NANOSCALE PROPERTIES

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Fundamentals of Nanoscience

Seventh Semeter

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Outline

- **Nanoscale Properties**
  - **Surface Area to Volume Ratio**
  - **Quantum Confinement Effect**
- **AuNPs as an Example for Nanoscal Properties**
- **Characteristics of Nanoscale materials**

Objectives

- To understand the different in properties between the Bulk materials and Nanomaterial.

Flash card

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Q\ Define the term of Nanostructures.

Q\ Discus some Examples of Nanostructures.

Q\ what is the relationship between Nanostructures and Nanomaterial?

Q\ what are the factors that affect the classification of Nanomaterial?

Flashpoint,

- NPs can be of different shapes, sizes, and structures. They can be spherical, cylindrical, conical, tubular, hollow core, spiral, etc., or irregular. The size of NPs can be anywhere from 1 to 100 nm. If the size of NPs gets lower than 1 nm, the term atom **clusters** is usually preferred. NPs can be crystalline with single or multi-crystal solids, or amorphous. NPs can be either loose or agglomerated.
- NPs can be uniform, or can be composed of several layers. The layers often are:
  - (a) **The surface layer**, which usually consists of a variety of small molecules, metal ions, surfactants, or polymers.
  - (b) **The shell layer**, which is made of a chemically different material from the core layer.
  - (c) **The core layer**, which is the central portion of the NP.

Nano scale Properties

- A property describes how a material acts under certain conditions.

- The prosperities of Nano scale materials are very much different from those at larger scale, due to :
  - Increase Surface Area Ratio to Volume Ratio
  - Quantum Confinement Effect
  - Surface charge/interaction, Crystallography, Composition effects

- These factors can change or improve or enhance the following properties:
  - Physical properties (hardness, melting point, diffusion rate) & chemical properties (reactivity, reaction rates)
  - Electrical properties (conductivity)
  - Optical properties (color, transparency)
  - Thermal properties (melting point)
  - Magnetic properties
  - Mechanical properties (a hundred time stronger)

- This makes materials more reactive (sometimes inert materials in larger bulk form can become reactive when produced in their tiny Nano scale)

➢ Physical properties

- Physical properties of nanoparticles are dependent on:
  - Size and Shape of the nanoparticle (spheres, rods, platelets, etc.)
  - Surface ligands or capping agents
  - Composition and Crystal Structure
  - The medium in which they are dispersed

Surface area to volume ratio,

- **Increase Surface Area to Volume Ratio,** As objects get smaller they have a much greater surface area to volume ratio.
- Nanomaterial have a relatively **larger surface area** compared to the same mass of material produced in a larger/bulk form.

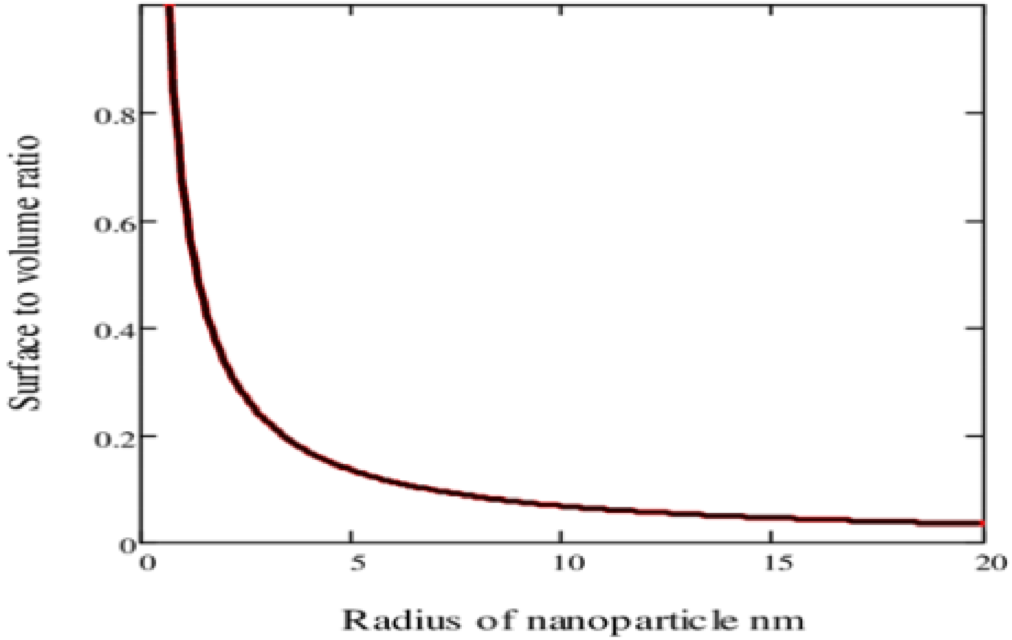
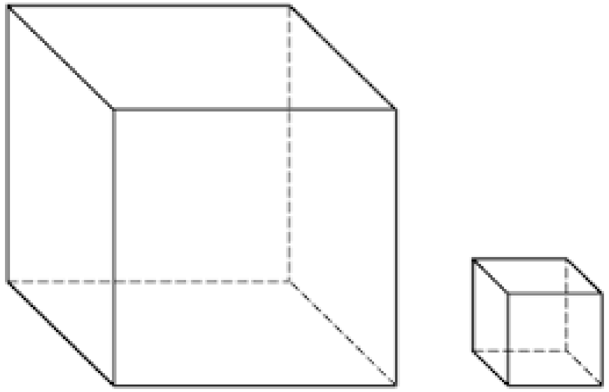


Figure: Surface Area to Volume Ratio relationship curve.

10 cm cube has a surface area of 600 cm^2 and a volume of 1000 cm^3 (ratio = 0.6:1)



2 cm cube has a surface area of 3000cm^2 and a volume of 1000cm^3 (ratio = 3:1)
note: the total number of cubes will be equal to 125 cube

Example,

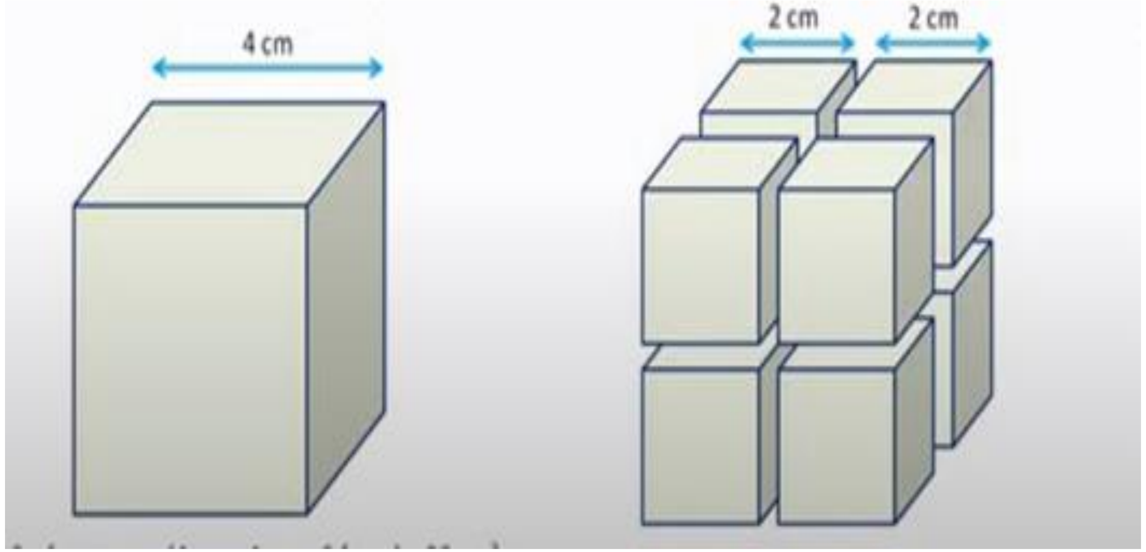
All cubes in the shown figure have the same volume, by breaking the cube in to multiple cubes the amount of surface will increase. Suppose that the arm of each cube is equal to 4cm . Find the surface area to volume ratio for each group of cubes.

Cube of 4 cm,

surface area = 4cm * 4cm* 6 faces = 96 cm^2

Volume = 4cm * 4cm * 4cm = 64 cm^3

Surface area \ volume ratio = 96\64 = 1.5:1



Cube of 2 cm,

surface area = 2cm * 2cm* 6 faces * 8 cubes = 192 cm^2

Volume = (2cm * 2cm * 2cm) * 8 cubes = 64 cm^3

Surface area \ volume ratio = 192 \64 = 3:1

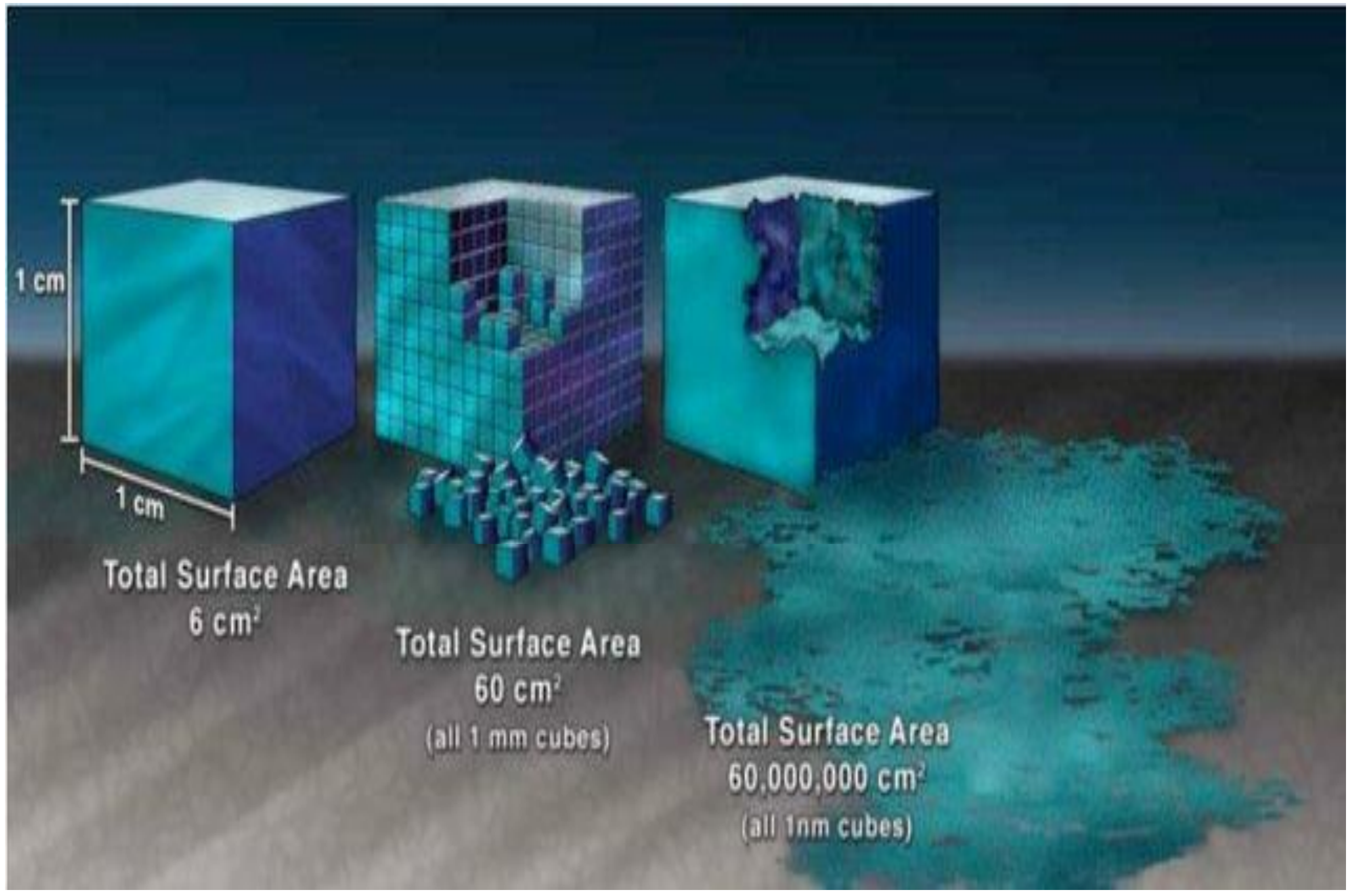
Class Activity,

- The consequence is that the surface-to-volume ratio of the material — compared to that of the parent bulk material — is increased.
- How would the total surface area increase if a cube of 1 cm were progressively cut into smaller and smaller cubes, until it is composed of 1 nm cubes?

✓ **cube of 1 cm,** surface area = 6 cm^2

✓ **cube of 1 mm,** surface area = 60 cm^2

✓ **cube of 1 nm,** surface area = 60.000.000 cm^2



➢ Thermal properties

- Melting point depression with Size,

◦ According to the nanomaterial thermal properties, the surface atoms are less constrained than interior atoms and thus can vibrate more freely about their equilibrium which result in better specific heat and thermal conductivity in nanomaterial.

◦ Also, have lower melting temperature/point.

◦ Surface atoms requires less energy to move because they are in contact with fewer atoms of the substance.

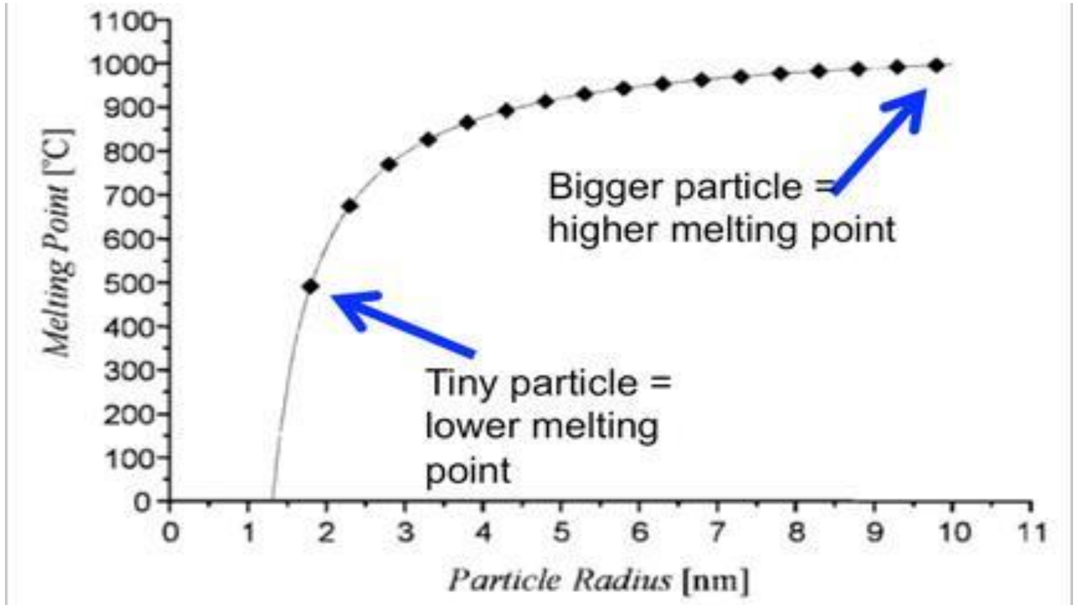


Table: Melting point\ particle radius relationship curve.

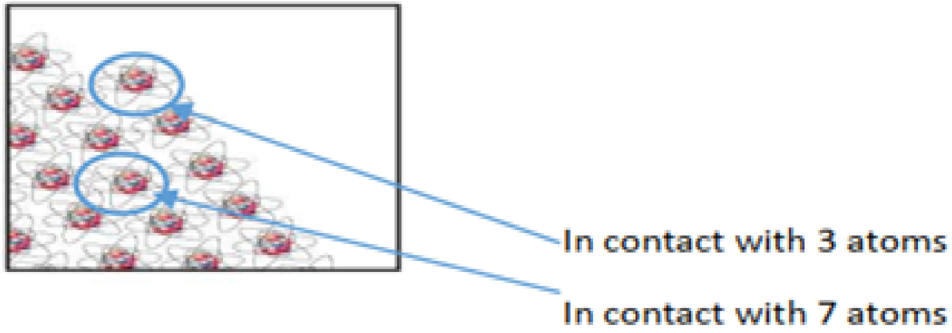
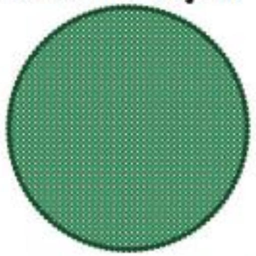


Table: surface atoms in contact with fewer atoms .

Thus,

- The total volume of a bulk material remains unchanged when it is subdivided into Nano scale materials, but the collective surface area increases. In comparison to bulk materials, this results in an increase in the surface to volume ratio at the Nano scale. The surface molecules or atoms have a high surface energy and a tendency to agglomerate.
- The melting temperature of a bulk material is not dependent on its size, but the melting point of nanomaterial decreases as the particle

	At the macroscale	At the nanoscale
The majority of the atoms are…	…almost all on the inside of the object 	…split between the inside and the surface of the object 
Changing an object's size…	…has a very small effect on the percentage of atoms on the surface	…has a big effect on the percentage of atoms on the surface
The melting point…	…doesn't depend on size	… is lower for smaller particles

➢ Electrical properties

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- Nanomaterial can increase conductivity in ceramics, ⟶ but also increase electric resistance in metal!

- Electron conduction is delocalized in bulk materials, which means electrons can move freely in all directions. When the scale is reduced to the Nano scale, the quantum effect takes over; electron delocalization occurs along the axis of nanotubes, Nano rods, and nanowires.

- Due to electron confinement, the energy bands are replaced by discrete energy states, causing conducting materials to behave as either semiconductors or insulators.
- Carbon nanotubes, for example, can be either conductors or semiconductors depending on their nanostructure.

- This is happen due to the "Quantum Phenomenon" or what is calls as Quantum size effect.

Quantum Confinement Effect,

Electrons can only exist at 'Discrete Energy Levels', where the QDs are nanomaterial that display the ***effect of quantization of energy***.

- In bulk materials electrical conductivity: Free electrons yield an energy continuum with no forbidden energy levels. The energy levels become discrete/quantized and then form bands with forbidden zones when move from bulk to nano scale.
- Hence, bulk metals are good electrical conductors. In the reverse, in Nano scale materials from the same material, the energy levels will have more forbidden zones & *reduces the electrical conductivity* of nanomaterial.
- Due to decreasing size, band-gap increases.

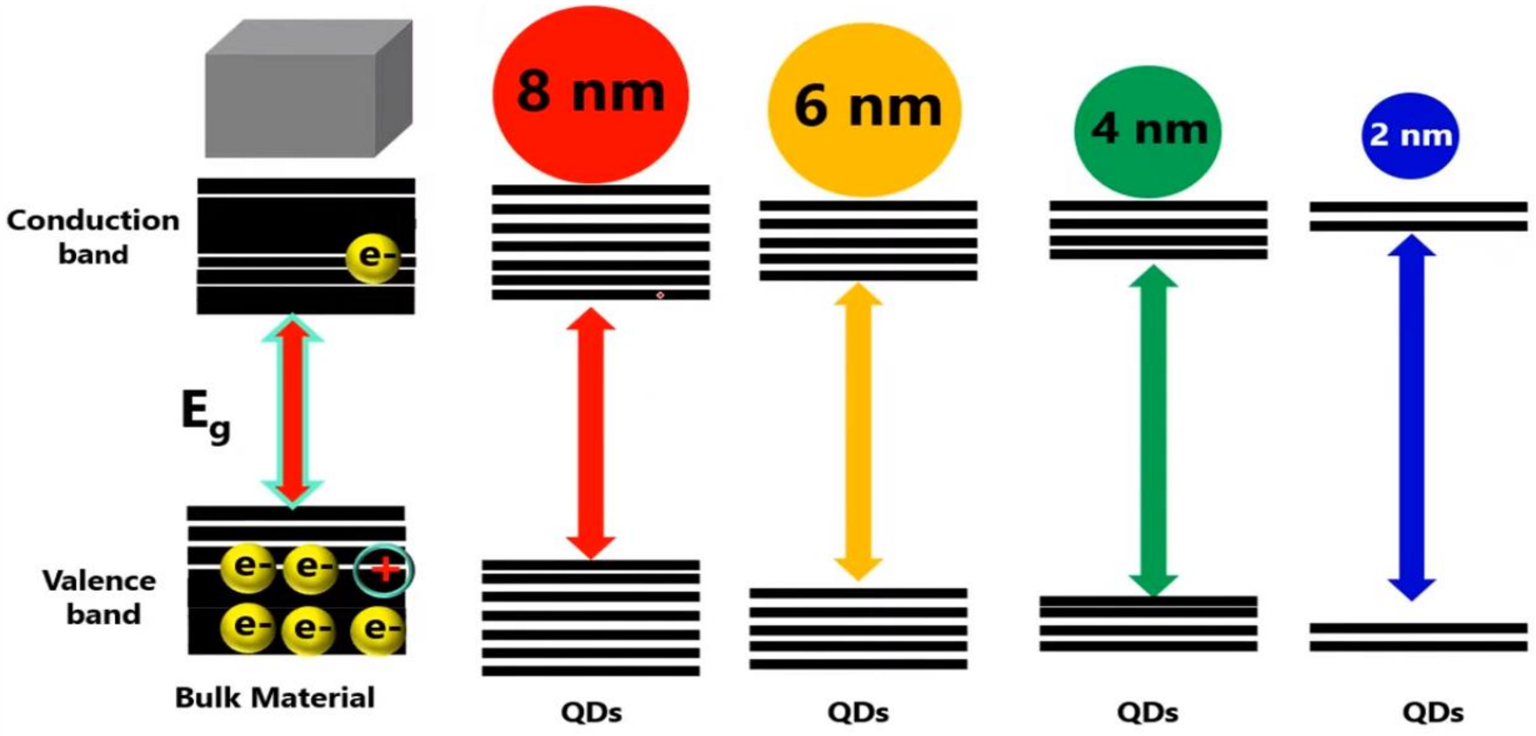

Figure: QDs and the effect of effect of quantization of energy.

- **Quantum effects**
  - The overall behavior of bulk crystalline materials changes when the dimensions are reduced to the Nano scale.
  - For 0-D nanomaterial, where all the dimensions are at the Nano scale, an electron is confined in 3D space. No electron delocalization (freedom to move) occurs.
  - For 1D nanomaterial, electron confinement occurs in 2D whereas delocalization takes place along the long axis of Nanowire, Nanorod, Nanotube.
  - In the case of 2D nanomaterial, the conduction electrons will be confined across the thickness but delocalized in the plane of the sheet.
- **Electrons confinement**
  - For 0D nanomaterial the electrons are fully confined.
  - For 3D nanomaterial the electrons are fully delocalized
  - In 1D and 2D nanomaterial, electron confinement and delocalization coexist.

  - The effect of confinement on the resulting energy states can be calculated by quantum mechanics. An electron is considered to exist inside of an infinitely deep potential well from which it cannot escape and is confined by the dimensions of the nanostructure.

Example,

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◦ **Conductivity of Nanotubes:**

- Nanotubes are long, thin cylinders of Carbon, a hundred times stronger than steel and have unique electrical properties.
- CNT electrical properties change with diameter, twisting configuration, and numbers of walls.
- They can be either conducting or semi-conducting in their electrical; behavior.

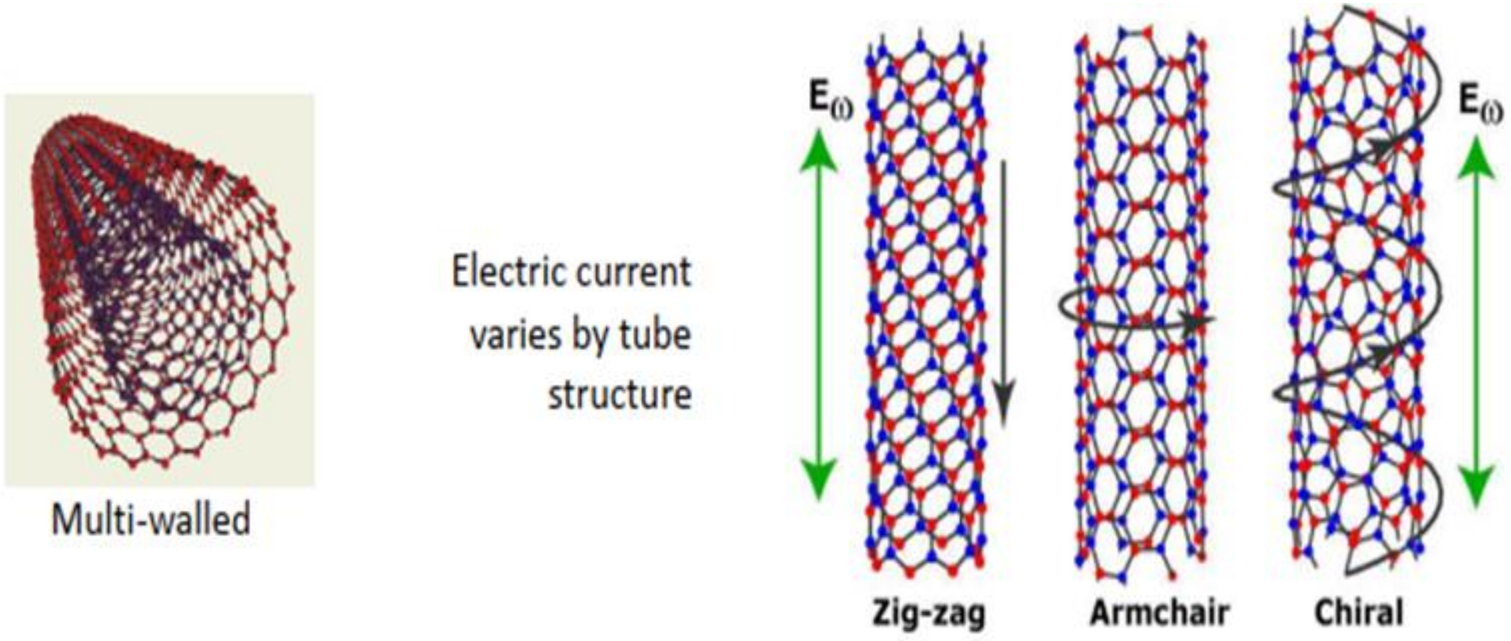
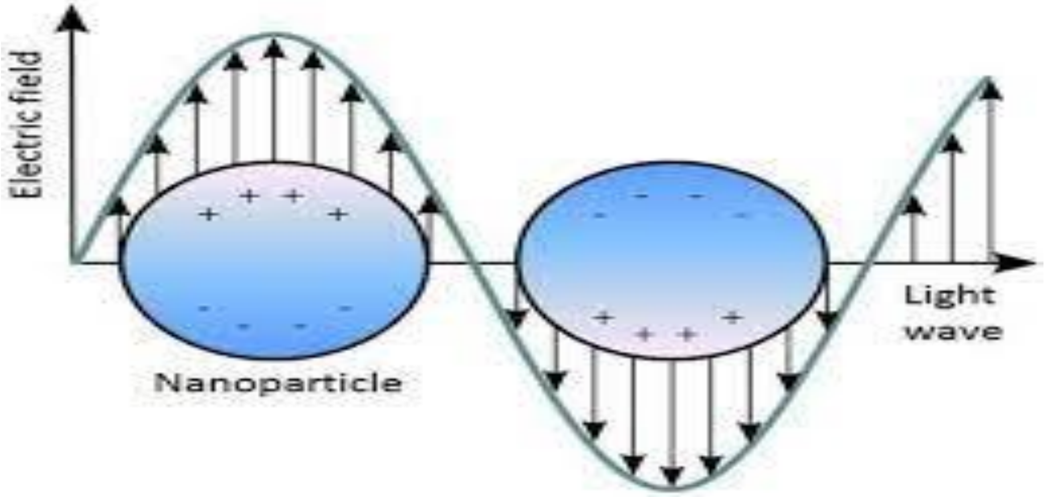


Fig.: Electrical conductivity of CNT.

➢ **Optical properties**

- QDs Nanomaterial has Optoelectronic properties (optical-electronic properties) of quantum phenomenon which is vary due to size and shape.
- THE Optoelectronic properties result in Change in Color, *Localized Surface Plasmon Resonance (LSPR)* is an optical property of nanoparticles. The line width is influenced by the size of nanoparticles. by decreasing the size of nanoparticles, the emission light position changes.



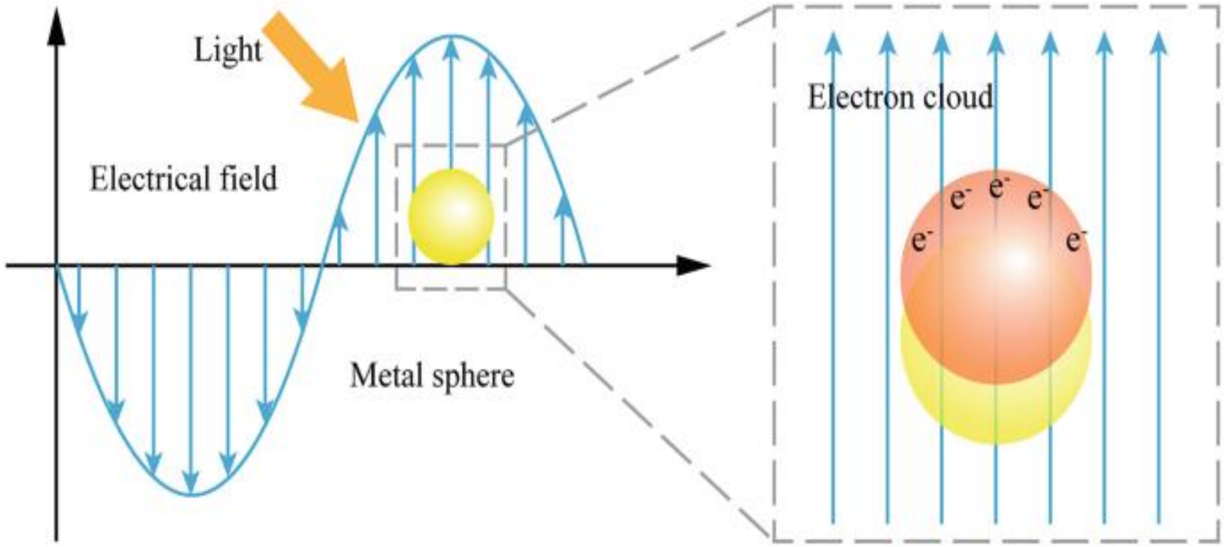
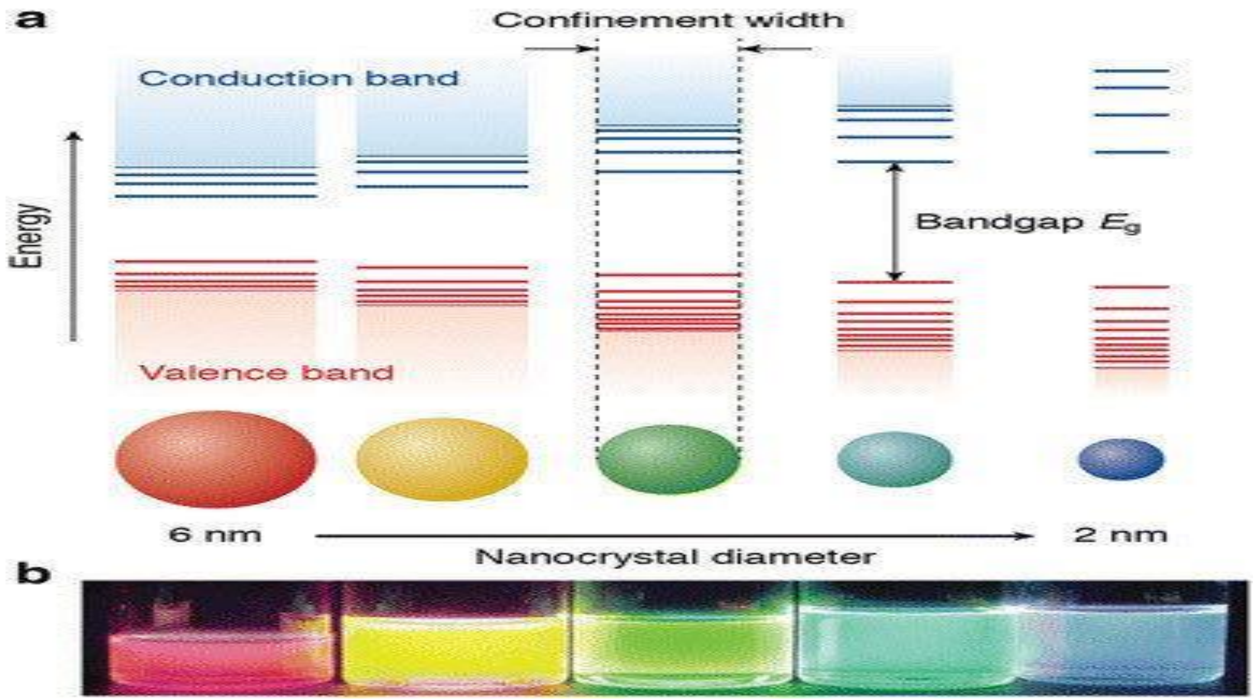
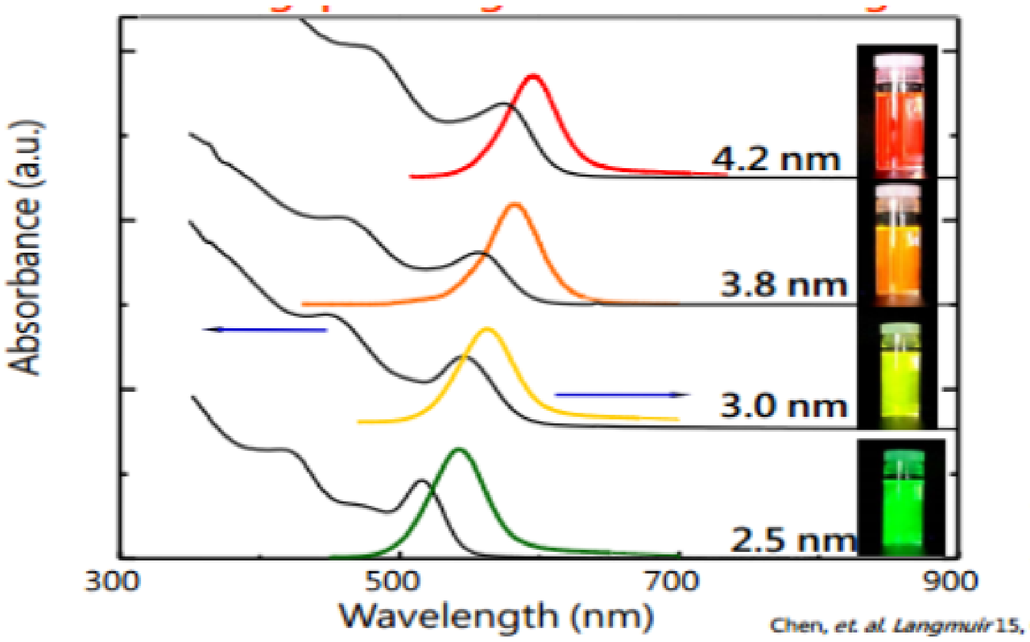


Figure: Localized Surface Plasmon Resonance (LSPR)

- Typically QDs are in the range of 2-10 nm.
- Larger QDs (5-6nm) in diameter emit longer wavelength with orange or red color. While smaller QDs (2-3nm) emit shorter wavelength, resulting blue, yellow and green colors.
- When the size of the nanomaterial decreases, the peak emission shifts toward shorter wavelengths.





Adapted from Ref.: [(15) (PDF) Excited-State Dynamics in Colloidal Semiconductor Nanocrystals (researchgate.net]

Figure: QDs Nanomaterial Optoelectronic properties diagram.

➢Magnetic properties

- The magnetic behavior of elements can change at the Nano scale because of the size of magnetic NPs. The Nano structuring of bulk magnetic materials alters the curves, resulting in soft or hard magnets with improved properties at the Nano scale.
- Nonmagnetic bulk materials can become magnetic at the Nano scale. For example, gold and platinum are non-magnetic in bulk but magnetic on the Nano scale.
- Superparamagnetic nanoparticles are not magnetic when located in a zero magnetic field, but they quickly become magnetized when an external magnetic field is applied. When returned to a zero magnetic field they quickly revert to a non-magnetized state. Which give the possibility of using such systems as magnetic memories, but also initiated the fundamental investigation of the core switching mechanism itself. They may pave the way to an alternative magnetic data storage technology.

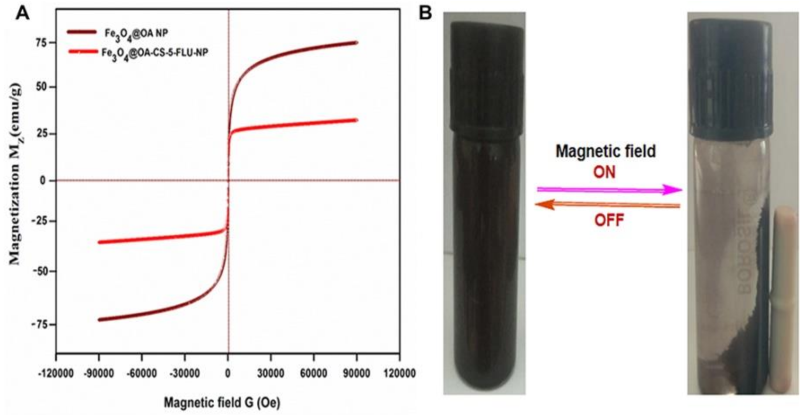


Figure: NMs Magnetic properties.

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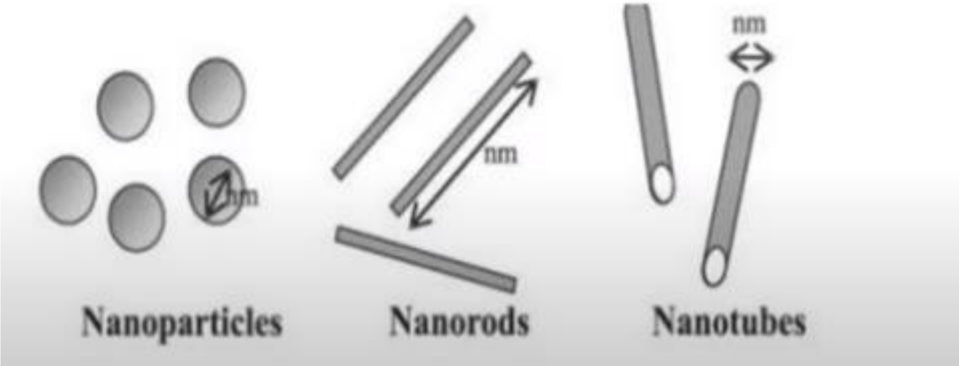
➢ **NMs Mechanical properties**

- Mechanical properties of materials depend upon the
  - composition of material,
  - bonds between atoms
  - presence of impurity.
- When the size of materials is reduced to Nano scale, material tend to be *single crystals*.

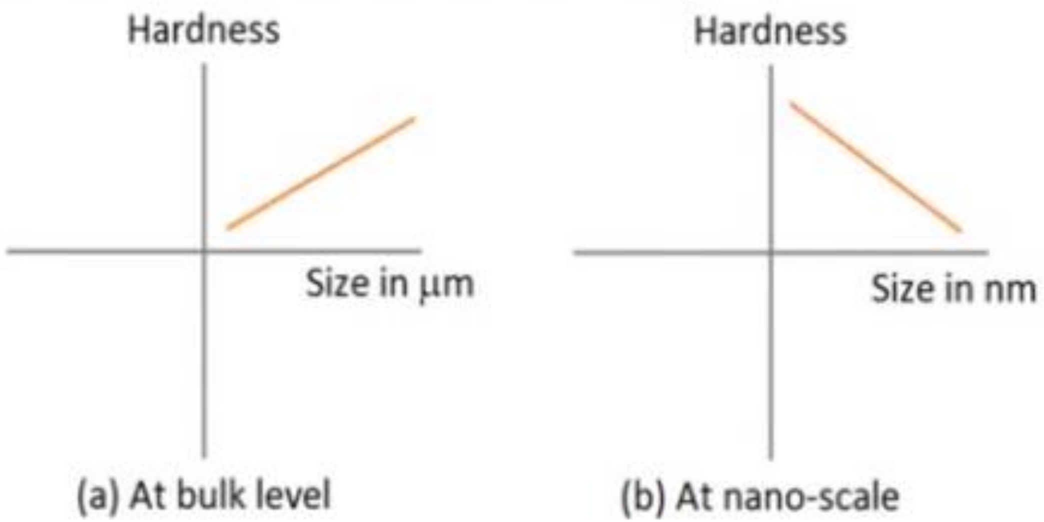
Figure: *single crystals.*



- The measurements of Elastic properties, Damping capacity, Plastic properties, Mechanical strength, Tough and Hardness increase with Light weight in NMs compared to the bulk material.

- Strength and hardness of nanostructured materials increase with decreasing grain size and grain boundary deformation. The increase in mechanical strength is simply due to a lower probability of defects and an increase in imperfection. It improved alloy hardness and toughness as well as ceramic super plasticity.
  - EX1: plastic deformation in nanocrystallind material, i.e. if stress is removed the recovery to original shape/ size is recovered more effectively.
  - Ex2:, Carbon Nanotubes are 100 times stronger than steel but six times lighter.
- The success of composite materials is that embedded particles can significantly improve the mechanical strength of the matrix.

Figure: Material hardness at Bulk level and Nano scale.



- Usage of nanomaterial in vehicles, undergo reduction in its weight, *which lead to decrease in gasoline consumption* and *reduces the cost of spacecraft launching*. Totally economy of the country will increase.

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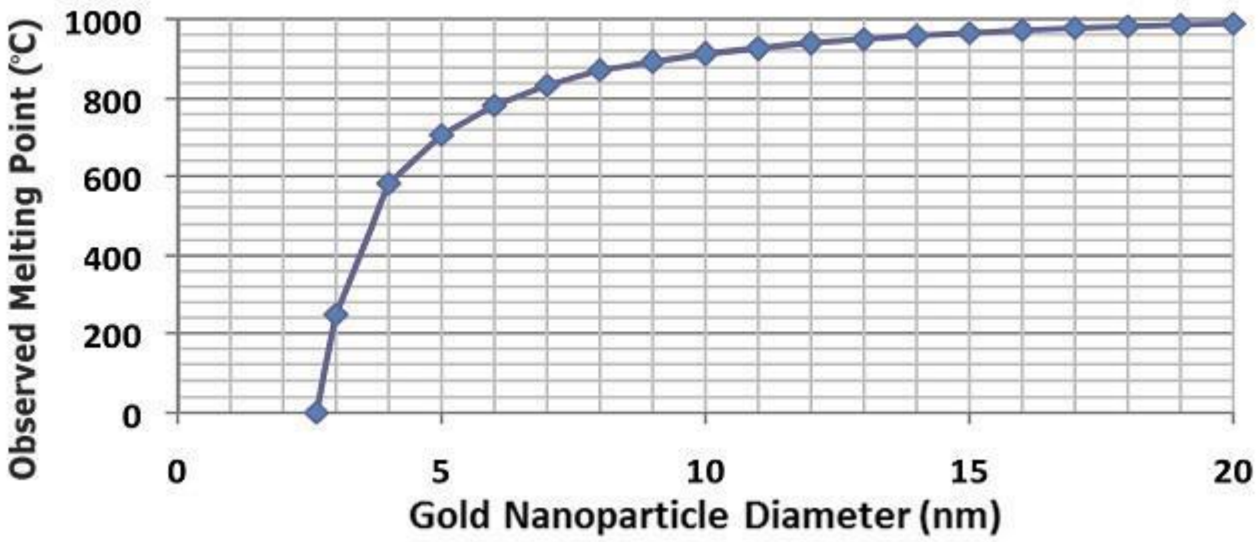
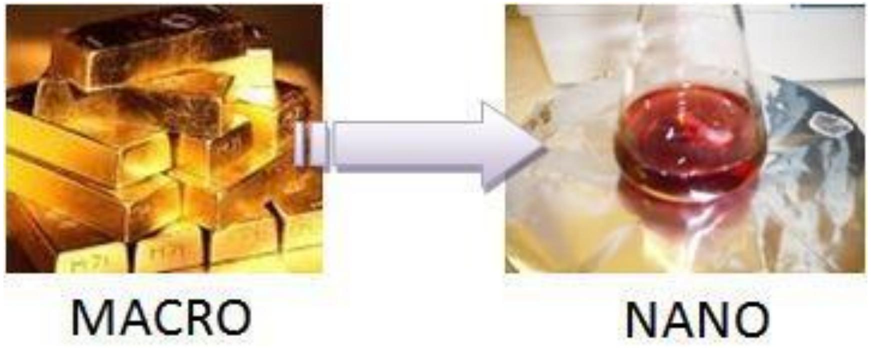
Example of the change in physical and chemical properties between gold and gold nanoparticles:





Properties	Gold (Au)	Gold Nano
Color	Yellow	Red
Electrical Conductivity	Conductive	Loses conductivity at 1-3 nm
Magnetism	Non-magnetic	Becomes magnetic at 3 nm
Chemical Reactivity	Chemically inert	Explosive and catalytic

Characteristics of Nanoscale materials

1. Fiber that is stronger than spider web
2. Metal 100 times stronger than steel and 1/6 its weight
3. Catalysts that respond more quickly and to more agents
4. Plastics that conduct electricity
5. Coatings that are nearly frictionless – (shipping industry)
6. Materials that change color and transparency on demand
7. Materials that are self repairing, self cleaning, and never need repainting
8. Nanoscale powders that are five times as light as plastic but provide the same radiation protection as metal.

Question, Why nanomaterials have different charachterstics?

Answer: Nanomaterials have different surface effects compared to micromaterials or bulk materials, mainly due to three reasons;

(a) Dispersed nanomaterials have a **very large surface area and high particle number per mass unit**

(b) The **fraction of atoms at the surface in nanomaterials is increased**

(c) The atoms situated at the surface in nanomaterials **have fewer direct neighbor**

References

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- Mekuye, B., Abera, B., (2023). Nanomaterials: An overview of synthesis, classification, characterization, and applications. *Nano select Wiely*, DOI: 10.1002/nano.202300038. Retrived From: Nanomaterials: An overview of synthesis, classification, characterization, and applications - Mekuye - 2023 - Nano Select - Wiley Online Library