to make 1-D nanotubes and nanowires. Catalyst nanoparticles are used to promote nucleation. Nanowires of other materials such as silicon (Si) or germanium (Ge) are grown by vapour-liquid-solid (VLS) methods.

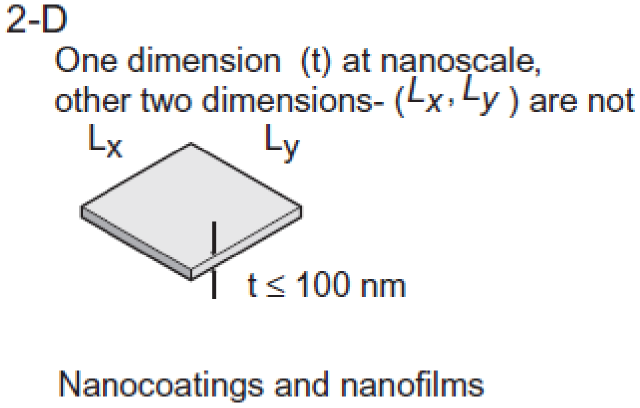
Classification of nanomaterials

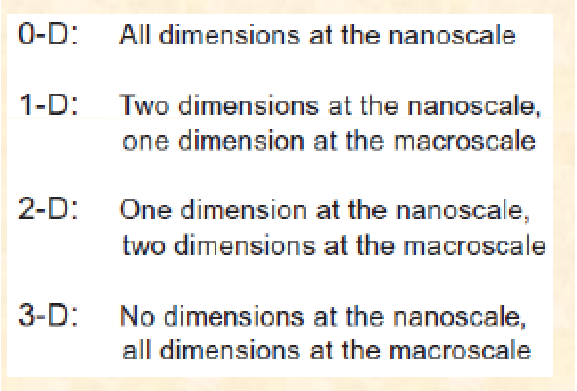
Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).

(1) zero-dimensional (0-D),
(2) one-dimensional (1-D),
(3) two-dimensional (2-D), and
(4) three-dimensional (3-D).









0-D:	All dimensions at the nanoscale
1-D:	Two dimensions at the nanoscale, one dimension at the macroscale
2-D:	One dimension at the nanoscale, two dimensions at the macroscale
3-D:	No dimensions at the nanoscale, all dimensions at the macroscale

Zero dimensional nanomaterials

Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm). The most common representation of zero-dimensional nanomaterials are nanoparticles and quantum dots or nano-clusters - self-assembled nanoislands and chemically synthesized nanoparticles

Nanoparticles can be amorphous or crystalline, be single crystalline or polycrystalline, be composed of single or multi-chemical elements, exhibit various shapes and forms, exist individually or incorporated in a matrix, be metallic, ceramic, or polymeric.

One-dimensional nanomaterials

One dimension is outside the nanoscale. This leads to needle like-shaped nanomaterials. 1-D materials include nanotubes, nanorods, and nanowires.

1-D nanomaterials can be amorphous or crystalline, single crystalline or polycrystalline, chemically pure or impure, standalone materials or embedded in within another medium, be metallic, ceramic, or polymeric. Typical example— carbon nanotube and silicon nanowires

Two-dimensional nanomaterials

Two of the dimensions are not confined to the nanoscale. 2-D nanomaterials exhibit plate-like shapes. They include nanofilms, nanolayers, and nanocoatings.

2-D nanomaterials can be amorphous or crystalline, made up of various chemical compositions, used as a single layer or as multilayer structures, deposited on a substrate, integrated in a surrounding matrix material, be metallic, ceramic, or polymeric. Typical example—semiconductor quantum wells.

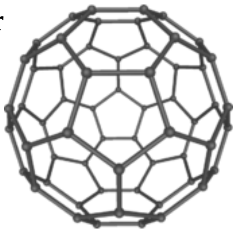
Three-dimensional nanomaterials

Bulk nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm. Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale. In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations.

With respect to the presence of features at the nanoscale, 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

Fullerenes

Fullerene is any molecule in the form of a hollow sphere, ellipsoid or tubular structure composed entirely of carbon. They are commonly referred to as "Buckyballs" – named after Buckminster Fuller who designed geodesic physical structures and buildings based on this geometry. Discovered in 1985 by Smalley, Curl and Kroto., it is the roundest and most symmetrical large molecule known to man.



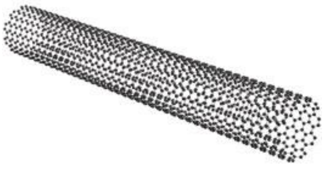
Using a laser to vapourise graphite rods in an atmosphere of helium gas, these chemists obtained cage like molecules composed of 60 carbon atoms joined together by single and double bonds to form a hollow sphere with 12 pentagonal and 20 hexagonal faces.

The C_{60} molecule undergoes a wide range of novel chemical reactions. It readily accepts and donates electrons, a behaviour that suggests applications in batteries and advanced electronic devices.

Graphene

It is one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honeycomb (hexagonal) crystal lattice. It can be viewed as an atomic-scale chicken wire made of carbon atoms and their bonds. The carbon-carbon bond length in graphene is about 0.142 nm. Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes and fullerenes. It has the ability to conduct electrons and is transparent. Those qualities make graphene a tantalizing alternative for use as a transparent conductor, the sort now found in everything from computer displays and flat panel TVs to ATM touch screens and solar cells.

Carbon nanotubes (CNT) - Graphene is the basic structural building block of carbon nanotubes. Carbon nanotubes (CNT) also known as 'buckytubes' have a cylindrical



nanostructure in the form of a tube and an engineered CNT typically has a nanoscale thick wall, geometrically shaped similar to a Buckyball, with a nanoscale diameter, and a length that may exceed 100 nm. Carbon nanotubes are manufactured as single wall carbon nanotubes (SWCNT) or multiwall carbon nanotubes (MWCNT). They are synthesized in a variety of ways, including arc discharge, laser ablation and chemical vapor deposition. With respect to tensile strength, carbon nanotubes are the strongest and stiffest materials yet discovered, more than 5 times stronger than Kevlar. Since CNTs have a very low density, their specific strength is 300 times greater than stainless steel, though under compression CNTs appear to be a lot weaker.

Nanotubes properties

1. Molecular perfection: essentially nearly free of defects
2. Electrical conductivity: probably the best conductor of electricity on a nanoscale level that can ever be possible
3. Thermal conductivity: comparable to diamond along the tube axis
4. Mechanical: probably the stiffest, strongest, and toughest fiber that can ever exist
5. Chemistry of carbon: can be reacted and manipulated with the richness and flexibility of other carbon molecules.
6. Self-assembly: strong van der Waals attraction leads to spontaneous roping of many nanotubes.

Quantum dots

Quantum dots, also known as nanocrystals, are another form of nanomaterial and are a specific type of semiconductor. They are 2-10 nanometers (10-50 atoms) in diameter, and because of their electrical characteristics, they are [electrically] tunable. The electrical conductivity of semiconductors can change due to external stimulus such as voltage or exposure to light, etc. As quantum dots have such a small size they show different properties to bulk material. Hence the 'tunability', for example, sensitivity to different wavelengths of light, can be adjusted by the number of atoms or size of the quantum dot. Quantum dots are typically made from CdSe, ZnS or CdTe compounds,

Quantum dots (QD) are semiconductor nanostructures that act as artificial atoms by confining electrons and holes in 3-dimensions. Quantum dots absorb light, then quickly re-emit the light but in a different colour. They have extremely sharp (delta-function-like) density of the available energy states and the strong confinement of electron and hole wave functions inside the dots. As a result, electrons are confined to specific – discrete – energy levels, similar to conditions that resemble those in an individual atom.

The confinement can be due to electrostatic potentials, (generated by external electrodes, doping, strain, impurities), the presence of an interface between different semiconductor materials (e.g. in core-shell nanocrystal systems), the presence of the semiconductor surface (e.g. semiconductor nanocrystal), or a combination of these.

In fluorescent dye applications, emission frequencies increase as the size of the quantum dot decreases, resulting in a colour shift from red to blue in the light emitted. Excitation and emission of the quantum dot are therefore highly tunable. Because the size of the crystals can be controlled during synthesis, the conductive properties can be carefully controlled.

Main applications: optical and optoelectronic devices, quantum computing, and information storage. Semiconductors with QDs as Material for Cascade Lasers. Semiconductors with QDs as Material for IR Photodetectors and Injection Lasers with QDs

Nanoparticles

Nanoparticles (NP) are synthesized or machined. They range in size from 2 nm to 100 nm. Nanoparticle materials vary depending on their application. Because Nanoparticles are invisible to the naked eye, they are usually supplied suspended in a liquid. The color is due to the refraction of light the surface area of the particular nanoparticle reflects. Different sized nanoparticles exhibit different colours based on its surface area.

Nanofibers and Nanowires

Nanofibers are slightly larger in diameter than the typical nanomaterial definition, though still invisible to the naked-eye. Their size ranges between 50 nm - 300 nm in diameter and are generally produced by electro spinning in the case of inorganic nanofibers or catalytic synthesis for carbon nanotubes. Nanofibers can be electrostatically aligned and biochemically aligned. Similar to nanofibers are nanowires, though nanowires are considerably smaller in diameter, of the order of 4 nm and conduct electricity.

Electron confinement or Quantum effects

The phenomenon of altering of a material's electronic properties as it decreases in size is referred to as the quantum size effect. The overall behavior of bulk crystalline materials changes when the dimensions are reduced to the nanoscale.

For 0-D nanomaterials, where all the dimensions are at the nanoscale, an electron is confined in 3-D space. No electron delocalization (freedom to move) occurs.

For 1-D nanomaterials, electron confinement occurs in 2-D, whereas delocalization takes place along the long axis of the nanowire/rod/tube.

In the case of 2-D nanomaterials, the conduction electrons will be confined across the thickness but delocalized in the plane of the sheet.

The effect of confinement on the resulting energy states can be calculated by quantum mechanics, as the "particle in the box" problem. An electron is considered to exist inside of an infinitely deep potential well (region of negative energies), from which it cannot escape and is confined by the dimensions of the nanostructure.

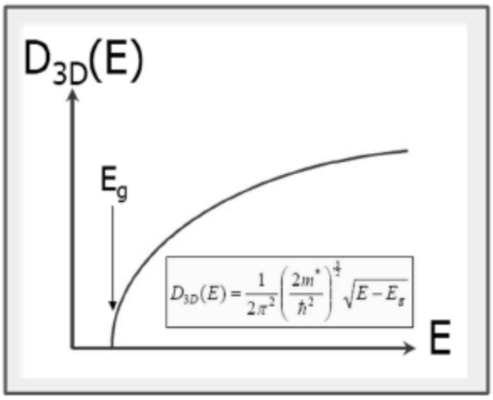
(0-D) $$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2 + n_y^2 + n_z^2\right)$$

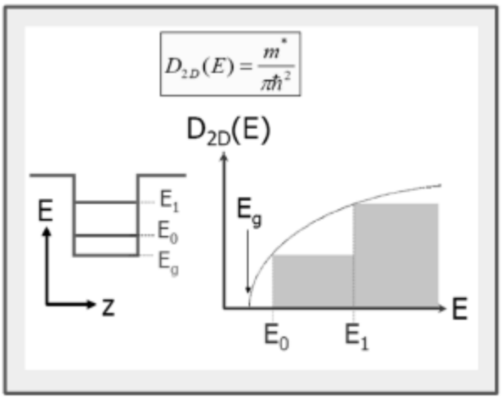
(1-D) $$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2 + n_y^2\right)$$

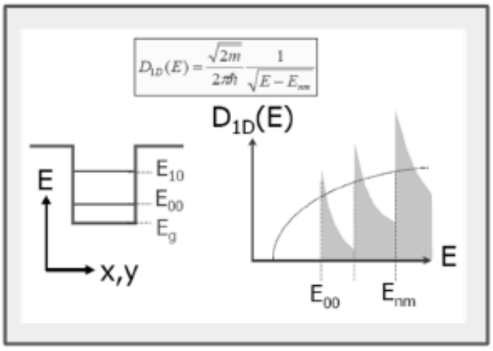
(2-D) $$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2\right)$$

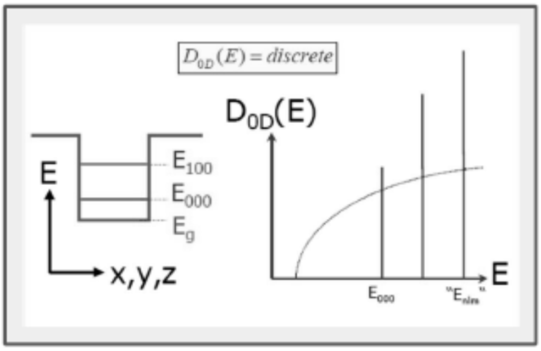
The above expressions give the energies in different dimensional nanoparticles. In the expression h is Planck's constant, m is the mass of the electron, L is the width (confinement) of the infinitely deep potential well, and n_x, n_y and n_z are the principal quantum numbers in the three dimensions x, y, and z. The smaller the dimensions of the nanostructure (smaller L), the wider is the separation between the energy levels, leading to a spectrum of discreet energies.

Density of states – Energy levels









The density of states is the number of quantum states per unit energy. In other words, the density of states, denoted by $g(E)$, indicates how densely packed quantum states in a particular system. Consider the expression $g(E)dE$. Integrating the density of the quantum states over a range of energy will produce a number of states. $N(E) = \int_E^{\Delta E} g(E)dE$. Thus $g(E)dE$ represents the number of states between E and dE. (In the diagram *D(E) dE = g(E)dE)* The above diagrams show that as we move to 3D from 0D the energy levels become discrete. The number of quantum states become important in the determination of optical properties of a material such as a semiconductor (i.e. carbon nanotubes or quantum dots).

Properties of nanomaterials

1. Surface properties :

When a bulk material is subdivided into materials on the nano scale, the total volume remains the same but the collective surface area is increased. This results in increase of surface to volume ratio at nanoscale as compared to bulk materials. The ratio of surface area to volume of a material is given by $\frac{area}{volume} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$. Thus as the radius of a given material is decreased, its surface to volume ratio increases. This results in more number of atoms or molecules on the surface as compared to its number inside the volume in a nanomaterial.

The molecules or atoms at the surface of a nanomaterial possess high surface energy and have high reactivity and have greater tendency to agglomerate. Thus, as the nanomaterials have s significant proportion of atoms existing at the surface, this has profound effect on reactions that occur at the surface such as catalysis reactions and detection reactions.

The melting point of nanomaterials are reduced as compared to bulk counterpart due to larger surface atoms present.

2. Electrical properties :

In bulk metals, the valence and conduction bands overlap, while in metal nanoparticles there is a gap between these bands. The gap observed in metal nanoparticles can be similar in size to that seen in semiconductors (< 2 eV) or even insulators (> 2 eV). This results in a metal becoming a semiconductor. For example, carbon nanotubes can be either conductors or semiconductors depending on their nano structure. Another example is super capacitors which has effectively no resistance which disobey ohm's law.

3. Optical properties :

Nanomaterials, in general have peculiar optical properties as a result of the way light interacts with their nano structure. In nanosized semiconductors there exists discrete energy states. Thus bands split and become discrete. Light of only certain wavelengths of certain dimensions are absorbed. This leads to emission of certain monochromatic wavelengths. Due to quantum confinement, energy gap increases. Thus more energy is required for absorption. Higher energy means shorter wavelength of light is emitted resulting in blue Shift. Tuning the nanosize of a semiconductor means tuning of bandgap leading to light of certain wavelength being emitted. Thus the same material emits different colours depending on its size.

Scattering of light depends on the size of a particle. By using nanomaterials in sunscreens, the wavelength of scattered light shifts towards shorter wavelengths and appear transparent instead of white. Metallic Nanoparticles show changes in colour (gold or silver nano particles) in spectra due to Surface Plasmons (a group of surface conduction that travel parallel to metal interface). Due to localization of these electrons, they oscillate leading to resonance when light of suitable frequency is absorbed them.

4. Magnetic properties

The magnetic properties of a magnet are described by its magnetisation curve (called hysteresis curve which is the variation of intensity of magnetisation with applied magnetic field). These curves show the property like whether a magnet can be used as permanent magnet or a electromagnet etc…. The size of the material can change the property of a magnet by changing the magnetisation curves. Thus nanostructuring of bulk magnetic materials leads to changes in the curves which can produce soft or hard magnets with improved properties.

5. Mechanical properties

Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply due to the reduced probability of defects. Carbon nanotubes are 100 times stronger than steel but six times lighter.

Applications of nanotechnology in various fields:

Nanotechnology offers an extremely wide range of potential applications from electronics, optical communications and biological systems to new materials.

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

1. Fuel cells

A fuel cell is an electrochemical energy conversion device that converts the chemical energy from fuel (on the anode side) and oxidant (on the cathode side) directly into electricity. The heart of fuel cell is the electrodes.

Microbial fuel cell is a device in which bacteria consume water-soluble waste such as sugar, starch and alcohols and produces electricity plus clean water. This technology will make it possible to generate electricity while treating domestic or industrial wastewater. Microbial fuel cell can turn different carbohydrates and complex substrates present in wastewaters into a source of electricity. The efficient electron transfer between the microorganism and the anode of the microbial fuel cell plays a major role in the performance of the fuel cell. The organic molecules present in the wastewater possess a certain amount of chemical energy, which is released when converting them to simpler introduction to Nanomaterials molecules like CO_2 The microbial fuel cell is thus a device that converts the chemical energy present in water-soluble waste into electrical energy by the catalytic reaction of microorganisms.

Carbon nanotubes (CNTs) have chemical stability, good mechanical properties and high surface area, making them ideal for the design of sensors and provide very high surface area due to its structural network. Since carbon nanotubes are also suitable supports for cell growth, electrodes of microbial fuel cells can be built using of CNT. Due to three-dimensional architectures and enlarged electrode surface area for the entry of growth medium, bacteria can grow and proliferate and get immobilized. Multi walled CNT scaffolds could offer self-supported structure with large surface area through which hydrogen producing bacteria can eventually grow and proliferate.

2. Catalysis

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

3. Phosphors for High-Definition TV

The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolution of monitors.

4. Next-Generation Computer Chips

The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. By achieving a significant reduction in their size, the microprocessors, which contain these components, can run much faster, thereby enabling computations at far greater speeds.

5. Nanowires for junctionless transistors

Transistors are made so tiny to reduce the size of sub assemblies of electronic systems and make smaller and smaller devices, but it is difficult to create high-quality junctions. In particular, it is very difficult to change the doping concentration of a material over distances shorter than about 10 nm. Researchers have succeeded in making the junctionless transistor having nearly ideal electrical properties. It could potentially operate faster and use less power than any conventional transistor on the market today.

The device consists of a silicon nanowire in which current flow is perfectly controlled by a silicon gate that is separated from the nanowire by a thin insulating layer. The entire silicon nanowire is heavily n-doped, making it an excellent conductor. However, the gate is p-doped and its presence has the effect of depleting the number of electrons in the region of the nanowire under the gate. The device also has near-ideal electrical properties and behaves like the most perfect of transistors without suffering from current leakage like conventional devices and operates faster and using less energy.

6. Elimination of Pollutants

Nanomaterials possess extremely large grain boundaries relative to their grain size. Hence, they are very active in terms of their chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

7. Sun-screen lotion

Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO_2 provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO_2) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin colour while working better than conventional skin-lotions.

8. Sensors

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