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Nano Science and Technologies

1.1 Concepts of Nanoscience and Nanotechnologies

1.1.1 Introduction

Nanoscience and Nanotechnologies are very important multidisciplinary areas dealing with matters, materials and structures/composites with at least one dimension roughly between 1 and 100 nanometers. As the physico chemical characters of these nano materials differ

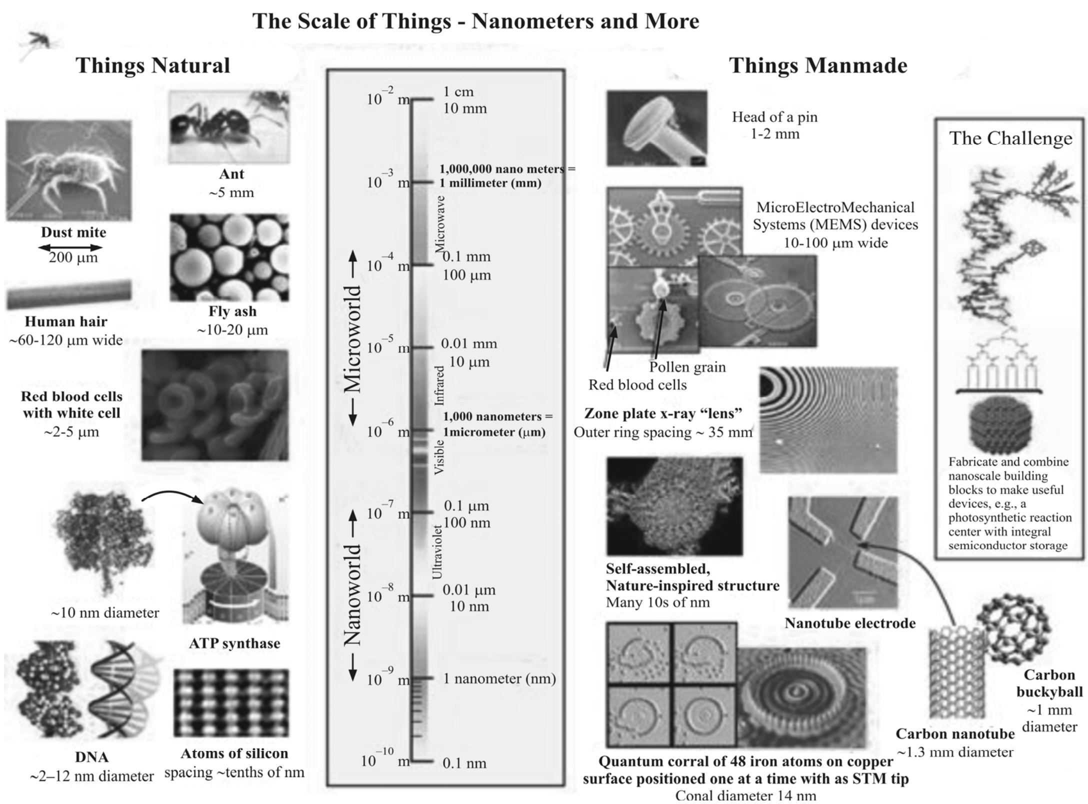

Figure 1.1 Scale of materials with micro and nano dimensions (1).

significantly from those at a macro scale leading to exhibition of extraordinary properties, these are finding wide range of applications with great potential to lead and provide innovative breakthroughs that can be applied to real life situations. In-view of their extensive and ever expanding applications in modern scientific world in different disciplines there is a great need to understand clearly the fundamental and basic concepts governing the Nanoscience and technologies which are discussed in this book.

Various natural and man-made materials which possess micro and nano scale dimensions are presented in Fig. 1.1. The prefix "nano" means one billionth. One nanometer (abbreviated as 1 nm) is 1/1,000,000,000 of a meter, which is close to 1/1,000,000,000 of a yard. For example a human hair measures 50,000 nanometers across a bacterial cell measures a few hundred nanometers across and ten hydrogen atoms in a line make up one nanometer.

1.1.2 What is Nanoscience?

As materials at the nanoscale exhibit properties (i.e., chemical, electrical, magnetic, mechanical and optical) quite different from the bulk materials and sometimes with enhanced performance, the basic scientific concepts governing these special properties fall under nanoscience. Thus "Nanoscience is the study of materials, phenomena, properties, and applications at the smallest length scale at which we can control matter"

Nanoscience is an interdisciplinary science which integrates knowledge from various vertical fields like Physics, Chemistry, Biology, Medicine, Informatics, and Engineering (Figure 1.2) and expands areas of material science and engineering.

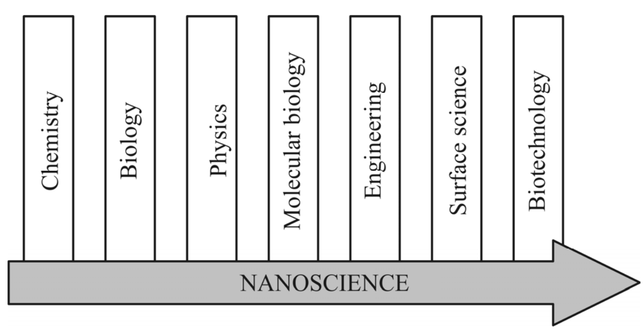

Figure 1.2 Nano science -horizontally integrating multi disciplinary science.
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1.1.3 What are Nano Technologies?

The main objectives of nanotechnologies are

(i) To Produce nano materials with extraordinary properties by controlling and manipulating the dimensions of their fundamental blocks of matter at nanoscale i.e at atomic/molecular level

(ii) To model, simulate, design and manufacture novel nanodevices / nano composites of highly specific properties and assemble them into nano systems with revolutionary functional abilities for high end applications

(iii) To study and explore the extraordinary properties/performance of nanomaterials for their highly efficient and cost effective applications to save energy and resources.

Thus nanotechnologies offer innovative approaches in smart material production by development of convergent (hybrid) technologies covering various industrial sectors (Figure 1.3).

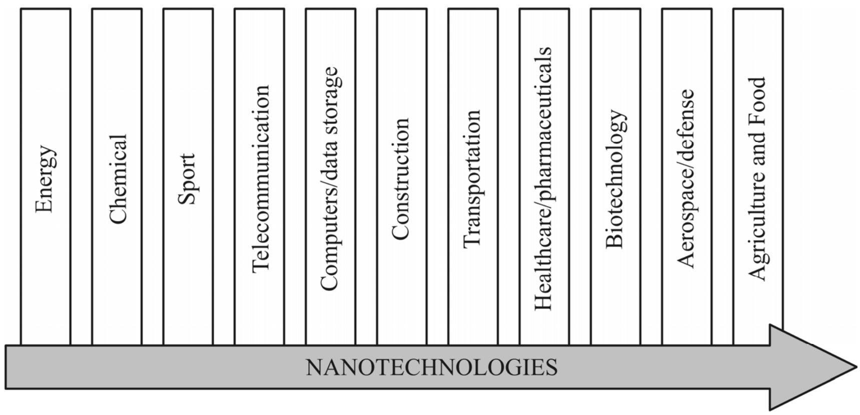

Figure 1.3 Nano Technologies-horizontal converging technologies.
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1.1.3.1 Scope and Potential of Nano Technologies

With advancement of highly precise nanotechnology tools and techniques, it is now become possible to produce a number of novel nano structures/devices with tailored and controlled nano-dimensions which are finding extensive applications in different disciplines. These new nano-production process can tune the properties, responses and functions of living and non-living matter to desired levels/specifications. Nanomaterials have a relatively larger surface area when compared to the same mass of bulk material produced in a larger form. Nano particles can make materials more chemically reactive and affect their strength or electrical properties.

The following materials based on their size and shape, fall under Nano materials which have great industrial importance: (a) Nano particles, (b) Nano capsules, (c) Nano fibers, (d) Nano wires, (e) Fullerenes (carbon 60), (f) Nano tubes, (g) Nano springs, (h) Nano belts, (i) Quantum dots, (j) Nano fluids etc.

Extensive applications of these new nanomaterial are now being realized in different areas like electronic and mechanical devices, in optical and magnetic components, quantum computing, tissue engineering, and other biotechnologies, medical applications etc. With advancement of new instrumentation/nanotools both for characterization and production, the scope of nanotechnologies are ever expanding rapidly in global markets.

1.1.4 Definition of Nanotechnology

US National Science and Technology Council (2) defines nanotechnology as : "*The essence of nanotechnology is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. The aim is to exploit these properties by gaining control of structures and devices at atomic, molecular, and supramolecular levels and to learn to efficiently manufacture and use these devices*".

In short, nanotechnology is the ability to build micro and macro materials and products with atomic precision.

United States National Science Foundation (3) defines nanoscience / nanotechnology as studies that deal with materials and systems having the following key properties.

1. **Dimension:** At least one dimension from 1 to 100 nanometers (*nm*).
2. **Process:** Designed with methodologies that shows fundamental control over the physical and chemical attributes of molecular-scale structures.
3. **Building block property:** They can be combined to form larger structures.

Nano science, in a general sense, is quite natural in microbiological sciences considering that the sizes of many bioparticles dealt with (like enzymes, viruses, etc) fall within the nanometer range.

Our ability to control and manipulate nanostructures will make it possible to exploit new physical, biological and chemical properties of systems that are intermediate in size, between single atoms, molecules and bulk materials.

As per British Standards Institute (BSI) the following definitions are also used.

Nano material: Material with one or more external dimensions, or an internal structure, which could exhibit novel characteristics compared to the same material without nanoscale features.

Nano particle: Particle with one or more dimensions at the nanoscale.

Nano composite: Composite in which at least one of the phases has at least one dimension on the nanoscale.

Nano structured material: Having a structure at the nanoscale.

1.1.5 How Laws of Physics differ at the Nano Scale-Quantum Size Effects

Due to extremely small size of nanomaterials approaching nearly the size of single atoms or molecules, they possess extremely small mass with negligible gravitational forces. However they exhibit dominant electromagnetic forces resulting special electrical, magnetic and spectral properties which can be explained by Quantum mechanics model for describing the motion and energy of atoms and electrons.

1.1.5.1 Wave-Corpuscle Duality of Matter

Quantum mechanics theory is mainly based on the Heisenberg's uncertainty principle which deals with wave - corpuscle duality of matter particularly applies to subatomic particles like electron, positron, photon etc. Thus, electrons exhibit wave behaviour and their position is represented by a wave (probability) function. Werner Heisenberg uncertainty principle states that the position and momentum of an object cannot simultaneously be determined (4). For example the more precisely the position is determined the less precisely the momentum will be known. Nanotechnology which deals with position and momentum of atoms and molecules can be assessed by Quantum mechanical treatment involving Heisenberg uncertainty principle (4) (Figure 1.4).

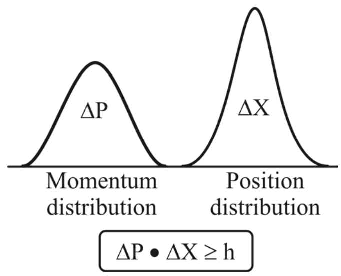


Figure 1.4 Heisenberg uncertainty principle.

1.1.5.2 Tunneling Effect

Any particle/body/object can pass through a potential barrier only if it acquires sufficient energy to jump over the barrier and the probability of finding the object which has lower energy than needed to jump the barrier on the other side of it will be zero as per classical physics. (Figure 1.5). However in quantum mechanical treatment, a particle with energy less than that

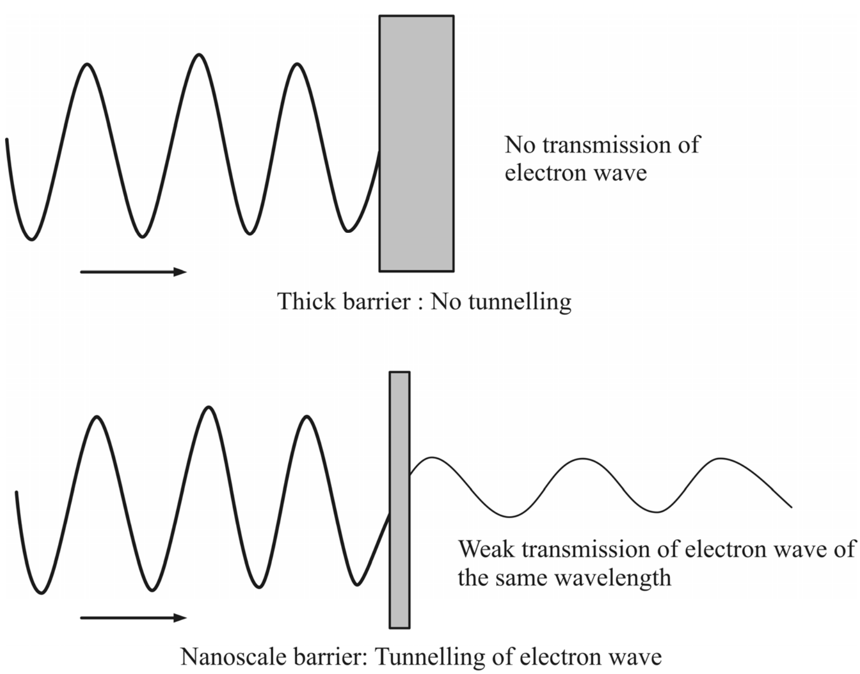


Figure 1.5 Quantum tunneling.

required to jump the barrier will have a finite probability of being found on the other side of the barrier. As shown in Figure 1.5 one can imagine that the particle passes into a 'virtual tunnel' through the barrier. Penetration of a particle/electron into an energy region that is classically forbidden (5) is known as tunneling effect. When a particle (an electron) with lower kinetic energy is able to exist on the other side of an energy barrier with higher potential energy, thus defying a fundamental law of classic mechanics then it is considered tunneling of particle/electron takes place.

In some nanomaterials as the thickness of the potential barrier will be comparable with the wavelength of the particle/electron the tunnel effect can be observed. The intensity of the current generated by the tunneling electron gives information about the thickness of the potential boundary layer of the nano material and this principle is used in 'Scanning Tunneling Microscopy' (STM). Conductive surfaces with nano scale texture can be imaged by measuring the tunneling current between a non-contact surface and the substrate. Hence the STM has become an important research tool in nanotechnology for characterization of surfaces with nano scale resolution.

1.1.5.3 Quantum Confinement

The electronic energy levels are continuous in the bulk materials whereas in nano particle/crystal /metals, they are discrete (finite density of states). So the electronic wave function in these nano materials will be confined in space of their physical dimensions and are not free to move as in the bulk of the material. This phenomenon is called Quantum confinement and therefore Nano Crystals are also referred to as quantum dots (QDs). In nanomaterials as their size approaches to that of electron wavelength in one or more dimensions, quantum mechanical characteristics of the electrons that are not manifest in the bulk material can start to contribute to or even dominate the physical properties of the material. Further the quantum mechanical (wave like) properties of electrons inside matter are also influenced by variations on the nanoscale.

Thus by proper nanoscale design of nanomaterials it is possible to vary their micro and macroscopic properties, such as charge capacity, magnetization and melting temperature, without changing their chemical composition.

For example, the ability of nano gold as well as of other noble metals and semiconductors relies on quantum confinement which is a very successful model for describing the size dependent electronic structure of nanometer sized materials. According to this theory electrons are confined in all three dimensions causing matter to behave completely different in terms of its optical and electronic properties.

1.1.5.4 Reasons for Quantization of Energy in Nano Materials

When the particle size decreases as in nanoparticles, the spacing of the electronic levels and the bandgap increases (Figure 1.6) in-view of the fact that the electron hole pairs are now much closer together and the Coulombic interaction between them can no longer be neglected giving an overall higher kinetic energy.

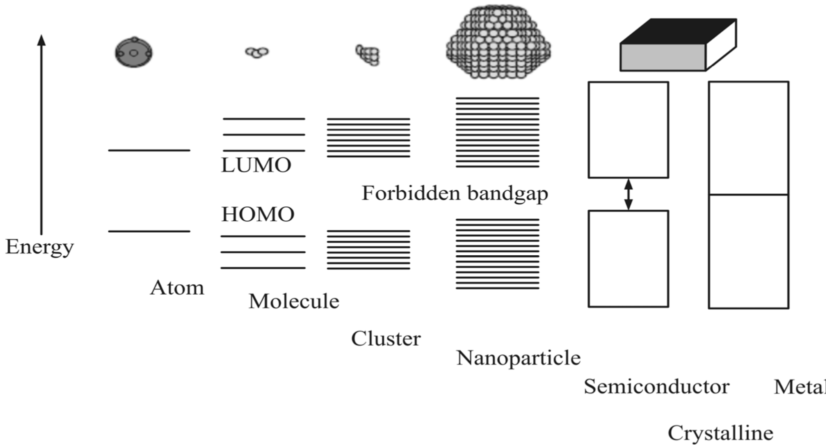


Figure 1.6 Size dependent quantization of energy levels HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).

Further due to the spatial confinement of the charge carriers, the edge of the valance and conduction bands split into discrete, quantized, electronic levels similar to electronic levels in atoms and molecules. Thus in nano particles size quantization arises as their size is comparable to the de Broglie wavelength of its charge carriers (*i.e.,* electrons and holes). For example Quantum dots are nanomaterials which display the effect of quantization of energy.

1.1.5.5 Random Molecular Motion

Above absolute zero temperature molecule undergo motion due to their kinetic energy which is called random molecular motion. While these motions will be insignificant in case of macro molecules when compared to their size, whereas in the case of nanomaterials they are of the same scale as their size and will have great influence on their properties and how they behave for example influence on Brownian motion.

1.1.6 Quantum Size Effects on Physical Properties

In nano materials as their size in one or more dimensions approach the size of an electron wavelength, quantum mechanical characteristics of the electron start contributing or even dominate their physical properties unlike in bulk materials.

Nano materials/particle whose dimensions are in between one and hundred nano meters, will have an electronic structure which falls in between discrete electronic structure exhibited by atom or molecule and the band structure exhibited by bulk material. This aspect will be responsible for corresponding changes in their respective physical properties. These size dependent changes in physical properties of nano materials from bulk are called as Quantum size effects. Quantum size effects can be exploited to design and production of tailor made nano materials for highly specific applications.

Crystals also exhibit quantum size effects which depend on the type of bonding and complex quantum mechanical models are required to predict the evolution of such properties. However to compare experimental data and theoretical predictions for changes in physical properties with particle size, very well defined conditions are needed.

1.1.6.1 Different Categories of Quantum Confined Nano Materials

As discussed above due to quantum confinement of electrons, nanomaterials exhibit hybrid /mixed electronic structures leading to special physical properties which have great potential for commercial applications. These nano structures can be classified as given below based on the degree of freedom of electrons existing in them

1. **Three Dimensional Systems - Nano particles**: in which the electrons have degrees of freedom in all three dimensions i.e length, breadth and height.

   As they exhibit high performance and special properties like chemical reactivity and optical behavior in comparison with corresponding bulk materials, nano particles are of great commercial interest.

   Example - high performance: Nano particles can be arranged into layers on surfaces, providing a large surface area and hence enhanced activity as catalysts.

   Example - special properties: Titanium dioxide and zinc oxide become transparent at the nanoscale and have potential applications in sunscreens.

   Other range of potential applications:

   Regular applications in cosmetics, textiles and paints and special high end applications like drug delivery systems where they could be to used to deliver drugs to a specific target site in the body.

2. **Two dimensional Quantum Well Systems-Nanowires, nanotubes etc.**

   When the electron can move only in two directions and have restrictions in one dimension they are termed as Quantum well which is a two dimensional system. They will have only two dimensions length and breadth like in nano wires and nano tubes and as their electronic property is quantized as the spatial distance is very very small they are termed as quantum wells.

   Quantum wells are formed in a semiconductor by having a material like gallium arsenide sandwiched between two layers of a material with a wider band gap like aluminum arsenide. These structures can be grown by molecular beam epitaxy or chemical vapor deposition with control of layer thickness down to monolayers.

   Single Quantum Well (SQW)**:** A single quantum well structure is formed by hetro epitaxial growth in an ultra thin layer of binary, tertiary, quaternary, or quintanary, semi conductor alloys on a suitable substrate. Examples are InP on a GaAs (InP/GaAS), AlGaAs on a GaAs (Figure 1.7) and Si on Ge(Si/Ge) systems.

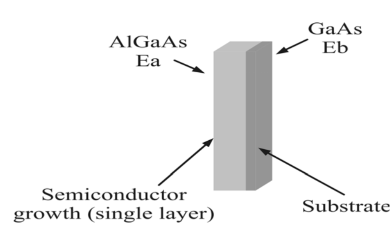


Figure 1.7 Single quantum well : AlGaAs on a GaAs.

Double Quantum Well (DQW) Systems**:** A double quantum structure is a hetero structure in which a small band gap ultra thin layer is sandwiched between wide band gap layers. Often the wide band gap materials are of the same semiconductor. An example is: AlGaAs/GaAs/AlGaAs double quantum well (Figure 1.8) (system(DQW).

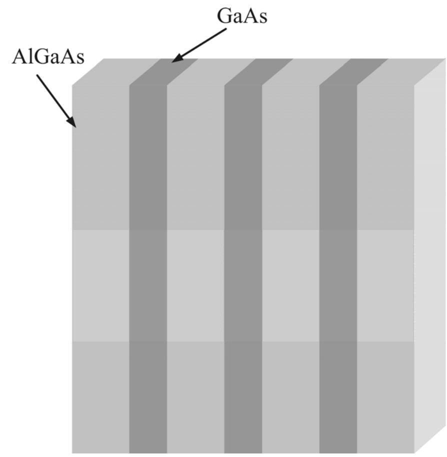


Figure 1.8 AlGaAs/GaAs/AlGaAs double quantum well.

Multiple Quantum Well System (MQW)**:** A multiple quantum system is a hetero structure in which alternating layers of small band gap and wide band gap layers are grown on each other (Figure 1.9). Often the wide band gap materials form a barrier to prevent communication between the electrons in various quantum wells.

3. **One Dimension nano systems-Quantum wires, surface coatings:** These nanomaterials will have only one parameter either length (or) breadth (or) height. Like Quantum Wire which is a one-dimensional system where the electron can move in one direction and restricted in two directions.

Quantum Wires: These are ultra fine wires or linear arrays made-up of Nano dots, formed by self-assembly. Nanowires have potential high end applications in high-density data storage, either as magnetic read heads or as patterned storage media, in electronic and opto-electronic Nano devices, for metallic, interconnects of quantum devices and Nano devices.

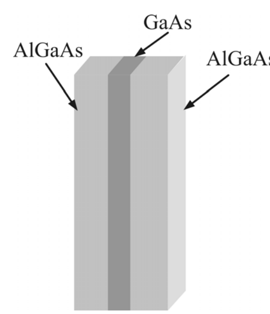


Figure 1.9 AlGaAs/GaAs – multiple quantum well system.

Nano wires can be prepared by growth techniques such as: Chemical Vapor deposition (CVD) Electroplating using a number of materials such as silicon, gallium nitride and indium phosphide.

As in quantum wires two dimension are reduced and on dimension remains large the electrical resistivity of quantum wire cannot be calculated using conventional formula.

$$R = \rho \frac{l}{A}$$

(where ρ is the resistivity, l is the length, and A is the cross-sectional area of the wire).

This equation is not valid for quantum wires. For calculating electrical resistivity of a conducting material we need two dimensions which are not present in a quantum wire and so it will not obey conventional formula applicable for bulk materials.

General properties of Nano wire:

Diameter – tens of nanometers,

Single crystal formation common crystallographic orientation along the nanowire axis, Minimal defects ----------------- within wire,

Minimal irregularities --------- within nanowire arrays.

Some examples of nano wires are shown in Figure 1.10.

Magnetic Nano Wires: Example: Cobalt, gold, copper and cobalt-copper nanowire arrays (Figure 1.10) important for storage device applications.

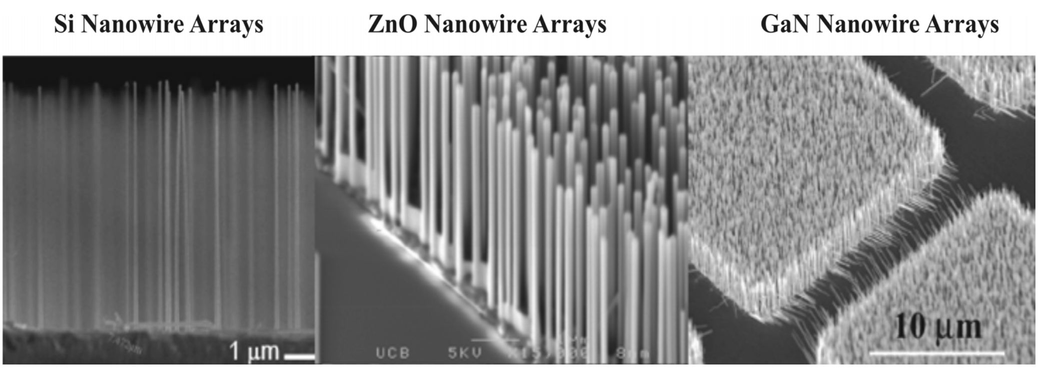


Figure 1.10 Cobalt nanowires on Si substrate.

4. **Zero Dimension: Quantum Dots:** In a quantum dot all three dimensions are reduced to zero. These belong to the extreme case of size reduction in which all three dimensions reach the low nano meter range. A quantum dot is a semiconductor nano structure that confines the motion of conduction band electrons, valence band holes or exitons (bound pair of conduction band electrons and valence band holes) in all three spatial directions (Figure 1.11).

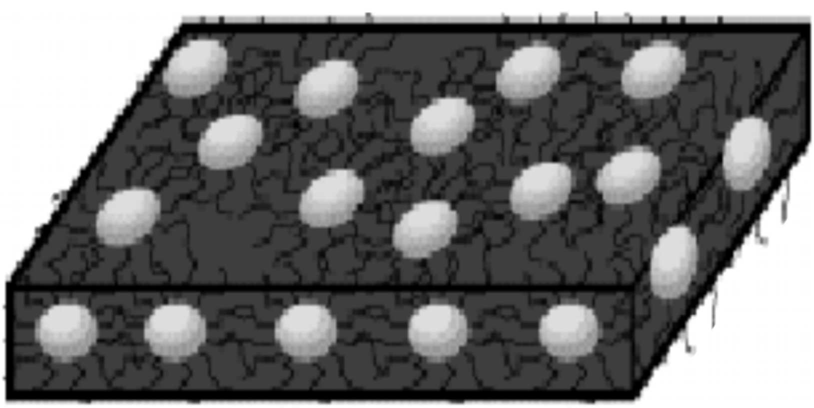


Figure 1.11 Quantum dots.

The quantum confinement effects with variation of sizes are summarized in Figure 1.12.

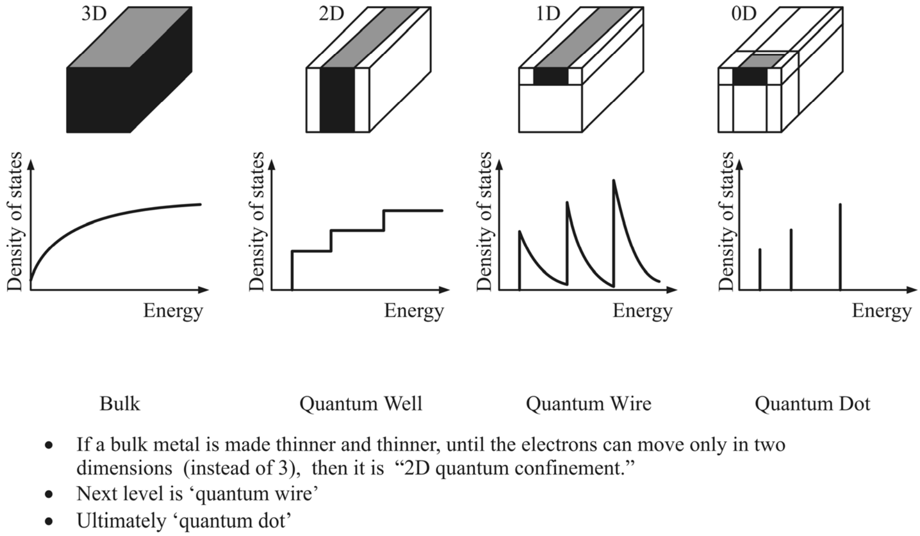


Figure 1.12 Summary of quantum confinement in with variation of size of nano particle.

1.1.7 What is Nano Chemistry?

Macromolecules formed due to combination of small molecules display three dimensional structures through intermolecular bonding possess large nano surfaces which can act as nano devices while the bonds as device components. These three dimensional macromolecules which possess large nano surfaces and intermolecular bonding find extensive applications as molecular switches, actuators, electronic wires and the nanoscience dealing with these macro molecules is known as nano-chemistry or supra molecular chemistry. The various critical functions the nano surfaces and internal boding can perform which have great scientific and commercial importance are given below

(i) **Intermolecular bonding:** The total activation/surface energy can be significant even if there are large no of weak interactions like hydrogen bonding and van der Waals bonding due to large surface area. For example DNA (which has a cross-section of 2 nm): the two helixes are held together by numerous hydrogen bonds due to which they possess large surface areas and small forces can be applied to very large areas which makes their nano chemistry interesting for various applications.

(ii) Macro molecules with nano-surfaces as nano devices, bonds as nano components: Ferritin a biological macro molecules can trap or release some ions in certain environment which can be exploited as nano device -application as molecular switches. Nano surfaces of a number of macro molecules now exploited as molecular switches, actuators and electronic wires.

(iii) **Surfaces perform numerous functions:**

(a) Nano Surface chemistry deals with chemical, physical and biological interactions on nano surfaces.

(b) In macromolecular nano chemistry the term interface, rather than surface, is often used, to emphasize the fact that it is a boundary between two phases: the material and the surrounding environment (liquid, solid or gas).

(c) If a bulk material is subdivided into an ensemble of individual nanomaterials, the total volume remains the same, but the collective surface area is greatly increased.

(d) In nano surface chemistry the chemical groups at the material interface determine its properties. Properties like catalytic reactivity, electrical resistivity, adhesion, gas storage and chemical reactivity depend on the nature of the interface which will have a profound effect on reactions that occur at the surface such as such as catalysis reactions, detection reactions, and reactions that, to be initiated, require the physical adsorption of certain species at the material's surface.

(iv) Atoms and molecules at the interface have enhanced reactivity and a greater tendency to agglomerate: surface atoms and molecules are unstable, they have high surface energy.

(a) Nano materials are inherently unstable, therefore there are various methods that nanomaterials adopt to minimise their inherent high surface energy. One of the ways of reducing the surface energy in nanoparticles is agglomeration. Surface energy is an additive quantity. The surface of 10 identical nanoparticles is equal to the sum of the surface energy of each individual nanoparticle. If these were to agglomerate, and become one large particle, the over- all surface energy would be reduced.

(b) Nano particles have a strong intrinsic tendency to agglomerate. To avoid this, surfactants can be used. This also explains why when nanoparticles are used in research and industry they are often immobilised on a solid support or mixed within a matrix. Even in commercial products that claim to contain nanoparticles (such as sunscreens) microscope images show that they are actually present in the form of agglomerates of > 100 nm dimensions.

1.2 Classification of Nano Materials

Based on their origin nano materials can be classified as

(i) Natural/non engineered nano sized materials available in the environment like proteins, viruses,

(ii) Engineered nano materials which are produced by fabrication process by manipulating/ controlling/modifying nano characteristics of materials like nano composites, nano fibers, nano tubes devices, quantum dots etc.

1.2.1 Natural/Non Engineered Nano Materials

Due to their inherent nano structure certain natural (plant, animal and Mineral) materials without any modification or processing exhibit unusual properties particularly in interaction with light, water and other materials. For examples the colours seen in opals butter flies is attributed to interaction with light. Certain biological molecules also exhibit nano structures which mainly due to arrangement of ten to hundreds of molecules into shapes and forms in the nano scale.

Thus some natural molecules with nano structures will provide models which can be solution to complex problems and the details of some of these examples are discussed below:

1.2.1.1 Nature's Examples for Non Engineered Nano Materials

Natural nano structure compounds exhibit remarkable properties and follow simple laws given below which are highly inspiring to follow

(i) Nature runs on sunlight and uses only the energy it needs.

(ii) Natural nanomaterials are extremely energy efficient.

(iii) Nature organize materials to function and recycles everything — waste products are minimized in nature.

(iv) Nature rewards cooperation although it encourages diversity

(v) Characterized by a surprising level of adaptability and multifunctionality.

Thus these natural nano materials can provide a model for designing radically improved artificial materials for many applications, such as solar cells, fuel cells, textiles, drug delivery systems, etc.

1.2.1.1.1 Examples of Natural Nano Materials

The following are some examples of naturally available nano materials.

(i) ***Nano particles from natural erosion and volcanic activity*****:** Minerals, such as clays, are nanostructured: clays are a type of layered silicate characterized by a fine 2D crystal structure. Among clays, mica has been the most studied.

Mica is made up of large sheets of silicate held together by relatively strong bonds. Smectic clays, such as montmorillonite, have relatively weak bonds between layers. Each layer consists of two sheets of silica held together by cations such as Li^+, Na^+, K^+ and Ca^{2+}. The presence of the cations is necessary to compensate for the overall negative charge of the single layers. The layers are 20-200 nm in diameter laterally and form into aggregates called tactoids, which can be about 1 nm or more thick.

(ii) ***Naturally occurring clays include montmorillonite (MMT) and hecrite*****:** The fine nanostructure of clays determines their properties. When water is added, the clay swells, but the volume change is rather unusual. It is several times the original volume due to the 'opening' up of the layered structure by the water molecules that replace the cations. Clay swelling is a significant factor in soil stability and must be taken into account when building roads etc.

(iii) ***Natural colloids, such as milk and blood (liquid colloids), fog (aerosol type), gelatin (gel type)*****:** In these materials when nano particles are dispersed in the medium (liquid or gas) but do not form a solution, rather a colloid. All these materials have the characteristic of scattering light and often their colour (as in the case of blood and milk) is due to the scattering of light by the nano particles that make them up.

(iv) ***Mineralised natural materials, such as shells, corals and bones*****:** Many of these materials are formed by calcium carbonate crystals that self-assemble together with other natural materials, such as polymers, to form fascinating three-dimensional architectures. For instance, a shell is grown by a layer of cells that first lays down a coating of protein supported by a polysaccharide polymer like chitin. The proteins act like a nano-assembly mechanism to control the growth of carbonate crystals. Around each crystal remains a honey comb – like matrix of protein and Chitin. This relatively 'flexible envelope' is fundamental for the mechanical properties of the shell and mitigates cracking. The size of each crystal is around 100 nm. The result is that the nacre of mollusc shells has extraordinary physical properties (strength, resistance to compression, etc.).

(v) ***Materials like skin, claws, beaks, feathers, horns, hair*:** These materials are made largely of very flexible proteins like keratin, elastin and collagen. Keratins have a large glycine and alanine content.

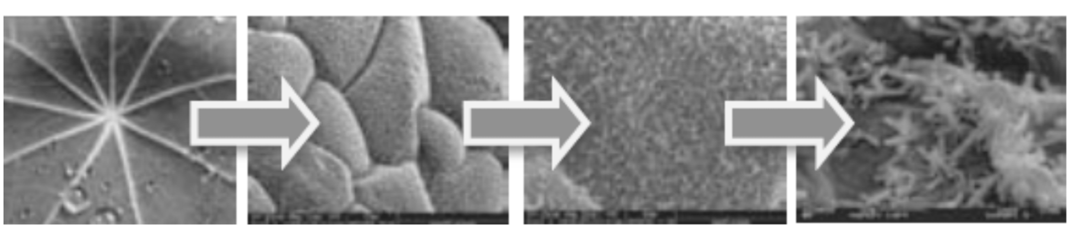
(vi) ***Insect wings and opals*:** The colours seen in opals and butterflies are directly related to their fine structure, which reveals packed nanostructures that act like a diffraction grid and induce iridescence. In the case of opals, this is due to packed silica spheres in the nano metre range, uniform in size and arranged in layers.

Spider silk: Silk is the material with the greatest known strength — about five times that of steel of the same weight. The extraordinary properties of spider silk are due to the proteins that make up the silk (mainly fibroin) and its supramolecular organization which is at the nano scale level.

(vii) ***Lotus leaves and similar (nasturtium)*:** The nano structure of these leaves is responsible for their extraordinary surface properties and their ability to 'self-clean'. The leaves of the lotus plant have the outstanding characteristic of totally repelling water because they are super hydrophobic (Figure 1.13).

Self-cleaning properties of the lotus plant are produced by a combination of the micro structure of leaves and epidermal cells on their rough surfaces which are covered with wax crystals (6). These crystals provide a water-repellent layer, which is enhanced by the roughness of the surface, making it a super hydrophobic surface, with a contact angle of about 150°. Figure 1.13 presents the progressive magnification of lotus leaf where on the right, nanocrystals a few tens of nanometres in size are shown.

The consequence is that water droplets roll off the leaf surface and, in doing so, drag dirt away from it, as shown in Figure 1.13 This effect, 'self-cleaning', renders the lotus leaf clean and resistant to dirt. The same effect is found in other leaves such as those of nasturtium (Tropaeolum) and some Cannas, and in some animals such as the water strider.



Macro (A) Macro (B) and (C) Nano (D)

Figure 1.13 Progressive magnification of lotus leaf.
(Image credit (A): A.Snyder, Exploratorium; (B, C): A.Marshall, Stanford University, (D): A. Otten and S. Herminghaus, Göttingen, Germany).

(viii) ***Nano Adhesives of Lizard (Geckos') Feet*****:** The structure of the Lizard foot is on of the best example for the relationship between function and nanostructure. The ability of Lizards to walk upside down, against gravity, even on wet or dirty surfaces is mainly due to the nanostructure of their feet. (Figure 1.14)

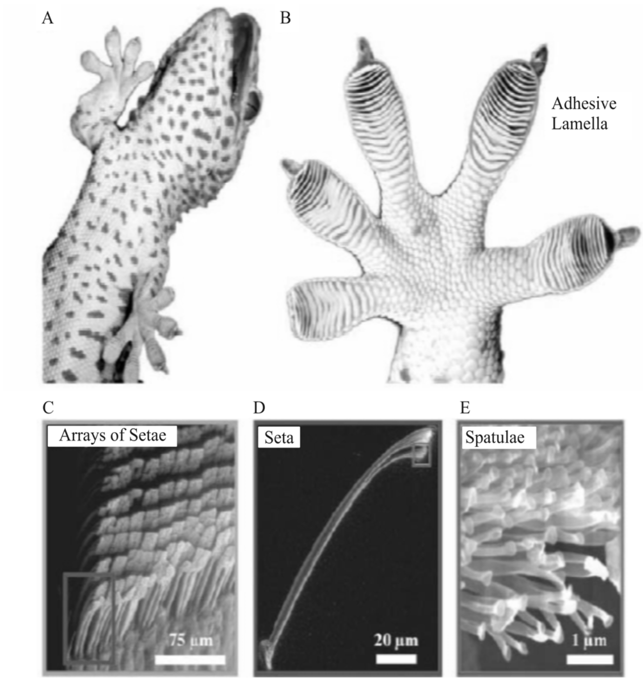


Figure 1.14 Lizards amazing feet with 10 N adhesive force (7).

The adhesion Characters of Lizard Feet and its mechanism are summarized in Table 1.1.

Table 1.1 Adhesive characters of lizard feet and mechanism of adhesion (8).

A lizard from southeast Asia which…	
Can generate – 10 B of adhesive force	
Can run up to – 1 m/s	
Can generate sheer stress of – 0.1 N mm^{-2} (–1 atm)	
Can walk on Any surfaces	
(hydrophobic/hydrophilic/rough/smooth/charged/uncharged…)	
What is the mechanism for such an amazing adhesion?	
– micro-suction?	No. adhesion works in vacuum.
– friction?	No. measured friction constant too low.
– micro-interlocking?	No. it walks on very smooth surface.
– capillary force?	No. it walks in ionized air.
– adhesion by glue?	No. there are no skin glands on their feet.

A lizard can cling to virtually any surface at any orientation; walk on smooth or rough surfaces, even upside down on a glass surface; and walk on a dirty or wet surface maintaining full contact and adhesion to it. As it walks, a lizard does not secrete any sticky substance, and its feet do not have any suction-like features (even at microscopic sizes). The reason for the lizards amazing properties lies in the nanostructures that are present on its feet. The lizard foot has a series of small ridges called scansors which contain numerous projections called setae. Each seta is about 100 μm long and has a diameter of about 5 μm. There are about half a million of these setae on the foot of a lizard. Each seta is further subdivided into about a thousand 200 nm-wide projections called spatulae (Figure 1.14). As a result, the total surface area of the lizards feet is enormous. The lizard spatulae are very flexible, so they essentially mould themselves into the molecular structure of any surface. The result is a strong adhesion which is entirely due to van der Waals forces. A single seta can resist a force of 200 μN, or approximately 10 atmospheres of stress. This is a very good example of the effect of large surface area on small forces. Another very interesting property of lizards is that their feet don't get dirty as they walk, even if they walk on a surface covered with sand, dirt, water, etc. Their feet stay clean even on dirty surfaces and full adhesion is maintained. The phenomenon has been investigated and it was found that the feet remain clean because it is more energetically favourable for particles to be deposited on the surface than to remain adhering to the lizard spatulae. If a lizard walks over a dirty surface, it takes only few steps for its feet to be totally clean again, and adhesion is not compromised.

Nano Photonic Crystals of the wings of butterflies: Butterflies often display extraordinary colours and iridescence due to nano photonic crystals. The shift in colour of butterfly when observed at different angles which is a consequence of the wing surface and its interaction with light. The wings of Morpho rhetenor are formed by rows of scales arranged like tiles on a roof (Figure 1.15). Each scale is about 70 × 200 μm and has a smaller structure on its surface, a very intricate and highly ordered nano metre organisation of ridges. Each ridge is about 800 μm wide. The spaces between them form a natural photonic crystal that can generate constructive and destructive Interference. The SEM (Figure 1.15) analysis of the cross-section of the ridges on the wings shows and an even more intricate structure that looks like fir trees.

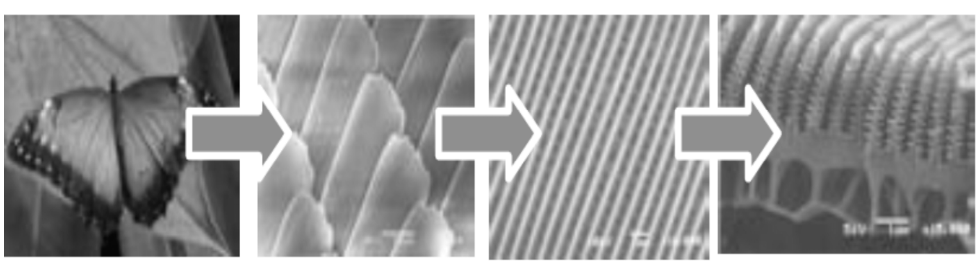


Figure 1.15 SEM analysis of the cross-section of the ridges on the wings of butterfly (Images credit: (far left): Wiki Commons, Creative Commons Attribution Share Alike 3.0; (all other images): S. Yoshioka, Osaka University).

Learning nanotechnologies from nature: Natural nano materials are of interest not only to understand (and appreciate) the amazing properties of biological materials but also to gather inspiration for the design and engineering of new materials with advanced properties. Some examples of nano technologies developed by mimicking natural systems are presented in Table 1.2.

Table 1.2 Biomimetics by inspiration from natural materials.

Biomimetric Material	Inspired from
Polymers	Substructure of nacre
Structural elements	Wood, ligaments and bone
Electrical conduction	Eels and nervous system
Photoemission	Deep-sea fish and glow-worms
Photonic crystals	Butterfly and bird wings
Hydrophobic surfaces	Lotus leaves and human skin
Adhesives	Geckos' feet
High tensile strength fibre	Spider silk
Artificial intelligence and computing	Human brain

1.2.2 Engineered Nano Structured Materials

1.2.2.1 Classification of Engineered Nano Materials/Devices

Nano structures which are produced by controlled manipulation of their microstructure at atomic level are termed as Engineered Nano Materials. The quantum confined nano materials discussed earlier also fall under this category.

These are classified by Gleiter into three categories (9).

1. Nano materials /structures/devices with reduced dimensions or dimensionality in the form of isolated substrate supported, or embedded nano sized particles or thin wires or thin films come under first category. The fabrication techniques normally used to attain this kind of nano structure are Chemical vapor deposition, (CVD), Physical Vapor Deposition (PVD), various aerosol techniques precipitation from the vapor, super saturation liquids or solids. The examples of technological application of this type of nano materials are catalysts, semiconductor devices utilizing multi layer quantum well structures.
2. Nano materials/devices in which nano sized microstructure is limited to a thin surface region of a bulk material fall under second category. CVD. PVD, ion implantation and laser beam treatments are widely used procedures to modify chemical composition and atomic structure of solid surfaces at nano scale level. Surfaces with enhanced corrosion resistance, hardness, ware resistance or protective coatings are examples widely used present day technologies. In these technologies the properties of a thin surface layer is improved by creating a nano meter sized micro structure in a thin surface region. Such process or nano devices/systems find wide application in next generation electronic devices such as highly integrated circuits, terabit memories, single electron transistors, quantum computers etc.
3. The third category consists of bulk solids with a nano meter scale micro structure. Those are the solids in which chemical composition, the atomic arrangement and or the size of building blocks (Crystalites or atomic or molecular groups) forming the solids varies on a length scale of few nano meters through the bulk.

Another classification of engineered nano structure materials/systems/as defined by Richard W. Siegel depends on the number of dimensions which lie within nano meter range

(i) 3D systems confined in all three dimensions e.g., Structures typically composed of consolidated equiaxed crystallites.

(ii) 2D systems confined in two dimensions ex: filamentary structures where length is substantially greater than the cross sectional dimensions.

(iii) 1D systems confined in one dimension ex: layered or laminate structures.

(iv) Zero-D –zero structures such as pores, nano particles quantum dots etc., which are discussed earlier pages.

Thus three dimensional structures or bulk materials with a nano meter sized micro structure are assembled of nano meter sized building blocks or grains that are mostly crystallites. The schematic model of various nano structured material is shown in Figure 1.16.

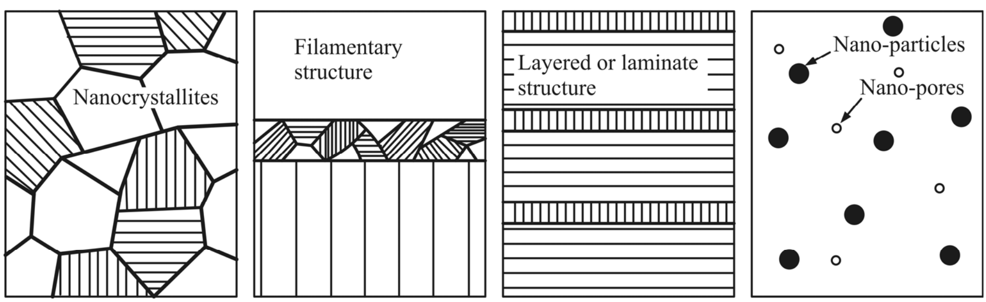


Figure 1.16 Schematic of nano structured materials with 3D, 2D, 1D and zero D confinement of electrons.

These building blocks differ in their atomic structure, their crystallographic orientation and/or their chemical composition. Incoherent or coherent interfaces may be formed between them depending on an atomic structure, the crystallographic orientation and/or chemical composition or adjacent crystallites. In other words materials assembled of nano meter sized building blocks are micro structurally heterogeneous consisting of building blocks (crystallites) and the regions between adjacent blocks (e.g., grain boundaries).

The latter three categories can be further grouped into four families as shown in Figure 1.17.

In the most simple case all grains and interfacial regions have the same chemical composition. e.g., Semicrystalline polymers (consisting of stacked lamellae separated by non-crystalline region), multilayers of thin film crystallites separated by an amorphous layer (a-Si:N:H/nc-Si) etc.

In the second case, materials are classified with different chemical composition of grains. Possibly quantum well structures are the best example of this family.

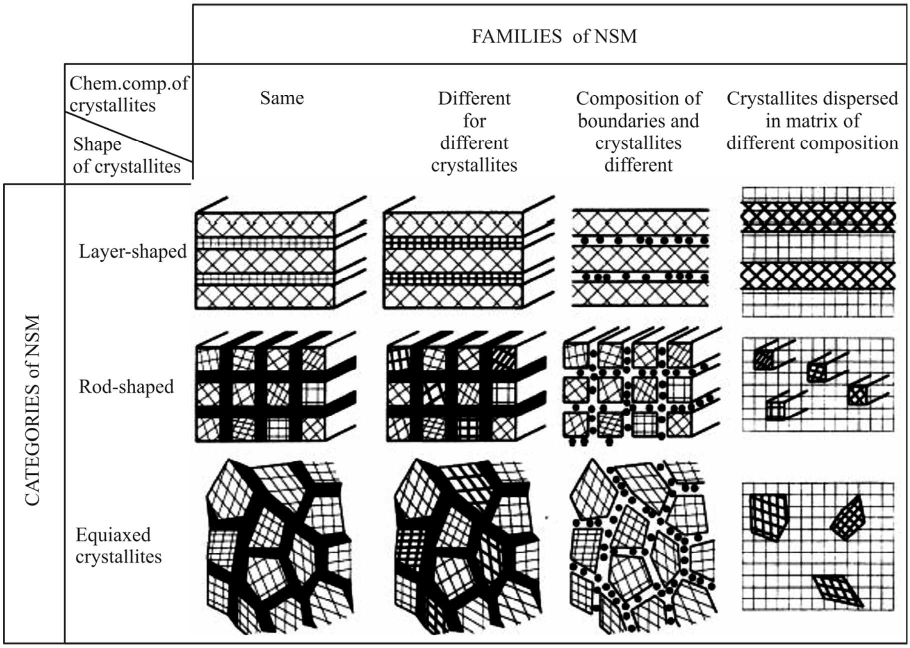


Figure 1.17 Relation between categories & families of nano structured materials (NSM) (Gleiter H., Acta Mater., 2000, vol. 48).

In the third family includes all materials that have a different chemical composition of its forming matter (including different interfaces) e.g., ceramic of alumina with Ga in its interface.

The fourth family includes all nanomaterials formed by nanometer sized grains (layers, rods or equiaxed crystallites) dispersed in a matrix of different chemical composition. Precipitation hardened alloys typically belong to this family. E.g., Nanometer sized Ni_3Al precipitates dispersed in a nickel matrix-generated by annealing a supersaturated Ni-Al solid solution- are an example of such alloys. Most high-temperature materials used in modern jet engines are based on precipitation-hardened Ni_3Al/Ni alloys.

1.3 History of Nano Technology

A number of practices since long time fall under nanotechnology though not recognize as such. For example the high quality steel which is rust free and exhibit other outstanding properties, made in India at the beginning of first millennium is known to contain carbon nano tubes. The permanent hair dye used by Greeks 2000 years back involves deposition of 5nm lead sulfide crystals. Metal nano particles were used by medieval artists in producing colored stained glass decorations. However in modern times research towards miniaturization in semiconductor industry lead to various developments in nanotechnology. While earlier nanotechnology being used without proper scientific understanding, in ancient times, the present knowledge due the development of advanced instrumentation for characterization and other scientific tools like computation are greatly helping for understanding the nano-structure activity relation and design of tailormade nano materials for specific applications.

The understanding of modern nano technology can be considered has begun from December 1959 from the Lecture of Richard Feynman a Physicist titled "There is Plenty Room at the Bottom"(10) at American Physical Society at California Institute of Technology.

Feynman said it should be possible to build machines small enough to manufacture objects with atomic precision, and that if information could be written on an atomic scale, "all of the information that man has carefully accumulated in all the books in the world can be written in a cube of material one two-hundredths of an inch wide—about the size of the smallest piece of dust visible to the human eye." He claimed that there were no physical laws preventing such achievements, while noting that physical properties would change in importance (e.g., gravity becoming less important), though surface phenomena would begin to dominate behavior. It is suggested to name the nanometer scale as the *Feynman* (φ nman) *scale* after Feynman's great contributions to nanotechnology (1 *Feynman* [φ] $\equiv 10^{-9}$ *meter* $=10^{-3}$ *Micron* [μ]=10 *Angstrom*s [Å]).

In 1974, Norio Taniguchi first used the word "nanotechnology" (11), in regard to an ion sputter machine, to refer to "production technology to get the extra-high accuracy and ultra- fine dimensions, i.e., the preciseness and fineness of the order of one nanometer."

In the 1980s, Eric Drexler authored the landmark book on nanotechnology, "Engines of Creation" (12) in which the concept of molecular manufacturing was introduced to the public at large. It is due to Drexler that much of the public's imagination has been captured by the potential of nanotechnology and nano manufacturing. In 1985, fullerenes, or "buckyballs," were discovered (13). By the 1990s, nanotechnology was advancing rapidly. In 1990, the first academic nanotechnology journal was published, in 1993 the first Feynman Prize was awarded, and by 2000 President Bill Clinton announced the U.S. National Nanotechnology Initiative (NNI). NNI and other nanotechnology proponents now anticipate the development of nano-enabled tools to help address many current challenges facing the United States and the international community, in the following areas:

(a) Clean, secure, affordable energy,
(b) Stronger, lighter, more durable materials,
(c) Low-cost filters to provide clean drinking water,
(d) Medical devices and drugs to detect and treat diseases more effectively with fewer side effects,
(e) Lighting that uses a fraction of the energy associated with conventional systems,
(f) Sensors to detect and identify harmful chemical and biological agents, and
(g) Techniques to clean up harmful chemicals in the environment.

1.4 Unique Physico-Chemical, Mechanical, Electrical, Optical and Magnetic Properties of Nano Materials

1.4.1 Reasons for Nano Materials Exhibiting different Properties from Bulk

The unique (different) physical properties of nanomaterials in comparison with bulk mainly occur due to the following reasons

1. Gravitational forces become negligible and electromagnetic forces dominate,
2. Quantum mechanics is the model used to describe motion and energy instead of the classical mechanics model,
3. Greater surface to volume ratios.
4. Large fraction of surface atoms,
5. Large surface energy,
6. Spatial confinement, and
7. Reduced imperfections.

1.4.2 Specific Properties of Nano Materials which have Great Role in Routine Applications

(a) Size dependent Properties: The most fundamental properties of nano materials and devices depend on their size. For example, a nanoscale wire or circuit component does not necessarily obey Ohm's law (as discussed earlier), the foundation of modern electronics. Ohm's law relates current, voltage, and resistance, but it depends on the concept of electrons flowing down a wire like water down a river, which they cannot do if a wire is just one atom wide and the electrons need to traverse it one by one.

(b) Impact of combined size and outer electronic structure effects: This coupling of size with outer electronic structure is the most fundamental chemical, electrical, and physical properties of materials is key to all nano science. Anything smaller than a nanometer in size is just a loose atom or small molecule floating in space as a little dilute speck of vapor. So the nanoscale is unique because it is the size scale (Figure 1.18) where the familiar normal properties of materials like conductivity, hardness, or melting point meet the more exotic properties of the atomic and molecular world such as wave-particle duality and quantum effects. So at the nano scale dimension, the principles of classical physics are no longer capable of describing their behavior (movement, energy, etc). At these dimensions, quantum mechanics principles apply. The same material (i.e., gold) at the nanoscale can have properties like optical, mechanical, electrical, etc., which are very different from (even opposite to) the properties the material has at the macro scale (bulk).

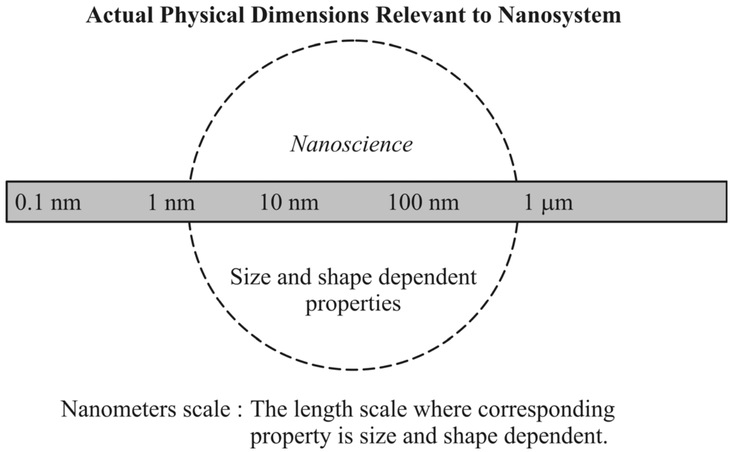


Figure 1.18 Length scale where materials exhibit size dependent properties.

(c) Role of Higher % Surface Atoms in Nano Systems: The macroscopic physical properties of a substance (melting point, boiling point, conductivity etc.) are determined by studying a pure sample in quantities big enough to be measured under normal laboratory conditions. One mole of any material contains 6.022×10^{23} molecules (Avagadros number); Properties are usually measured by looking at large ($\sim 10^{23}$) aggregations of atoms or molecules. We assume that the result should be true for any size of group of water molecules. This is not correct for many materials: as the size of the material is reduced in the nano scale regime where only hundreds to tens of thousand atoms will be present with large proportion of surface atoms (Example1). It is possible that the same material will display totally different properties (different melting point, conductivity etc). This is because matter at the nano scale no longer follows Newtonian physics but rather quantum mechanics.

Example 1: Typical Nano system of carbon may contain 100 to few thousand molecules at the surface which are less bounded by bulk atoms (Figure 1.19)

C Atom details

Bohr radius = 0.5292Å ≈ 0.05 nm

C atom (VdW radius) = 0.17 nm

In a 1nm line: 3C atoms

In a 1nm × 1nm surface: 9C atoms

In a 1nm × 1nm × 1nm cube: 27 C atoms

In a 100 nm × 100 nm × 100 nm cube: 2.7×10^{7} C atoms

In a 1m × 1m × 1m cube: 2.7 × 1028 C atoms

Example 2: Nano Systems % of Surface atoms

Example of Gold Nano particle

Sphere of radius 12.5 nm contains total approx. 480,000 atoms.

Surface contains approx. 48,000 atoms.

So, approx. 10% atoms are on the surface.

Sphere of radius 5 nm contains total approx. 32,000 atom surface contains approx. 8000 atoms.

So, approx. 25% atoms are on the surface.

Surface atoms will have un-used electrons which make them very reactive and excellent platform for catalysis.

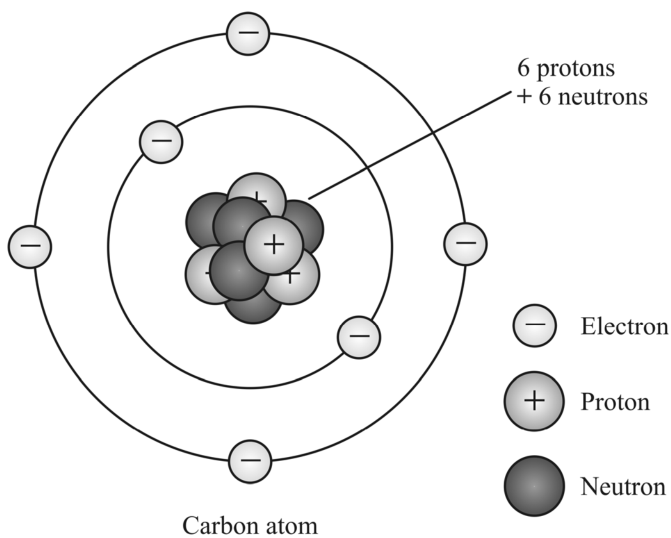


Figure 1.19 Electronic structure of carbon atom.

1.4.3 Unique Physical Properties of Nano Materials

1.4.3.1 Lower Melting Point or Phase Transition Temperature with Reduced Lattice Constants

Melting Point is the temperature at which the atoms, ions, or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a "fixed" position in a solid. Surface atoms require less energy to move because they are in contact with fewer atoms of the substance (Figure 1.20).

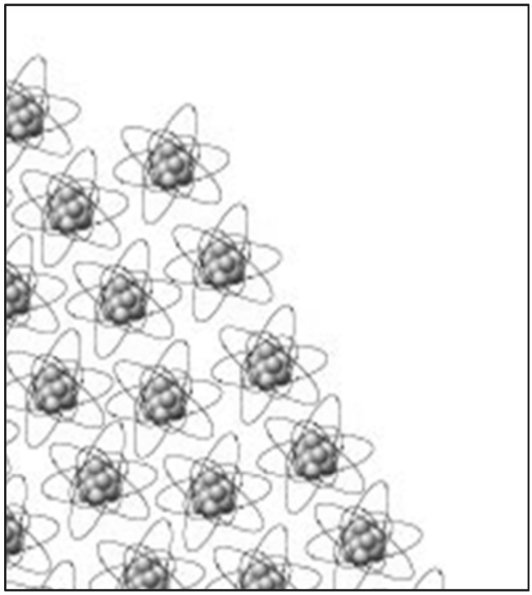


Figure 1.20 Nano structure showing that surface atoms are bound by lower number of atoms than in the bulk (14).

Low melting points for nano materials

Nano materials exhibit significantly lower melting point or phase transition temperature and appreciably reduced lattice constants. As can be seen in Figure 1.21 the melting points of many nano particles decrease dramatically when their size gets below 5 nm

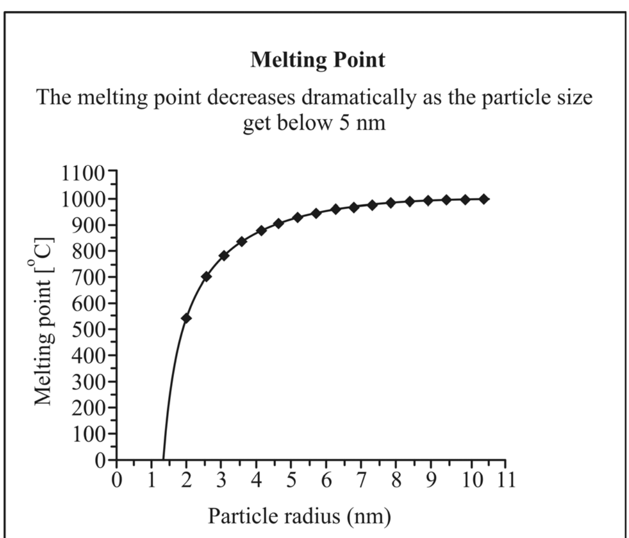


Figure 1.21 Dramatic decrease of melting point of nano particles below 5 nm (15).

This is due to a huge fraction of surface atoms out of total number of atoms.

As an example the variation of melting points of gold as a function of particle diameter are presented in Figure 1.22.

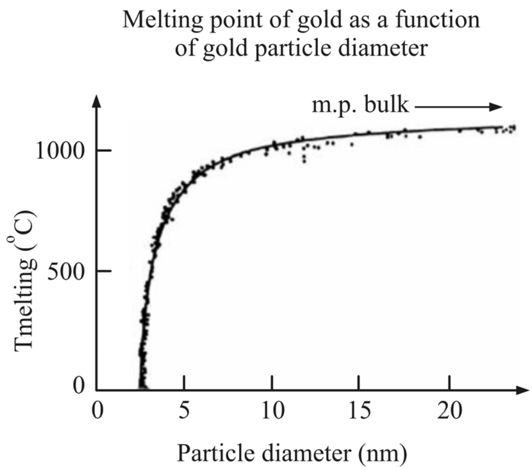


Figure 1.22 Decrease in melting point of gold nano particles as their size decreases (16).

1.4.3.2 Gravitational and Electromagnetic Forces at Nano Scale

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

Gravitational force is a function of mass and distance and is weak between (low-mass) Nano sized particles (Figure 1.23).

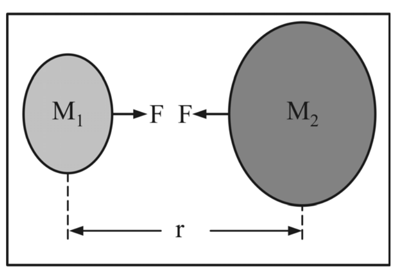


Figure 1.23 Gravitational force decreases with size (17).

At the nano scale, inertia and gravity would make no difference. The bacterium swimming through the water comes to a stop in a distance less than the diameter of the hydrogen atom. Attractive forces, such as van der Waals forces, and viscous forces between small objects are much stronger than the forces of gravity and inertia at that scale. As a result, all of these molecules and machines and cell parts are in constant motion, being pushed and pulled around in quick, random trajectories.

Electromagnetic force is a function of charge and distance is not affected by mass, so it can be very strong even when we have Nano sized particles (Figure 1.24).

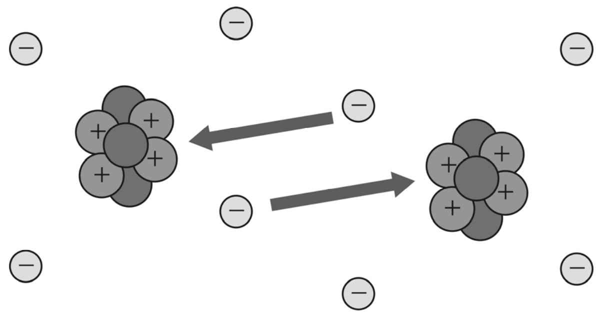


Figure 1.24 Electromagnetic forces become dominant as the size decreases in nano particles (18).

1.4.3.3 Enhanced Mechanical Strength

As nanomaterials in general possess very high tight packing with reduced probability defects compared to bulk material they exhibit enhanced mechanical strength and tensile strength by one or two orders. However some nano materials like carbon nano tubes exhibit exceptional mechanical properties due to their structure. Carbon nano - tubes (single walled and multi walled, Figure1.25) are extremely small tubes possessing honey - cube structure of graphite but exhibit quite different properties compared to graphite.

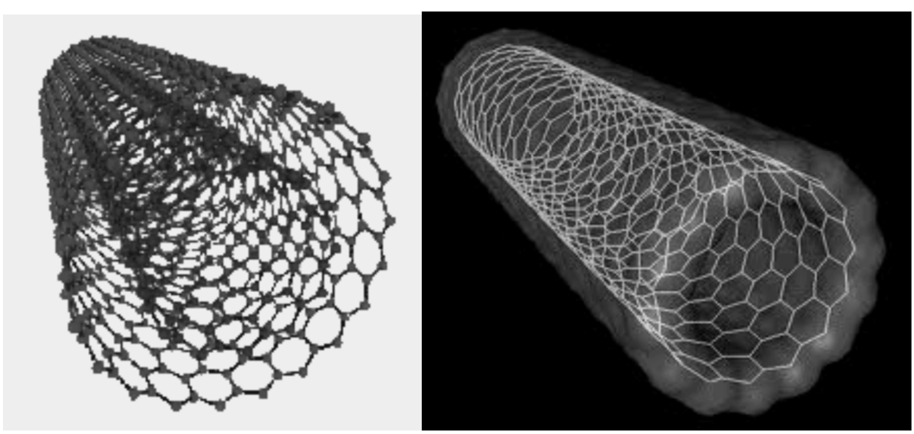


Figure 1.25 Single walled and multi walled carbon nano tubes.

Carbon nanotubes composed of entirely of sp2 bonds (carbon double bonds) as in graphite are stronger than diamonds which have sp3 tetrahedral and can be aligned into 'ropes' held together by van der Waals forces. Further they are 100 times stronger than steel with one sixth of its weight due to which they find extensive application in aviation and automotive industries. Similarly they are also used in tennis racket for increasing its strength without adding much weight.

Table 1.3 presents the summary of mechanical properties of carbon nanotubes (19).

Table 1.3 Mechanical properties of carbon nano tubes.

Material	Young's Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm^3)
Single-wall nonotube	800	> 30	1.8
Multi-wall nanotube	800	> 30	2.6
Diamond	11400	> 20	3.52
Graphite	8	0.2	2.25
Steel	208	0.4	7.8
Wood	16	0.008	0.6

- Young's modulus is a measure of how stiff, or elastic a material is and the higher the value, the less a material deforms when a force is applied.
- Tensile strength describes the maximum force that can be applied per unit area before the material snaps or breaks.
- A third interesting measure of a material is its density, which gives an idea of how light it is.

From Table 1.3, it can be concluded that wood is very light but weak, whereas nanotubes are many times stronger than steel and yet much lighter.

1.4.3.4 Improving Existing Materials

By preparing the composites with nano crystalline materials the mechanical properties of existing materials can be tremendously increased. If the grain size of industrial metallic materials (which is around 10,000nm) is reduced to 100 nm nano crystals they exhibit highly improved mechanical properties (toughness, hardness, etc.). However if in the crystalline structures any defects exist materials may fracture when subject to mechanical stress as the defects allow cracks to propagate. By adding some nano particles in the lattice the movements of cracks can be impeded. Further to mechanical properties, in certain cases the magnetic, electrical, catalytic and corrosion resistance properties can also be tremendously improved compared to bulk materials with large grains. Hard coatings composed of nanocrystalline find great application for protecting sharpness of cutting tools and greatly improving their performance and life span. Similarly addition of nano particle to alumina based ceramics and polymers composites for significantly improving the mechanical properties is extensively used currently for various industrial process of great commercial importance.

1.4.3.5 Increased Surface to Volume Ratio and Enhanced Surface Energy

Large surface area with higher surface energy: One of the distinguishing properties of nanomaterials is that they have an increased surface area resulting higher surface energy, large surface active molecules and greater reactivity than corresponding bulk materials. The 'active surface' increases when the size of the nano catalysts is decreased resulting greater the ratio of surface-to-volume (Figure 1.26).

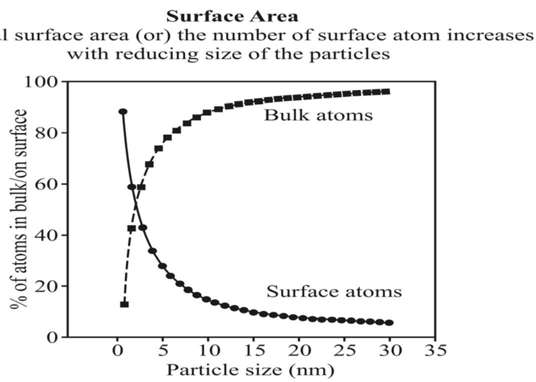


Figure 1.26 Increase in surface area and number of surface atoms with decreasing size of nano particles.

Let us consider one Cubic Volume shown in Figure 1.27 its the Surface Area is 6 m^2.

Total Surface area = height × width × number of sides × number of boxes

Total Volume = height × width × length × number of boxes

Surface to volume ratio = total surface area/total volume.

When it is divided into eight pieces its Surface Area becomes 12 m^2, similarly. When the same volume is divided into 27 pieces its Surface Area becomes 18 m^2.

Thus we find that when the given volume is divided into smaller pieces the Surface Area increases. Hence as particle size decreases a greater proportion of atoms are found at the surface compared to those inside (Figure 1.27). Nano particles have a much greater surface area per given volume compared with larger particles. It makes materials more chemically reactive.

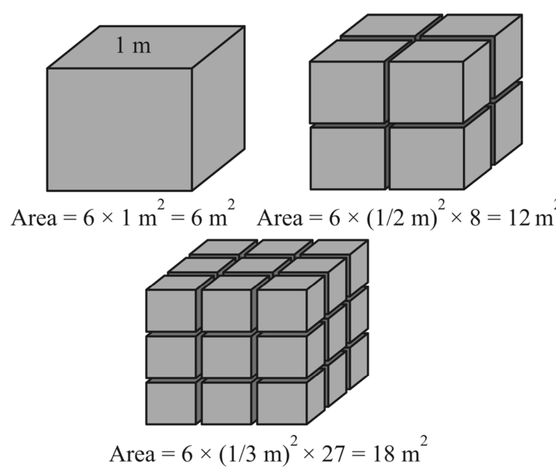


Figure 1.27 Surface area of cubes of 1m,1/2m and 1/3m lengths of each side.

This increased reactivity for surface area to volume ratio is widely taken advantage in nature, one biological example being the body's digestive system. Within the small intestine, there are millions of folds and sub folds that increase the surface area of the inner lining of the digestive tract. These folds allow more nutrients and chemicals to be absorbed at the same time, greatly increasing our body's efficiency and the rate at which we digest food.

Thus nano particles, nanostructures and nano materials possess a large fraction of surface atoms per unit volume. The ratio of surface molecules to interior molecules changes dramatically (Table 1.4) if one successively divides a macroscopic object into smaller parts. The total surface energy increases with the overall surface area, which in turn is strongly dependent on the dimension of the material.

Table 1.4 Variation in cross section, total mass, no of molecules and fraction of molecules at the surface of a nano cluster with size (19).

Size (mm)	Cross section (10^{-18} m^2)	Mass (10^{-36} kg)	No. of molecules	Fraction of molecules of surface (%)
0.5	0.2	0.65	1	
1	0.8	5.2	8	100
2	3.2	42	64	90
5	20	650	1000	50
10	80	5200	8000	25
20	320	42000	64000	12

Surface Energy γ is the energy required (or produced) to create a unit area of a new surface, therefore,

$$\gamma = (\partial G/ \partial A)_{ni, T, P}$$

G: Gibs free energy of the surface

A: Surface area of the particles

Due to the dangling bonds on the surface, surface atoms or molecules are under an inwardly directed force and the bond distance between molecules and the sub-surface molecules becomes smaller. An extra force or energy is required to pull the surface to its original positions.

This energy is defined as surface energy, γ

$$\gamma = Nb\ \varepsilon\ \rho a /2 \qquad \text{.....(1.1)}$$

Nb: number of broken bonds

ε: bond strength

ρa = number of atoms or molecules per unit surface area = density

Table 1.5 presents the (typical data of nano $CaCO_3$) how the surface energy increases with decreasing size in nano systems.

Table 1.5 Surface area and surface energy variation with size of nano $CaCO_3$ (20).

Size (nm)	Surface area (m^2 mol^{-1})	Surface energy (J mol^{-1})
1	1.11×10^9	2.55×10^4
2	5.07×10^8	1.17×10^4
5	2.21×10^8	5.09×10^3
10	1.11×10^8	2.55×10^3
20	5.07×10^7	1.17×10^3
10^2	1.11×10^7	2.55×10^2
10^3 (1 μm)	1.11×10^6	2.55×10

1.4.3.5.1 Nano Particle-Nano Particle Interactions

The fate of nano particles either to be individual or collective by formation of aggregates/agglomerates is decided by the nature of possible interactions due to attractive or repulsive forces between them and this influences their physico chemical behavior in a given environment. Weak Vander walls forces or strong polar/electrostatic or covalent forces are main forces of attraction between nano particles.

The nano particle-nano particle interaction forces and nano particle-fluid interactions are of key importance to describe physical and chemical processes, and the temporal evolution of free nanoparticles. As small number of surface molecules involved surface active layer which mainly determine the nature of physico chemical properties of nano particles both surface energy, charge and solvation are relevant parameters to be considered.

For example the particle charges in the liquids can be stabilized by electrochemical forces at the surfaces. The viscosity and polarizability of the liquid medium in which nano particles exist influence the interparticle interaction leading to particle aggregation and by the modification of the surface layer, the tendency of a nano particle colloid to coagulate can be enhanced or hindered.

For nano particles suspended in air, charges can be accumulated by physical processes such as glow discharge or photoemission. In gas suspensions, aggregation is crucially determined by the size and diffusion, and coagulation typically occurs faster than in the liquid phase as the sticking coefficient is closer to unity than in liquids.

1.4.3.6.1 Interaction of Light with Matter

The optical properties of materials are mainly due to interaction of light with matter and in this size of the material plays important role. For example some nano materials exhibit different colors when compared to bulk materials (21).

In general light (I) incident on a material can be transmitted (T), absorbed (A) or reflected (R):

$$I = T + A + R$$

Absorption (A) is a molecular phenomenon and the energy level of the substance (depends on the electronic transitions, vibrations and rotations) that determines the wavelength of light that can be absorbed and not on the size of the molecule or cluster. Chromophores and fluorophores are examples of organic materials that have specific electronic transitions.

Reflection occurs when light strikes a smooth surface and the incident wave is directed back into the original medium. The reflected wave will have same geometrical structure as the incident wave.

Transmission (T) which is complimentary to absorption is equal to incident light minus the absorbed + reflection+ scattered light together.

Scattering (S) is a physical phenomenon which occurs when radiation is incident on a substance with dimensions comparable with incident wave length. Scattering contributes to colour or transparency of the material and depends on cluster size, refractive index of the cluster and suspension medium. In Scattering process no energy transition occurs unlike in absorption while energy simply reflected in many directions and there will not be any change in the wavelength of the incident light and outgoing light. Further multi scattering may also occur as in a colloid after first scattering the out going light may encounter with another cluster, be redirected again and maximum scattering occurs for wave lengths as large as the cluster size. For example with a cluster size 200nm maximum scattering will be observed at 400 nm which falls in the visible region giving colour to the system.

1.4.3.6.2 Color Generation from Nano Particles and Nanostructures

Due to the typical interaction of light with nano structures, they exhibit peculiar spectral properties. Particularly metal nano particles exhibit optical properties different from their bulk mainly due to localized surface plasmon resonance. For example d electrons in bulk silver or gold are able to travel entire material with a mean free path for the blk atoms around ~50nm while for nano particles less than 50nm no scattering takes place and all interactions with the surface electrons. When the incident wave length of light is much larger than the size of the nano particle, resonance conditions will be setup between incident light and surface plasmon free electrons of the nano particles which make the free electrons to oscillate as shown in Figure 1.28. The surface electron density of the nano particle will be polarized to one surface and oscillates when the wave front of the incident light passes through it resulting a standing oscillation. Absorption and scattering spectroscopy can be used to identify the resonance condition which is found to depend in the size, shape and dielectric constant of both the metal and surrounding material which is termed as localized surface plasmon resonance (LSPR).

The surface geometry changes as the size or shape of the nano particle varies leading to shift in electric density on the surface which causes a change in the oscillation frequency of the electrons resulting different cross sections for absorption and scattering reflecting as varying optical properties (Figure1.28).

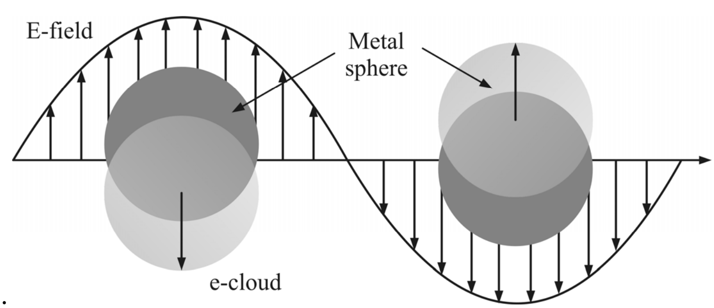


Figure 1.28 Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei (21).

The dielectric constant of the surrounding environment will influence oscillation frequency as varying dielectric constant will provide varying ability to the surface to accommodate electron charge density of the nano particle. Thus either by changing the solvent or capping with material which produces changed dielectric function of the nano particle or by varying their charge and shape, the shift the LPSR can be achieved which can be made as basis for noble metal nano particles as sensitive sensors. For example if a ligand, such a protein, attaches to the surface of the metal nanoparticle, its LSPR energy changes and can be used for their detection. Similarly many chemically bonded molecules can be detected by the observed change they induce in the electron density on the surface, which results in a shift in the surface plasmon absorption maximum (Figure 1.29). Similarly, the LSPR effect is sensitive to other variations such as the distance between the nanoparticles, which can be changed by the presence of surfactants or ions. The LSPR effect has been observed not only on metal nanoparticles but also in nano rings, voids in metal films and other nanostructures.

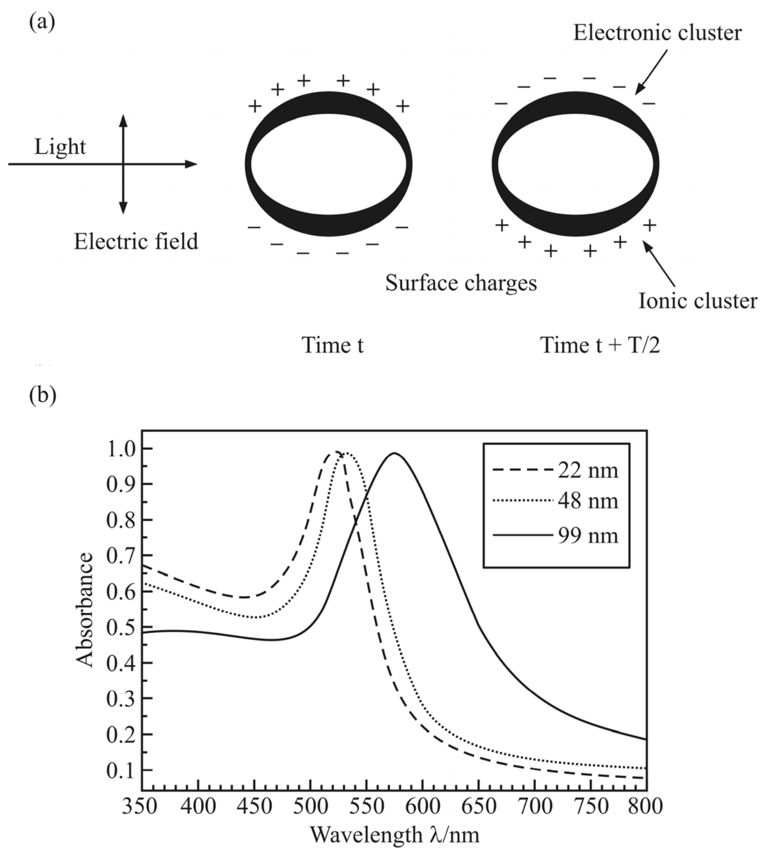


Figure 1.29 LPSR absorption spectra of spherical gold nano particles and their size dependence (21).

One of the consequences of the LSPR effect in metal nanoparticles is that they have very strong visible absorption due to the resonant coherent oscillation of the plasmons. As a result, colloids of metal nanoparticles such as gold can display different colours (Figure 1.30).

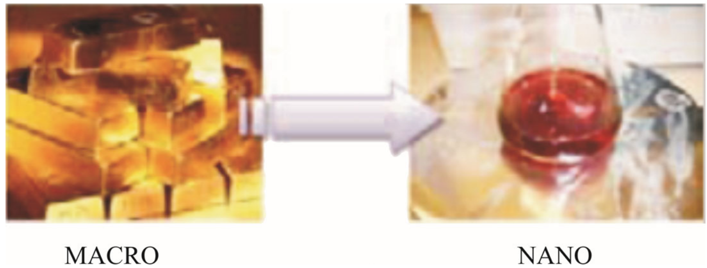


Figure 1.30 (macro (bulk) gold-yellow and nano Gold (1.5 nm) ruby red (22). (Image. LPillppooni iNano Arhus University Creative common Share Alike 3.0).

Figure 1.31 shows how colloids of gold and silver nano particles change their colour with size. The properties of metal nanoparticles make them useful in sensing.

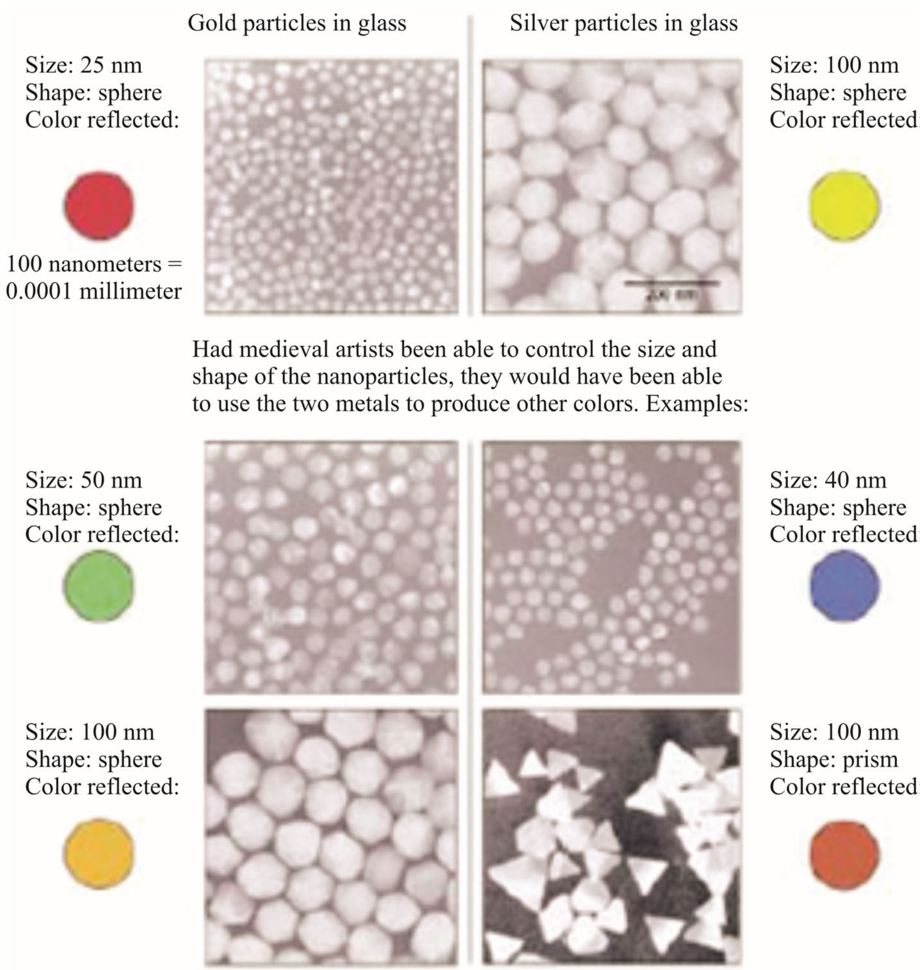


Figure 1.31 Changes in colours of colloids of gold and silver with size (22).

1.4.3.6.3 Quantization and Energy Level Spacing

As already mentioned, nano sized semiconductors possess quantized energy states; therefore, the conduction and the valence bands in the materials will split into discrete levels leading to monochromatic emission due to charge transfer between these discrete energy levels. Further due to quantum confinement the band gap in the nano semiconductors also increases resulting (more energy difference between band gap) blue shift (lower wave length). Even the same blue shift can be observed in the fluorescent light exhibited by semiconductor nano crystals and the band gap (the wave length absorbed/emitted by the crystal) can be tuned by tuning their size. In-view of this phenomenon same nano crystal for example CdSe emits different colours based on its size (Figure 1.32). In-view of this CdSe/Quantum dots find applications as alternative to dye in fluorescence spectroscopy, dye sensitized solar cells, light emitting sources.

Thus quantum confinement in nano crystals cause splitting of energy levels in discrete way resulting discrete features in their emission/absorption spectra and concentration of oscillator strength in just few transitions.

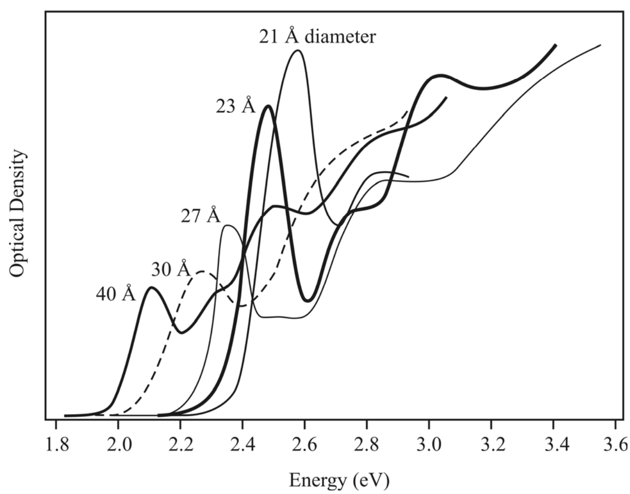


Figure 1.32 Optical absorption vs size for CdSe nano crystals shows the shift to higher energy in smaller sizes, as well as the development of discrete structure in the spectra and the concentration of oscillator strength into just a few transitions (23).

1.4.3.6.4 Electrical and Electronic Properties of Nano Materials

Electrical conductivity of bulk metals is based on their electronic band structures, and the mobility of electrons is related to their mean free path between two collisions with the lattice. The collective motion of electrons in a bulk metal obeys Ohm's law,

V = RI, where, V is the applied voltage, R is the resistance of the material and I is the current. As the electronic band structure changes into discrete energy levels as in nano materials, Ohm's law is no longer valid. If one electron is transferred to a small particle, the Coulomb energy of the latter increases by $EC = e^2/2C$, where C is the capacitance of the particle. If the temperature is low such that $kT < e^2/2C$, single electron tunneling processes are observed. Thermal motion of the atoms in the particle can initiate a change in the charge and the Coulomb energy so that further electrons may tunnel uncontrolled. Hence, the I-V characteristic of a quantum dot is not linear, but staircase-like. No current flows up to $VC = \pm e/2C$. If this value is reached, an electron can be transferred. Following this, an electron tunnelling process occurs if the Coulomb energy of the particle is compensated by an external voltage of $V = \pm ne/2C$. This behaviour is called Coulomb blockade. The charging energy increases with decreasing the size of the quantum dot.

Further some nano materials exhibit electrical properties that are absolutely exceptional. Their electrical properties are related to their unique structure. Two of these are fullerenes and carbon nanotubes. For instance, carbon nanotubes can be conductors or semiconductors depending on their nanostructure. Carbon nanotubes are long, thin cylinders of carbon. Their electrical properties change with diameter, "twist", and number of walls. They can be either conducting or semi-conducting in their electrical behavior.

1.4.3.6.4.1 Applications of Special Electrical Properties of Nano Materials

The following are some examples where the special electrical conductivity of nano materials are exploited for micro electronics applications

- The use of carbon nanotubes in semiconductor chips,
- Research into the use of a variety of nanomaterials in lighting technologies (light emitting diodes or LEDs and organic light emitting diodes or OLEDs), with commercial use expected in the near future,
- Use of 'quantum dots' in lasers, along with ongoing research into application of other nano materials in laser technology,
- A variety of nano materials used in lithium-ion batteries, or which are being researched for this use,
- Potential use of carbon nanotubes and other nanomaterials in fuel cells and by the solar industry for use in photovoltaics,
- Research into use of nanomaterials to produce lead-free solder, as well as the development of solder-free assembly technology.

Molecular electronics is one of the emerging field with wide range of applications. Some single molecules with nano structures exhibit exceptional control of electron transport and find applications the molecular functions of electronic devices and these molecules can be tailored for using as a working circuit as shown in Figure 1.33.

Figure 1.33 Schematic of molecules crafted into working circuit (24).

1.4.3.6.5 Magnetic Properties of Nano Particles

Magnetic materials are those that exist in a state of permanent magnetization without the need to apply a field. The strength of magnet is measured in terms of saturation magnetization and coercivity (surface area per unit volume) of the grains. There are three categories of magnetism diamagnetism, paramagnetism, and ferromagnetism. Diamagnetism is a fundamental property of all atoms and the magnetization is very small and opposed to the applied magnetic fields direction. However many materials exhibit para magnetism (In materials with un paired electron) where a magnetization develops parallel to the applied magnetic field as the field increased from zero.

Ferromagnetism is the property of those materials which are intrinsically magnetically ordered which develop spontaneously magnetization without the need to apply field. The ordering mechanism is the quantum mechanical exchange mechanism.

In general the magnetic behavior of a material depends on the structure of the material and on its temperature. In order to 'feel' a magnetic field, a material must have a non-zero net spin (unpaired electrons) (transition metals). The typical size of expected magnetic domains is around 1 μm. When the size of a magnet is reduced, the number of surface atoms becomes an important fraction of the total number of atoms, surface effects become important, and quantum effects start to prevail. When the size of these domains reaches the nanoscale, these materials show new properties due to quantum confinement, for example the giant magneto resistance effect (GMR). This is a fundamental nano effect which is now being used in modern data storage devices.

In magnetic nano particles, the energy of magnetic anisotropy may be that small that the vector of magnetization fluctuates thermally; this is called super paramagnetism. Such a material is free of reminisce, and coercitivity. Touching superparamagnetic particles are loosing this special property by interaction, except the particles are kept at distance. Combining particles with high energy of anisotropy with super para magnetic ones leads to a new class of permanent magnetic materials.

Magnetic nano particles (MNPs) are of particular interest in fundamental importance, as well as a strong technological interest, ranging from fields as diverse as medicine applications to potential high density magnetic recording memories, and soil treatments. They exhibit very different macroscopic magnetic properties when compared with their bulk counterpart. Most of these differences are due to the effects of the small scale, leading to a significant increase in the fraction of atoms on the surface, as compared with those in the particle. In the case of MNPs, the effects of mutual magnetic interactions have to be added, in a complex way, to those of the reduced dimensions (25). Magnetic nano particles (MNPs) have potential for use in a number of biomedical applications, ranging from drug localization and magnetic hyperthermia to gene transfection and enhancement of medical images (26).

Magnetic particles have received a considerable attention due to their potential employment in the fields of high-density magnetic storage devices (due to their size and anisotropic behavior, which permits the use of smaller bit size that favors the attainable recording density), contrast enhancers for magnetic resonance imaging, magnetic vectors for cell targeting and drug delivery, wiring materials for audio and radio frequency transformers, high temperature space power systems etc.

Historically, the first magnetic nanoparticles used in magnetic fluids was magnetite (Fe_3O_4 in 1960 by NASA (27, 28). In Chapter VI more details on Ferro fluids are presented.

Different types of magnetic material include some alloys such has FePt, NiPt and NiPd (29,30), which can be used in the magnetic fluid and ferrites: MFe_2O_4 (M = Mn, Ni, Co, Zn, Fe) (31,32,33), γ-Fe_2O_3 (34).

Many magnets made up of nano crystalline yittrium samarium-cobalt grains possess very unusual magnetic properties due to their large surface area. Typical applications of these high power rare earth magnets include power generators in submarines, automobile alternators, Land based power generators and motors for ships, ultra sensitive instruments, MRIs etc.

1.4.3.6.6 Catalytic Properties of Nano Materials

Any substance which increases a chemical reaction rate without being consumed or chemically altered is called catalyst. Enzymes which are naturally available catalysts facilitate a number biological reactions to take place with minimum energy consumption and higher kinetic rate. A number of man made catalysts like metal particles fixed on a oxide surface are in use. However they are less energy efficient when compared to natural catalysts.

As most of the catalyzed reactions occur on the surface of a catalyst active surface of the catalysts is very important as higher the catalysts' active surface, the greater will be the efficiency of the catalyst. The active surface of the catalysts increases when its size is decreased. Thus the smaller the catalyst particles, the greater the surface-to-volume ratio. Further the spatial structure of the catalysts also plays important role in the catalyst activity.

The particle size and molecular structure of the catalyst can be controlled using nanotechnology. Hence, this technology has great potential to expand catalyst design with benefits for the chemical, petroleum, automotive, pharmaceutical and food industries.

The use of nanoparticles that have catalytic properties allows a drastic reduction in the amount of material used, with resulting economic and environmental benefits.

For example bulk gold is a noble metal, stable non toxic and resistant to oxidation and chemical attack, while nanoscale gold particles can catalyse chemical reactions. In a number reactions finely dispersed gold nanoparticles on oxide supports are found to be catalytically very active with high selectivity than those of the commonly used transition metal catalysts such as platinum, rhodium palladium. As metals like platinum and palladium (commonly used in catalysis such as car catalytic converters) are toxic and are also very rare metals, hence very expensive, dispersed nano gold particles find extensive applications in a number of industrial process

Nanoparticles of transition element oxides attached gold or platinum clusters also exhibit interesting catalytic properties.

Nano structural materials with high surface area can be used as nano *catalysts* decompose 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. Nano catalysts based on platinum group metals (PGM) and Pt-Ru alloys are some of the most frequently used catalysts in fuel cell technology though their high cost limit their application. Using bimetallic nano particles the cost can be reduced to certain extent.

1.4.3.6.7 Nano Biotechnology Applications

In nature we have a number of important biological molecules which possess highly precise and functional nanostructures like, proteins, DNA, cellular components, membranes etc. These functional biological molecules are build up of simple molecular building blocks which are arranged as complex three dimensional nano structures with dynamic interaction patterns. They can be integrated with nanoparticles (of the same dimensions) like nano gold in colloidal form by adopting physical principles and chemical synthesis techniques . Many of these biomolecules consist of long macromolecular chains which are folded and shaped by cooperative and weak interaction between side groups, H-bridges and salt bridges. Here, functionalized nanoparticles, such as colloidal gold (35), may intrude into the complex folded structures (36, 37). This allows labelling the functional biological molecules for following complex reaction paths. This types of applications fall under **nano biotechnology** where nano and macro structures are integrated to understand the functional mechanism of macro biological molecules by following typical n properties of tagged nano particles.

These nano tagging techniques are finding extensive applications in immune labelling (38) and related surface functionalization techniques to target nanoparticles to biomolecules as markers for high resolution Transmission Electron Microscopy and optical imaging systems. Quantum dots (39) and magnetic nano particles (40) are also finding potential applications in this direction.

Thus nano biotechnology will be a powerful combination of biology with nano materials science.

1.4.4 Summary of Importance of Properties of Nano Materials and their Applications

The promise and essence of the nanoscale science and technology is based on the demonstrated fact that materials at the nanoscale have properties (i.e., chemical, electrical, magnetic, mechanical and optical) quite different from the bulk materials as discussed above Some of such properties are, somehow, intermediate between properties of the smallest elements (atoms and molecules) from which they can be composed of, and those of the macroscopic materials. Compared to bulk materials, it is demonstrated that nanoparticles possess enhanced performance properties when they are used in similar applications.

New phenomena are being observed and exploited for various applications and some examples are summarized below.

- Atomic diffusion through interfaces becomes an efficient mechanism of transport of matter at relatively low temperatures comparing to conventional matter. This effect can be used for example to considerably increase the sensitivity of a gas sensor, the kinetics of hydrogen diffusion in a hydrogen storage device, or lower the operation temperature of Solid Oxide Fuel Cells.

- If the crystal size is smaller than the electron mean free path, the electronic conductivity and the temperature coefficient is found to decrease because of grain boundary scattering.
- Phonon spectra are modified due to the effect of surfaces and the small size of particles – so called phonon confinement effects.
- Band gap changes in nano sized semiconductor particles leads to a blue shift of luminescence.
- Size induced control of luminescence relaxation in oxide nanoparticles leads to changes in the optical properties and therefore interesting optoelectronic device applications.
- Reduction of the size of quantum dots to the point where only a few electrons are present in each one is the basic technology for spintronics.
- Surface effects in magnetic materials control the magnetic properties of thin layers, leading to more efficient data storage devices and more sensitive magnetic sensors. Examples are Giant Magnetic Resistance, GMR.
- For metals with grain size less than 100 nm, mechanical properties change strongly because of the contribution of grain boundaries. This mechanism can lead to the development of materials with superior strength and ductility, and thus improved service performance.
- Thermodynamic phase equilibria are shifted or changed due to the contribution of interfaces or interface related strains, to the free energy of the system. This allows production of new non-equilibrium materials which exhibit properties not previously known.
- Tribological properties are changed tremendously when the interacting materials are in the nanoscale. These changes facilitate reduced friction and wear in MEMS applications, microsystems and microsurgical instruments.

Some special applications of nano material properties are presented in Table 1.6.

Table 1.6 Effects of nanomaterials and applications due to the reduced dimension.

Effect of Nanoscale	Applications
Higher surface-to-volume ratio, enhanced reactivity	Catalysis, solar cells, batteries, gas sensors
Lower percolation threshold	Conductivity of materials, sensors
Increased hardness/wear resistance with decreasing grain size	Hard coatings, tools, protection layers
Narrower bandgap with decreasing grain size	Opto-electronics
Higher resistivity with decreasing grain size	Electronics, passive components, sensors
Improved atomic transport kinetics	Batteries, hydrogen storage
Lower melting and sintering temperature	Processing of materials, low temperature sintering materials
Improved reliability, fatigue	Electronic components, MEMS

1.5 Current Industrial Applications of Nano-Technologies

Presently nanotechnologies became part of convergent new technologies, which offer synergies between nanotechnology, biotechnology, information technology, and cognitive sciences (such as psychology, neuroscience, biology or computer science). Each of these is currently progressing at a rapid rate, experiencing qualitative advancements, and interacting with more established fields such as mathematics, environmental technologies.

Figure 1.34 presents broad areas where nano technologies have great potential for industrial applications. Many of these biomolecules consist of long macromolecular chains which are folded and shaped by cooperative and weak interaction between side groups, H-bridges and salt bridges. Here, functionalized nanoparticles, such as colloidal gold (35), may intrude into the complex folded structures (36, 37).

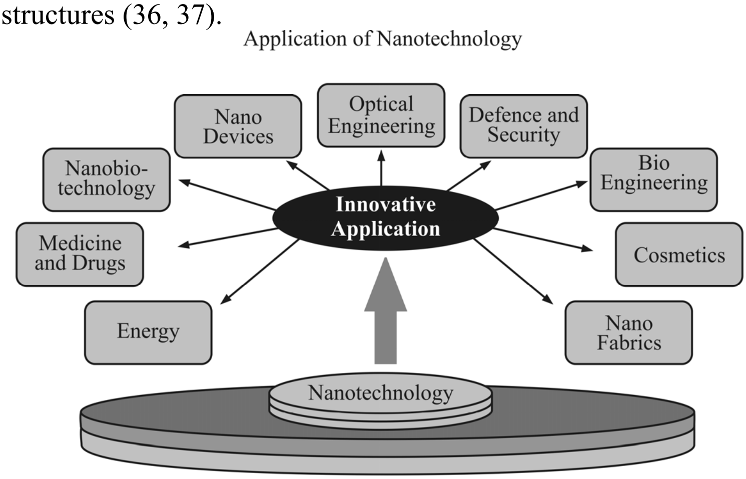


Figure 1.34 Broad areas of industrial applications of nano technologies.

As can be seen from Figure 1.34 Nanotechnology is entering into all aspects of science and technology including, but not limited to, aerospace, agriculture, bioengineering, biology, energy, the environment, materials, manufacturing, medicine, military science and technology. It is truly an atomic and molecular manufacturing approach for building chemically and physically stable structures one atom or one molecule at a time. Presently some of the active nanotechnology research areas include nanolithography, nano devices, nano robotics, nano computers, nano powders, nano structured catalysts and nano porous materials, molecular manufacturing, diamond, carbon nanotube and fullerene products, nano layers, molecular nanotechnology, nano medicine, nano biology, organic nanostructures to name a few.

1.5.1 Improving Product Performance

Currently nano technologies are being used for improving the product performance in the following industrial process.

(i) By combining nanoscale particles of inorganic clays with polymers as well as other nanoparticle reinforced materials, highly Wear-resistant tires can be produced,

(ii) Using nanoscale particles that have the best properties of both dyes and pigments as well as advanced ink jet systems, the printing quality can be greatly improved,

(iii) Nano layers with selective optical barriers and systems on a chip can be made by controlling layer thickness to better than a nanometer which plays key role in producing vastly improved new generation of lasers, magnetic disk heads,

(iv) Advanced chemical and bio-detectors based on nanometal particles are finding extensive applications in bio process control and pollution control,

(v) A number advanced drug delivery systems and drug targeting capabilities, are emerging in bio medical applications using nano bio technologies,

(vi) Nano metallic particles combined with silica- tungsten slurries can be used to Chemical-mechanical polishing, hard coatings and high hardness cutting tools,

(vii) Nanotechnologies currently used by leading businesses and industrial process for a variety of technical and innovative applications. Examples include:

- (a) Exxon Mobil is using zeolites, minerals with pore sizes of less than 1 nm, as a more efficient catalyst to break down or crack large hydrocarbon molecules to form gasoline.
- (b) IBM has added nano scale layering to disk drives, thus exploiting the giant magneto resistive effect to attain highly dense data storage.
- (c) Gilead Sciences is using nanotechnology in the form of lipid spheres, also known as liposomes, which measure about 100 nm in diameter, to encase an anticancer drug to treat the AIDS-related Kaposi's sarcoma.
- (d) Carbon Nanotechnologies, a company co-founded by buckyball discoverer Richard E. Smalley, is making carbon nanotubes more affordable by using a new and more efficient manufacturing process.
- (e) Nano phase Technologies is utilizing nano crystalline particles, incorporated into other materials, to produce tough ceramics, transparent sun blocks, and catalysts for environmental uses, among other applications.

1.6 Engineering Principles and Initiatives of Nano Technology

1.6.1 Process Engineering, Design and Manufacturing

To prepare some smart materials/devices with certain desired properties nanotechnology can be used as an engineered manipulation of atoms and molecules in a defined and repeatable manner. These nano size building blocks are intermediate systems in size lying between atoms and small molecules and microscopic and macroscopic systems and composed of a limited and countable number of atoms. Molecular Building Blocks (MBBs) are distinguished for their unique properties (e.g., graphite, fullerene molecules made of a number of carbon atoms, e.g., C60, C70, C240, etc.

Earlier mechanical engineers and material scientists used to discuss jointly to plan for the design and characterization of smart materials. At present with the availability of advanced computing and new developments in material science, more precise modeling approaches are available for researchers for processes design and manufacture materials, with desirable performance and properties. However the present challenge is modelling short-term nano/micro-scale material behavior, through meso-scale and macro-scale behavior into long-term structural systems performance which will provide in better understanding and design of materials and structures in all physical scales.

1.6.2 Fabrication Techniques for Engineered Nano Materials

There are a wide variety of techniques that are capable of creating nanostructures with various degrees of quality, speed and cost. These manufacturing approaches fall under two categories: ‘bottom-up’, and ‘top-down’. In recent years the limits of each approach, in terms of feature size and quality that can be achieved, have started to converge. A diagram illustrating some of the types of materials and products that these two approaches are used is shown in Figure 1.35.

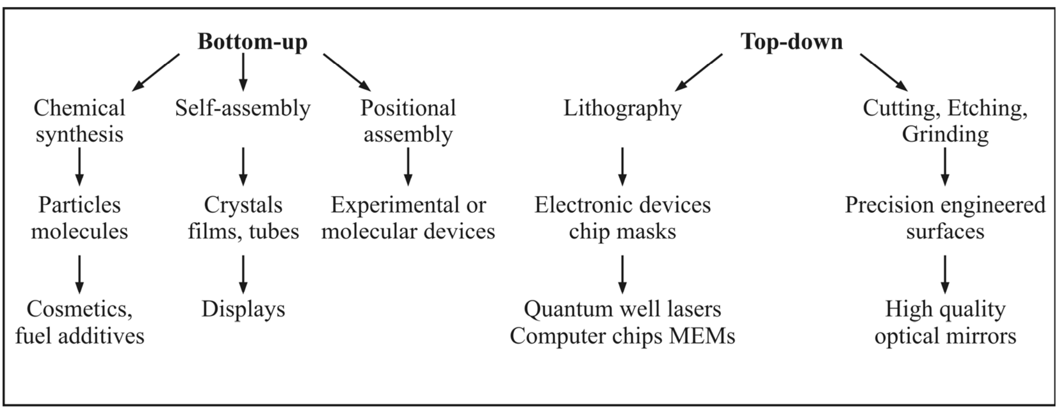


Figure 1.35 The use of bottom-up and top-down techniques in manufacturing.

1.6.2.1 Bottom-Up Manufacturing

Bottom-up manufacturing involves the building of structures, atom-by- atom or molecule-by-molecule which can be classified into three categories: (i) chemical synthesis, (ii) self-assembly, and (iii) positional assembly.

1.6.2.1.1 Chemical Synthesis

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.

The generic chemical process of nanomaterial manufacture, and applications involve precursors, primary/secondary building units, reactions in liquid/vapour phase, nano material production and characterization (Figure 1.36) in which all general production engineering principles apply.

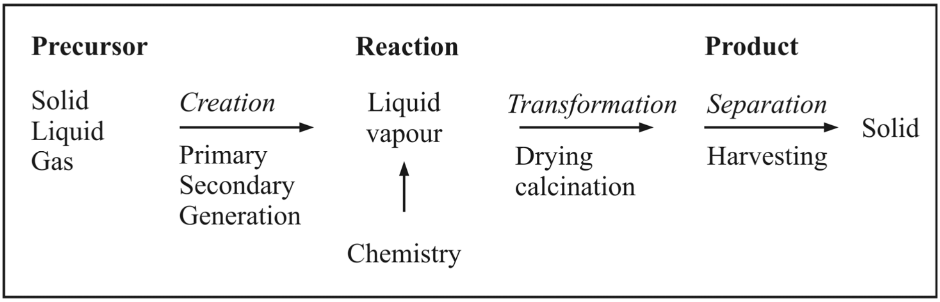


Figure 1.36 The generic processes that are involved in the production of nano particles.

1.6.2.1.1.1 Unit Operations

The first step in chemical synthesis is the creation of a new phase or state where the nanoparticles either form or can be formed by a chemical step. Thus 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. After formation of nanoparticles takes place, usually a chemical reaction will be performed to generate the desired material through phase transformation or even solid-state reaction. As the potential exposure of the workforce to nanoparticles will be greatest when these materials are processed in a gaseous environment; the worker exposure 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. Processing and handling ability is very important for nanomaterials. Production of nanoscale and nanostructured materials, is still at the laboratory scale of synthesis (kilograms per day scale of operation or even less) and further optimized studies are required for scaleup.

1.6.2.1.1.2 Resource Management and Environmental Issues

Life cycle assessment (LCA) (sometimes referred to as ‘cradle-to-grave’ analysis) is necessary to assess the potential benefits of nanotechnologies. LCA will help to understand (a) the efficiency in the usage of various raw materials (like energy, water, reacting chemicals), (b) emissions over the complete supply chain from the ‘cradle’ of primary resources to the ‘grave’ of recycling, (c) resultant environmental issues and allow to compare them with the benefits of new nano products.

1.6.2.1.2 Self Assembly

A bottom-up production process in which atoms or molecules arrange themselves into ordered nanoscale structures by physical or chemical interactions between the units is called self assembly. Examples of natural process like formation of self salt -crystals and snowflakes, with their intricate structure, come under this category. As in Self assembly, products and components form themselves by combination of atoms and molecules, these process involve less energy, produce low wastes and of great economic and environmental interest.

However, present understanding on self assembly process extends only to the creation of simple systems while in-depth understanding of (a) thermodynamics (b) kinetics of processes at the nanoscale (c) advances in the characterization techniques and (d) improved computer modelling, are expected to facilitate the production of more complex systems. Further by using external force or field (for example: electric or magnetic) to accelerate the often slow self-assembly process (directed Self assembly) will be a future engineered process option under development which is of great interest in industrial point of view.

1.6.2.1.3 Positional Assembly

The final bottom-up technique is positional assembly, whereby atoms, molecules or clusters are deliberately manipulated and positioned one-by-one. Positional assembly is extremely laborious and is currently not suitable as an atomic-scale industrial process. The fact that very simple structures can be fabricated atom-by-atom has lead to speculation that tiny nanoscale machines could be made which could be used in parallel to manufacture materials atom-by-atom.

1.6.2.2 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 30 years. These methods are discussed in detail in Chapter 4.

Top-down methods offer reliability and device simplicity, 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.

1.6.3 Precision Engineering

In general, ultra-precision engineering and manufacture are essential aspects in micro-electronics, production of the flat low-damage semiconductor wafers used as substrates for computer chips, manufacture of the precision optics used to print the patterns on the wafers etc. In addition, the techniques of ultra-precision engineering are also used in a variety of consumer products such as computer hard disks, CD, DVD players etc.

Ultra-precision machine tools can now achieve very high performance in terms of both the accuracy with which form can be defined (up to 1 part in 10^7, or better than 100 nm over distances of tens of centimeters) and the surface finishes that can be achieved (0.5-1 nm root mean square surface roughness). Adopting nanotechnologies advanced materials for cutting tools, based on diamond or cubic boron nitride; very stiff, precise machine tool structures; new linear and rotary bearing designs employing fluid films; and sensors for size control combined with numerical control and advanced servo-drive can be achieved. Further very precise process conditions and temperature control can also be achieved by convergent nano technologies (41).

1.6.3.1 Lithography

Manufacturing in the Integrated Chip Technology (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. (See for more details in Chapter 4).

1.6.4 Characterization

The characterization of materials like the determination of their shape, size, distribution, mechanical and chemical properties is an important part of the nano technologies utilization at industrial scale as it serves two broad purposes: as quality control, and as part of the research and development of new processes, materials and products. Sophisticated tools, such as the STM, AFM and TEM, enable surface and interfacial characterization of materials at the nanoscale, allowing individual atoms to be observed and analyzed provided break through in the application of nanotechnologies at large scale. These characterization techniques are discussed in Chapter 5. This will lead to greater understanding of the relationship between form and material properties, and enabling the control of processes at the nanoscale and the design materials with specific properties.

Table 1.7 gives 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 nano particles.

Table 1.7 Estimated global production rates for various nanomaterials and devices based on international chemical journals and reviews and market research (BCC 2001). These rates are intended for guidance only, as validated numbers are commercially confidential.

Application	Material/device	Production 2005-2010	Projected (tones/annum) 2011-2020
Structural applications	Ceramics, catalysts, composites, coatings, thin films, powders, metals	10^3	10^4-10^5
Skincare products	Metal oxides (titanium dioxide, zinc oxide, iron oxide)	10^3	10^3 or more
ICT	Single wall nanotubes, nano electronics, opto-electro materials (titanium dioxide, zinc oxide, iron oxide), organic light-emitting diodes (OLEDs)	10^3	10^3 or more
Biotechnology	Nanoencapsulates, targeted drug delivery, bio-compatible, quantum dots, composites, biosensors	1	10
Instruments, sensors, characterization	MEMS, NEMS, SPM, dip-pen lithography direct write tools	10^2	10^2-10^3
Environmental	Nanofiltration, membranes	10^2	10^3-10^4

1.7 Future Nano Technologies

1.7.1 High Precision Engineering Process

There are strong drivers for increased precision, energy efficiency and cost effectiveness in process engineering which involve miniaturization, improved wear and reliability, automated assembly and greater interchangeability, and reduced waste, thus there is a great demand for miniaturization and automatization driven by micro e electronics and computer modeling. Techniques such as electron beam lithography (EBL), focused ion beam (FIB), reactive ion etching (RIE) and femtosecond pulsed laser ablation are becoming more accurate and cheaper to apply in a production context. Some examples of future applications of high-precision engineering process are given below.

1.7.2 Integrated Chip Technologies (ICT)

Ultra high precision techniques based on application of nanotechnologies are needed in the production of microchips and their operation. Production of large diameter wafers are finding extensive use in improving nano device efficiency and cost effectiveness.

1.7.3 Optics

Innovative ductile-mode grinding processes, together with electrolytic in-process dressing (ELID), should result in the elimination of polishing in the production of high-quality optical devices. This is likely to be of particular importance in the production of the optics for extra-large astronomical telescopes such as the proposed 50 m and 100 m systems.

1.7.4 Transport

Precision manufacturing based on nanotechnologies will lead to weight reductions in airframe wings and to improve the performance of internal combustion chambers. Precision-machined parts will be more reliable, because of reduced wear, requiring fewer replacement parts and less energy consumption. For example, the ability to produce surfaces with controlled textures through finishing to 10 nm average roughness followed by laser surface treatment is expected to lead to improved power transmission trains with losses through slip reduced by up to 50%.

1.7.5 Medical

It is hoped that the use of ultra-precision machining techniques to produce improved surface finishes on prosthetic implants should lead to lower wear and better reliability.

1.7.6 The Chemical Industry

Chemical industry is growing with great advances in the use nanoscale ‘building blocks’ to assemble organized nano structures, that can in turn be manufactured into commercially useful nano - products. Some of these nano scale structures when integrated with functional biological molecules can be used as drivers to control meso-and macro-scale properties of materials which have direct relevance to industry. It is expected in the coming decades, many of the needs of commerce and society likely to met through application of nano materials revolutionizing synthesis and smart fabrication.

1.8 Human Health and Environmental Risks of Nano Materials

1.8.1 Human Heath Impacts of Nanomaterials

Engineered Nano-particles (ENP) due to their small size when inhaled can pass through the alveolar region of the lungs, from there will be able to cross the blood–air–tissue barrier, enter the bloodstream, and reach target organs (42-44) (11) leading to their injury causing serious health issues. The ability of nanoparticles to enter the body across specific pathways depends on their physico chemical properties.

Nanoparticles may enter the body by the following pathways: By inhalation through the respiratory tract, by permeation through the skin and by ingestion through the digestive tract. (Figure 1.37).

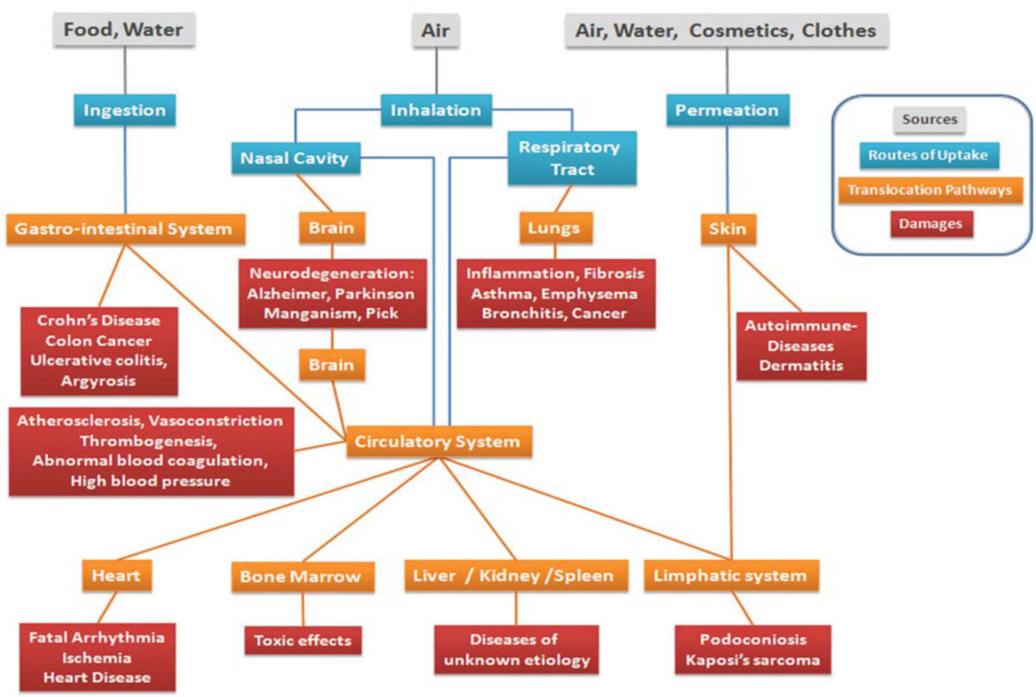


Figure 1.37 The predominant routes of NPs exposure, uptake, translocation and potential risks. (45).

At present through out the globe a number of research groups are working on the toxicity of Engineered nano particles (ENPs) on animal models or in-vitro studies and reporting a wealth of information. However as these data are produced under different experimental conditions it is difficult to compare them though one can understand the trends. For development of a risk management strategy for safe handling of nano materials it is necessary rationalize the data collected from different laboratories and prepare a risk assessment frame work.

So systematic studies on the toxicological, ecotoxicological, and exposure data under standard protocols are planned by various research groups to perform a complete risk analysis.

A number of global research funding agencies at present are supporting R&D projects on toxic effects of nano materials and on social ethical problems arising out of new nanotechnologies on priority basis as the success of nanotechnologies depend on their safe handling.

1.8.2 Health Risk Assessment of Nano Materials

The most frequently encountered nanomaterials in our daily life include zinc oxide nanoparticles (ZnONPs), titanium dioxide nanoparticles (TiO2NPs), silica nanoparticles (SiO2NPs), silver nanoparticles (Ag-NPs), gold NPs (AuNPs), polymeric nanoparticles (PNPs), carbon nanotubes (CNT)s, cabon nanofibers etc.

Potential human health risks are predicted when exposed to some nanomaterials like nano-particles, nano-spheres, nano-tubes, nano-fibers as they have a size comparable to biomolecules (e.g. proteins, DNA) and may interact with them in an adverse manner, leading to toxic effect by passing through protection barriers in cells. The small size of nanoparticles will enable that a high proportion inhaled from the air reaches and is deposited in the deep lung. The size of nanoparticles appears to influence their uptake into cells.

1.8.2.1 Types of nano particles under toxicological study

The European Center for Ecotoxicology and Toxicology of Chemicals (ECETOC) Task Force on Nanomaterials has developed a decision-making framework for the grouping and testing which categorized four main groups (MGs), of nanomaterials (46) 78.

(i) encompassing soluble nanomaterials (MG1s),

(ii) bio -persistent high aspect ratio nanomaterials (MG2s),

(iii) passive nanomaterials (MG3s), and

(iv) active nanomaterials (MG4s).

For detailed understanding the mechanism of their toxicity and resultant health risks a number of research groups are taking R&D programs with approved proto calls focusing on all relevant aspects of a nanomaterial’s life cycle and biological pathways and their toxicity.

1.8.2.2 Relation between Physico Chemical Properties and toxicity of nano particles

It is now generally recognized that the mechanisms underlying NPs uptake, translocation, biological and toxicological effects, depend strongly on their relationship with their physico chemical properties like (i) size, (ii) shape, (iii) surface charge, (iv) surface area, (v) hydrophilicity, (vi) agglomerate (vii) aggregate formation, (viii) solubility, and (ix) chemical nature.

So much attention needed in understanding the relationship between the exact NPs property and toxicity.

1.8.3 Environmental Effects of Nanotechnology

To understand the environmental risks of nano particles we need to understand.

What is their impact on environment?

What happens when materials containing nanoparticles reach landfills and degrade?

Could this cause harm to ecosystems?

The knowledge of the risks of the particles to the flora and fauna is sparse. The application of nanoparticles to the soil or water sources, for example as fertilizers, may hold many unknown risks. We also know that as surface area increases, the rates of chemical reactions will also increase such that substances which are normally inert in normal forms become explosive as finely divided powders. How will the increased reactivity of nanomaterials affect the environment?

Nanotechnology have a number of beneficial environmental effects also. Global warming, not surprisingly, is a major consideration in new technologies. As nanotechnologies allow the manufacture of materials with less energy consumption and fewer waste gases, it is likely the production of green house gases will decline which may lead to an abatement of the global warming process. Because nanotechnology employs a bottom up manufacturing process, there will be a decrease in industrial waste, both in terms of wasted energy and solid waste production.

However as environmental systems are highly overlapping complex systems detailed modeling studies with supporting ground truth studies are needed for arriving at final conclusions on impacts of nano materials in ecosystems.

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Web Sites

Paper by R. Feynman entitled 'There's plenty of room at the bottom':

http://www.zyvex.com/nanotech/feynman.html

Institute of nanotechnology:http://www.nano.org.uk/

European Society for Precision Engineering and Nanotechnology

(EUSPEN): http://www.euspen.org/

Images of quantum corrals:http://www.almaden.ibm.com/almaden/media/image_mirage. html

Molecular abacus:http://www.research.ibm.com/topics/popups/serious/nano/html/show.html

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