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Nanotechnology

Nanoscience is the study of phenomena and objects at the nanoscale and nanotechnology deals with the ability to develop and use the technology to manipulate and observe at nanoscale.

In short nanoscience is the study of nanostructures and nanotechnology is the application of these knowledge in different industries.

Nanoscale

The word nano is derived from a Greek word 'nanos' meaning dwarf or extremely small and is equal to one billionth part of a unit.

$$1\ nm = 10^{-9}\ m.$$

Significance of Nanoscale

Most of the properties of the solid depends on the size of the solid. For bulk materials properties like resistivity, density, elasticity etc. are averaged properties. When the size of the material becomes smaller, this averaging no longer works and the properties of material change drastically in nanometer range.

Two main factors causes the significant change in properties of nanomaterials from their bulk counterpart are

1. Increase in surface area to Volume ratio.
2. Quantum confinement effect.

These factors can enhance the properties such as reactivity, strength & electrical characteristics.

1. Surface area to volume ratio.

For spherical nanoparticles The surface to volume ratio is

$$\frac{S.A}{\text{Volume}} = \frac{4\pi R^2}{4/3\,\pi R^3} = \frac{3}{R}.$$

Hence the S.A to volume ratio increases as the radius R decreases; since it is inversely proportional to radias.

As the particle size decreases a greater portion of atoms are found at the surface compared to those inside. For example a particle size 30 nm has 5% of its atoms on its surface & at 3 nm 50% of its atoms on surface.

Thus nanoparticles have a greater surface area per unit mass compared with larger particle.

In catalytic chemical reactions, the reaction occurs at the surface. In nanosized materials the surface atoms are more reactive and hence the properties will be different from its bulk counterpart.

2. Quantum Confinement effect : (λ of an $\bar{e}$ 1.23nm)

Quantum confinement is the restricted motion of randomly moving electrons in specific energy levels when the dimension of the material approaches the de-Broglie wavelength of $\bar{e}$. When this occurs the properties changes significantly because energy levels become discrete and motion of electrons become restricted.

Based on the no. of dimensions, they are confined, nanostructures are classified as three

i Nanosheets [Quantum well]

In nanosheets confinement is present in only one dimension. ie carriers are allowed to move freely in 2 Dimensional plane.

Suppose the confinement is present along z-direction to a small distance, and the $\bar{e}$s are free to move along x and y directions.

Then Schrodinges eqn. in this case is

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V(z)\right]\psi(z) = E_z\psi(z)$$ [Time independent form].

The wave fn and energy in this case is

$$\psi(z) = \sqrt{2/L}\ \sin\frac{n_z\pi z}{L_z}\ e^{ik_x x}\cdot e^{ik_y y}.$$

$$E_n = \frac{n^2h^2}{8mL_z^2} + \frac{h^2k_x^2}{8m} + \frac{h^2k_y^2}{8m}.$$

eg: A typical example of nanosheet is graphen the thinnest 2-D material in the world. It consists of a single layer of carbon atoms with hexagonal lattices.

Advantages :- Improved chemical & thermal stability in aqueous solution, enhanced conductivity, excellent electrochemical capacitance etc.

2. Nanowire / Quantum wire

In nanowire, carriers are confined in 2D and allowed to move freely along one dimension. Suppose carriers are confined in the y and z directions to small distances L_y and L_z respectively and are free to move along x-direction. Then the wave fn. and energy values will be

$$\psi(x,y,z) = \sqrt{2/L_y}\cdot\sqrt{2/L_z}\ \sin\left(\frac{n\pi y}{L_y}\right)\sin\left(\frac{n\pi z}{L_z}\right)e^{ik_x x}.$$

The corresponding energy eigen values are

$$E_n = \frac{h^2}{8m}\left[\frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] + \frac{h^2 k_x^2}{8m}$$

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2 k^2}{8m}$$

$$\lambda = h/p$$

$$p = h/\lambda$$

$$p = \left(\frac{h}{2\pi}\right)\left(\frac{2\pi}{\lambda}\right) = \hbar k$$

eg: Nanowires include inorganic molecular wires, which can have a diameter of 0.9 nm & be hundreds of micrometers long.

- Nanowire can also be made from CNTs.

Motion of charge carriers in CNT is an example of 2D confinement.

3. Quantum dot

If the carriers are confined in 3Ds, then the nanostructure is called a quantum dot.

In this case S.E. is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r).$$

The corresponding wave fn. and energy is

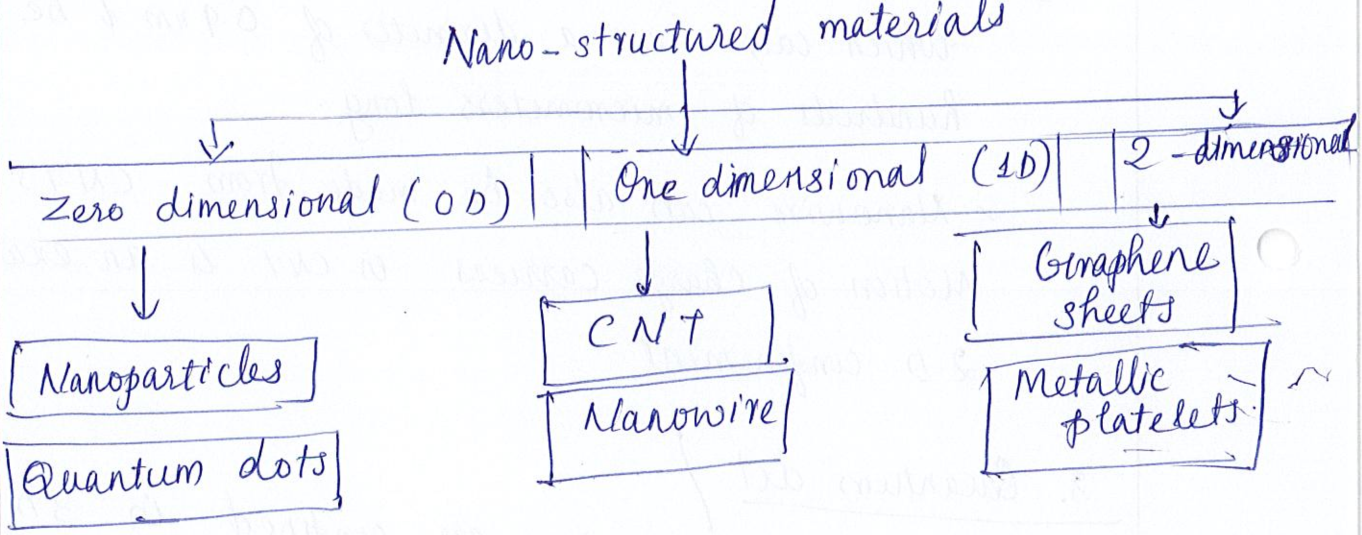
$$\psi_n(x,y,z) = \sqrt{2/L_x}\,\sqrt{2/L_y}\,\sqrt{2/L_z}\cdot \sin\frac{n_x\pi x}{L_x}\,\sin\frac{n_y\pi y}{L_y}\,\sin\frac{n_z\pi z}{L_z}$$

and

$$E_n = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

Quantum dots are very small semiconductor particles, only several nanometres in size, having optical & electronic properties, that differ from large particles due to quantum mechanics.

Nanoparticles with a fraction of nanometer to a few tens of nanometes size can be treated as examples of three dimensional confinement of carriers.



Properties of Nanomaterials.

1. Mechanical Properties

The mechanical properties of nanomaterials may reach theoretical strength, which is higher in magnitude than that of a single crystal in bulk form. The enhancement in mechanical strength is mainly due to reduced probability of defects.

- It is observed that nanoparticles of metals, semiconductors and molecular crystals have lower melting points compared to their bulk form, when the particle size is less than 100 nm.
- The probability of having dislocation is very small for nanowires of smaller cross-sections. Therefore nanowires have mechanical strength much greater than that of thick ones.
- The enhanced mechanical strength is due to high internal strength and less surface defects.
- Nanostructured materials have higher or lower strength & hardness compared to coarse-grained ones, depending on the methods used to vary the grain size.

eg: Cu with an average grain size of 6 nm has 5 times higher hardness over a sample of grain size 50 μm.

⇒ Pure nanocrystalline Cu has yield strength in excess of 400 MPa, ie 6 times higher than that of coarse - grained Cu.

⇒ Modulus of elasticity / young's modulus is also high for nanostructures than that of their bulk counterpart.

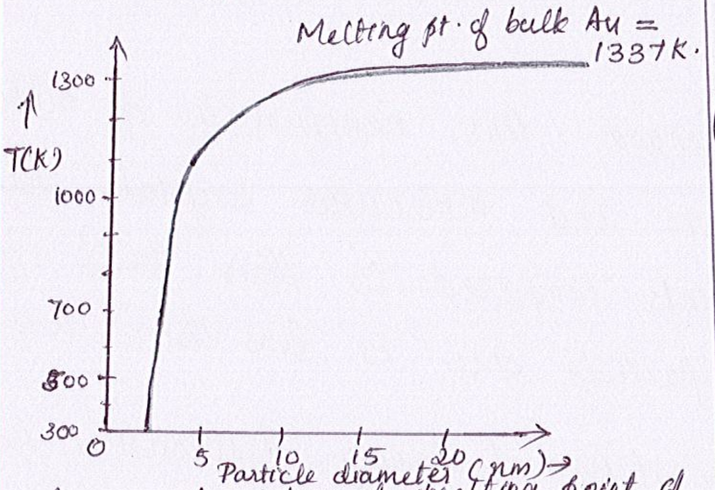


Fig (i): Variation of melting point of gold with particle size.

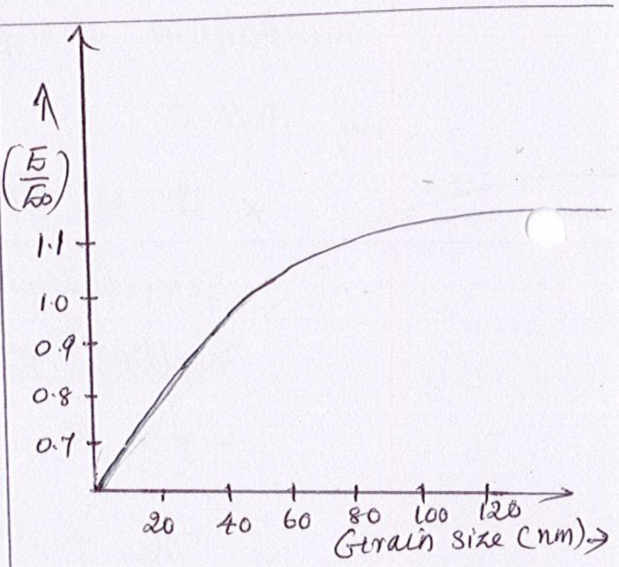


Fig (ii): The variation of young's modulus of nanomaterial (E) to that of bulk (E_0) as a fn of grain size is plotted.

2. Electrical Properties

Size plays an important role in the electrical properties of nanomaterials based on four mechanisms.

- Surface scattering
- Change of electronic structure
- Quantum Transport
- Effect of microstructure.
- Increased perfection.

⇒ Electrical conductivity decreases with a reduced dimension due to increased surface scattering.

⇒ However electrical conductivity can be increased due to better ordering in micro-structure.

⇒ As the bulk materials reduces its size, continuous energy bands are replaced by discrete energy levels and bandgap increases as the size decreases. As a result some metal nanowires undergo transition to become semiconductors and semiconductors might become insulators, when their diameters are reduced below a critical diameters.

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

3. Optical Properties

The optical properties of nanomaterials are due to two reasons. 1. Increased energy level spacing.
2. Surface Plasmon Resonance (SPR).

⇒ The energy level separation in a nanocluster depends on the size of the nanoclusters, which affect the energies needed for the transition of electrons to excited states.

⇒ Clusters of different sizes will have different absorption spectra. Hence the clusters of different size exhibit different colours.

eg: Nanoscale gold particles can be orange, purple, red or greenish depending on the size of the cluster.

⇒ Surface Plasmon Resonance (SPR) is the coherent excitation of all the free $\bar{e}$s within the conduction band upon interaction with e.m. field leading to an inphase oscillation. This takes place when the size of the nanoparticle is smaller than wavelength of incident radiation.

Quantum Dots.

Quantam dots are semiconductors whose excitons are confined in all three dimensions of space.

Quantum dots are very small semiconductor particles with a size comparable to Bohr radius of the excitons. [separation of electrons & holes].

Typical dimension : 1 – 10 nm.

It can be large as several μm.

Shapes : cubes, spheres, pyramids etc.

Applications of quantum dots.

- Photovoltaic devices : solar cells.
- LEDs.
- Biosensors, imaging.
- Photodetectors
- LASERs etc.

Quantum dots

Quantum dots are artificial nanostructures that can possess many varied properties, depending on their material and shape.

Nanoparticles of semiconductors – quantum dots – were created in the early 1980s. If the semiconductor particles are made very small enough, quantum effects come into play. ie which limit the energies at which ēs and holes can exist in the particle. As the energy is related to wavelength or colour, this means that the optical properties of the particle can be finely tuned depending on its size. Thus the particles can be made to emit or absorb specific wavelengths of light, merely by controlling their size.

The properties of a quantum dot are not only determined by its size, but also by its shape, composition, structure etc.

Applications – In the areas such as electronics, photonics, information storage, imaging, medicine used as catalysis etc.

Nanowire

A nanowire is a nanostructure, with the diameter of the order of a nanometer ($10^{-9}m$). It can also be defined as the ratio of the length to width being greater than 1000. Alternatively, nanowires can be defined as structure that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length.

Many different types of nanowires exist, including superconducting (eg: YBCO), metallic [eg: Ni, Pt, Au], semiconducting [eg: silicon nanowires InP, GaN) and insulating [eg: SiO_2, TiO_2]

What are nanowires?

Nanowires are microscopic wires that have a width measured in nanometers. Typically their width ranges from 40 nm to 50 nm, but their length is not so limited. Since they can be lengthened by simply attaching more wires end to end or just by growing them longer, they can be as long as desired.

- Diameter of nanowires range from a single atom to a few hundreds of nanometers.
- Length varies from a few atoms to many microns.

Different names of nanowires in literature is given below;

⇒ Whiskers fibers : 1D structures ranging from several nanometers to several hundred microns.

⇒ Nanowires : Wires with large aspect ratios (eg: > 20)

⇒ Nanorods : Wires with small aspect ratios. (eg: ≤ 20)

⇒ NanoContacts : Short wires bridged between two larges electrodes.

Advantages of NW

NW devices can be assembled in a rational and predictable because;

- Nanowires can be precisely controlled during synthesis
- Chemical composition.
- diameter
- length.
- doping / electronic properties.

NWs thus represent the best-defined class of nanoscale building blocks, and this precise control over key variables has correspondingly enabled a wide range of devices and integration strategies to be pursued.

Applications of Nanotechnology

⇒ Nano materials with greater surface area helps in the development of super capacitors with increased energy density and power output than conventional materials.

⇒ Aerogels are new form of insulation based on nanotechnology which is more effective than traditional insulation. They are lighter, smaller & provide improvements wherever superior thermal, fire & acoustic barriers are needed.

⇒ Nanomaterials have environmental applications :- It is used as a catalysts to react with toxic gases such as CO, Nitrogen oxide in automobile catalytic converters. This can avoid environmental pollution from burning petrol & coal. Nanomaterials are also used for removing pollutants from ground water, soil etc.

eg.. Magnetic iron oxide nano particles are used for removing arsenic from ground water.

⇒ In Medical field :- Nanoparticles can be used to deliver drug to specific type of cells such as cancer cells. It only attracts the diseased cells & thus reduces the damage of healthy cells in the body

⇒ Nanoparticles are used for anti-bacterial treatments.

⇒ CNT based alloys have high strength & reduced weight - so this can be used as automobile frames.

⇒ Nano-powders & coatings will increase the durability of paint coatings.

⇒ Nanoparticles are used for the early detection of diseases.

⇒ Nanoparticles are used to enhance the contrast in MRI, probing of DNA structure in stem cell research etc.

⇒ Nanomaterials are used in spark plugs

Spark plug – It is a device for firing the explosive mixture in an internal combustion engine
* It is a device for delivering an electric current
* To ignite air/fuel mixture, electrical energy is transmitted through spark plug.

⇒ carbide – compound of carbon.

⇒ erosion resistant – erosion means gradual destruction of something.

Electrical properties

* surface scattering
* change of electronic structure
* quantum transport
* effect of microstructure.

⇒ Yarn – knitted together could be used as sensors.
Nanomaterials for clothing & Textile products

⇒ Superplastics – a state in which a solid crystalline material is deformed well beyond its breaking point.

⇒ sintering – The process of forming a solid mass of material by heat or pressure.

NANO TECHNOLOGY

Nano means 10^{-9}. A nanometer is 1 billionth or 10^{-9} of a meter. Nanomaterials could be defined as those materials which have structured components with size less than 100nm.

$$1\text{nm}=10^{-9}\text{m}$$

Properties of Nano particles are over other materials:-

Most of properties of solid depends on size of solid. The properties of nanoscale materials are very much different from those at a larger scale. Two principal factors cause the properties of nanomaterials to differ significantly from other materials: (1). Increased surface to volume ratio and (2) quantum effects. These factors can change or enhance the properties such as reactivity, strength and electrical characteristics.

Nanoscience and nano technology

Nano technology is an emerging engineering discipline that applies methods from nanoscience to create products. The difference between nanoscience and nano technology is that between theory and practice. Nanoscience is the study of phenomena and objects at the nanoscale and nano technology deals with the ability to develop and use the technology to manipulate and observe at nanoscale. Nano science is the study of nano structures and nano technology is the application of these knowledge in different industries.

Increase in surface to volume ratio.

Nano materials have a relatively large surface area when compared to the larger form of the materials of same volume (or mass)

Let us consider a sphere of radius r

Its surface area = $4\pi r^2$

Volume = $\left(\frac{4}{3}\right)\pi r^3$

Surface area to its volume ratio = $\frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

When the radius of sphere decreases its surface area to volume ratio increases. When size decreased the surface area increases and properties like surface reactivity, catalytic activity, electrical and thermal conductivity melting point, mechanical strength, magnetic property change remarkably.

Given volume is divided into smaller pieces, the surface area increases. When particle size decreased, a greater proportion of atom are found at the surface compared to those inside.

30nm – 5% of atoms at its surface
10nm – 20% of atoms at its surface
3nm – 50% of atoms at its surface

Thus nano particles have a much greater surface area per given volume compared with larger particles. It makes material more chemically reactive as chemical reaction occurs at surfaces. In some cases materials which are chemically inert in their bulk form became reactive in their nano scale form eg. Gold. This affects their strength or electrical properties.

When gold is reduced to nanoscale, it's colour, melting point and chemical properties will change. Nanogold does not act like bulk gold. Opaque substances become transparent.

Quantum confinement effect (Reduction of dimensionality)

Quantum effects can begin to dominate the behaviour of matter at the nanoscale effecting optical, electrical and magnetic behaviour of materials. Quantum confinement is the restricted motion of randomly moving electron in specific energy levels, when the dimension of a material approaches the de-Broglie wavelength of electron. When this occurs the properties change significantly because energy levels become discrete and motion of electrons becomes restricted. Based on the number of dimension that are confined, nanostructures are classified as quantum well (nanosheet), quantum wire(nanowire), and quantum dots.

a) Nanosheets

In nanosheets confinement is present in only one dimension. That is carriers are allowed to move freely along a two dimensional plane.
Suppose the confinement is present along z direction to a small distance L_z and free to move along X and Y directions/ Schrodinger equation in this case is

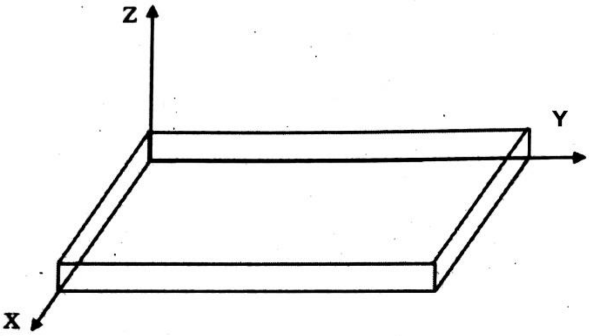
$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+V(z)\right]\psi(z)=E_z\psi(z)$$

The wavefunction and energy in this case is

$$\psi_n(x,y,z) = \left(\frac{2}{L_z}\right)^{\frac{1}{2}} sin\left(\frac{n_2\pi\, z}{L_z}\right) e^{ik\, x^x} e^{ik\, y^y}$$

$$E_n = \frac{\pi^2 n_2^2 \hbar^2}{2mL_z^2} + \frac{\hbar^2 K_x^2}{2m} + \frac{\hbar^2 K_y^2}{2m}$$

A thin layer of low bandgap semiconductor sandwiched between two layers of another semiconductor with a large bandgap is an example to this kind of confinement.



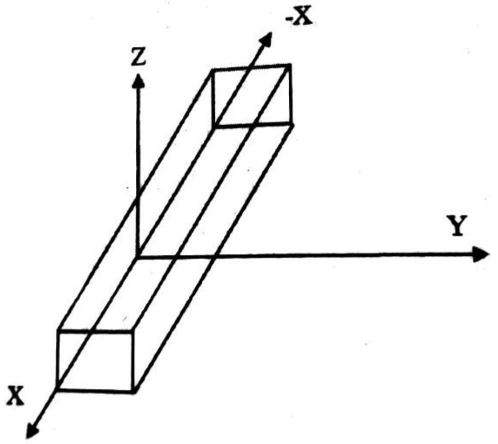
Particles can move along x and y directions freely, and confined along z direction by a small distance L_z

b) NanoWire

In a nanowire, carriers are confined in tow dimension and allowed to move freely along one diemesion. Suppose the carriers are confined in Y and Z directions to small distance L_y and L_z respectively and free to move in X direction then the wave function and energy will be.

$$\psi_n(x,y,z) = \left(\frac{2}{L_y}\right)^{\frac{1}{2}} \left(\frac{2}{L_z}\right)^{\frac{1}{2}} sin\left(\frac{n_2\pi\, y}{L_y}\right) sin\left(\frac{n_2\pi\, z}{L_z}\right) e^{ik\, x^x}$$

$$E_n = \frac{\pi^2 \hbar^2}{2m}\left[\frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] + \frac{\hbar^2 K_x^2}{2m}$$



Motion of carrier in carbon nanotube is an example for this kind of confinement

c) Quantum dot

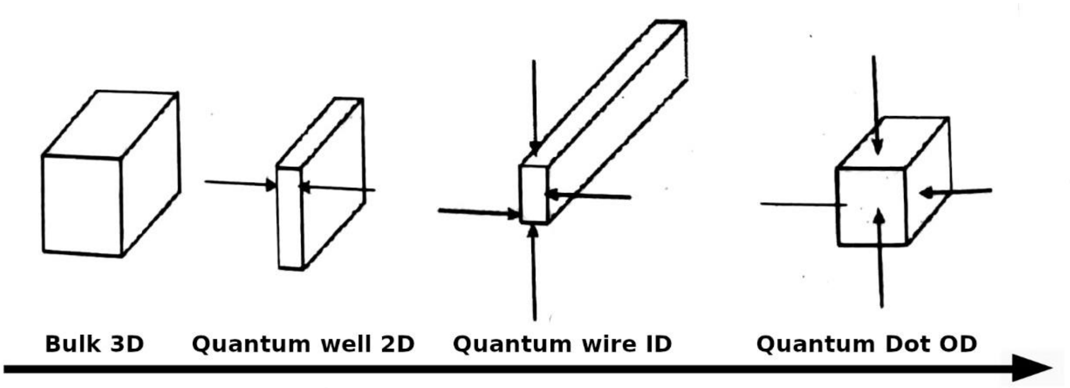
If the carriers are confined in three dimensions, then the nanostructure is called a quantum dot. In this case Schrodinger equation is

$$\frac{-\hbar^2}{2m}\nabla^2\psi\overline{(r)} + V\overline{(r)}\psi\overline{(r)} = E\psi\overline{(r)}$$

The corresponding wavefunction and energy is

$$\psi_n(x,y,z) = \left(\frac{2}{L_x}\right)^{\frac{1}{2}}\left(\frac{2}{L_y}\right)^{\frac{1}{2}}\left(\frac{2}{L_z}\right)^{\frac{1}{2}} sin\left(\frac{n_2\pi\, x}{L_x}\right) sin\left(\frac{n_2\pi\, y}{L_y}\right) sin\left(\frac{n_2\pi\, z}{L_z}\right)$$

$$E_n = \frac{\pi^2\hbar^2}{2m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$



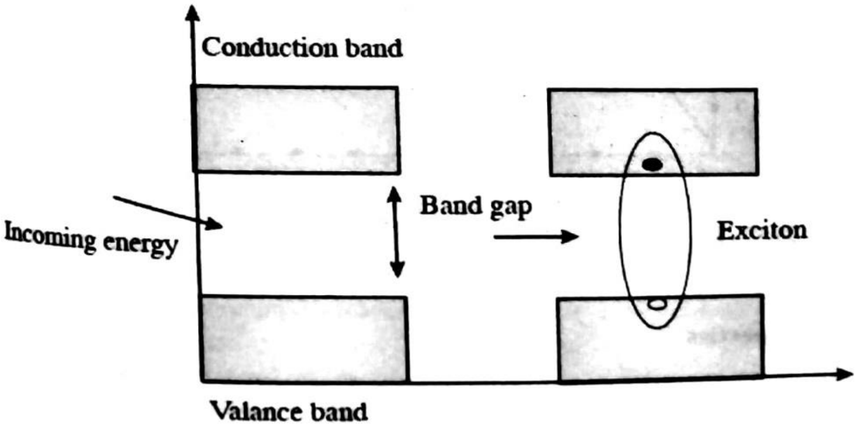
Spatial confinement

Nano particles with a fraction of nanometre to a few tens of nanometre size can be treated as example of three dimensional confinement of carriers.

Excitons

When an atom at a lattice site loses an electron, the atom acquires a positive charge and is called a hole. If the hole remains localised at the lattice site and the detached negative e electron remains in its neighbourhood, it will be attracted to the positively charged hole through coulomb interaction and can bound to form a hydrogen type atom. This bound pair of electron-hole is known as exciton.

Exciton has the properties of a particle. It is mobile and able to move around the lattice. The electron and hole forming a given exciton could be physically close to each other or separated by a few lattice spacing. The exciton radius can be taken as an index of the extent of confinement experienced by nanoparticle. For weak confinement, $d>a_{eff}$ and for strong confinement, $d<a_{eff}$ if $d>>a_{eff}$ there is no confinement. Under weak confinement condition , the exciton can undergo unrestricted translational motion and in strong confinement condition translational motion is restricted. Weakly bound electron hole pair is called mott-wannier exciton and strong bound exciton is called Frenkel exciton.



Structure	QC	Number of Free direction
Bulk solid	0	3
Quantum well / Nanosheet	1	2
Quantum wire	2	1
Quantum dot/ Nanocrystal	3	0

Properties:-

The physical, chemical, electronic and magnetic properties depend on the size of the material.

1. **Electrical properties:-**

In nanoscale electrical properties depend on size. The resistance of a material is due to the scattering of conduction electrons with vibrating atoms and impurities. The mean distance travelled between two successive collision is called mean free path and scattering length. When the dimension of solid become comparable to this quantity, the scattering probability decreases and hence electrical properties change. When its size is in the order or mean free path or deBroglie wavelength of electrons or holes which carry current, electronic structure of the system changes completely.

The change in electrical properties can not be generalized. In nano ceramic and magnetic nano composites the electrical conductivity increases with reduction in particle size and decreases in metals.

Energy of particles inside a potential box

$E_n = \frac{n^2h^2}{8mL^2}$ Where $n^2 = n_1^2 + n_2^2 + n_3^2$

In metal L = 1cm, separation between consecutive energy level is in the order of 10^{-14}eV. Ie energy levels are continuous.

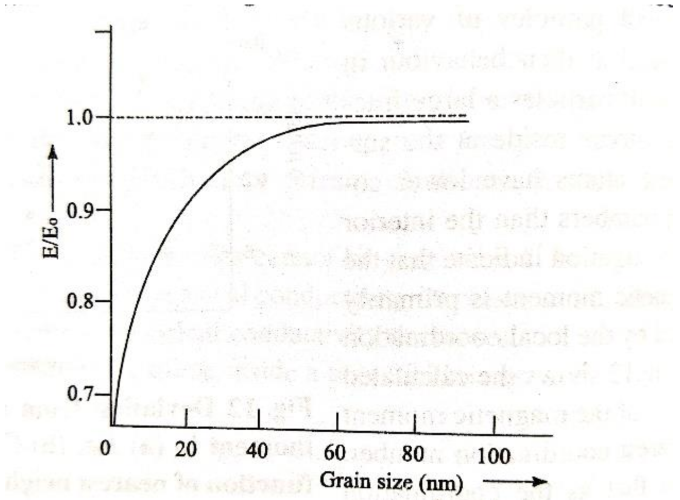
When L= 100nm, separation between energy levels is in the order of 10^{-4}eV. Thus we conclude that energy levels are discrete in nano sized materials.

2. **Optical properties:-**

Depending on particle's size, different colours are seen. Gold nanospheres of 100 nm appears orange in colour while 50nm nanosphere appear green in colour. In nano sized semiconductors particles quantum effects come in to play and optical properties are varied by controlling its size. This particle can be made to emit or absorb specific wavelength of light according to their size.

3. **Mechanical properties:-**

In nanomaterials mechanical properties like hardness, young's modules, yield strength, fracture toughness etc. show significant variation. At nanoscale, strength of metal enhances. For instance nanocrystalline nickel is as strong as hardened steel. Copper with average grain size of 6mm has five times higher micro hardness compared to a sample having grain size of 50μm. The variation of ration of young's modulus of nanocrystalline materials (E) to that of material having conventional grain size (E_o) as a function of grain size is given below



Ratio of Young's modulus of nanocrystalline materials to (E_0) of conventional grain size material as a function of grain size.

Some observations of the mechanical behaviours of nanostructured materials prepared by gas condensation method are

1. 30-50% lower elastic modulus than for conventional grain size materials
2. 2-7 times higher hardness and strength for nanocrystallines pure metals (10nm grain size)
3. Super plastic behaviours in brittle ceramic

Applications

Nano particles are "the small particles with a big future", Because of their extremely small particle size, they have extremely large specific surface area. Hence they are chemically very active. They are stronger and more ductile. They have electric state quite different from those of bulk.

1. Material Technology
   - Harder metals
   - Fillers in replacement in body part and metal -car tyres
   - Sunscreen, self cleaning windows,
   - lipsticks
   - Lubricants
2. Information Technology
   - Information storage – High density data storage

- Quantum electronic devices
- Efficient display devices
- Photonic crystals

3. Biomedical
    - Tagging of DNA and DNA chips with bio sensitive nano particles
    - controlled drug delivery
    - Bio implant material, Artificial heart valves
4. Energy storage
    - Hydrogen storage devices
    - Improved fuel efficiency
    - Fabrication of ionic batteries
    - Magnetic refrigeration.