Materials

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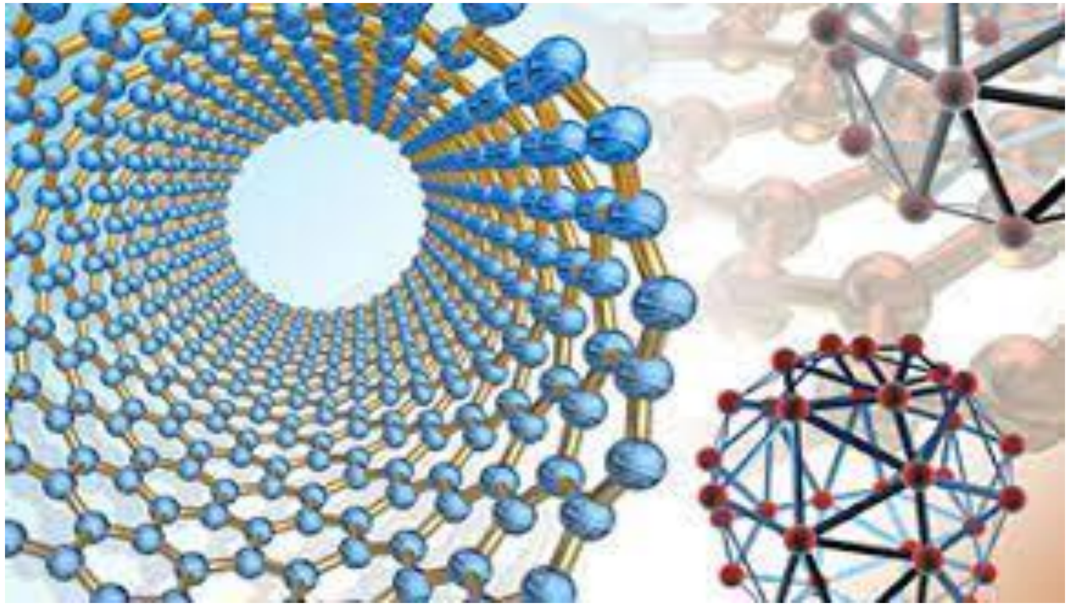
Applied Sciences and Humanities

CHAPTER-3

MATERIALS

What are Nanomaterials?

- Nanomaterials are commonly defined as materials with an average grain size less than 100 nanometers.
- Nanomaterials have extremely small size which having at least one dimension 100 nm
- One billion nanometers equals to one meter



Ref. https://revolutionized.com/nanomaterials/

What are Nanomaterials?

- A nanomaterial can be defined as a material with external dimensions in the nanoscale or with internal structure or surface structure in the nanoscale.

- According to this definition, most of the materials around us would qualify as nanomaterials, as their internal structure is modulated at the nanoscale.

- A differential approach for the term of "nanoparticle" was proposed in 2011 by the European Commission.

- The European commission suggests that a nanomaterial should consist of 50 % or more of particles having a size between 1 and 100 nm.

What are Nanomaterials?

- The European Union agencies suggest that the following definition should apply to the term "nanomaterial"

- Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm.

- By derogation from the above statement, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.

What are Nanomaterials?

- ‘Particle’, ‘agglomerate’ and ‘aggregate’ are defined as follows:

(a) ‘particle’ means a minute piece of matter with defined physical boundaries;

(b) ‘agglomerate’ means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;

(c) ‘aggregate’ means a particle comprising of strongly bound or fused particles.

What are Nanomaterials?

For the better understanding, nanomaterials are again organized into two types as follows:

i. Carbon based materials

ii. Metal and Semiconductor based materials

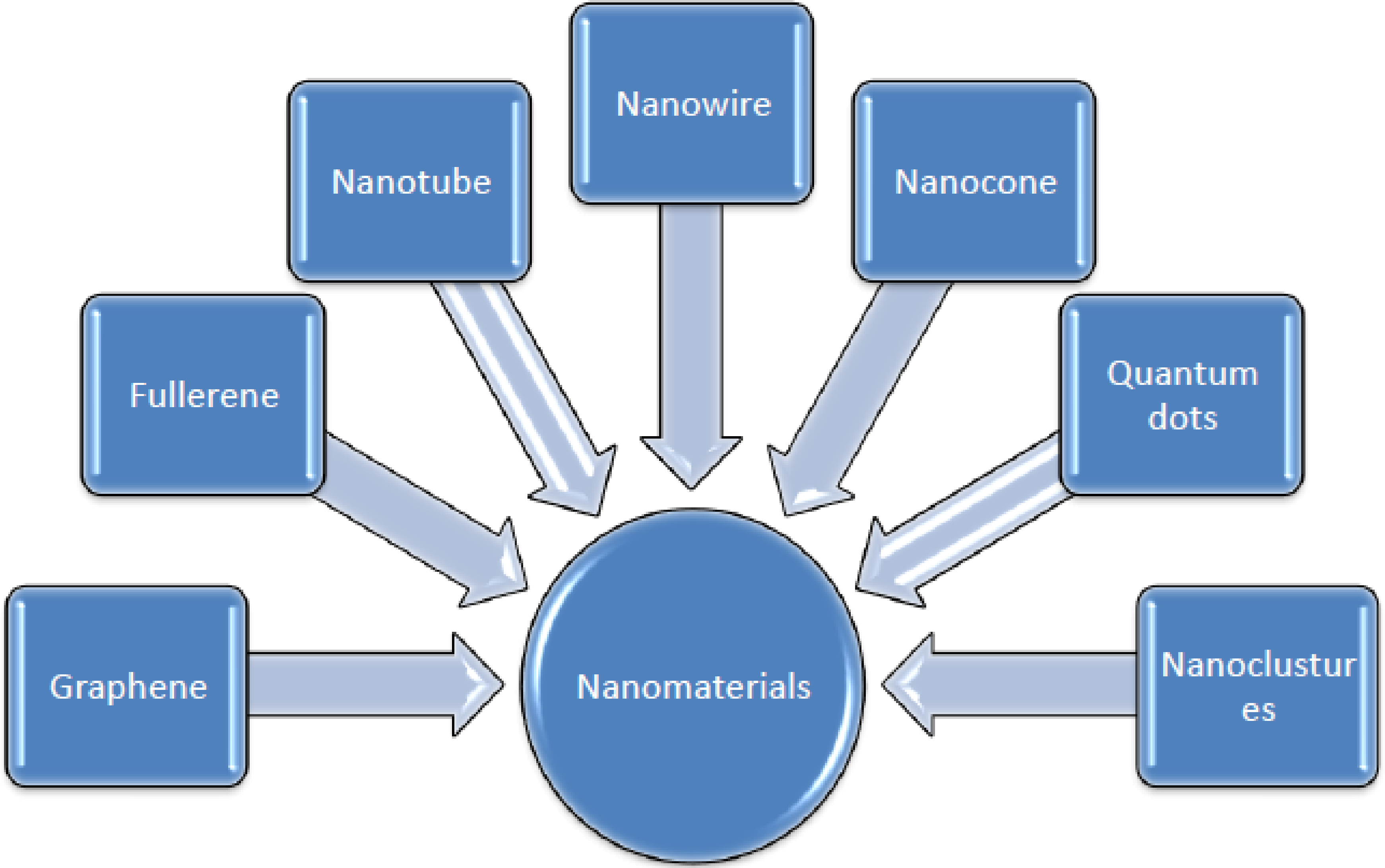
(i) **Carbon based materials:** These are composed of carbon, taking the form of hollow spheres, ellipsoids or tubes.

- The spherical and ellipsoidal forms are referred as fullerenes, while cylindrical forms are called nanotubes.

(ii) Metal and Semiconductor based materials: These include quantum dots, nanogold, nanosilver and metal oxides like TiO_2.

- A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, whose size is on the order of a few nanometers to a few hundred nanometers.

What are Nanomaterials?



Why nanomaterials ?

Nanotechnology exploits benefits of ultra small size, enabling the use of particles to deliver a range of important benefits

Small particles are 'invisible' :
Transparent Coatings/Films are attainable

Small particles are very weight efficient:
Surfaces can be modified with minimal material

- The behavior of nanomaterials may depend more on surface area than particle composition itself.
- Relative-surface area is one of the principal factors that enhance its reactivity, strength and electrical properties.

Why nanomaterials ?

- we can say the mechanical, electrical, optical, electronic, catalytic, magnetic, etc. properties of solids are significantly altered with great reduction in particle size. For example:

- Silver foil does not react with dilute HCl but silver nanoparticles rapidly react with dilute HCl.

- Gold and silver both are chemically inert but their nanoparticles show catalytic property.

- Gold nanoparticles are deep red but its bulk material (gold pieces) is gold-coloured.

Classification of Nanomaterials

- The classification of nanomaterials is based on the number of dimensions as shown in Fig. 3.1.
- Nanostructured materials are classified as: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanomaterials.

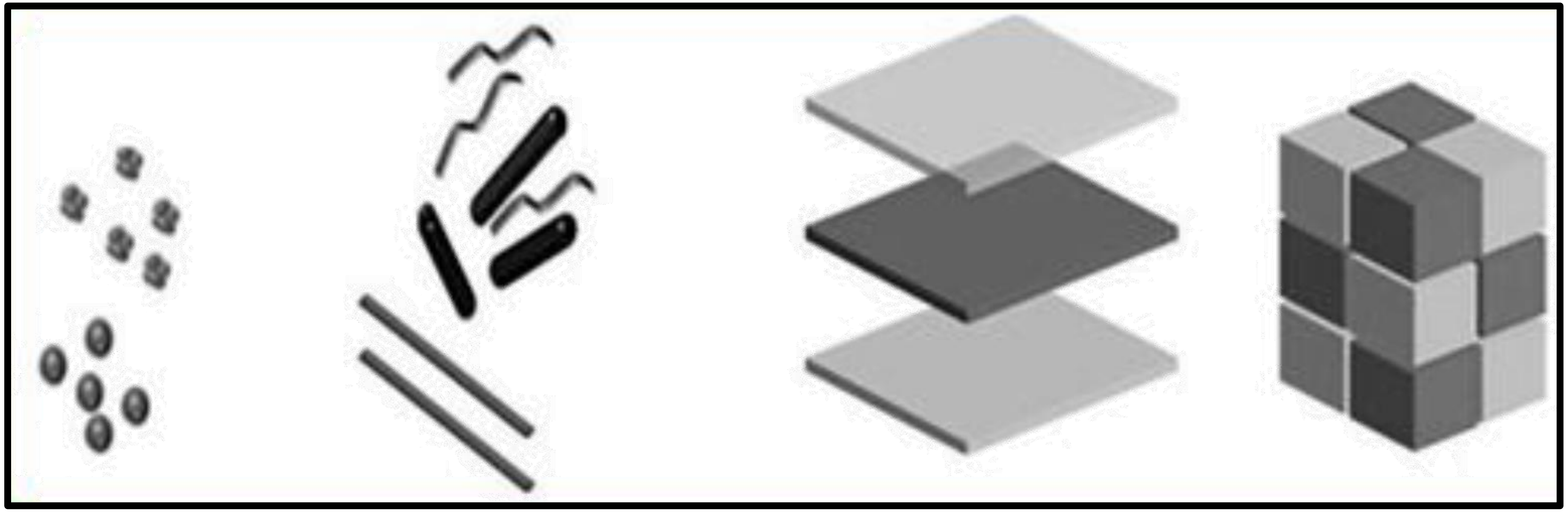
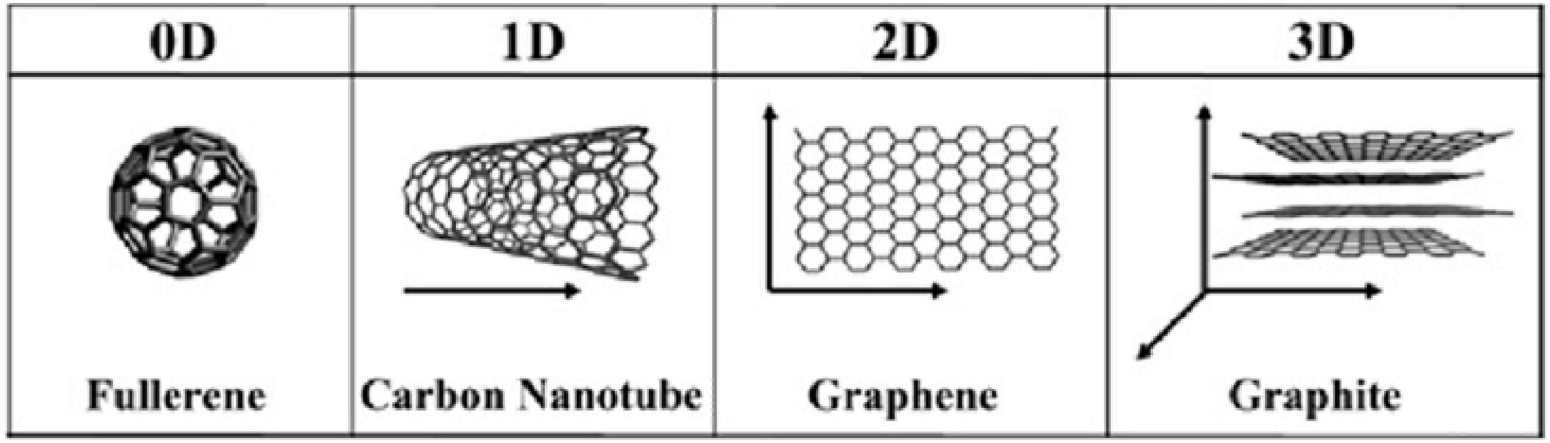


Fig. 3.1. The classification of nanomaterials is based on the number of dimensions

Classification of Nanomaterials

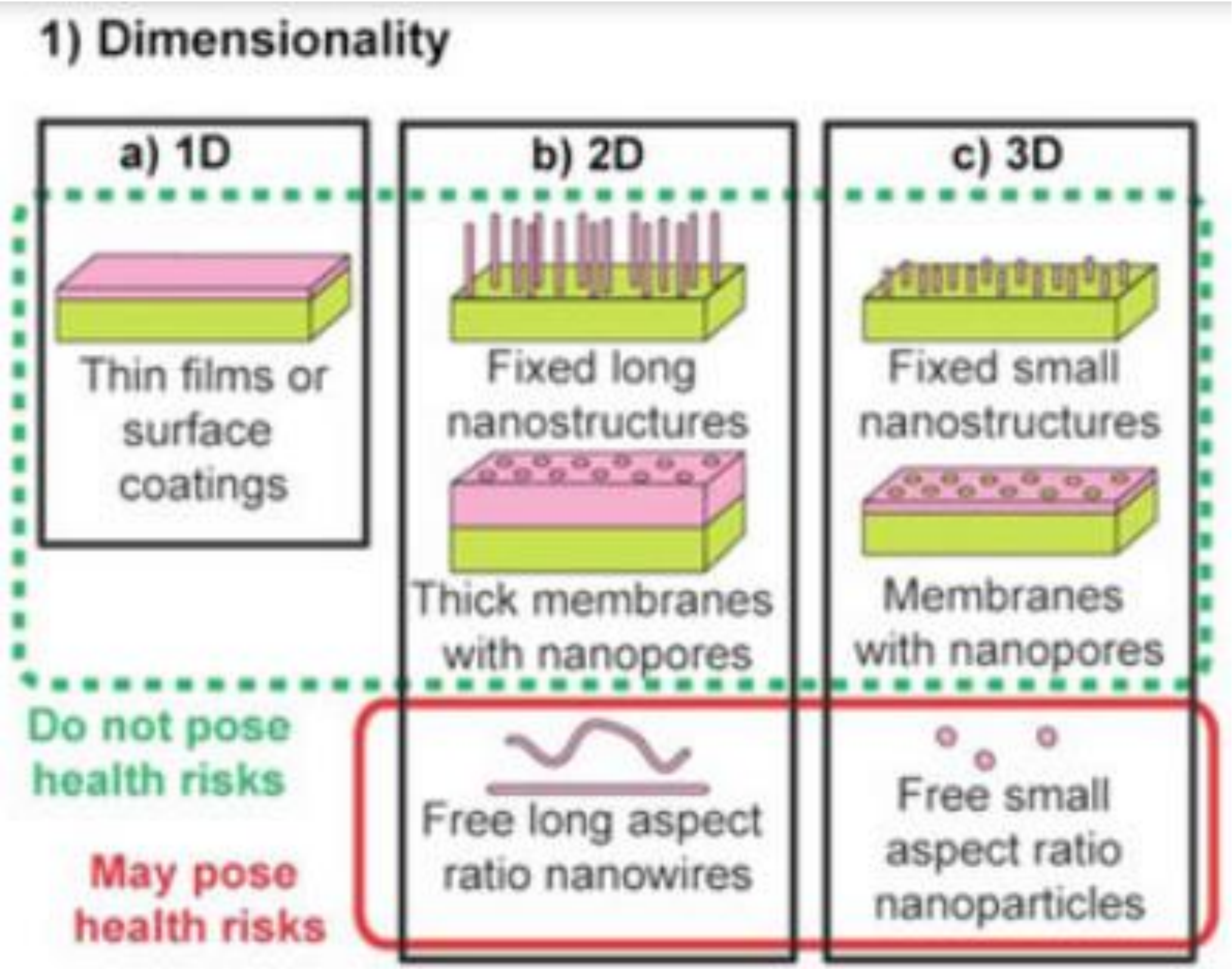
- The classification of nanomaterials is based on the number of dimensions.
- Nanomaterials can be nanoscale in one dimension (surface films), Two dimensions (strands or fiber), Three dimensions (particles)
- They can exist in single or fused forms with spherical, tubular, and irregular shapes.



3.1 Dimensionality

- From the point of view of their dimensionality, nanomaterials can be classified as nanomaterials with one, two, and three dimensions within the nanoscale.

- Materials with one dimension in the nanoscale are also called thin films or surface coatings attached on a substrate usually made from a different material.



Classification of Nanomaterials

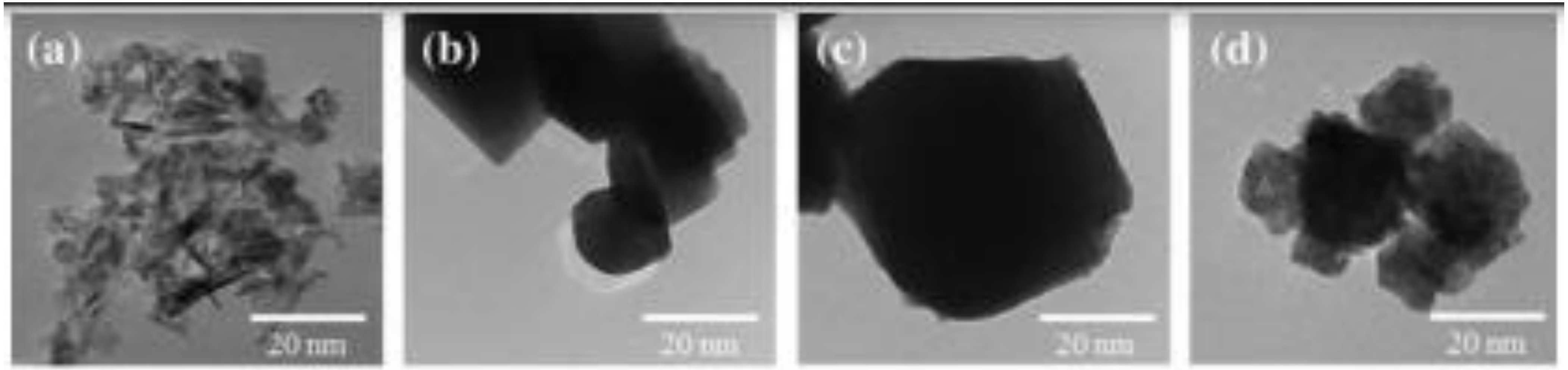
- Nanomaterials with two dimensions in the nanoscale are either nanoparticles attached onto a substrate, porous thin films with pores in the nanoscale, or free long aspect ratio nanoparticles, wires, or tubes.

- Finally, nanomaterials with three dimensions within the nanoscale can be fixed small nanostructures on a substrate, membranes with nanopores on a substrate, or nanoparticles. In this chapter one will focus mainly on nanomaterials.

- One must emphasize that while the nanomaterials fixed on a substrate or those with nanopores do not pose a health risk, the free nanoparticles can become airborne and may be very toxic to human health.

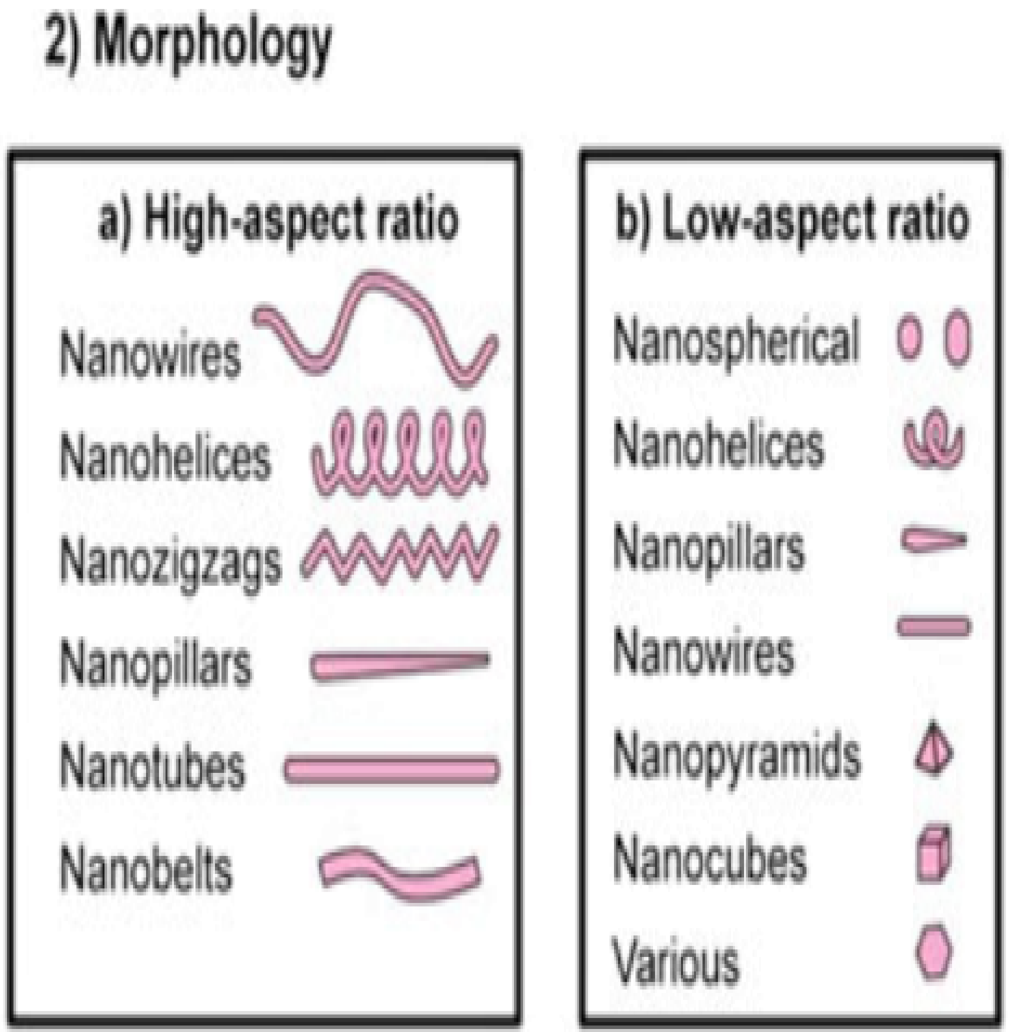
- Figure 3 shows transmission electron microscopy (TEM) images of various metal oxide nanoparticles: Al, Sb, Bi and Co.

- When we think of long aspect ratio nanoparticles, we think carbon nanotubes, however, a wide range of materials can be synthesized as nanoparticles with long aspect ratio.



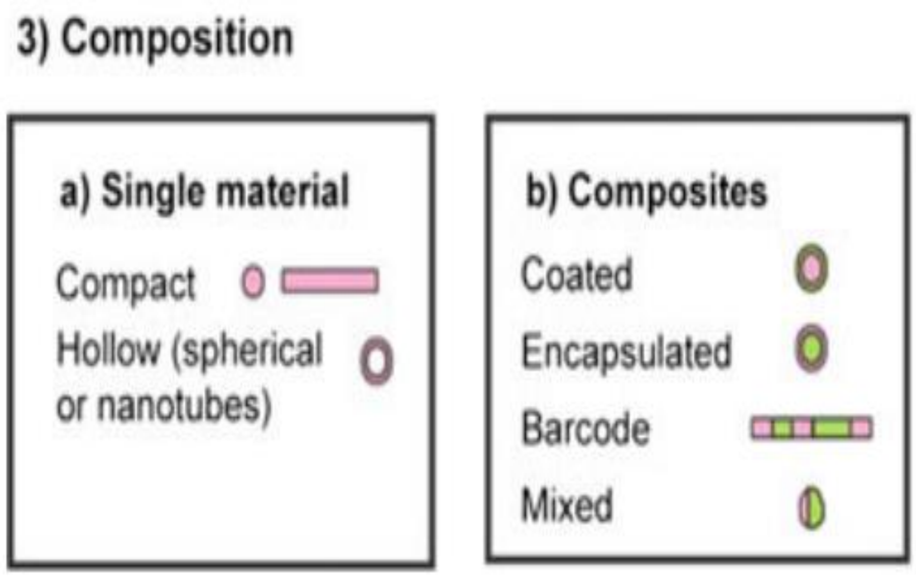
3.2 Morphology

- A classification of nanomaterials according to their morphology divides them in low- and high aspect ratio particles, see Fig. 2.
- The high aspect ratio nanoparticles can have different shapes, such as nanowires, nanohelices, nanozigzags, nanopillars, nanotubes, or nanobelts.
- The low aspect ratio nanoparticles can have many shapes as well, such as spherical, helical, pillar-like, pyramidal, cubes, among others.



3.3 Composition

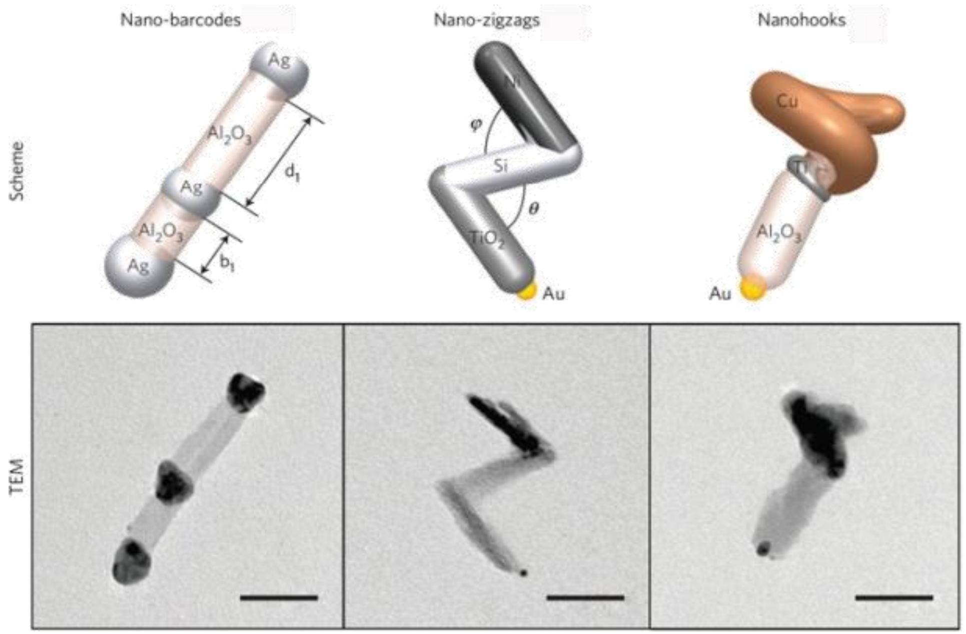
- According to their composition, nanoparticles can be made of a single material, compact or hollow.
- Nanomaterials can also be comprised of two or more materials that can be as coatings, encapsulated, barcode, or mixed.
- Nanoparticles can be made of a single material or composite materials.
- Many nanoparticles will oxidize in the presence of air and form a thin film at their surface.



3.3 Composition

- Nowadays nanoparticles comprising different composite materials are easily fabricated using a physical vapor deposition process at grazing incidence over a nanoseeded pattern, involving the manipulation of substrate motion and temperature.

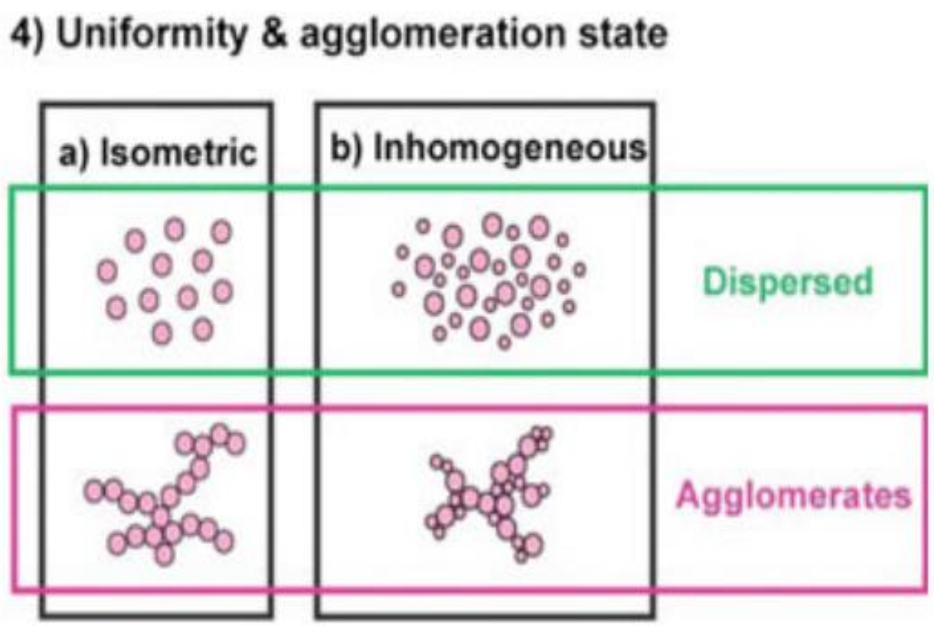
- This technique of deposition at a glancing angle incidence can be used to manipulate the morphology of single materials as well.



Composite or hybrid nanoparticles with progressively lower symmetry. Columns from left to right show: nano-barcodes, nanozigzags combining magnetic, semiconducting and insulating materials, and nanohooks with defined chirality. First row, structure models; second row TEM images.

3.4 Uniformity and Agglomeration State

- According to their uniformity, nanoparticles can be classified as isometric and inhomogeneous.
- From the point of view of their agglomeration status, nanoparticles can be dispersed or agglomerate.
- Their agglomeration state depends on their electromagnetic properties, such as surface charge and magnetism.



Basic characteristic properties of nanomaterials Nanomaterials

- Nanomaterials have structure sizes smaller than 100 nm in at least two dimensions. These Nanomaterials can have various shapes and structures such as spherical, needle-like, tubes, platelets, etc.

- Chemical composition is another important parameter for the characterization of Nanomaterials, which comprise nearly all substance classes e.g. metals/ metal oxides, polymers, compounds as well as biomolecules.

- Under ambient conditions nanoparticles tend to stick together and form aggregates and agglomerates.

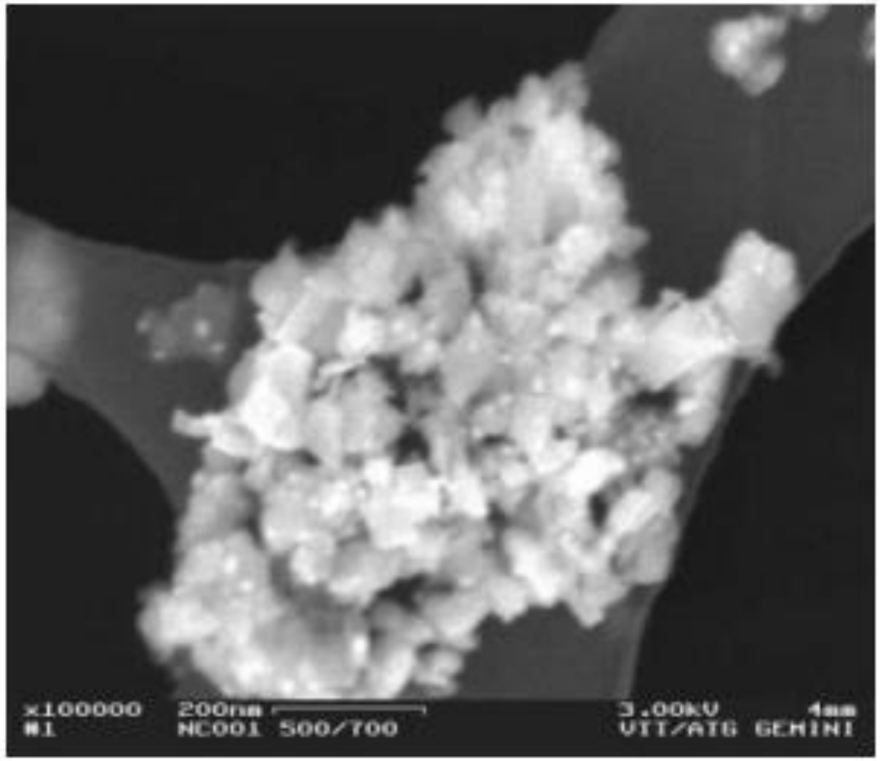
- These aggregates/ agglomerates have various forms, from dendritic structure to chain or spherical structures with sizes normally in the micrometer range.

Basic characteristic properties of nanomaterials Nanomaterials

- The properties of nanoparticles can be significantly altered by surface modification.

- For the characterization of Nanomaterials it is further important in which medium the nanoparticles are dispersed e.g. in gaseous, liquid or solid phase.

- The following figure summarizes relevant parameters for the characterization of Nanomaterials.



Basic characteristic properties of nanomaterials

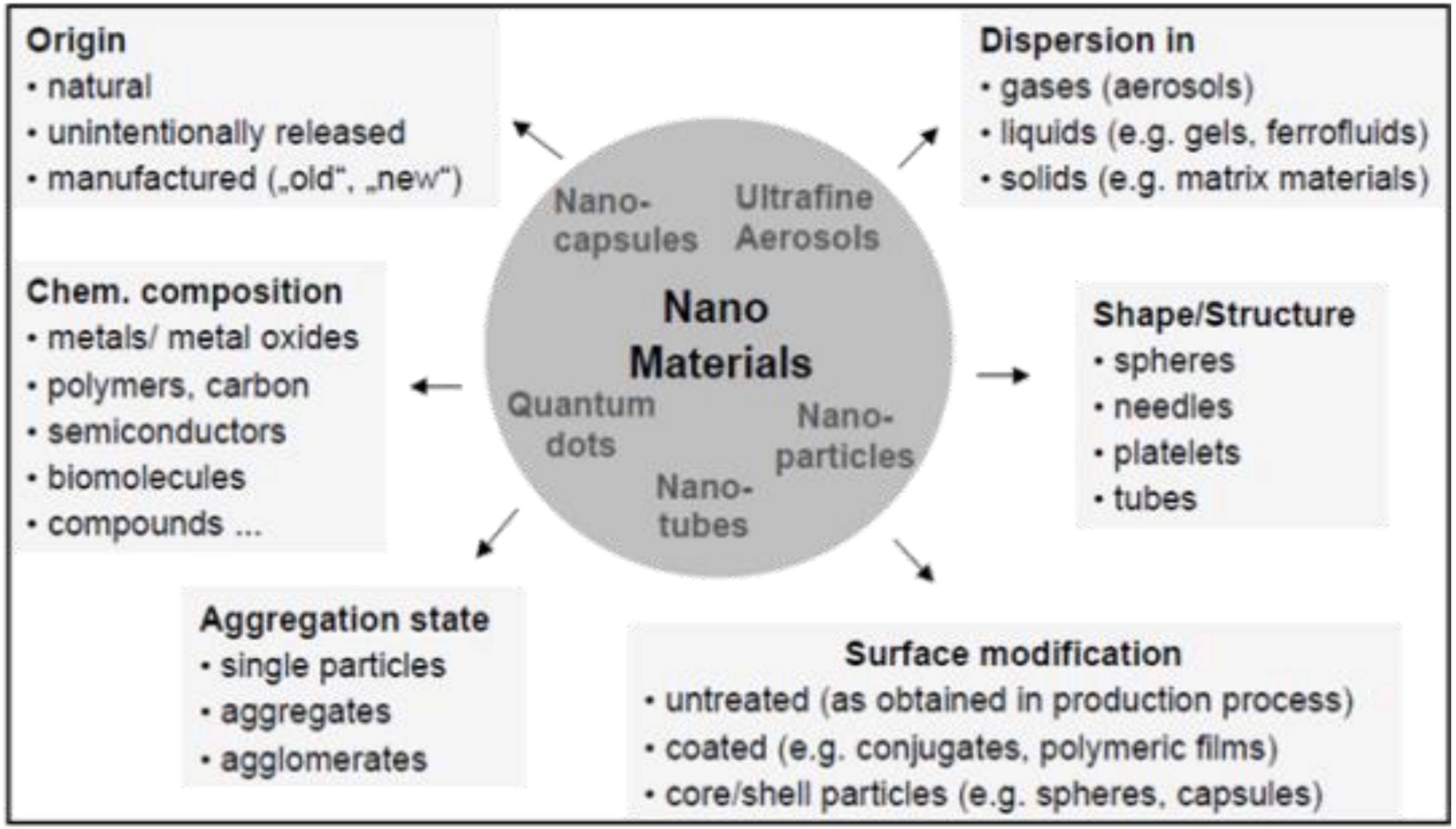


Fig. Characterization Parameters of Nano Particulate Materials

Classifications of Magnetic Materials

- ***Halite*.** The NaCl structure is composed of two interpenetrating fcc sublattices, with cations and anions alternating along [100] directions. Cations are octahedrally coordinated by anions and vice versa.
- ***Wurzite*.** The ZnS structure is composed of two interpenetrating hcp sublattices, so that cations and anions alternate along the 001 direction. Here the cations are tetrahedrally coordinated by anions and vice versa. The structure lacks a center of symmetry, and compounds with this structure may be piezoelectric or pyroelectric.
- ***Spinel*.** The structure of $MgAl_2O_4$ is based on an fcc array with 32 oxygen ions where 1/8 of the tetrahedral interstices (A-sites) are occupied by Al and 1/2 the octahedral interstices (B-sites) are occupied by a mixture of Mg and Al. This is known as the *inverse cation distribution*. The B-sites form a lattice of corner-sharing tetrahedra, which leads to frustration of antiferromagnetic superexchange in spinel ferrites with the normal cation distribution (Fe^{3+} on B-sites).

- ***Corundum (sapphire)*****.** This structure of Al_2O_3 is based on an hcp oxygen array, where Al occupies 2/3 of the octahedral interstices. The structure is rhombohedral, but it is often indexed on a larger hexagonal cell with 32 oxygen ions.

- ***Rutile*****.** This structure of TiO_2 can be regarded as a distorted hcp oxygen array, where Ti occupies 1/2 of the octahedral interstices. Each hcp sheet is deformed into a centered cubic array; so the structure is tetragonal with just four oxygen ions in the unit cell. TiO_2 can also crystallize in the anatase structure.

- ***Perovskite*****.** The $CaTiO_3$ structure is pseudocubic. Here the Ca and O ions together form an fcc lattice, and the Ti ions occupy 1/4 of the octahedral interstices, coordinated only by oxygen. The cell tends to be rhombohedrally or orthorhombically distorted, depending on the cation:oxygen radius ratios.

Classifications of Magnetic Materials

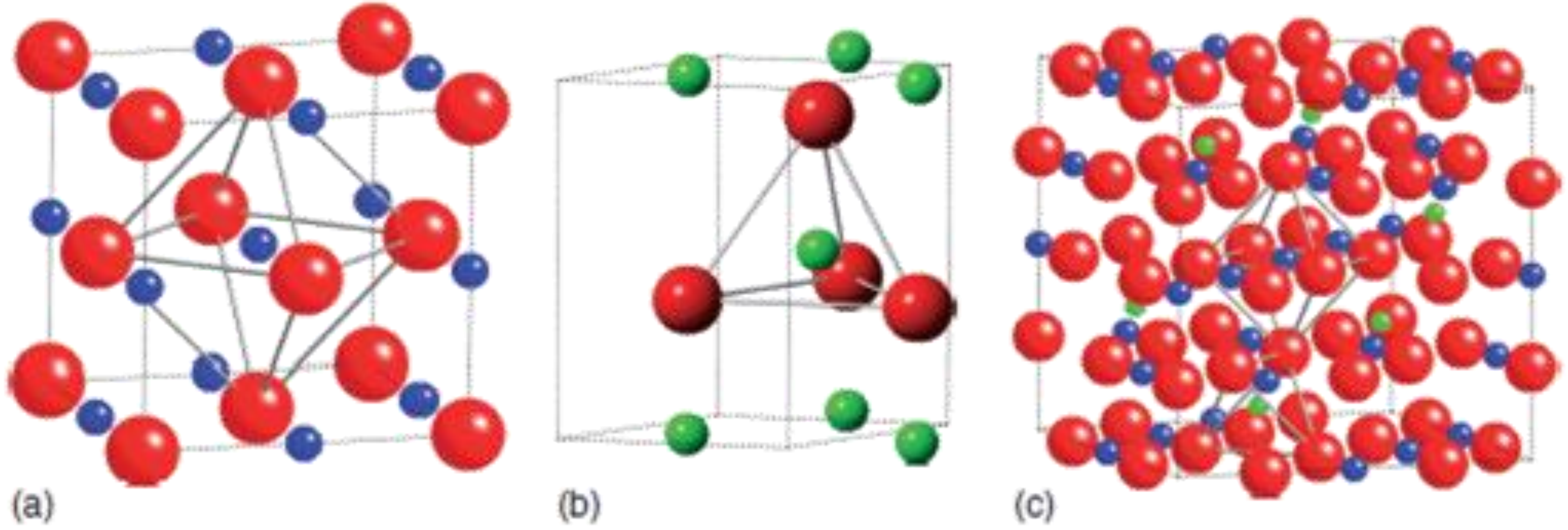
- ***Garnet*.** Pyrope, $Ca_3Fe_2Si_3O_{12}$, has a big cubic unit cell containing 96 oxygen atoms. The calcium is coordinated by eight oxygens; iron is in octahedral sites and silicon is in tetrahedral sites.

- ***Magnetoplumbite*.** $PbFe_{12}O_{19}$ has a tall hexagonal cell containing 76 oxygen ions. The structure can be considered as an hexagonal ABABAABABA stack of oxygen and lead ions, with the iron sites coordinated only by oxygen. There are three octahedral sites, a tetrahedral site and a five-coordinated trigonal bipyramidal site.

- ***Pyrochlore*.** This is a mineral with the ideal formula $Ca_2Nb_2O_7$. The structure is derived from that of fluorite (CaF_2), where the fluorine anions form a simple cubic array, with calcium in alternate body-centers, forming an fcc cation array. In pyrochlore, the lattice parameter is doubled, 7/8 of the fluorine sites are occupied by oxygen but 1/8 are vacant, and the structure includes an array of corner-sharing Ca tetrahedra. There are 56 oxygen ions in a cubic cell.

Classifications of Magnetic Materials

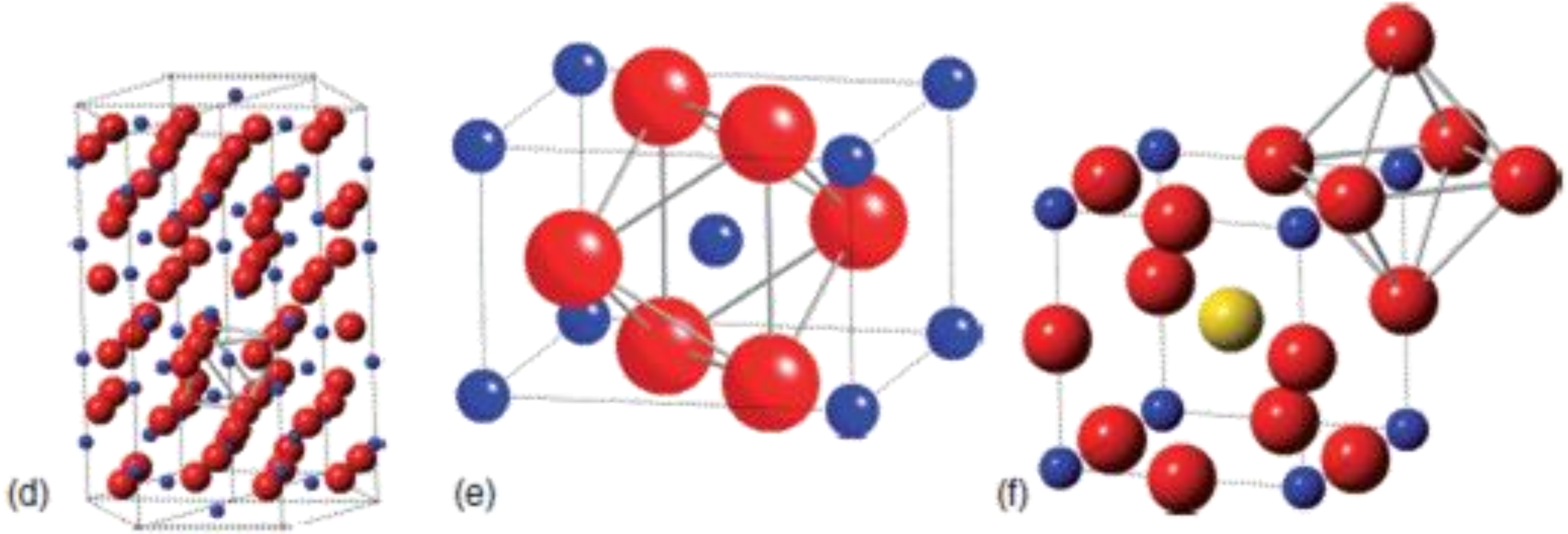
- Some common semiconductor and oxide structure types are shown below. However, few oxides are nonmagnetic but they are important due to their structures.



(a) Halite(MgO – NM) (b) Wurzite (ZnO – NM) (c) Spinel ($MgAl_2O_4$ – NM)

Where NM* referred as Non Magnetic

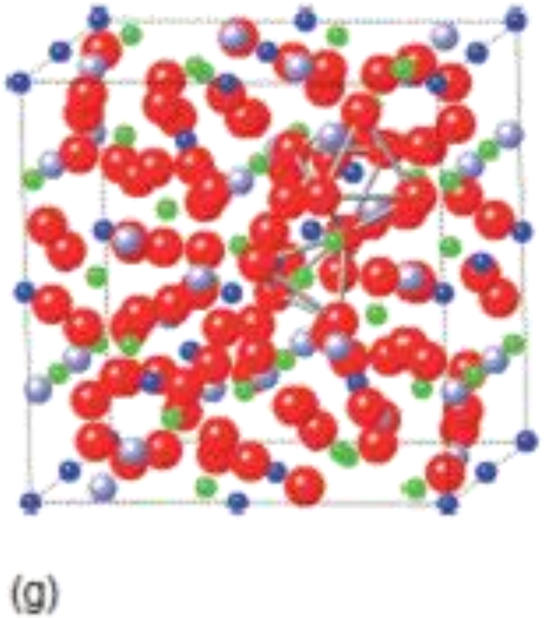
Classifications of Magnetic Materials



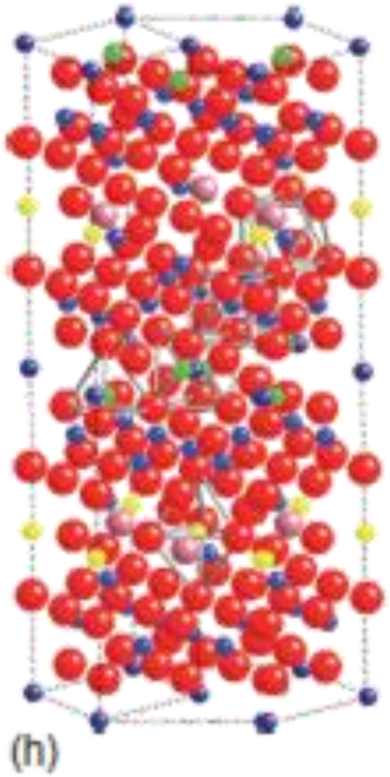
(d) corundum (Al_2O_3 – NM) (e) rutile(TiO_2 – NM) (f) perovskite

Where NM* referred as Non Magnetic

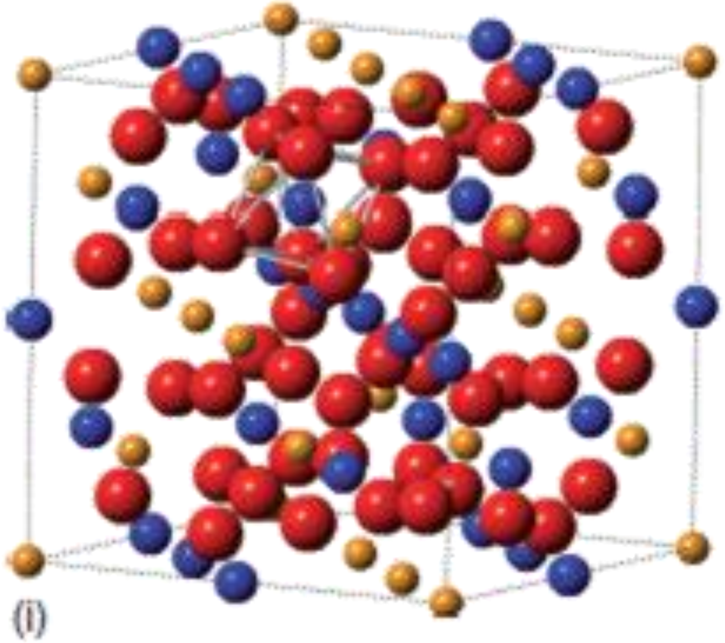
Classifications of Magnetic Materials



(g) garnet



(h) magnetoplumbite



(i) pyrochlore

Materials of the Future- Smart Materials:

- Smart (or intelligent) materials are a group of new and state-of-the-art materials now being developed that will have a significant influence on many of our technologies.
- Actuators may be called upon to change shape, position, natural frequency, or mechanical characteristics in response to changes in temperature, electric fields, and/or magnetic fields.
- Four types of materials are commonly used for actuators: shape memory alloys, piezoelectric ceramics, magnetostrictive materials, and electrorheological/ magnetorheological fluids.

I. Shape memory alloys are metals that, after having been deformed, revert back to their original shapes when temperature is changed.

II. Piezoelectric ceramics expand and contract in response to an applied electric field (or voltage); conversely, they also generate an electric field when their dimensions are altered.

Novel Materials

Materials of the Future- Smart Materials:

- The behavior of magnetostrictive materials is analogous to that of the piezoelectrics, except -- responsive to magnetic fields. Also, electrorheological and magnetorheological fluids are liquids that experience dramatic changes in viscosity upon the application of electric and magnetic fields, respectively.

- Materials/devices employed as sensors include optical fibers, piezoelectric materials (including some polymers), and microelectromechanical devices.
-

For example, one type of smart system is used in helicopters to reduce aerodynamic cockpit noise that is created by the rotating rotor blades.

- Piezoelectric sensors inserted into the blades, monitor blade stresses and deformations; feedback signals from these sensors are fed into a computer controlled adaptive device, which generates noise cancelling antidose.

Novel Materials

Nanoengineered Materials :

- Until very recent times the general procedure utilized by scientists to understand the chemistry and physics of materials has been to begin by studying large and complex structures.

- To investigate the fundamental building blocks of these structures that are smaller and simpler. This approach is sometimes termed "top-down" science.

- However, with the advent of scanning probe microscopes, which permit observation of individual atoms and molecules.

- It has become possible to manipulate and move atoms and molecules to form new structures and, thus, design new materials that are built from simple atomic-level constituents (i.e., "materials by design").

Novel Materials

Nanoengineered Materials :

- We call this the "bottom-up" approach, and the study of the properties of these materials is termed "nanotechnology".

Materials produced out of nanoparticles have some special features, e.g.

(i) very high ductility

(ii) very high hardness ~4 to 5 times more than usual conventional materials

(iii) transparent ceramics achievable

(iv) manipulation of colour

(v) extremely high coercivity magnets

(vi) developing conducting inks and polymers.

Novel Materials

Nanoengineered Materials :

- Material science has expanded from the traditional metallurgy and ceramics into new areas such as

a. electronic polymers,
b. complex fluids,
c. intelligent materials,
d. organic composites,
e. structural composites,
f. biomedical materials (for implants and other applications),
g. biomimetic,
h. artificial tissues,
i. biocompatible materials

PROPERTIES OF LOW DIMENSION MATERIAL

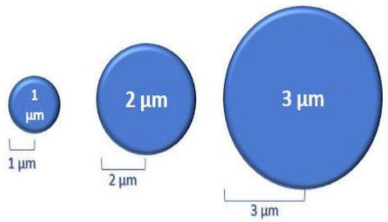
At the Macro Scale, the Physical and Chemical properties do not dependent on the size of the material, but at the nanoscale everything will change including colour, melting point, electrical properties, electronic properties, magnetic properties and chemical properties. This is due to the difference in the nature of interactions between atoms in nanostructures and in bulk materials. Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale.

The various properties have been explained below:

1. **PHYSICAL PROPERTIES**
2. **THERMAL PROPERTIES**
3. **ELECTRICAL PROPERTIES**
4. **OPTICAL PROPERTIES**
5. **MAGNETIC PROPERTIES**

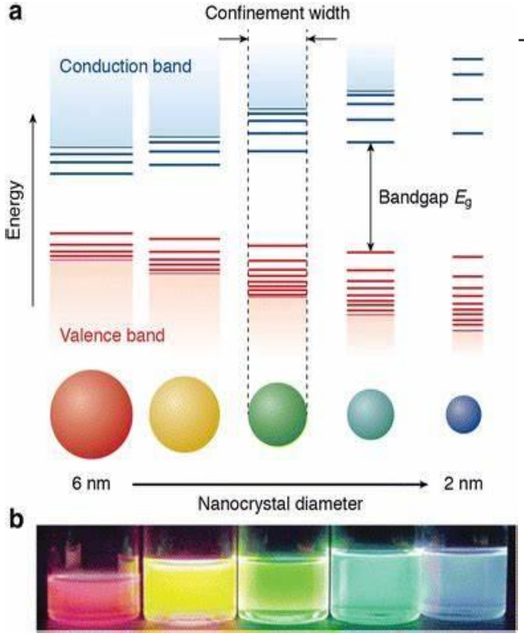
1. PHYSICAL PROPERTIES

THE VARIOUS PHYSICAL PROPERTIES ARE EXPLAINED GIVEN BELOW:

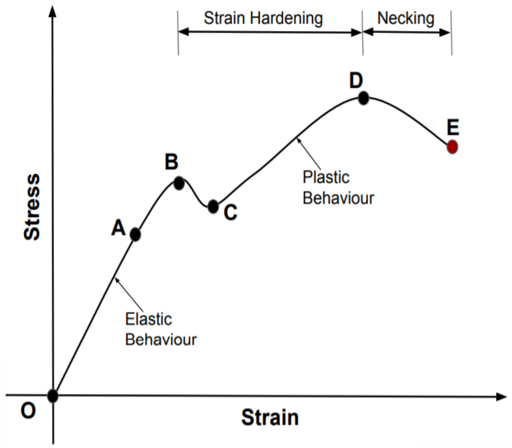


$Diameter_{(sphere)}$	1 µm	2 µm	3 µm
$Surface\ Area_{(sphere)} = 4\pi r^2$	3.14 μm^2	12.56 μm^2	28.26 μm^2
$Volume_{(sphere)} = \frac{4\pi r^3}{3}$	0.52 μm^3	4.19 μm^3	14.18 μm^3
Surface Area-to-Volume Ratio	6:1	3:1	2:1

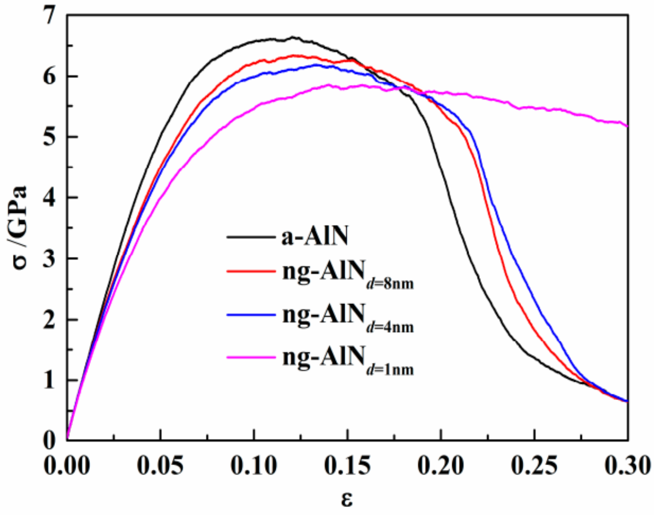
1.SURFACE AREA TO VOLUME RATIO



2.QUANTUM CONFINEMENT



3.ELASTICITY

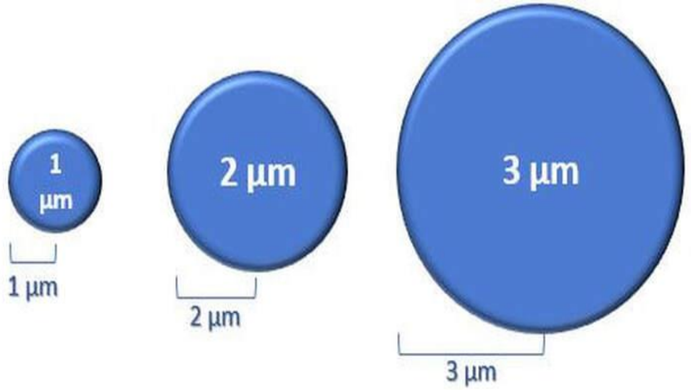


4.HARDNESS AND DUCTILITY

- This value is **very large** for **nanomaterials**.
- To understand this concept, consider a spherical material of radius 'r‘

$$\text{Dispersion(F)} = \frac{\text{Surface area of the sphere}}{\text{Volume of the sphere}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

- **As the size of the sphere decreases, Dispersion increases**.
- Alternatively, if the material is cubic, as it is divided into small cubes, then also the surface area to volume ratio increases.
- Hence, the nanomaterials possess large value of surface area to volume ratio as compared to the bulk material.



Diameter$_{(sphere)}$	1 µm	2 µm	3 µm
Surface Area$_{(sphere)}$ $= 4\pi r^2$	3.14 μm^2	12.56 μm^2	28.26 μm^2
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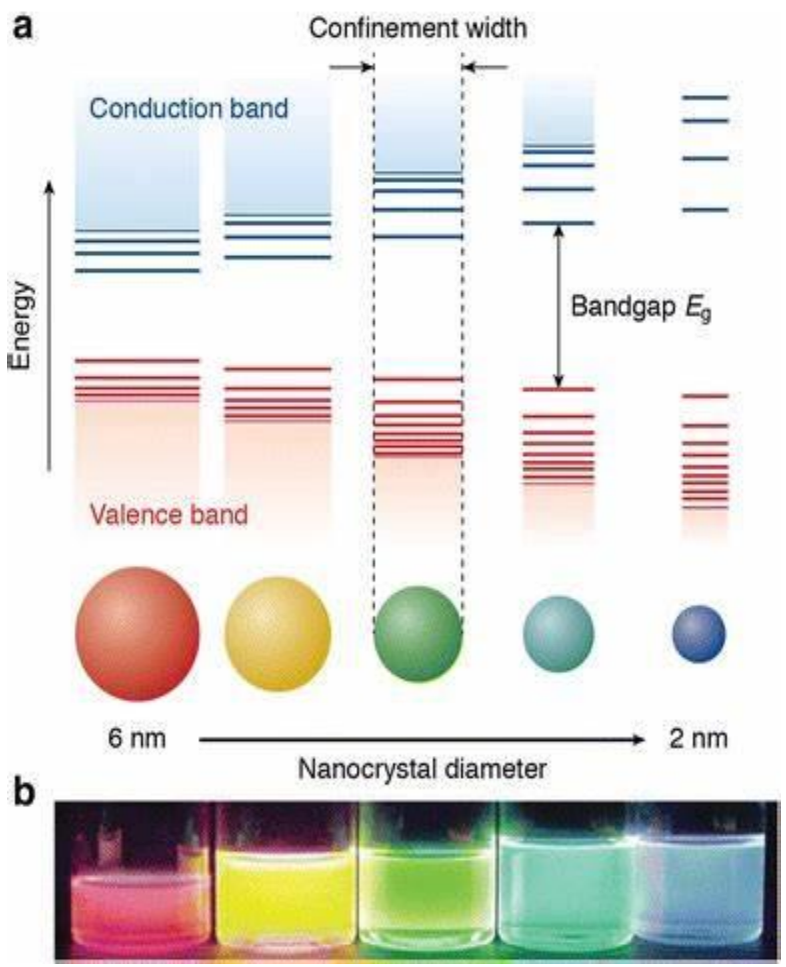
Surface Area-to-Volume Ratio	**6:1**	**3:1**	**2:1**

volume-to-surface-area-ratio_2.jpg (995×731) (scientistcindy.com)

1.2 QUANTUM CONFINEMENT

- One of the most direct effect of reducing the size of materials to nanoscale is the appearance of quantization effects due to the confinement of the movement of electrons.
- This leads to the discrete energy levels depending on the size of the structure.
- The **quantization confinement** can be observed **only when the diameter of the material is of the same magnitude as the wavelength of the electron wave-function.**
- Quantum confinement effects describe electron in terms of energy levels, potential well, valence band, conduction band and energy bandgap.
- In other words, the energy spectrum becomes discrete measured as quanta rather than continuous as in bulk materials. This situation of discrete energy levels is called **quantum confinement**.
- Quantum confinement describes how the electronic and optical properties change when the material size is at nanoscale.



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1.3 ELASTICITY

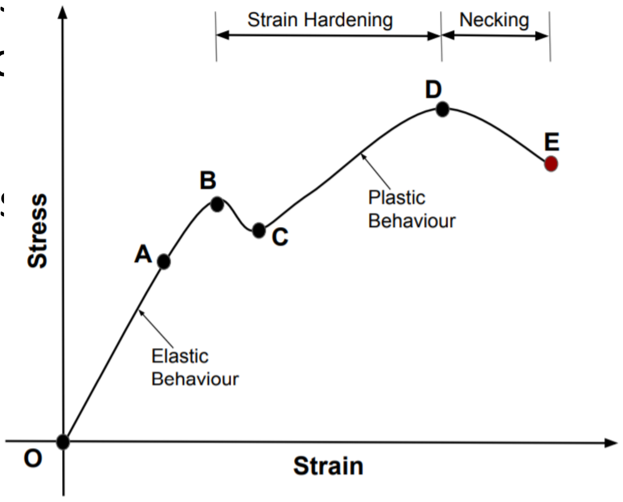
- Elasticity characterizes the ability of a material to resist elastic deformation, i.e., stiffness.
- The elastic moduli of materials reflect the forces that bind multiple atoms together. Therefore, measuring and understanding elasticity not only helps us to understand atomic interactions but also it is important for material applications.
- The Young's modulus “E”, shear modulus “G”, bulk modulus “K” and poisons ratio ϑ are also important.
- The relationship between stress and strain are represented by three moduli,

$$\sigma = E\varepsilon$$

$$\tau = G\gamma$$

$$p = -K\Delta V V_0$$

- Where σ, τ and p are normal and shear stress, and hydrostatic pressure, respectively. ε, γ, $\Delta V V_0$ are normal, shear and volumetric strain, respectively.
- Due to the nonlinear surface effect, nanomaterials may exhibit a nonlinearly elastic property though the inside of nanomaterials or the corresponding bulk one is linearly elastic. Moreover, it is found that externally applied loading should be responsible for the softening of the elastic modulus of a Nano-film.



OA : Proportional Limit
B : Upper Yield Stress Point
C : Lower Yield Stress Point
D : Ultimate Stress Point
E : Fracture

Stress-Strain-Curve-For-Ductile-Materials.png (1078×645) (smlease.com)

1.4 HARDNESS AND DUCTILITY

- Hardness and strength of conventional grain size materials (grain diameter, d > 1 m) is a function of grain size. The dependence of yield stress on grain size in metals is well established in the conventional polycrystalline range (micrometer and larger sized grains).

- Yield stress, for materials with grain size d, is found to follow the Hall– Petch relation:

$$\alpha_y = \alpha_0 k d^{-1/2}$$

where α_0 the friction stress apposing dislocation motion and k is a constant.

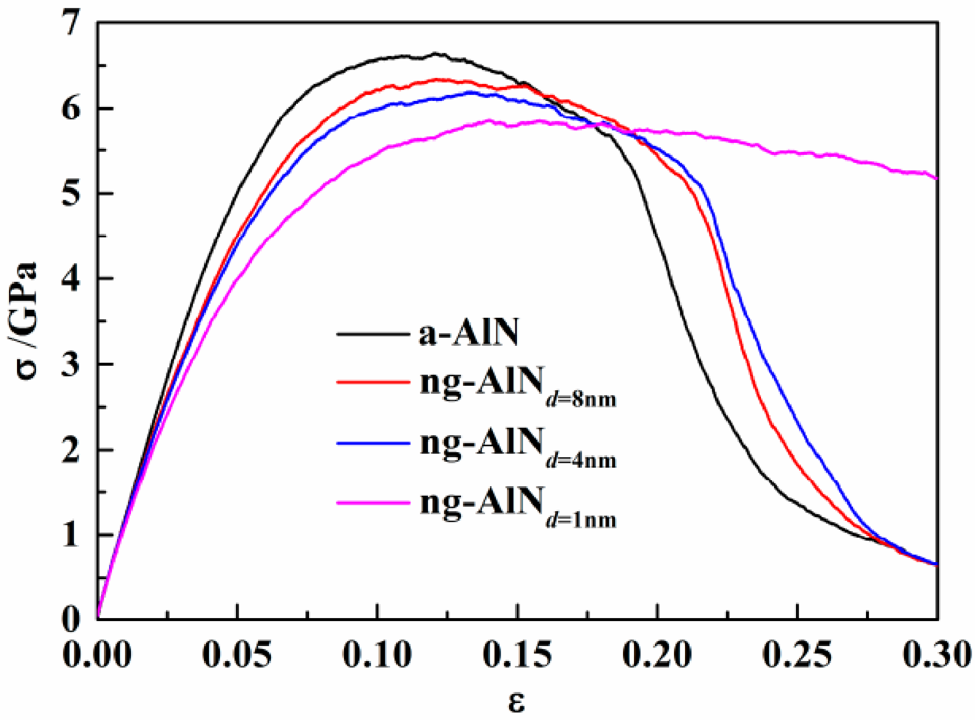
- It is clear that as grain **size is reduced through the nanoscale regime (< 100 nm), hardness typically increases** with decreasing grain size and can be factors of 2 to 7 times harder for pure nanostructured metals (10 nm grain size) than for large-grained (> 1 μm) metals.

- In the conventional grain size (> 1 μm) regime, usually a **reduction in grain size leads to an increase in ductility**. Thus one should expect a ductility increase as the grain size is reduced to nanoscale.

1.4 HARDNESS AND DUCTILITY

- Nucleation and propagation of cracks can be used as the explanation for the fracture stress dependence on grain size. Grain size refinement can make crack propagation more difficult and therefore, in conventional grain size material, increase the apparent fracture toughness.

- However, the large increases in yield stress (hardness) observed in nanocrystalline(NC) materials suggest that fracture stress can be lower than yield stress and therefore result in **reduced ductility**

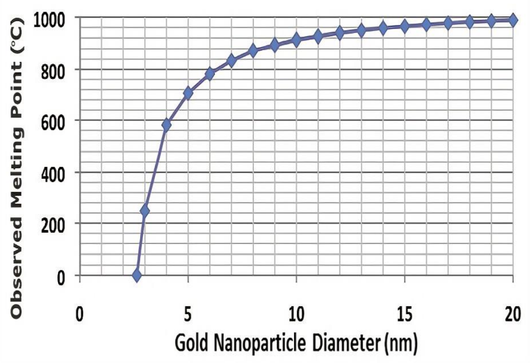


Super Ductility of Nanoglass Aluminium Nitride. Nanomaterials, 9(11), 1535 | 10.3390/nano9111535

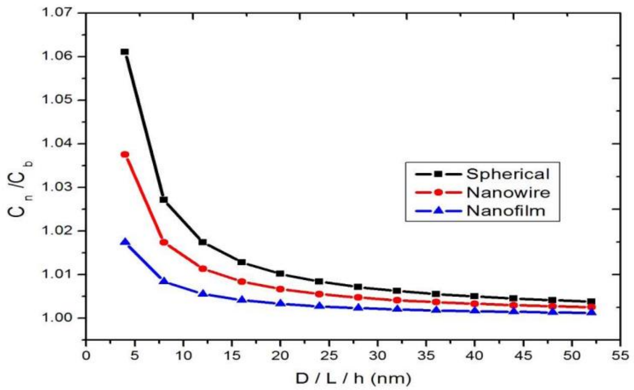
Tensile stress-strain (σ – ε) curves for a-AlN and ng-AlNs with average grain size of 8 nm, 4 nm, and 1 nm, respectively.

2. THERMAL PROPERTIES

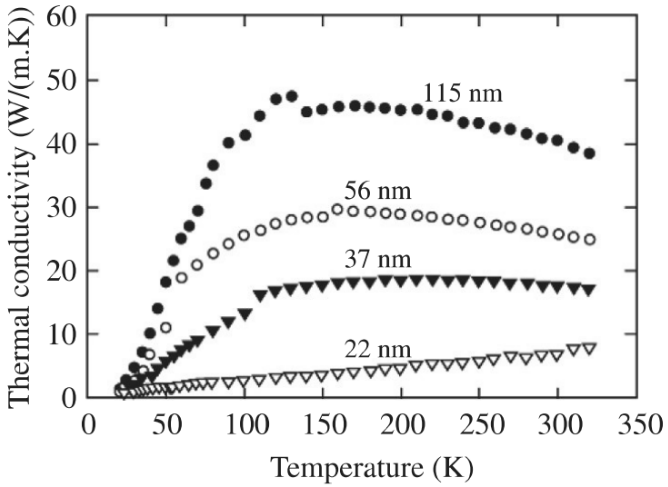
There is a change in thermal properties of some materials as they go from bulk to nanoparticles. A few of them are given below:



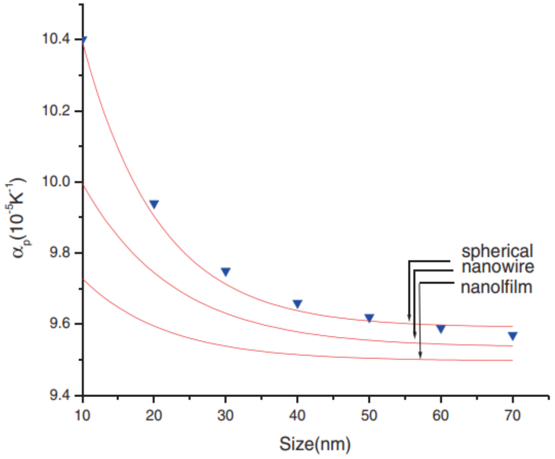
1.MELTING POINT



3.SPECIFIC HEAT



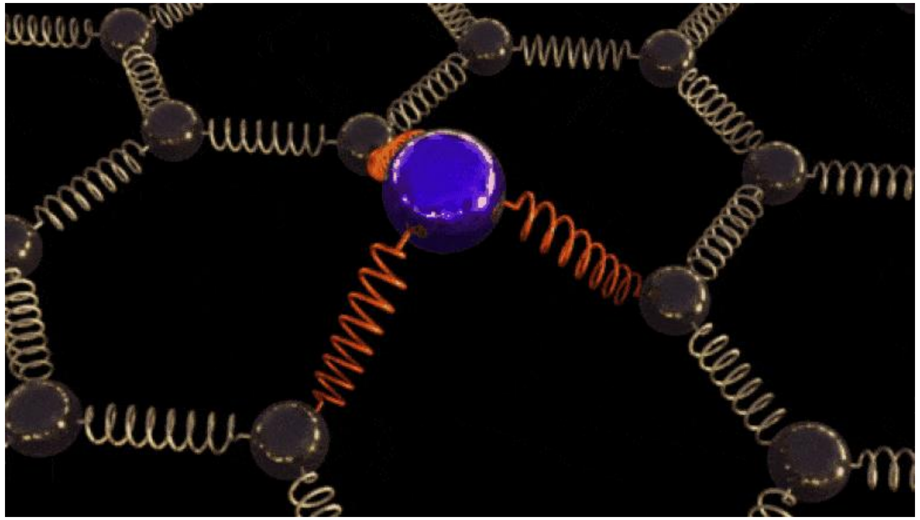
2.THERMAL CONDUCTIVITY



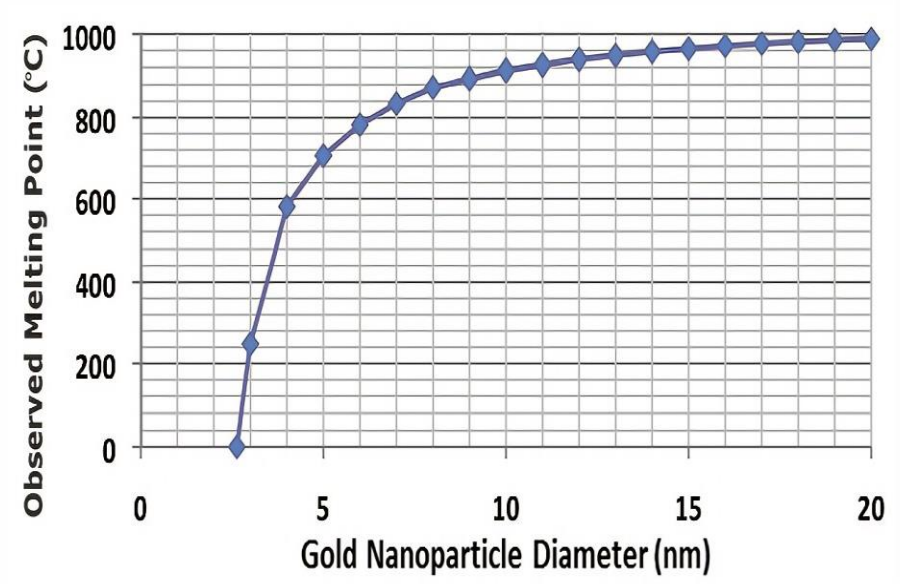
4.THERMAL EXPANSION

2.1 MELTING POINT

- The melting temperature for bulk material is independent on its size. However nanoparticle melting temperature depends on its dimension, due to higher value of surface by volume ratio. The deviation can be ten to hundred kelvin.
- The melting point of Nano-gold decreases from 1200 K to 800 K as the size of particles decreases from 300Å to 200Å
- At higher temperatures, there is breakdown in symmetry of nanoparticles due to high thermal vibrations of surface atoms in nanostructures
- Solid gold changes into liquid as it goes from bulk to nanomaterial at room temperature.



thermal vibration in nanomaterial gif - Bing



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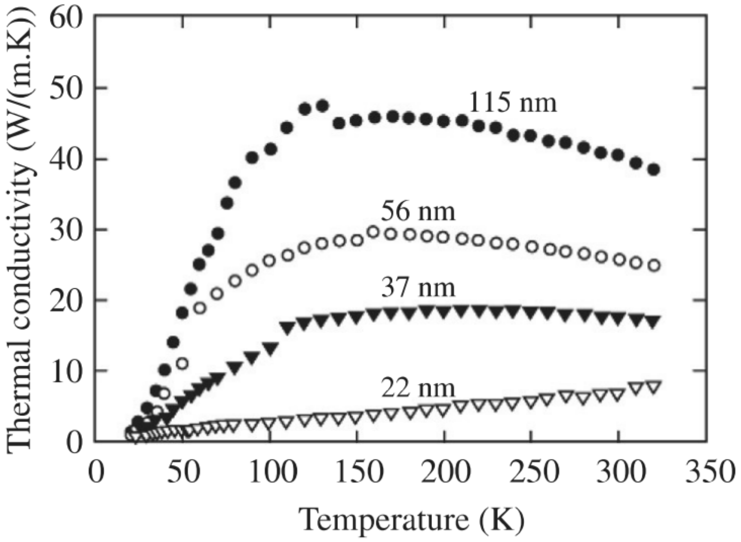
2.2 THERMAL CONDUCTIVITY

- Thermal conductivity can be determined accurately from electrical conductivity measurements.

- From the figure we can say that initially when we increase temperature the thermal conductivity of material is also increases, whereas further increases in temperature shows decrease in thermal conductivity of material.

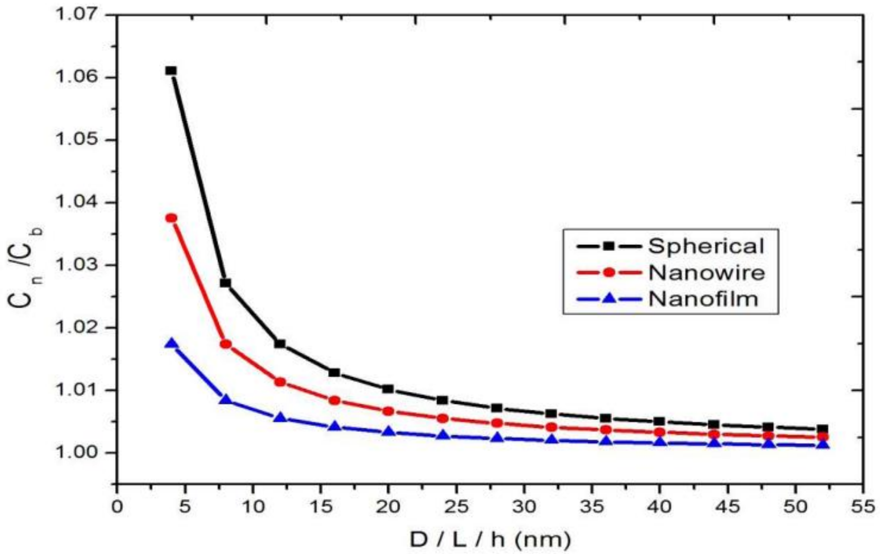
- The increase in thermal conductivity is explained by increase electron quantities and motion, the decreases in thermal conductivity after some temperature is a response to phonon scattering.



Thermal conductivity of pure single-crystal Si nanowires of various diameters

2.3 SPECIFIC HEAT

- For bulk material, specific heat is a function of temperature. Moreover, for nanomaterials, the **specific heat depends on temperature as well as on the size**, The reason for these changes corresponds to **increased relative surface area** and grain boundaries, which may be explained in terms of defects and impurities.
- The properties like melting temperature, specific heat and entropy have been investigated for nanoparticles by calculating its **Gibbs free energy.**
- The grain size less than 10nm , C_n/C_b (C_n and $C_b$is Specific Heat Capacity for Nano material and bulk material, respectively.) increases which indicates that **specific heat is inversely related to the grain size**.
- The specific heat values are somewhat higher than the corresponding bulk values while the thermal conductivity values are considerably lower. Therefore, we conclude that **specific heat has weak grain size dependence and thermal conductivity shows strong grain size dependence**.



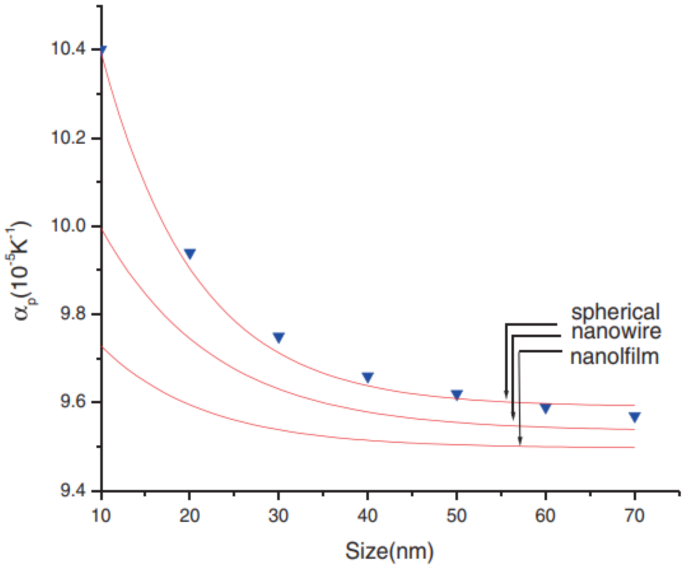
Effect of Shape on C_n/C_b nanoparticle

2.4 THERMAL EXPANSION

- It is easy to imagine that the **thermal expansion of a nanocrystal is different from that of a bulk crystal** because of the **proportion of grain boundaries increases** significantly as the **grain size decreases** to the **nanoscale** the increase in grain boundaries should affect the atomic bonding energy and vibrations near the equilibrium position, thus affecting thermal expansion.

- The experimental measurements show that the **thermal expansion coefficients of nanocrystalline materials are larger than those of their polycrystalline** counterparts which **depend on temperature** and **influenced by the effect of size**.

- The size-dependent thermal expansion coefficient of Se for different shapes of nanomaterial (spherical, nanowire and Nano-film) with increasing grain size, **It is seen that the thermal expansion coefficient increases with decreasing grain size.**



Size-dependent thermal expansion coefficient

3. ELECTRICAL PROPERTIES

- In bulk materials conduction electrons are delocalized and travel 'freely' till they are scattered by phonons, impurities, grain boundaries etc.

- In nanoscale conductors two effects become important:
  - **Quantum effect**: **Continuous ('nearly') bands** are **replaced** with **discrete energy states**
  - **Classical effect**: **mean free path** (MFP) for **inelastic scattering becomes comparable to the size of the system** (can lead to **reduction in scattering events**).

- **In metals**: Change **in DOS on reduction of size** of the system plays a major role (along with change in electronic and vibrational energy levels).

- In semiconductors **quantum confinement** of both the **electron and hole** leads to an **increase** in the **effective band gap** of the material **with decreasing crystallite size**.

- **These effects can lead to altered conductivity in nanomaterials.**

3. ELECTRICAL PROPERTIES

- The electrical conductivity and energy bandwidth of some materials change when they pass from bulk phase to nanoparticle phase.
  For example, **bulk silicon is an insulator; it becomes a conductor in the nanophase**.

- In nanoceramics and in nanomagnetic composites, **electrical conductivity increases with reducing particle size**.

- In **metals, electrical conductivity decreases with reducing particle size**. By reducing the size of metal particles from bulk to nano, the energy bands become narrower and hence the ionization potential energy increases.

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

4. OPTICAL PROPERTIES

- When talking about optical properties it usually refers to the **interaction of electromagnetic radiation with matter**. The simple picture one can start with is by considering a 'ray' of an electromagnetic wave of a single frequency entering a medium from vacuum. This ray could be reflected, transmitted (refracted) or absorbed.

- Absorption essentially involves activating some process in the material to take it to an excited state (from the ground state).
  These processes are:
  (i) Electronic Excitations (ii) Vibrational Excitations (iii) Rotational Excitations

- Bulk metal samples absorb electromagnetic radiation (say visible region). Thin films of metals may partially transmit, just because there is insufficient material to absorb the radiation. Au films few 10s of nm thick become partially transparent.

- In semiconductor quantum dots, optical absorption and emission shift to the blue (higher energies) as the size of the dots decreases.

- At very small sizes metal nanoparticles can develop a bandgap (can become a semiconductor or insulator).

4. OPTICAL PROPERTIES

- On decreasing the size the electron gets confined to the particle (confinement effects) leading to:
  (i) Increase In Bandgap Energy
  (ii) Band Levels Get Quantized (Discrete).

- Surface states (trap states), which lie in the bandgap become important → alter the optical properties of nanocrystals.

- The energy level spacing increases with decreasing dimension → Quantum Size Confinement Effect

- With reducing size of the particle the density of states becomes more quantized and the band gap shifts to higher energies (shorter wavelengths) → the absorption spectrum shows a blue shift.

- By changing the size of the nanoparticles the frequency of emission can be tailored.

5. MAGNETIC PROPERTIES

- When we go from bulk to 'nano' only the structure sensitive magnetic properties (like coercivity) is expected to change significantly

- Some of the possibilities when we go from bulk to nano are:
  I. Ferromagnetic particles becoming single domain
  II. Superparamagnetism in small ferromagnetic particles (i.e. particles which are ferromagnetic in bulk)
  III. Giant Magnetoresistance effect in hybrids (layered structures)
  IV. Antiferromagnetic particles (in bulk) behaving like ferromagnets etc.

- **There is a increase in magnetic moment, as we decrease the dimensionality of the system.**

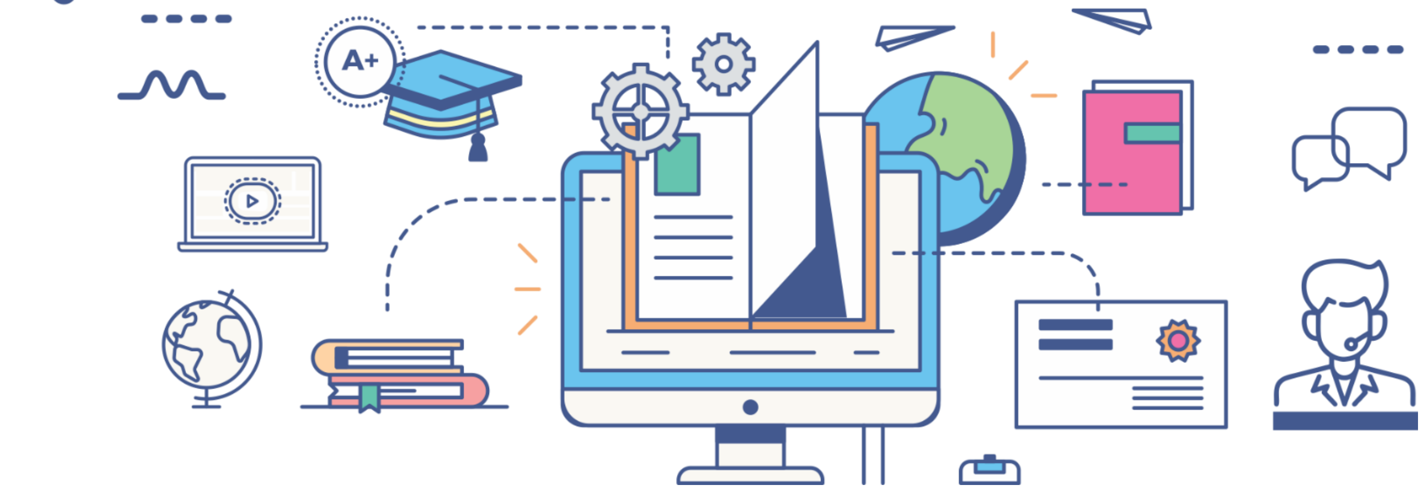
- **The thermal expansion increases with decreasing grain size effect.**

- The magnetic properties of nanomaterials are different from that of bulk materials. In small ferromagnetic particles, the magnetic properties are different from that of bulk material. They are saturated magnets.

5. MAGNETIC PROPERTIES

- In nanomaterials, we use single domains unlike large number of domains in bulk materials.
- The coercivity of single domain is very large.
- **Transition metals** are ferromagnetic in bulk but they exhibit super paramagnetism in the nanophase.
- Na, K and Rh are paramagnetic in bulk but in nanophase, they are ferromagnetic.
- Cr is anti- ferromagnetic in bulk, in nanophase it shows frustrated paramagnetic property.
- At higher temperatures, clusters show less magnetic moment called super paramagnetism because thermal vibrations change the alignment of magnetic moment.
- Clusters of non-magnetic element supported on metal substrates also show magnetism. This shows that small particles possess more magnetism than the bulk material

DIGITAL LEARNING CONTENT



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