

# 1

## Nano Science and Technologies

### 1.1 Concepts of Nano Science and Nanotechnologies

#### 1.1.1 Introduction

Nano science deals with the study of materials at atomic, molecular and structures level with at least one dimension roughly between 1 and 100 nanometers where their properties differ significantly from those at a macro scale.

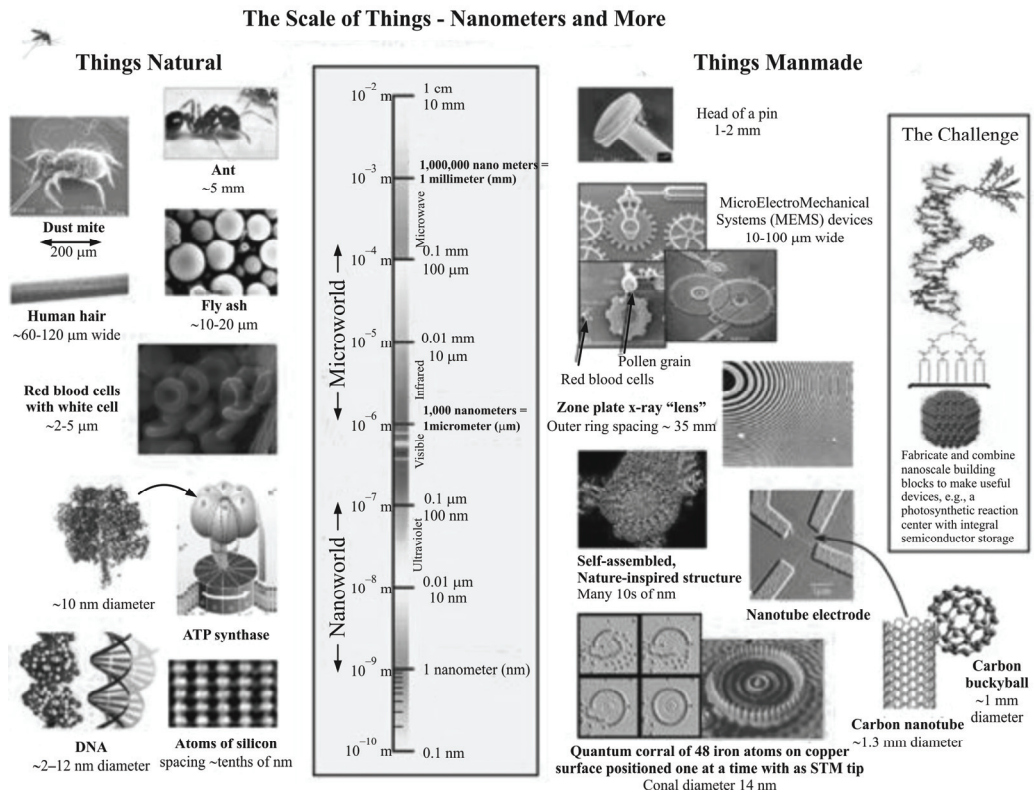
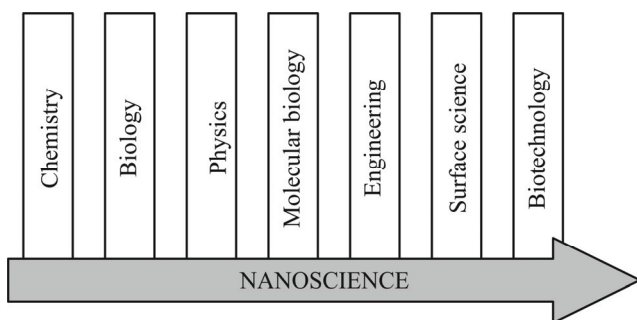


Figure 1.1 Scale of things in micro and nano world (1)

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. To get a sense of the nano scale, a human hair measures 50,000 nanometers across and a bacterial cell measures a few hundred nanometers across. The smallest things visualized with the unaided human eye are 10,000 nanometers across. Just ten hydrogen atoms in a line make up one nanometer. To provide better idea the scale of various natural and man-made things which fall in micro and nano scale are presented in Fig. 1.1.

### 1.1.2 What is Nano Science?

Nano Science being an interdisciplinary science became one of the leading scientific fields today since it combines knowledge from the fields of Physics, Chemistry, Biology, Medicine, Informatics, and Engineering. Nano science expands the borders of material science and engineering by adding biology, biochemistry, information science to physics and chemistry disciplines. Nano science is thus a "horizontal-integrating interdisciplinary science that cuts across all vertical sciences and engineering disciplines" (Figure 1.2).



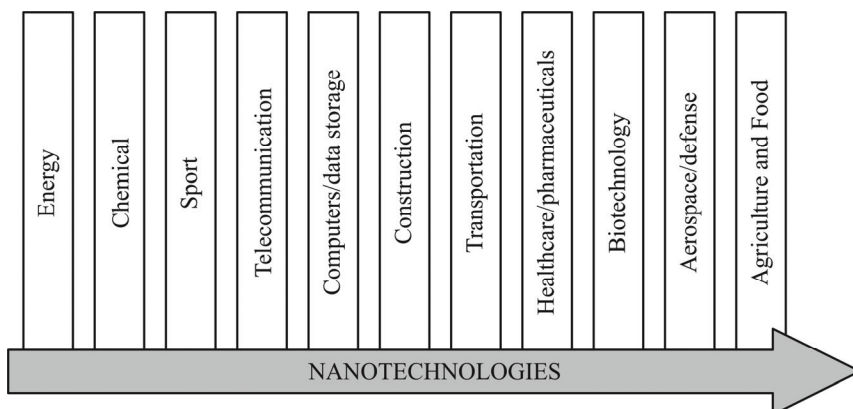
**Figure 1.2** Nano science -horizontally integrating multi disciplinary science  
(Source: L. Filippini, iNANO, Aarhus University, Creative Commons Share Alike 3.0)

### 1.1.3 What are Nano Technologies?

"Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometre scale."

The fundamental objective of nanotechnology is to model, simulate, design and manufacture nanostructures and nano-devices with extraordinary properties and assemble them economically into a working system with revolutionary functional abilities. Nanotechnology offers new innovative ways of material development by controlling and manipulating the fundamental building blocks of matter at nanoscale, that is, at the atomic/molecular level.

Nanotechnologies are also horizontal-enabling convergent technologies (Figure 1.3). They are "horizontal" because they cut across numerous industrial sectors; they are "enabling" since they provide the platform, the tools to realise certain products; and are "convergent" because they bring together sectors of science that were previously separated.



**Figure 1.3** Nano Technologies-horizontal converging technologies

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### 1.1.3.1 Scope and Potential of Nano Technologies

Nanotechnologies are newly emerging technologies with great potential to lead and provide innovative breakthroughs that can be applied to real life. Novel nano and biomaterials, and nano devices can be fabricated and controlled by nanotechnology tools and techniques, which investigate and tune the properties, responses, and functions of living and non-living matter, at sizes below 100 nm. The application and use of nanomaterials in electronic and mechanical devices, in optical and magnetic components, quantum computing, tissue engineering, and other biotechnologies, with smallest features, widths well below 100 nm, are the economically most important parts of the nanotechnology nowadays and presumably in the near future. The number of nano products is rapidly growing since more and more nano engineered materials are reaching the global market.

### 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

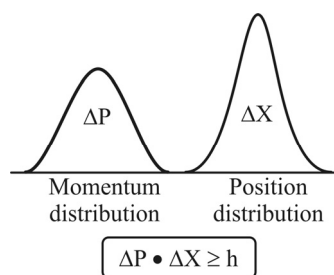
Nano materials are closer in size to single atoms and molecules than to bulk materials. Due to the very small size of nano materials, their mass will also be extremely small resulting gravitational forces to be negligible while electromagnetic forces become dominant in determining their behavior which can be explained by Quantum mechanics theory. Quantum mechanics is a scientific model that was developed for describing the motion and energy of atoms and electrons.

#### 1.1.5.1 Wave-Corpuscle Duality of Matter

Wave-corpuscle duality of matter for objects of very small mass, such as the electron, will have a more pronounced effect. Thus, electrons exhibit wave behaviour and their position is represented by a wave (probability) function.

According to Heisenberg's uncertainty principle (quantum mechanical approach) the position and momentum of an object cannot simultaneously and precisely be determined [4].

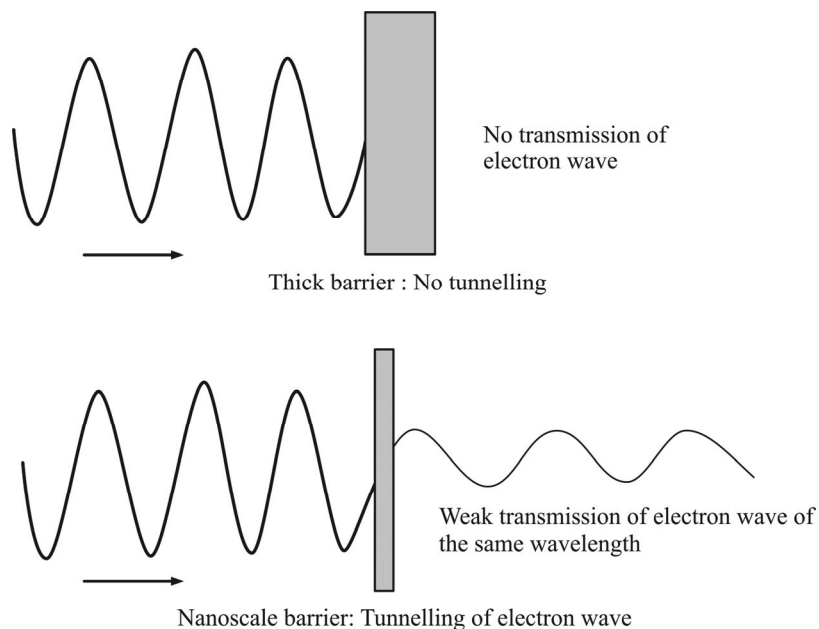
According to Werner Heisenberg "The more precisely the **position** is determined, the less precisely the **momentum** is known". Heisenberg's Uncertainty Principle applies only to the subatomic particles like electron, positron, photon, etc. It does not forbid the possibility of nanotechnology, which has to do with the position and momentum of such large particles like atoms and molecules. This is because the mass of the atoms and molecules are quite large and the quantum mechanical calculation by the Heisenberg Uncertainty Principle (4) places no limit on how well atoms and molecules can be held in place [Figure 1.4].



**Figure 1.4** Heisenberg uncertainty principle

### 1.1.5.2 Tunneling Effect

Tunneling is the penetration of an electron into an energy region that is classically forbidden (5). Electron (or quantum) tunneling is attained 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.



**Figure 1.5** Quantum tunneling

Classic physics states that a body can pass a barrier (potential barrier) only if it has enough energy to 'jump' over it. Therefore, if the object has lower energy than that needed to jump over the energy barrier (the 'obstacle'), in classic physics, the probability of finding the object on the other side of the barrier is zero. In quantum physics, a particle with energy less than that required to jump the barrier has 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. However it should be noted that in order to have a tunnel effect, the 'thickness' of the barrier (i.e. energy potential) must be comparable to the wavelength of the particle and, therefore, this effect is observed only at nano metre level. The intensity of the current generated by the tunneling electron gives information about the thickness of the boundary. 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.

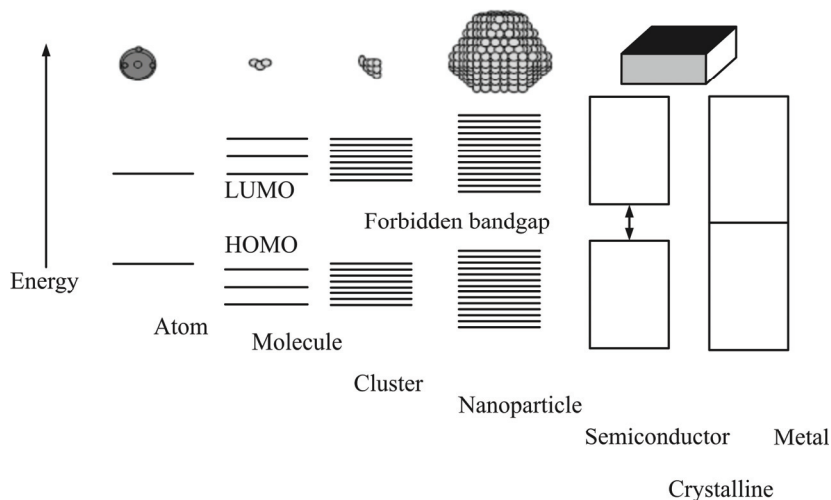
### 1.1.5.3 Quantum Confinement

In Nano particles/crystals, the electronic energy levels are not continuous as in the bulk but are discrete (finite density of states), because of the confinement of the electronic wave function to the physical dimensions of the particles. This phenomenon is called Quantum confinement and therefore Nano Crystals are also referred to as quantum dots (QDs).

In a nano material, such as a metal, electrons are confined in space rather than free to move in the bulk of the material. The quantum mechanical (wavelike) properties of electrons inside matter are influenced by variations on the nanoscale. By nanoscale design of materials 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. When the dimension of a material approaches the 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.

### 1.1.5.4 Reasons for Quantization of Energy in Nano Materials

In nano particles size quantisation arises because the size of a nanoparticle is comparable to the de Broglie wavelength of its charge carriers (*i.e.*, electrons and holes). (Quantum dots are nanomaterials that display the effect of quantization of energy). Due to the spatial confinement of the charge carriers, the edge of the valance and conduction bands split into discrete, quantized, electronic levels. These electronic levels are similar to those in atoms and molecules. The spacing of the electronic levels and the bandgap increases with decreasing particle size. (Figure 1.6). This is because 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)

### 1.1.5.5 Random Molecular Motion

Molecules move due to their kinetic energy (assuming the sample is above absolute zero). This is called random molecular motion and is always present. At the macro scale, this motion is very small compared to the sizes of the objects and thus is not influential on how the object moves. At the nanoscale, however, these motions can be of the same scale as the size of the particles and thus have an important influence on how they behave. One example of a random kinetic motion is Brownian motion.

### 1.1.6 Quantum Size Effects on Physical Properties

Thus when the dimension of a material approaches the 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.

Both physical and chemical properties are derived from atomic and molecular origin in a complex way. For example the electronic and optical properties and the chemical reactivity of small clusters are completely different from the better known property of each component in the bulk or at extended surfaces. Nano particles with a diameter between one and several tens of nanometers possess an electronic structure that is intermediate of the discrete electronic level of an atom or molecule and the band structure of a bulk material. The resulting size dependent role of physical properties is called the quantum size effect. Depending on their chemical composition the particles in the nano range display physical, chemical and biological properties which can be manipulated for the desired objectives. It is predicted that the behavior of the particles at the macro and nano range may be very different and the same material in bulk.

The origin of the quantum size effects strongly depends on the type of bonding in the crystal also. Complex quantum mechanical models are required to predict the evolution of such properties with particle size, and typically very well defined conditions are needed to compare experiments and theoretical predictions.

Nano materials 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 the 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

### 1.1.6.1 Different Categories of Quantum Confined Nano Materials

Under the influence of quantization of energy levels nanoscale materials will have special properties of great importance and can be grouped into the following categories based on the degree freedom of electrons in these nano structures.

- 1. Three Dimensional Systems:** Nano particles which have all three dimensions-length, breadth and height.

Nano particles are of interest because of the new properties (such as chemical reactivity and optical behaviour) that they exhibit compared with larger particles of the same materials. For example, titanium dioxide and zinc oxide become transparent at the nanoscale and have found application in sunscreens.

Nano particles have a range of potential applications: In the short-term application such as in cosmetics, textiles and paints. In the longer term applications such as drug delivery where they could be used to deliver drugs to a specific site in the body.

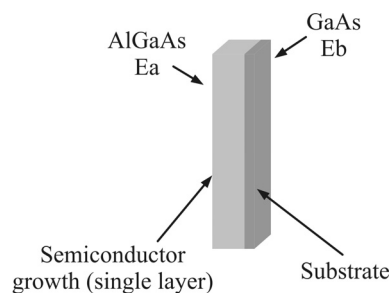
Nano particles can also be arranged into layers on surfaces, providing a large surface area and hence enhanced activity, relevant to a range of potential applications such as catalysts

- 2. Two Dimensional Quantum Well Systems:**

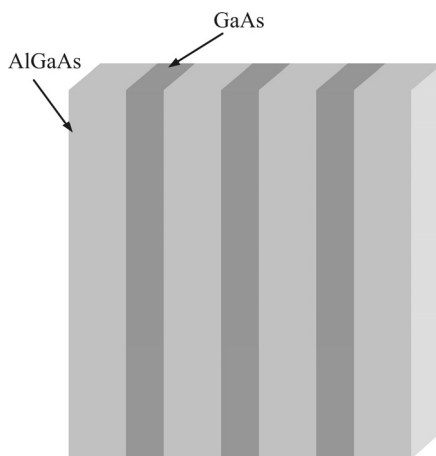
They will have only length and breadth for example, nano wires and nano tubes: Quantum well is a two dimensional system where the electron can move in two directions and restricted in one direction. They are called Quantum because; the electronic property is quantized as the spatial distance is very very small.

In Quantum Well one dimension is reduced to nano range while the other two dimensions remain large. Quantum well are formed in semiconductor by having a material like gallium arsenide sandwiched between two layers of a material with a wider band gap like aluminium arsenide. These structures can be grown 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 hetero epitaxial growth by an ultra thin layer of binary, tertiary, quaternary, or quinary, semiconductor 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

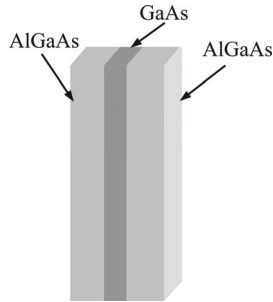


**Figure 1.8** AlGaAs/GaAs/AlGaAs double quantum well



**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)).

**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.



**Figure 1.9** AlGaAs/GaAs – multiple quantum well system

- 3. One Dimension:** It has only one parameter either length (or) breadth (or) height (example: very thin surface coatings).

Quantum Wire is a also one-dimensional system where the electron can move in one direction and restricted in two directions.

**Quantum Wires:** Quantum wires are ultra fine wires or linear arrays of Nano dots, formed by self-assembly. They can be made from a wide range of materials such as Semiconductor Nanowires made of silicon, gallium nitride and indium phosphide. Nanowires have potential 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. Nano wires can be prepared by growth techniques such as: Chemical Vapour deposition (CVD) Electroplating.

In quantum wires two dimension are reduced and on dimension remains large.

Therefore, the electrical resistivity of quantum wire can not be calculated using conventional formula (where  $\rho$  is the resistivity,  $l$  is the length, and  $A$  is the cross-sectional area of the wire).

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

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.

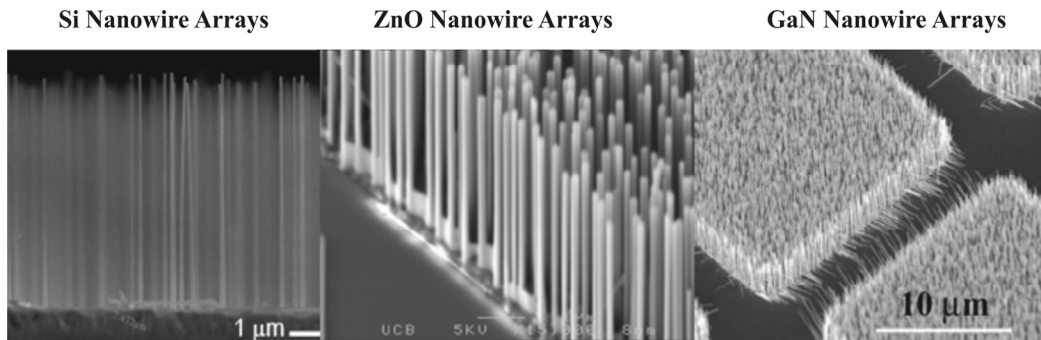


Figure 1.10 Cobalt nanowires on Si substrate

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 excitons (bound pair of conduction band electrons and valence band holes) in all three spatial directions (Figure 1.11).

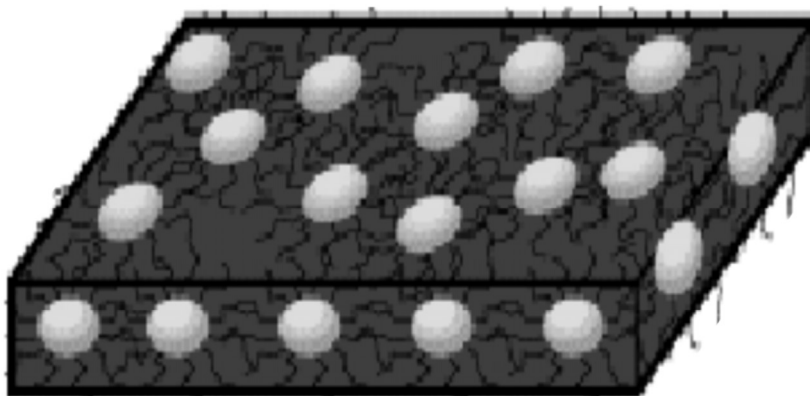
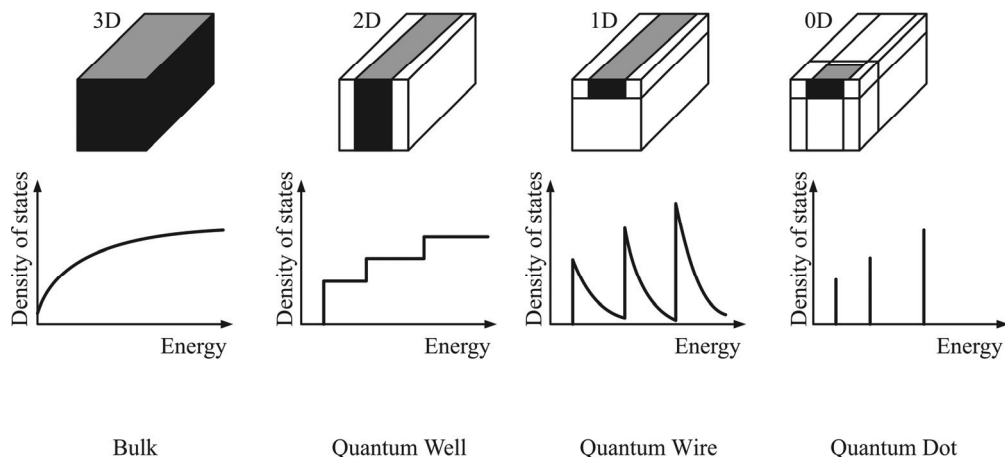


Figure 1.11 Quantum dots

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



- If a bulk metal is made thinner and thinner, until the electrons can move only in two dimensions (instead of 3), then it is “2D quantum confinement.”
- Next level is ‘quantum wire’
- Ultimately ‘quantum dot’

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

### 1.1.7 What is Nano Chemistry?

Nanomaterials often arise from a number of molecules held together or large molecules that assume specific three-dimensional structures through intermolecular bonding (macromolecules). Therefore, nanoscience also deals with supramolecular chemistry (i.e., the chemistry that deals with interactions among molecules), which is just a sub-area of the general field called 'chemistry'. In these macromolecules, intermolecular bonding and surfaces often plays a crucial role and perform numerous functions as given below

- Intermolecular bondings, such as hydrogen bonding and van der Waals bonding are weak interactions but in a large number they can have a total energy that can be quite significant. Consider, for instance, the structure of DNA (which has a cross-section of 2 nm): the two helixes are held together by numerous hydrogen bonds. This point becomes particularly relevant in nanoscience, where materials can have very large surface areas and, consequently, small forces can be applied to very large areas .
- In nanoscience, macromolecules are often considered as 'devices' that, for instance, can trap or release a specific ion under certain environmental conditions (pH etc.). A biological example of such a macro- molecule is ferritin.

Therefore, in nano science and nanotechnologies, where molecules can themselves be devices, bonds may also be device components. One area of study is for example, the use of molecules as molecular switches, actuators and electronic wires; physical and chemical properties depend on many of its surface properties.

- (iii) Surfaces perform numerous functions: they keep things in or out; they allow the flow of a material or energy across an interface; they can initiate or terminate a chemical reaction as in the case of catalysts. Nano Surface chemistry deals with chemical, physical and biological interactions on nano surfaces. In this context, the term interface, rather than surface, is often used, to emphasise the fact that it is a boundary between two phases: the material and the surrounding environment (liquid, solid or gas).
- (iv) 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.
- (v) 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.
- (vi) This has 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.
- (vii) Atoms and molecules that exist at the surface or at an interface are different from the same atoms or molecules that exist in the interior of a material. This is true for any material. 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.
- (viii) 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.
- (ix) 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**

Nano materials can be classified based on the basis of their origin as given below

- (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

Natural nano materials are those available in nature (Plant, animal and mineral), without human modification or processing and which possess un-usual properties because of their inherent nano structure. The arrangement of tens to hundreds of molecules into shapes and forms in the nanoscale range provide nano structure to biological molecules. The interaction of light water and other materials with these nanostructures gives the natural materials some remarkable properties. In nature, we encounter some outstanding solutions to complex problems in the form of fine nanostructures with which precise functions are associated.

### 1.2.1.1 Nature's Examples for Non Engineered Nano Materials

The physical origins of the remarkable properties of many biological materials are due to complex, often hierarchical structures. They are characterized by a surprising level of adaptability and multifunctionality. These 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.

Further in the formation and functioning of these natural nano structure characteristic follows very simple laws given below which are highly inspiring to follow

- (i) Nature runs on sunlight and uses only the energy it needs. Natural nanomaterials are extremely energy efficient.
- (ii) Nature organize materials to function and recycles everything — waste products are minimized in nature.
- (iii) Nature rewards cooperation although it encourages diversity and local expertise.

#### 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  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ . 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.

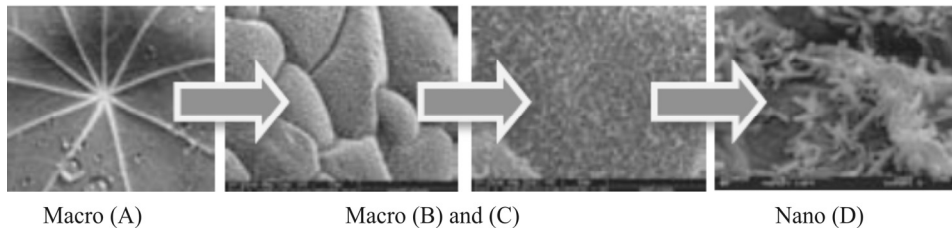
- (iv) **Mineralised natural materials, such as shells, corals and bones:** Many of these materials are formed by calcium carbonate crystals that self-assemble together with other natural materials, such as polymers, to form fascinating three-dimensional architectures. For instance, a shell is grown 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

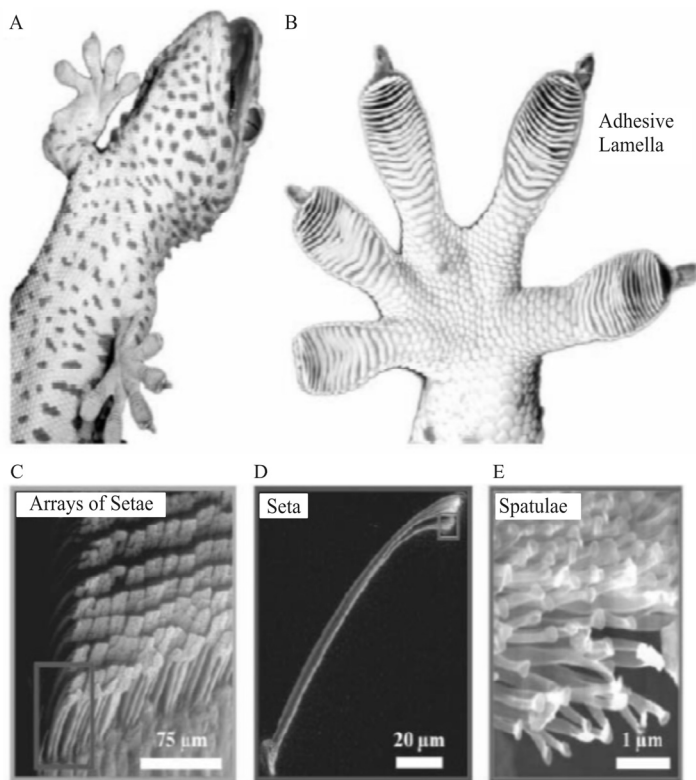
The consequence is that water droplets roll off the leaf surface and, in doing so, drag dirt away from it, as shown in Figure 1.13 This effect, 'self-cleaning', renders the lotus leaf clean and resistant to dirt. The same effect is found in other leaves such as those of nasturtium (*Tropaeolum*) and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



**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 one of the best examples 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)

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A lizard from southeast Asia which...	
Can generate – 10 B of adhesive force	
Can run up to – 1 m/s	
Can generate shear stress of – 0.1 N mm <sup>-2</sup> (–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.

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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  $\mu\text{m}$  long and has a diameter of about 5  $\mu\text{m}$ . 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  $\mu\text{N}$ , 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  $70 \times 200 \mu\text{m}$  and has a smaller structure on its surface, a very intricate and highly ordered nano metre organisation of ridges. Each ridge is about 800  $\mu\text{m}$  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

Biomimetic 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

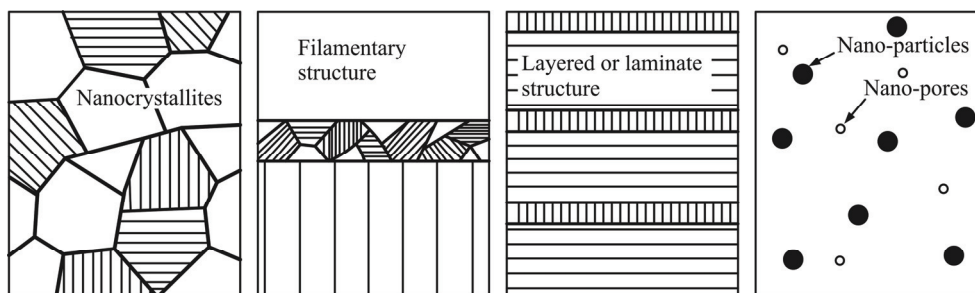
or solids. The examples of technological application of this type of nano materials are catalysts, semiconductor devices utilizing multi layer quantum well structures

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, wear 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.



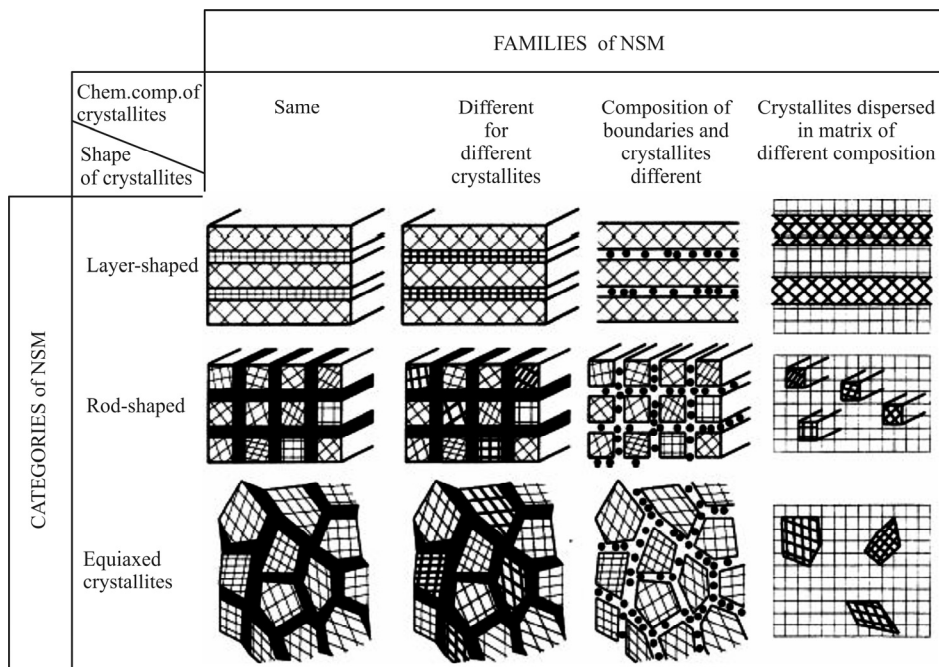
**Figure 1.16** Schematic of nano structured materials with 3D, 2D, 1D and zero D confinement of electrons

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  $\text{Ni}_3\text{Al}$  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<sub>3</sub>Al/Ni alloys.

### 1.3 History of Nano Technology

Nanotechnology is often regarded as an outcome of research in the latter part of the twentieth century, a product of the drive towards miniaturization led by the semiconductor industry. However, in a broader sense, nanotechnology has been in practice unrealized as such, for a long time. Two thousand years ago the ancient Greeks used a permanent hair-dyeing recipe that worked by depositing 5 nm lead sulfide crystals inside hair. High-quality steel made in India before the turn of the first millennium has been shown to contain — and owe its outstanding properties to carbide structures similar to modern carbon nanotubes. Medieval artists colored stained glass using metal nanoparticles.

The difference between these ancient examples of “nanotechnology” and the current situation is the ability to understand — or at least embark on a path towards understanding the fundamental principles underlying nano technological behavior, the ability to assess the current state of knowledge, and the ability to systematically plan for the future based on that knowledge.

The history of nanotechnology is generally understood to have begun in December 1959 when physicist Richard Feynman gave a speech, “There's Plenty of Room at the Bottom” (10), at an American Physical Society meeting at the California Institute of Technology in which he identified the potential of nanotechnology. 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* ( $\varphi$  nman) *scale* after Feynman’s great contributions to nanotechnology ( $1 \text{ Feynman } [\varphi] \equiv 10^{-9} \text{ meter} = 10^{-3} \text{ Micron } [\mu] = 10 \text{ Angstroms } [\text{Å}]$ ).

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
- Techniques to clean up harmful chemicals in the environment

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

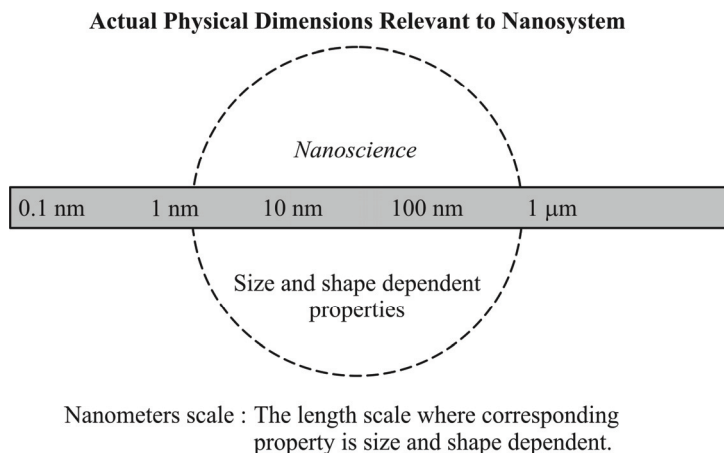
### **1.4.1 Reasons for Nano Materials Exhibiting different Properties from Bulk**

The unique (different) physical properties of nanomaterials in comparison with bulk are 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.

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. This coupling of size with 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 nanostructures aren't just smaller than anything we've made before, they are the smallest solid things it is possible to make. Additionally, the nanoscale is unique because it is the size scale (Figure 1.18) where the familiar day-to-day 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. Similarly 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

## 1.4.2 More % 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  $6.022 \times 10^{23}$  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 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 =  $0.5292\text{\AA} \approx 0.05\text{ nm}$

C atom (VdW radius) =  $0.17\text{ nm}$

In a  $1\text{ nm}$  line: 3C atoms

In a  $1\text{ nm} \times 1\text{ nm}$  surface: 9C atoms

In a  $1\text{ nm} \times 1\text{ nm} \times 1\text{ nm}$  cube: 27 C atoms

In a  $100\text{ nm} \times 100\text{ nm} \times 100\text{ nm}$  cube:  $2.7 \times 10^7$  C atoms

In a  $1\text{ m} \times 1\text{ m} \times 1\text{ m}$  cube:  $2.7 \times 10^{28}$  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.

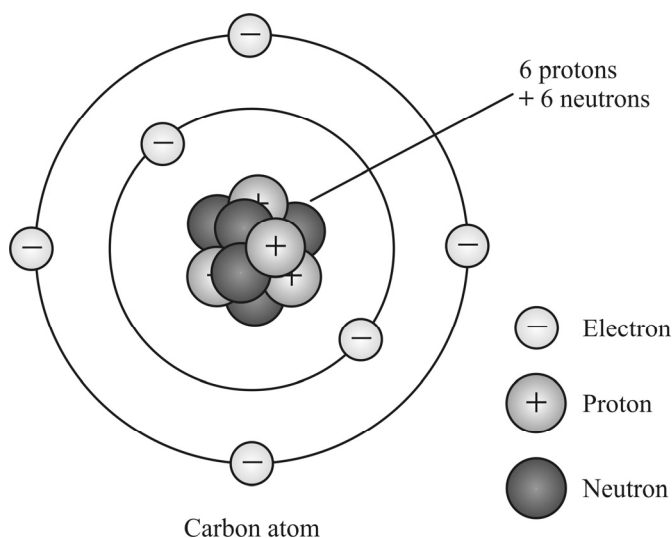
Surface contains approx. 48,000 atoms.

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

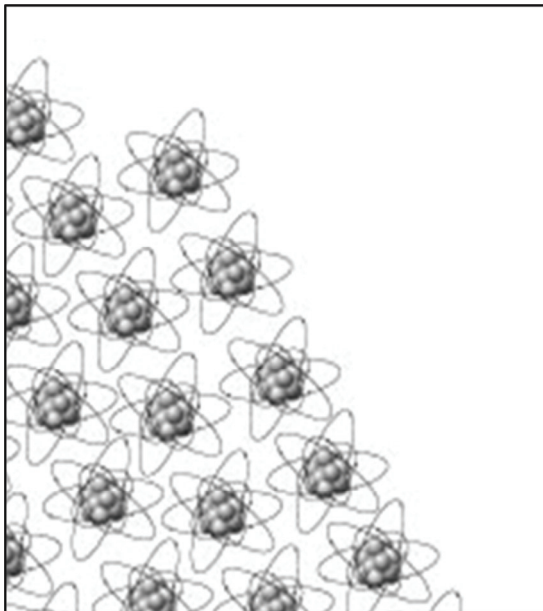


**Figure 1.19** Electronic structure of carbon atom

## 1.4.3 Unique Physical Properties of Nano Materials

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

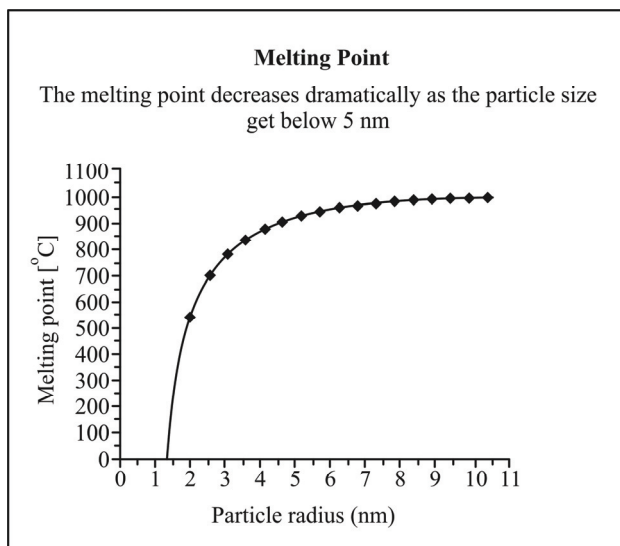
Melting Point is the temperature at which the atoms, ions, or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a “fixed” position in a solid. Surface atoms require less energy to move because they are in contact with fewer atoms of the substance (Figure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

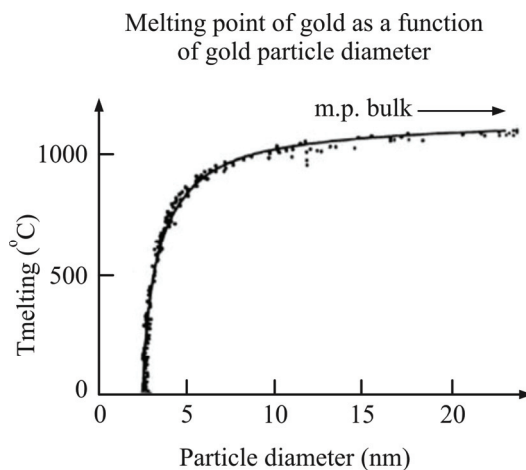


**Figure 1.21** Dramatic decrease of melting point of nano particles below 5 nm (15)



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.

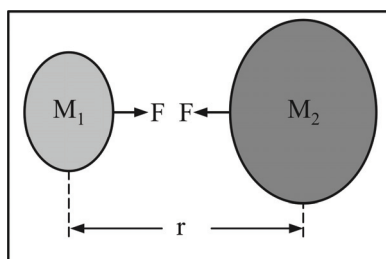


**Figure 1.22** Decrease in melting point of gold nano particles as their size decreases (16)

### 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.

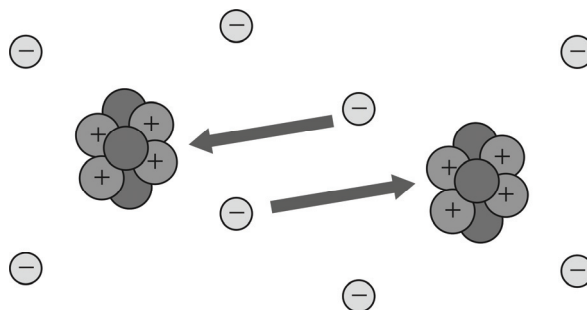
**Gravitational force** is a function of mass and distance and is weak between (low-mass) Nano sized particles (Figure 1.23).



**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).

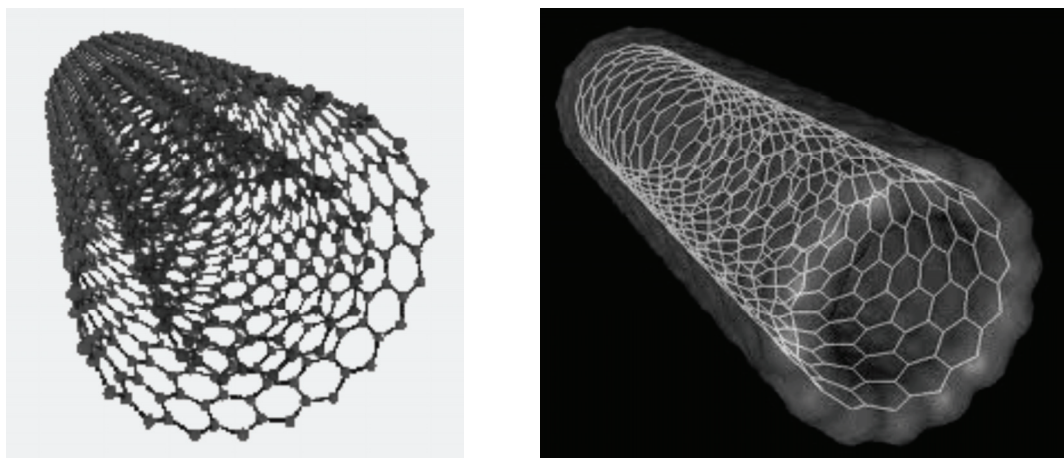


**Figure 1.24** Electromagnetic forces become dominant as the size decreases in nano particles (18)

### 1.4.3.3 Enhanced Mechanical Strength

Nano materials exhibit enhancement in the mechanical strength (by one or two orders of magnitude) which may be simply due to the reduced probability of defects. While there will be more room for deformation in bulk material the nano material being tightly packed offer higher mechanical strength and tensile strength.

Some nano materials have inherent exceptional mechanical properties which are connected to their structure. One such material is carbon nanotubes: these are extremely small tubes having the same honeycomb structure of graphite, but with different properties compared to graphite. They can be single-walled or multi-walled, as illustrated in Figure 1.25.



**Figure 1.25** Single walled and multi walled carbon nano tubes

The chemical bonding of nanotubes is composed entirely of sp<sup>2</sup> bonds (carbon double bonds) similar to those of graphite (whereas, in diamonds, all bonds are sp<sup>3</sup>). This bonding

structure, which is stronger than the sp<sup>3</sup> bonds found in diamonds, provides the molecules with their unique strength. Nanotubes naturally align themselves into 'ropes' held together by van der Waals forces.

Theoretical predictions say that carbon nanotubes are 100 times stronger than steel but only one sixth of its weight. Therefore, they are ideal in lightweight construction, for instance in the automotive and aviation industries. Carbon nanotubes are already used in some consumer products, such as tennis rackets to add strength (without compromising weight). The mechanical properties of carbon nanotubes are summarised in Table 1.3(19).

**Table 1.3** Mechanical properties of carbon nano tubes

Material	Young's Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm <sup>3</sup> )
Single-wall nanotube	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. 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 seen 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

Nanomaterials can also be used to improve the mechanical properties of existing materials. In this case, nano composites are formed. One example is nano crystalline materials, which are polycrystalline (i.e. made of many crystals which are identical but connected without orientation) and defined as materials with grain sizes from a few nano metres up to 100 nm. In contrast, the grain size in industrial metallic materials is about 10 000 nm or greater. These materials generally show improved mechanical properties (toughness, hardness, etc.).

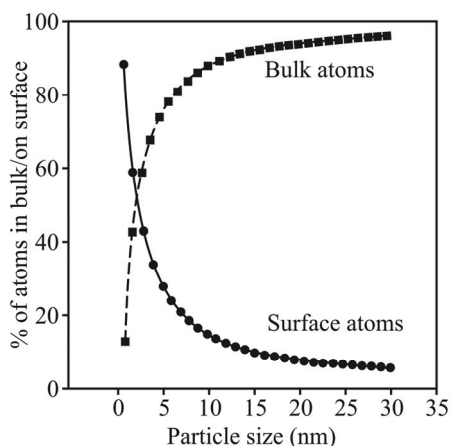
Within the crystalline structures, there can be defects (cracks or dislocations). If subjected to mechanical stress, the polycrystalline materials can fracture because these defects allow the crack to propagate. To impede the movement of cracks and dislocations tiny particles (nanoparticles) of another material can be added in the lattice.

Nano crystalline materials can have vastly improved mechanical, magnetic, electrical, and catalytic properties and greater corrosion resistance compared to conventional materials with large grains.

Nano crystalline materials are already used in the form of hard coatings to protect tools in industry, such as cutting tools, where they are making a great impact in improving tool

performance and lifespan. Nanoparticles added to a ceramic, such as alumina also increases its mechanical properties and the same applies to the addition of nanomaterials (such as carbon nanotubes) to polymers. The possibility of using nanomaterials for improving the mechanical properties of materials involves both inorganic and organic (polymeric) composites.

**Surface Area**  
The total surface area (or) the number of surface atom increases  
with reducing size of the particles



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

#### 1.4.3.5 Increased Surface to Volume Ratio and Enhanced 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.

A greater amount of a substance comes in contact with surrounding material. This results in better catalysts, since a greater proportion of the material is exposed for potential reaction.

The 'active surface' increases when the size of the increased active surface of a nano catalysts is decreased.

The smaller the catalyst particles, the greater the ratio of surface-to-volume (Figure 1.26).

The higher is the catalysts' active surface, the greater is the surface reactivity.

Total Surface area = height  $\times$  width  $\times$  number of sides  $\times$  number of boxes

Total Volume = height  $\times$  width  $\times$  length  $\times$  number of boxes

Surface to volume ratio = total surface area/total volume

Let us consider one Cubic Volume shown in Figure 1.27 its the Surface Area is 6 m<sup>2</sup>.

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

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.

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)

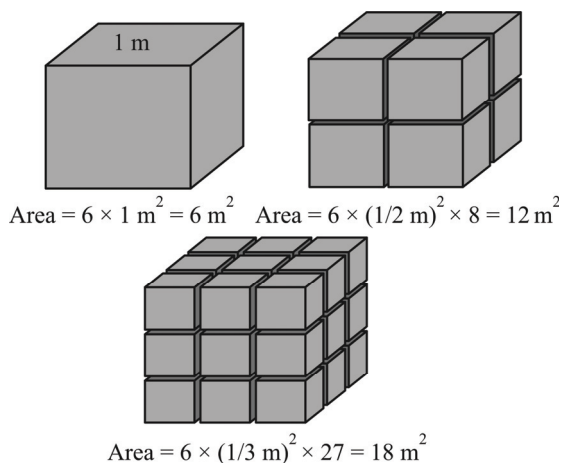
Size (mm)	Cross section ( $10^{-18} \text{ m}^2$ )	Mass ( $10^{-36} \text{ kg}$ )	No. of molecules	Fraction of molecules of surface (%)
0.5	0.2	0.65	1	
1	0.8	5.2	8	100
2	3.2	42	64	90
5	20	650	1000	50
10	80	5200	8000	25
20	320	42000	64000	12

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

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

G: Gibbs free energy of the surface

A: Surface area of the particles



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

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,  $\gamma$

$$\gamma = N_b \epsilon p_a / 2 \quad \dots(1.1)$$

Nb: number of broken bonds

$\epsilon$ : bond strength

$p_a$  = number of atoms or molecules per unit surface area = density

Table 1.5 presents the (typical data of nano  $\text{CaCO}_3$ ) how the surface energy increases with decreasing size in nano systems.

**Table 1.5** Surface area and surface energy variation with size of nano  $\text{CaCO}_3$  (20)

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

#### 1.4.3.5.1 Nano Particle-Nano Particle Interactions

At the nano scale, particle-particle interactions are either dominated by weak Van der Waals forces, stronger polar and electrostatic interactions or covalent interactions.

Depending on the viscosity and polarisability of the fluid, particle aggregation is determined by the interparticle interaction.

By the modification of the surface layer, the tendency of a 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 liquids, particle charge can be stabilised by electrochemical processes at surfaces.

Thus 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.

They remain difficult to characterise due to the small amount of molecules involved in the surface active layer.

Both surface energy, charge and solvation are relevant parameters to be considered. Due to the crucial role of the nano particle-nano particle interaction and the nanoparticle-fluid interaction, the term free nanoparticle can be easily misunderstood.

The interaction forces, either attractive or repulsive, crucially determine the fate of individual and collective nanoparticles. This interaction between nanoparticles resulting in aggregates and/or agglomerates may influence on their behaviour.

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 Special Optical Properties of Nano Materials

Some nanomaterials display very different optical properties, such as colour and transparency, compared to bulk materials (21).

##### 1.4.3.6.1 Interaction of Light with Matter

The 'colour' of a material is a function of the interaction between the light and the object. In general light (I) incident on a material can be transmitted (T), absorbed (A) or reflected (R):

$$I = T + A + R$$

As the size of the materials is reduced, scattering (S) of light can also contribute to its colour (or transparency).

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.

Absorption (A) is a process that involves energy transformation. The energy levels of a substance determine the wavelengths of light that can be absorbed. It is a molecular phenomenon, dependent on the chemical identity and structure of the substance (not on the size of the molecules or clusters), and involves electronic transitions, vibrations and rotations. Chromophores and fluorephores are examples of organic materials that have specific electronic transitions.

Transmission (T) is the ability of light to pass through a material: it is complementary to absorption.

Transmission of light is what is left after reflection, scattering and absorption have occurred.

Scattering (S) is the phenomenon that occurs when radiation hits a structure with dimensions comparable to the incident wavelength. Therefore, it is a physical process that depends on cluster size, the refractive index of the cluster and the refractive index of the suspension medium. It is a physical interaction only, no energy transformations occur during scattering (as opposed to absorption), energy is simply redirected in many directions. The wavelength of incoming light and that of the outgoing light are the same. After the light hits the clusters in the colloid and is redirected once, it can encounter another cluster and be redirected again. This phenomenon is called multiple scattering. At the 'macro' level, the overall effect can be that light is sent back the way it came (back scattering) or moves forward in the same direction it was moving initially (front scattering). Maximum scattering occurs for wavelengths twice as large as the cluster size. Therefore, if the cluster is about 200 nm, maximum scattering is observed at 400 nm, which lies within the range of the visible spectrum.

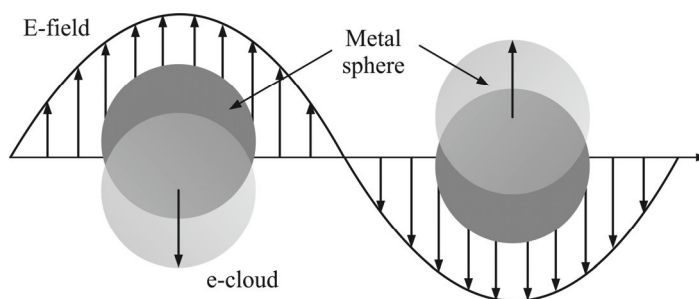
The formula indicated above still holds if scattering occurs. Scattering simply contributes to the 'reflection' (back scattering) and 'transmission' (front scattering) parts of the equation. Light that has been absorbed cannot be scattered.

#### 1.4.3.6.2 Colour Generation from Nano Particles and Nanostructures

Nano materials in general can have peculiar optical properties as a result of the way light interacts with their fine nanostructure. One of the distinguishing properties of metal nano particles in general is their optical properties, which are different from those of their bulk counterpart. This is due to an effect called localized surface plasmon resonance.

The free electrons in the metal (d electrons in silver and gold) are free to travel through the material. The mean free path in gold and silver is  $\sim 50$  nm, therefore in particles smaller than this, no scattering is expected from the bulk. Thus, all interactions are expected to be with the surface. When the wavelength of light is much larger than the nanoparticle size it can set up standing resonance conditions as represented in Figure 1.28.

Light in resonance with the surface plasmon oscillation causes the free-electrons in the metal to oscillate. As the wave front of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the light's frequency causing a standing oscillation. The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constants of both the metal and the surrounding material. This is referred to as the localized surface plasmon resonance (LSPR), since it is located at the surface. As the shape or size of the nanoparticle changes, the surface geometry changes causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering (Figure 1.29).



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

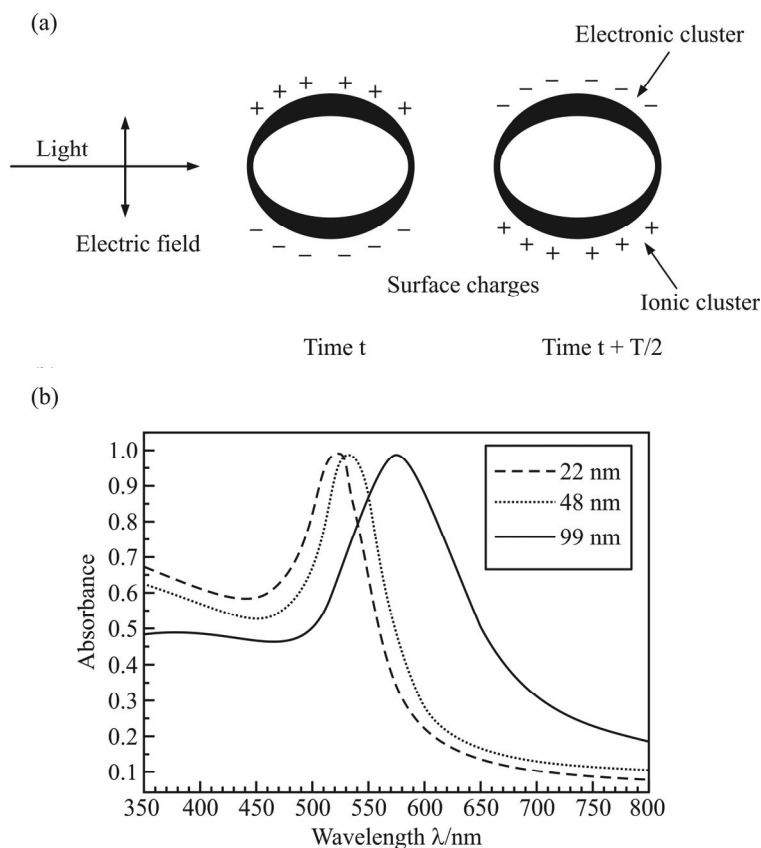
Changing the dielectric constant of the surrounding material will have an effect on the oscillation frequency due to the varying ability of the surface to accommodate electron charge density from the nanoparticles.

Changing the solvent will change the dielectric constant, but the capping material is most important in determining the shift of the plasmon resonance due to the local nature of its effect on the surface of the nanoparticle. 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). This is the basis for the use of noble metal nano particles as sensitive sensors.

Thus LSPR energy is sensitive to the dielectric function of the material and the surroundings decrease in size and to the shape and size of the nanoparticle. This means that if a ligand, such a protein, attaches to the surface of the metal nanoparticle, its LSPR energy changes. 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** LSPR 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).

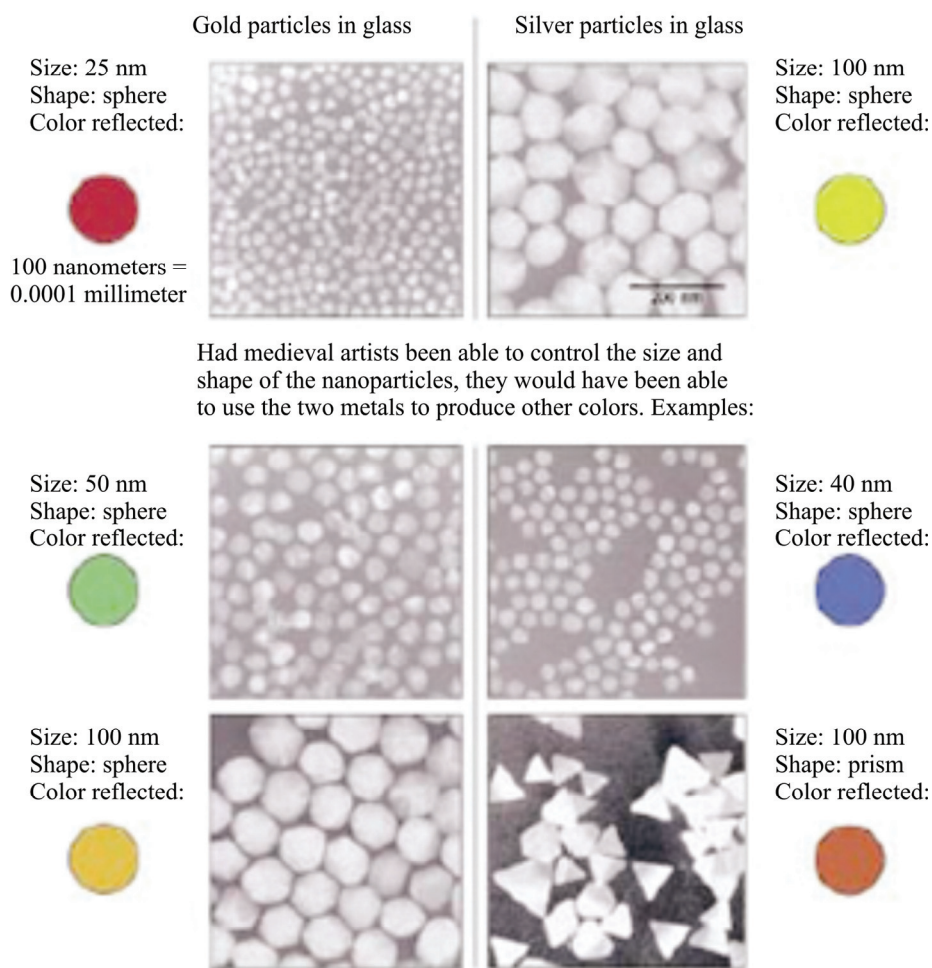


MACRO

NANO

**Figure 1.30** (macro (bulk) gold-yellow and nano Gold (1.5 nm) ruby red (22).  
(Image. LPillpooni 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.

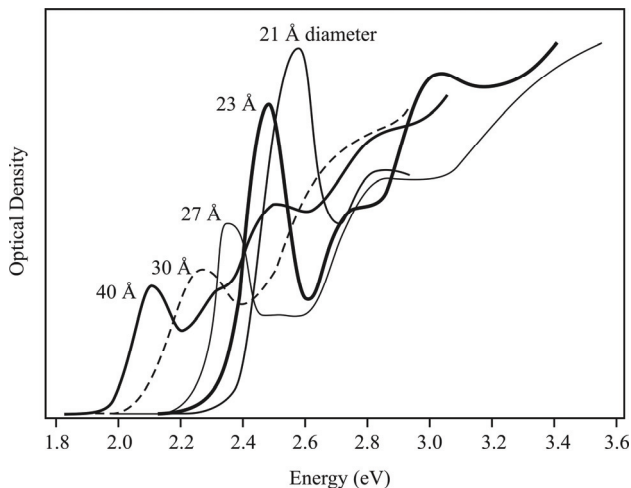


**Figure 1.31** Changes in colours of colloids of gold and silver with size

### 1.4.3.6.3 Quantization and Energy Level Spacing

As already mentioned, nano sized semiconductors have quantized energy states; therefore, the conduction and the valence bands split and become discrete. Charge transfer occurs between these discrete levels, so only wavelengths of a certain dimension are absorbed: as a consequence, emission is monochromatic. Quantum confinement causes the energy of the band gap to increase: therefore, more energy is needed in order to be absorbed by the band gap of the material. Higher energy means shorter wavelength (blue shift). The same applies to the wavelength of the fluorescent light emitted from the nano sized material, which will be higher, so the same blue shift will occur. Tuning the size of the semiconductor nanocrystal is a means of tuning the band gap and, therefore, the wavelength absorbed/emitted by the crystal. As a result, the same material (CdSe) emits different colours depending on its size (Figure 1.32). As the size is reduced, the electronic states may be viewed as superpositions of bulk states.

Hence, there is a shift to higher energy, the development of discrete features in the spectra, and concentration of the oscillator strength into just a few transitions. Qualitatively, all of these effects can be readily observed in the spectra of Figure 1.32, which show data for CdSe QDs are currently used as an alternative to conventional dyes in fluorescence microscopy and in other methods where dyes are used (e.g., dye-sensitised solar cells). QDs are also being studied as alternative light-emitting sources



**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

As discussed earlier electrical conductivity decreases with a reduced dimension due to increased surface scattering, while electrical conductivity of nanomaterial could be enhanced appreciably,

due to the better ordering of microstructure. Nano structuring of bulk magnetic materials can be used to design the magnetization curve of the material, leading to soft or hard magnets with improved properties.

For metals, the electron mean free path (MFP) determines the thermal and electrical conductivity and affects the color of the metal. For most of the metals, MFP is of the order of 5–50 nm. Reducing further this threshold, the electrons begin to scatter off the crystal surface, and the resistivity of the particles increases. For very small metal particles, the conduction and valence bands begin to break down into discrete levels. For gold particles, this causes a change in color from red to orange at sizes around 1.5 nm.

Depending on their chemical composition optical and electronic properties have generated much attention in studies of properties of particles approaching molecular dimensions.

#### 1.4.3.6.4.1 Electrical Properties of Metal Nano Particles

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, 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.

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.

#### 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.

The tremendous efforts and progress have been made in molecular electronics. In molecular electronics single molecules are expected to be able to control electron transport which offers the promise of exploring the molecular functions of electronic devices and molecules can now be crafted into a working circuit as shown in Figure 1.33.

When the molecules are biologically active bioelectronics devices could be developed. In molecular electronics control over the electronic energy levels at the surface of conventional semiconductors and metals is achieved by assembling on the solid surfaces, poorly organized, partial monolayers of molecules instead of more commonly used ideal ones. Once those surfaces become interfaces these layers exert electrostatic rather than electro dynamic control over the resulting devices based on both on the electrical monopole and dipole effects of the molecules. Thus electronic transport devices incorporating organic molecules can be constructed without current flow through these molecules.



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

Nanoelectronic devices have the advantage of having higher integrating densities and also exhibit interesting properties in the radiofrequency region, thereby offering challenges and opportunities alike.

#### 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  $\mu\text{m}$ . 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 remanence, and coercivity. Touching superparamagnetic particles are losing 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 ( $\text{Fe}_3\text{O}_4$  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 as FePt, NiPt and NiPd (29,30), which can be used in the magnetic fluid and ferrites:  $\text{MFe}_2\text{O}_4$  ( $\text{M} = \text{Mn, Ni, Co, Zn, Fe}$ ) (31,32,33),  $\gamma\text{-Fe}_2\text{O}_3$  (34).

Many magnets made up of nano crystalline yttrium 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

A catalyst is a substance that increases a chemical reaction rate without being consumed or chemically altered. Nature's catalysis are called enzymes and are able to assemble specific end products, always finding pathways by which reactions take place with minimum energy consumption.

Man-made catalysts are not so energy efficient: they are often made of metal particles fixed on an oxide surface, working on a hot reactant stream (to reduce the phenomenon, 'catalyst poisoning', which occurs when species dispersed in the atmosphere, such as CO, occupy the active sites of the catalysts is used).

One of the most important properties of a catalyst is its active surface where the reaction takes place. The 'active surface' increases when the size of the catalysts is decreased: the smaller the catalyst particles, the greater the surface-to-volume ratio.

The higher the catalysts' active surface, the greater the surface reactivity. Research has shown that the spatial organisation of the active sites in a catalyst is also important. Both properties (nanoparticle size and molecular structure/ distribution) 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.

A good example of how nano science can impact the development of catalytic materials is that of gold. Bulk gold noble metal is a stable non toxic and resistant to oxidation and chemical attack.

On the other hand, nanoscale gold particles can catalyse chemical reactions. It has been found that finely dispersed gold nanoparticles on oxide supports are catalytically very active. In many cases the catalytic activity and selectivity of dispersed gold nanoparticles exceed those of the commonly used transition metal catalysts such as platinum, rhodium palladium. This is an exciting result because 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.

Due to their large surface, nanoparticles made of transition element oxides exhibit interesting catalytic properties. In special cases, catalysis may be enhanced and more specific by decorating these particles with gold or platinum clusters.

Due to their enhanced chemical activity, nano structural materials can be used as *catalysts* to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

Fuel cell technology is another important application of the noble metal nanoparticles relating the catalysis of the reactions. In the present, the fuel cell catalysts are based on platinum group metals (PGM). Pt and Pt-Ru alloys are some of the most frequently used catalysts from this group. In fact, the use of these metals is one major factor for cell costs, which has been one of the major drawbacks preventing it from growing into a more important technology. One possibility to produce economical catalysts is the use of bimetallic nano particles.

#### **1.4.3.6.7 Nano Biotechnology Applications**

Nano biotechnology converges the angstrom, nano and micro scale worlds with the exploitation of physical principles, chemical synthesis capabilities and functional properties of biological nanostructures. Nature has made highly precise and functional nanostructures: DNA, proteins, membranes, filaments and cellular components. These biological nanostructures typically consist of simple molecular building blocks of limited chemical diversity arranged into vast numbers of complex three dimensional architectures and dynamic interaction patterns

A key feature of biological entities is the systematic organization of matter on the nanoscale. Developments in nano science and nano technology would allow us to place man-made nanoscale things inside living cells.

Nano particles may be of the same dimensions as some biological molecules such as proteins and nucleic acids. 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).

Evidence for such interactions is seen from the experience with 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. Other nanoparticle systems which are established for research purposes in cell systems include quantum dots (39) and magnetic nano particles (40).

It would also make it possible to make new materials using the self-assembly features of nature. Thus nano biotechnology will be a powerful combination of biology with materials science.



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

Thus 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.

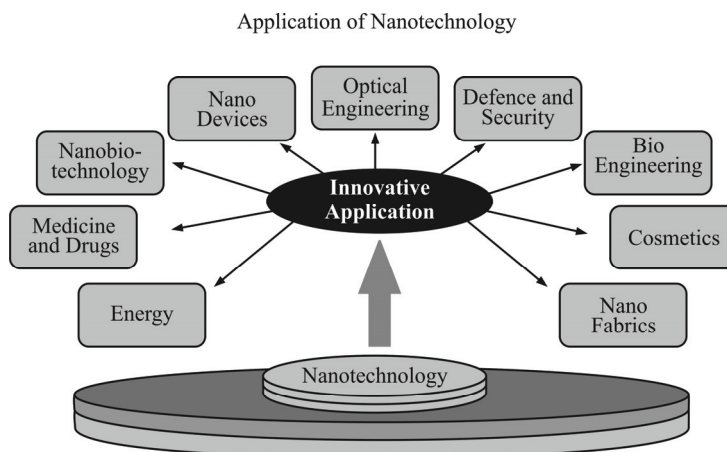
**Table 1.6** Effects of nanomaterials and applications due to the reduced dimension

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.



**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) Wear-resistant tires made by combining nanoscale particles of inorganic clays with polymers as well as other nanoparticle reinforced materials,
- (ii) Greatly improved printing brought about by nanoscale particles that have the best properties of both dyes and pigments as well as advanced ink jet systems,
- (iii) Vastly improved new generation of lasers, magnetic disk heads, nano layers with selective optical barriers and systems on a chip made by controlling layer thickness to better than a nanometer,
- (iv) Production of advanced chemical and bio-detectors,
- (v) Nano particles to be used in medicine with vastly advanced drug delivery and drug targeting capabilities,
- (vi) Chemical-mechanical polishing with nano particle slurries, 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**

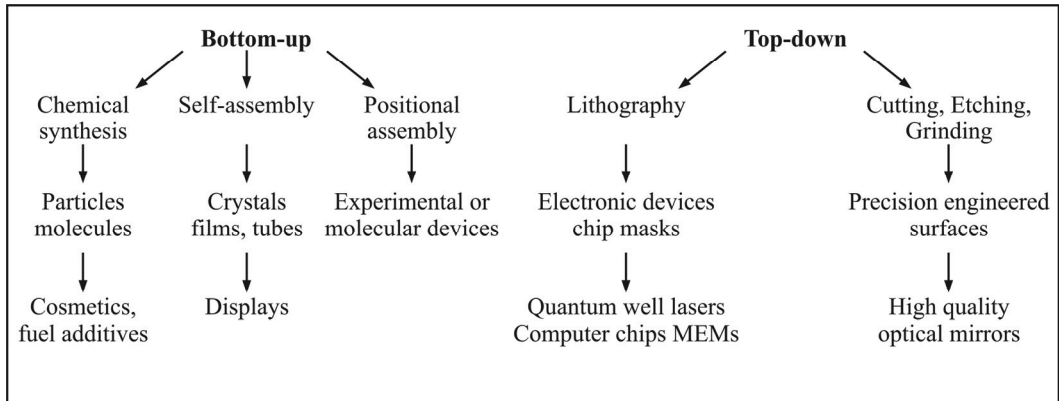
### **1.6.1 Process Engineering, Design and Manufacturing**

Nanotechnology is the engineered manipulation of atoms and molecules in a user defined and repeatable manner to build objects with certain desired properties. These nano size building blocks are intermediate systems in size lying between atoms and small molecules and microscopic and macroscopic system. These building blocks contain a limited and countable number of atoms. They can be synthesized and designed atom by atom. They constitute the means of our entry into new realms of nanoscience and nanotechnology. 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.

In the past, engineers and material scientists have been involved extensively with the characterization of given materials. Mechanics and materials engineering are really two sides of a coin, closely integrated and related. With the availability of advanced computing and new developments in material science, researchers can now characterize processes and design and manufacture materials with desirable performance and properties. One of the challenges is to model short-term nano/micro-scale material behavior, through meso-scale and macro-scale behavior into long-term structural systems performance. This will provide in better understanding and design of materials and structures across all physical scales, even though the seamless and realistic modeling of different scales from the nano-level to the system integration-level is not yet attainable.

### **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

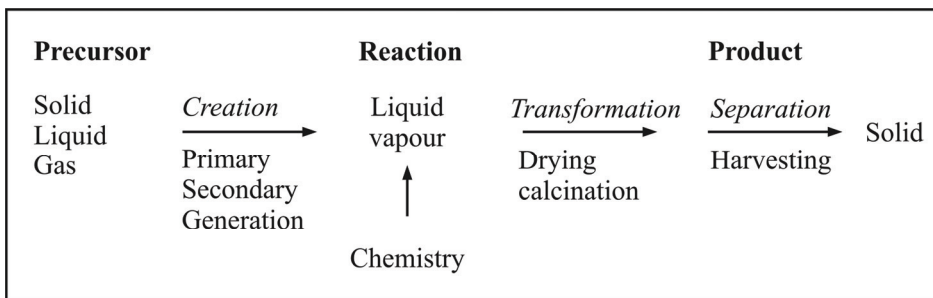
### 1.6.2.1 Bottom-Up Manufacturing

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

#### 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, produced using the techniques.

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

### **1.6.2.1.2 Unit Operations**

The precursor phase is the starting point, and the material can be in any physical state (or multiphase) or spatial arrangement to other components. The first step is the creation of a new phase or state where the nanoparticles either form or can be formed by a chemical step. In other words, the phase change itself could bring about nanoparticle formation (rare but possible) although generally the circumstances are created whereby nanoparticles can be made, for example vaporisation of a precursor mixture. Once in a state where nanoparticles can be made, usually a chemical reaction of some description is performed to generate the desired material. A further phase transformation or even solid-state reaction may be necessary to produce the final product. Potential exposure of the workforce to nanoparticles is likely to be greatest when these materials are processed in a gaseous environment; in such cases worker exposure will need to be monitored closely. However, nanoparticles have a tendency to agglomerate, and are therefore often manufactured from a liquid phase as this enables surface energies to be better controlled, reducing agglomeration. This also reduces the potential exposure level of workers. Processing and handling ability is very important for nanomaterials: mixing nanoscale particles together before agglomerating and (for example) sintering can generate wholly new complex nano phase materials which could not be made by any other method. Most genuinely nanoscale and nanostructured materials, however, are still at the laboratory scale of synthesis (kilograms per day scale of operation or even less).

### **1.6.2.1.3 Resource Management and Environmental Issues**

The potential benefits of nanotechnologies should be assessed in terms of life cycle assessment (LCA) (sometimes referred to as ‘cradle-to-grave’ analysis). LCA is the systematic analysis of the resource usages (for example, energy, water, raw materials) and emissions over the complete supply chain from the ‘cradle’ of primary resources to the ‘grave’ of recycling.

### **1.6.2.1.4 Self Assembly**

Self assembly is a bottom-up production technique in which atoms or molecules arrange themselves into ordered nanoscale structures by physical or chemical interactions between the units. The formation of salt crystals and snowflakes, with their intricate structure, are examples of self-assembly processes. Although self assembly has occurred in nature for thousands of years, the use of self assembly in industry is relatively new. There is an economic and environmental interest in processes through which materials or product components essentially form themselves, creating less waste and using less energy. However, current understanding extends only to the creation of fairly rudimentary systems. Improved understanding of thermodynamic and kinetic processes at the nanoscale, enabled through advances in the characterisation techniques, and improved computer modelling, are expected to aid the development of more complex systems. One potential engineered processing technique involves the use of an external force or field (for example, electric or magnetic) to accelerate the often slow self-assembly process, which is attractive in an industrial context. This is known as directed self assembly.

### 1.6.2.1.5 Positional Assembly

The final bottom-up technique is positional assembly, whereby atoms, molecules or clusters are deliberately manipulated and positioned one-by-one. Techniques such as SPM for work on surfaces, or optical tweezers in free space, are used for this. Positional assembly is extremely laborious and is currently not suitable as an atomic-scale industrial process. The utility and strength of SPM in industry lie in their ability to characterise and measure surfaces with atomic-level precision, rather than as fabrication tools.

The fact that very rudimentary structures can be fabricated atom-by-atom has led to speculation that tiny nanoscale machines could be made which could be used in parallel to manufacture materials atom-by-atom. The idea is to fabricate one or a few machines (or assemblers) that would first make copies of themselves, and then go on to make materials in parallel, in principle solving the problem of slow production speed.

### 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 complexity, although they are generally higher in energy usage, and produce more waste than bottom-up methods. The production of computer chips, for example, is not yet possible through bottom-up methods; however, techniques using bottom-up (or hybrid top-down/bottom-up) methods are under exploration.

## 1.6.3 Precision Engineering

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

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), although these are currently on simple shape surfaces and with low output levels. This capability, which is bringing benefits in several areas has been achieved through a combination of advances. These include: the use of 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 technologies. Very precise process and temperature control is needed to achieve this performance (the latter being of the order of  $\pm 0.01^\circ\text{C}$ ).

### 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 Chapter 4). The ability to pattern features in the nano metre range is fundamental to the success of the IT industry and the ITRS roadmap. The main lithographic tools can be conveniently separated into methods that use a focused beam of electrons or ions to write patterns, and those that rely on the projection of light through a mask to define a pattern over a complete semiconductor wafer. Electron- and ion-based methods are both capable of making sub-10 nm structures (with electron beam lithography having the greatest routine resolution), but they are too slow to be used directly in production. Optical lithography is used for production of semiconductor devices. Although it does not have the resolution of the beam-based techniques, it provides rapid throughput and cost-effective manufacture. Electron beam lithography is primarily used to fabricate the masks used for optical lithography, and ion beam techniques are mostly used to repair masks and for specialist device applications.

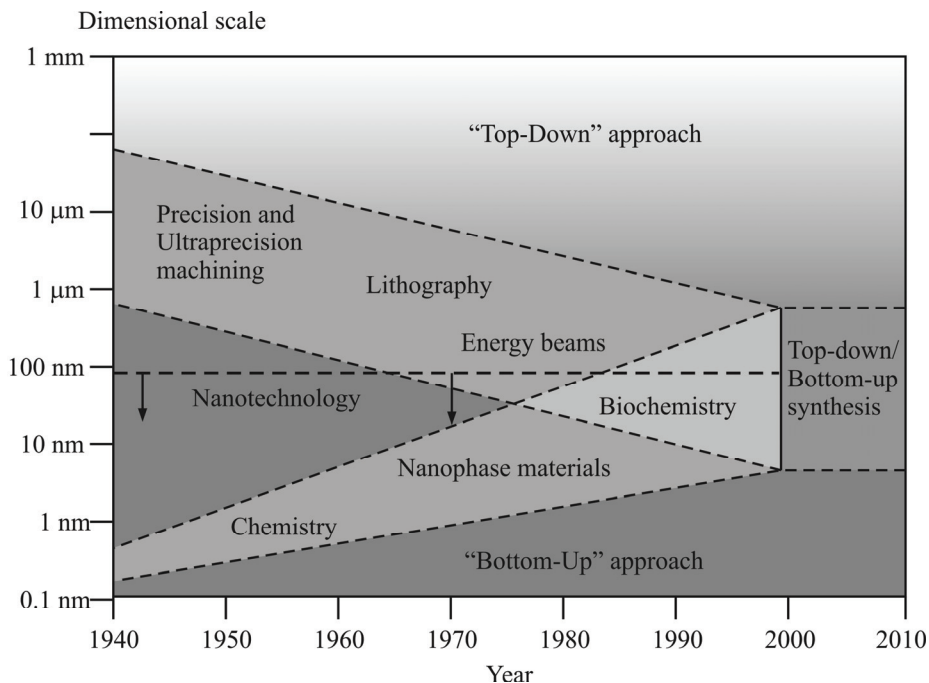
The requirement for ever-shrinking device structures has placed enormous technical demands on optical lithographic process, as the nanostructures have length scales similar to or less than the wavelength of the illuminating light (ultraviolet). Despite these difficulties, the ITRS roadmap implicitly expects optical lithography to keep track of future device dimensions until 2016 when the target critical device dimension reaches 22 nm.

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

### 1.6.4 Convergence of Top-Down and Bottom-up Techniques

The relationship between top-down and bottom-up manufacturing is illustrated in Figure 1.37. The 'top-down' section is an updated version of the diagram produced by Norio Taniguchi. The 'bottom up' section illustrates how bottom-up processes have evolved to control ever-larger structures through advances in chemical processing. Now the dimensions that can be controlled by either approach are of a similar order, and this is leading to exciting new hybrid methods of manufacture.





**Figure 1.37** The convergence of top-down and bottom-up production techniques (41)

### 1.6.5 Characterisation

The characterization of materials like the determination of their shape, size, distribution, mechanical and chemical properties is an important part of the industrial process. It serves two broad purposes: as quality control, and as part of the research and development of new processes, materials and products. Nanotechnology ‘breakthrough’ had occurred in the tools used to observe and measure properties and processes at the nanoscale level. Sophisticated tools, such as the STM, AFM and TEM, enable surface and interfacial characterisation of materials at the nanoscale, allowing individual atoms to be observed and analysed. (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. However, the commercialisation of such advanced functional materials requires that they can be made in a predictable, reliable way, and in sufficient quantities. Until that is achieved production will be limited to academia and R&D departments within industry.

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 Precision Engineering

There are strong drivers to reduce tolerances in engineering, including miniaturisation, improved wear and reliability characteristics, automated assembly and greater interchangeability, reduced waste and requirement for re-work. As the trend towards miniaturisation continues, research and the industrial application of energy beam processing methods will increase, driven in particular by the electronics and computer industries. 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 are given below.

### 1.7.2 Integrated Chip Technologies (ICT)

The machines used to fabricate chips depend fundamentally upon the use of ultra-high precision techniques for their manufacture and nano metrology techniques for their operation. The manufacture of larger-diameter semiconductor wafers with improved flatness and reduced sub-surface damage should lead to improved device yields and reduced costs.

### 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 (Euro50 and OWL), which will consist of many individually figured segments (Shore et al 2003).

### 1.7.4 Transport

Precision-machined parts should 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%. Precision manufacturing is predicted to lead to weight reductions in airframe wings and to improve the performance of internal combustion chambers.

### 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.

It is hoped that advances in precision engineering will enable the reduction of environmental impacts by, for example, reducing the use of lubricants.

### 1.7.6 The Chemical Industry

Long-term goal within the chemical industry is to use nanoscale ‘building blocks’ to assemble organised nano structures, that can in turn be manufactured into commercially useful products. From an understanding of the chemistry and physics of nanoscale materials, and top-down/bottom-up modelling and measurement, industry will concentrate on processes that use manufacturing at the nanoscale in a way that preserves the desired effect and function as nanoscale components are combined into macroscale materials and products. This will involve the development of technologies based on self-assembling materials, or more probably on directed-assembly methods, which allow for some form of massively parallel production, along with modelling and measuring tools. The vision is the manufacture of reproducible, accurate and designable nanomaterials.

The time-scale for the commercial exploitation of these types of highly organised structures or quantum materials is approximately 2020 and beyond, for use in the biotechnology and IT sectors. These materials will be extremely valuable, in excess of \$1,000,000 per tonne, with the production rates of the order of 10–10,000 tonnes a year. The price is expected to remain relatively high because, though the effect of the nanomaterial will be to add value to consumer products, it will only form a tiny fraction of the final product as sold.

The desired functionality is created through exploiting structure – property relationships. Measurement, modelling and simulation are essential for the characterisation and subsequent control of property and functional performance and therefore the production of desirable

materials. The development of measurement tools for use at the nanoscale will move from laboratory-based characterisation to in-line and on-line methods of monitoring and controlling accuracy at the 6-sigma level (99.9997% accurate) in terms of reproducible structure, texture and surface properties. The use of computer simulation based on advanced structure – property – process predictor codes will become the key technology for manufacture-by-design, where the characteristics of the material are effectively ‘dialled up’ through morphology, texture, structure and reactivity based on the interaction of materials across molecular- and nano-length scales. The structure or form of the material then dictates the processing options for economic, reliable and reproducible operation. The combination of measurement, modelling and manufacturing technologies will be the basis for intelligent material systems. It is also hoped that it will be possible to produce materials with less waste.

The synthesis and control of micro- and nano scale structures may yield unprecedented control of meso- and macro-scale properties in functional materials for use in applications of direct relevance to industry. It has been predicted (Chemical Industry 2003) that over the course of the century, many of the needs of commerce and society may be satisfied through a materials revolution involving synthesis and smart fabrication.

### **1.7.7 The Information and Communication Technology Industry**

Although the future of device fabrication is still centred around the lithographic processes there are other techniques that are increasingly being applied both to on-roadmap developments and to alternative approaches to device materials. Soft lithography techniques where a flexible master is used to stamp out patterns on a range of surfaces have been available for several years. The accuracy demands imposed by the silicon-based industry have, until now, prohibited the use of soft lithographies as the elastic nature of the stamp can cause small, but still unacceptable, physical distortions across a wafer surface. However, for small-area device fabrication and for applications where spatial tolerances are less restrictive, they offer a real alternative to conventional methods, although the fabrication of the master still requires optical or electron beam methods. Soft lithographies can be used for plastic electronics, as can alternative ink-jet based methods which use essentially the same technology as desk-top printers. Although plastic electronics are not truly in the nano-range in terms of critical dimensions, a relatively simple manufacturing technique that can deal with wet chemistries will enable cheap electronic and photonic devices. Such developments, combined with advances in directed self-assembly, may bring the semiconductor, materials and chemical industries closer together, in order to create novel alternative methods for chip production as the end of the roadmap approaches.

### **1.7.8 Molecular Manufacturing**

Molecular manufacturing systems will develop with precision on the atomic scale. These systems will expand our control of systems from the macro to the micro and beyond, while simultaneously reducing the cost associated with manufacturing products. Thus gaining molecular-level control over the structure of matter will bring a wide variety of positive applications.

Molecular machine systems will be able to sense and rearrange patterns of molecules in the human body, providing the tools needed to bring about a state of health, regardless of a disease's cause. Theorists envision creating machines that will be able to travel through the circulatory system, cleaning the arteries as they go; sending out troops to track down and destroy cancer cells and tumors; or repairing injured tissue at the site of the wound, even to the point of replacing missing limbs or damaged organs. The extent of medical repair systems is expected to be quite broad, with the cumulative impact being equally large.

## 1.8 Safety and Health Risks of Nano Materials

### 1.8.1 Potential Areas for Concern

Some nano particles, nano spheres, nano tubes, and nano fibers produced via nanotechnologies including adventitious by-products have the potential to raise concerns for humans (public health, consumer safety, and the health and safety of workers) and the environment. As nanomaterials, have a size comparable to biomolecules (e.g. proteins, DNA) there are a number of apprehensions that they may interact with biomolecules in an adverse manner, triggering a toxic effect by passing through protection barriers in cells. In medical applications nanomaterials are used precisely to target infected cells and deliver drug agents locally. They are designed to pass through cell membranes. Further 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 concerns that nano particles, nano tubes, and nano fibers raise constitute the most significant ones relating to nanotechnologies within the next 3–5 years. They require further studies. In this respect, more often the toxicological, ecotoxicological, and exposure data needed to perform a complete risk analysis which are lacking.

Experts are of the unanimous opinion that the adverse effects of nanoparticles cannot be predicted (or derived) from the known toxicity of material of macroscopic size, which obey the laws of classical physics. This has led the UK Royal Society and the Royal Academy of Engineering to recommend “that chemicals in the form of nanoparticles or nanotubes be treated as new substances under the existing Notification of New Substances (NONS) regulations and in the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)” (Chapter 8 “Regulatory issues”, Point 18, p. 71.

### 1.8.2 Environmental Effects of Nanotechnology

Nanotechnology have a number of beneficial environmental effects. On a broad scale, as the technology develops, 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.

## Environmental Risks

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?

Global warming, not surprisingly, is a major consideration in new technologies.

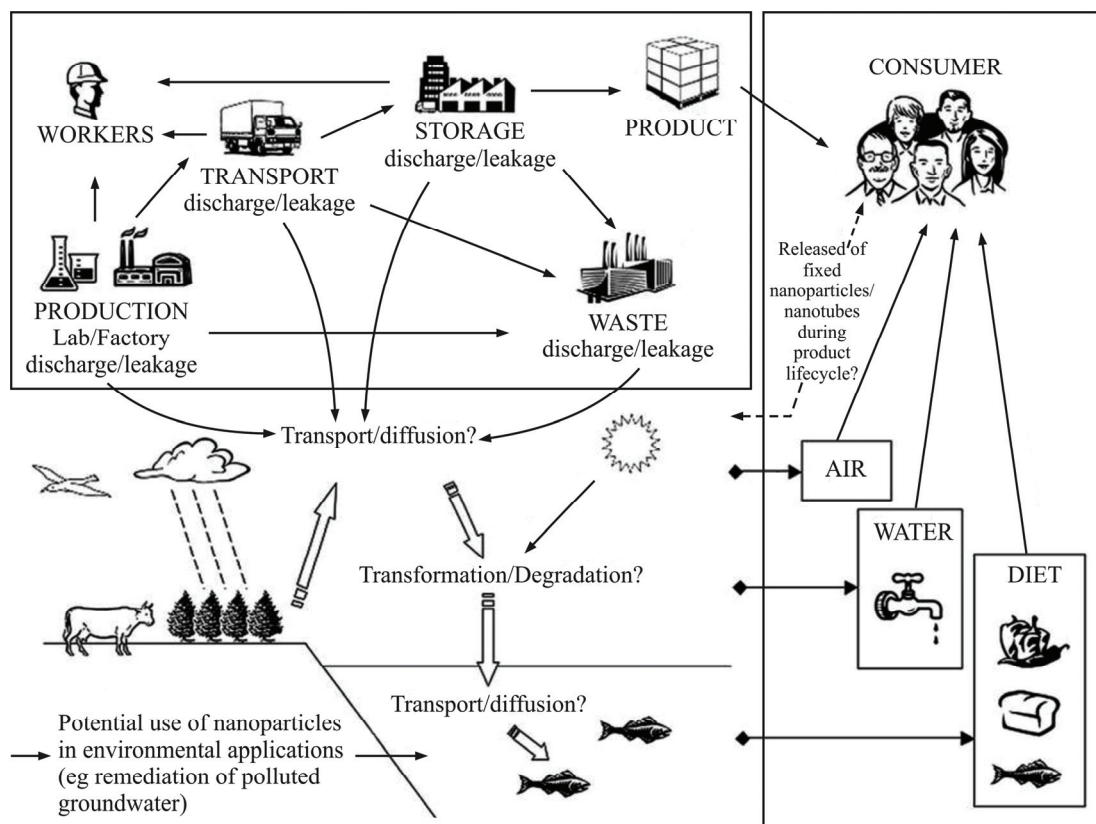
Nanotechnology may allow the manufacture of materials with less energy consumption and fewer waste gases, but the effect on global warming is yet to be determined. Current evidence suggests that nano technology may cause either warming or cooling of the atmosphere.

### 1.8.3 Nano Particles Impact on Human Health

Nanoparticles are produced by aeroplane and motor vehicle exhaust emissions, erosion of man-made materials (e.g., tyres), as well as by natural erosion and volcanic activity. Thus humans are exposed to small particles, often in very high concentration, and the mechanisms evolved for defence against microorganisms are also used to defend the body against such particles. So to understand the potential risks to humans from nanoparticles, it is necessary first to consider briefly the body's defences against particles in general and the properties that particles require to overcome these defences. Access to the human body can occur through the lungs, the skin or the intestinal tract. Each organ presents a barrier to penetration by microorganisms or other particles. Nevertheless, despite the defense mechanisms, certain particles have proved to have toxic effects on humans, just as have certain microorganisms. In general this is a consequence of properties that either allow them to evade or cause damage to defensive mechanisms. An understanding of these mechanisms is of importance to estimate the possible toxic effects of nanoparticles or nanotubes. Three types of particle in particular have provided relevant information: the minerals quartz and asbestos, and the particles associated with air pollution. There is some evidence that established protective measures against ultrafine particles would also be effective against engineered nano particles (ENPs), should these be classified as hazardous. So the question becomes: Are ENPs new hazardous materials and, if so, do these pose a risk for humans and/or the environment. But the risk associated with any material depends on the **exposure route and dose**. Some possible exposure routes for human exposure to nano particles are depicted in Figure 1.38.

In the last few years, a wealth of information has been reported by authoritative research groups on toxicity of ENPs though on animal models or *in vitro*. Another problem is that different testing methods are used in different laboratories, making it difficult to compare results. Research so far has mainly focused on two groups of materials: carbon-based nanomaterials (carbon nanotubes and fullerenes) and metal or metal-oxide nanoparticles (e.g. ultrafine titanium dioxide, TiO<sub>2</sub>). Several studies seem to indicate that some forms of carbon nanotubes show pulmonary toxicity and that this depends on the production method and the length and surface properties of the carbon tubes. Similarly, TiO<sub>2</sub> has been reported to cause

inflammation in the lungs when inhaled in high doses. The small size of nanoparticles ensures 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. Specialized phagocytic cells such as tissue macrophages and leukocytes in the blood generally take up larger particles. This is a mechanism evolved in higher animals for removal of potentially harmful bacteria, and is analogous to the feeding method of unicellular organisms. Nanoparticles in contrast, because of their small size, may pass into cells directly through the cell membrane with the possibility of interfering with important cell functions such as motility and ability to remove bacteria (42).



**Figure 1.38** Some possible exposure routes for nano particles and nano tubes based on current and potential future applications. (Adapted from National Institute for Resources and Environment, Japan [http://www.nire.go.jp/eco\\_tec\\_e/hyouka\\_e.htm](http://www.nire.go.jp/eco_tec_e/hyouka_e.htm))

Small size alone is not the critical factor in the toxicity of nanoparticles; the overall number and thus the total surface area (essentially the dose) are also important. Although nanoparticles may imply a toxic threat because of their small size and therefore large surface area per unit mass, any toxicity would be expected to be dependent upon inhalation or absorption into the body of a very large number. For nanoparticles with low surface reactivity, potential toxicity to humans and, presumably, other animals, should be considered in relation to the likely dose and

route of exposure. From the point of view of the lung, inhalation of small numbers of particles is unlikely to represent a significant risk. Inhalation of very large numbers, as may occur in a manufacturing process, should be controlled by regulation. For specific types of nanoparticle that may be expected to have a more reactive surface, perhaps because of a higher proportion or different combination of transition metals, greater caution would be advised and exposure should be minimised. Toxicological studies, both *in vitro* and *in vivo*, will be required for the investigation of any such substances to which people might be exposed.

Only a few types of manufactured nano particle such as titanium dioxide, carbon black, zinc oxide and iron oxide are currently in industrial production. There is, however, a realistic prospect of industrial production of other nanoparticles for therapeutic or diagnostic use, often based on metals with chemical coatings that confer particular properties with respect to uptake into the body, across natural tissue barriers, and into cells (43). There is also considerable interest in the possible production of nanotubes: some pilot manufacturing plants exist for CNTs, and nanotubes made of carbon and other elements are being extensively investigated in research laboratories. The greatest potential for exposure therefore over the next few years will be in the workplace, both in industry and in universities.

Overall, the scientific community agrees that progress has been made in the toxicological evaluation of nanomaterials. There is still much research to be done, but some key matrices have been identified. For example that surface area is a more important parameter than mass when dealing with engineered nanoparticles, and some targets and common behaviours have been also identified. The question is now how to make a risk assessment framework from these data, how to convert scattered numbers collected in numerous laboratories around the world into a risk management strategy for the safe handling of nanomaterials.

Research into the potential toxic effects of nanomaterials is now a priority in most funding institutions and agencies, as it is clear that the success of nanotechnologies will also depend on how the issue of safety is handled. Further it is also necessary to investigate the social and ethical issues expected to arise from the development of some nanotechnologies.

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5. Nanophysics and Nanotechnology: An introduction to the modern concepts in Nanoscience: Edward L. Wolf, *Wiley-VCH*, 2011.
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### **Web Sites**

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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/>

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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](http://www.almaden.ibm.com/almaden/media/image_mirage.html)

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

Nanoscience:<http://www.research.ibm.com/nanoscience/>

Ferroelectrics, microsystems and nanotechnology – the Cranfield University Nanotechnology web site:<http://www.nanotek.org/>

<http://www.nanostart.de/index.php/en/nanotechnology/nanotechnology-information/610-schneller-sparsamer-robuster-nanotechnologie-in-computer-handy-a-co>