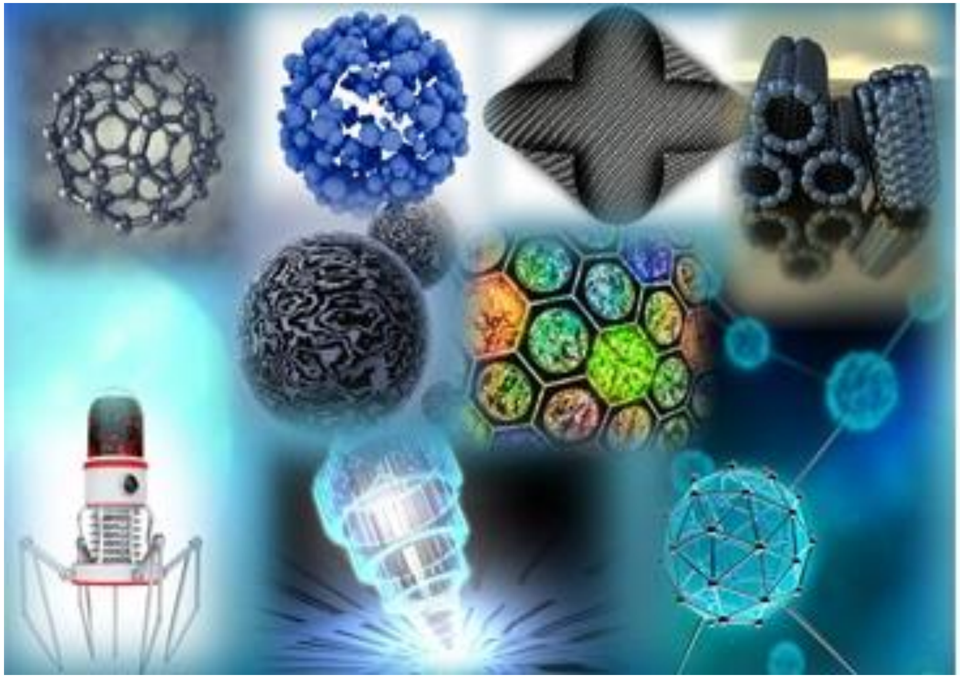
Physics of Nano



- Introduction to nanomaterials,
- Properties of nanomaterials,
- Types of nanomaterials,
- Synthesis of Nanomaterials- Top-down and Bottom-up approaches,
- Quantum confinement, Quantum well, Wire and Dot,
- Carbon Nano tubes (CNTs),
- Nanotechnology for medical and industrial applications.

Nanomaterials: Introduction

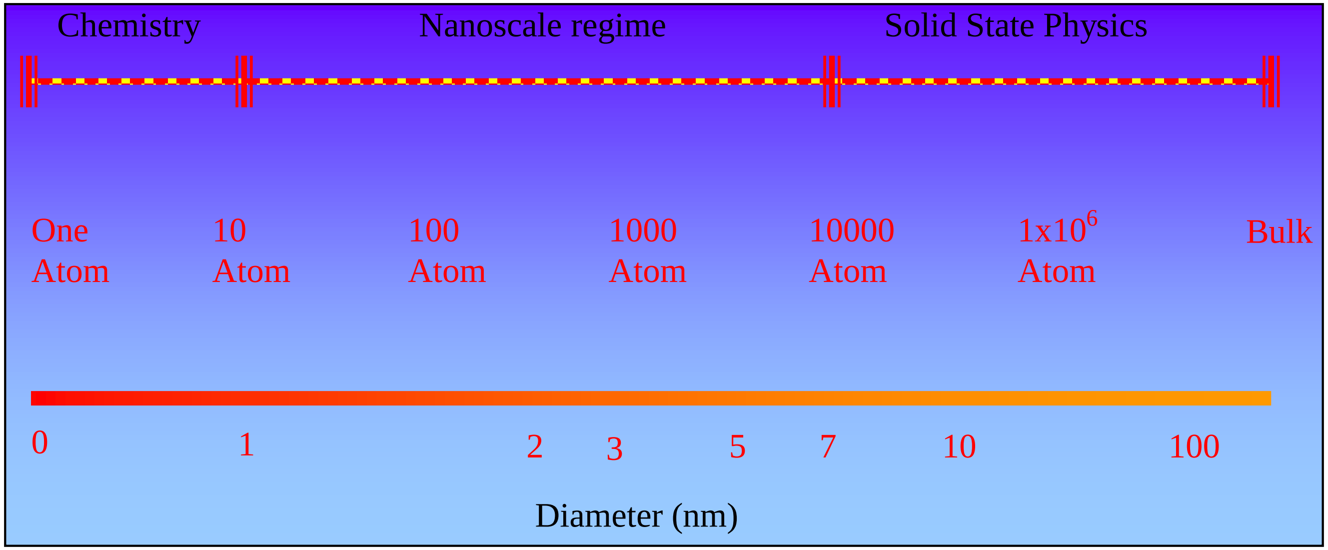
- Ultrafine microstructures of grain size of order nanometer (10^{-9}m) called nanostructured materials (NSMs).
- Currently, wider meaning,
  - Any material containing grains or clusters below 100 nm, or layers or filaments of that dimension, called as NSMs.
- Stimulated Interest in these materials owing to
  - Small size of building blocks (particle, grain, or phase)
  - High surface-to-volume ratio
- Expected to demonstrate unique
  - Mechanical
  - Optical
  - Electronic
  - Magnetic properties

Nanomaterials: Introduction

- Properties of NSMs depend on
  - **Fine grain size and size distribution** (« 100 nm)
  - **Chemical composition of constituent phases**
  - **Presence of interfaces, more specifically**
    - Grain boundaries
    - Heterophase interfaces
    - Or free surface
  - **Interactions between constituent domains**.
- Presence and interplay of these four features largely determine unique properties of NSMs

Size relationship of Chemistry, Nanoparticles and SSP

- Chem. & Phy. fields evolved in intermingled way & still inseparable in any practical sense
- Chemistry - atoms and molecules, a realm of matter whose dimensions are generally < 1 nm



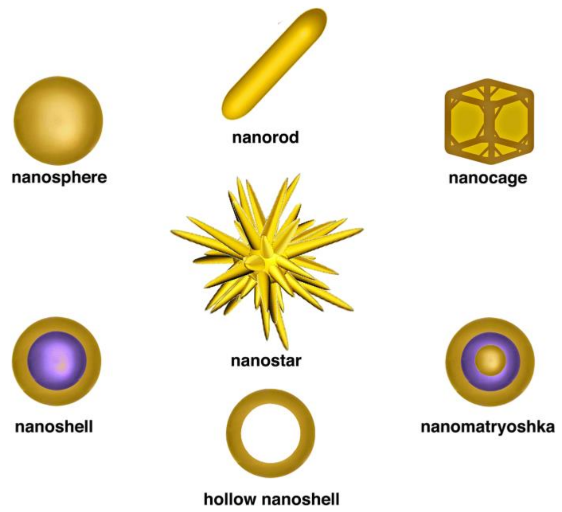
Size relationship of chemistry, nanoparticles, and solid-state physics

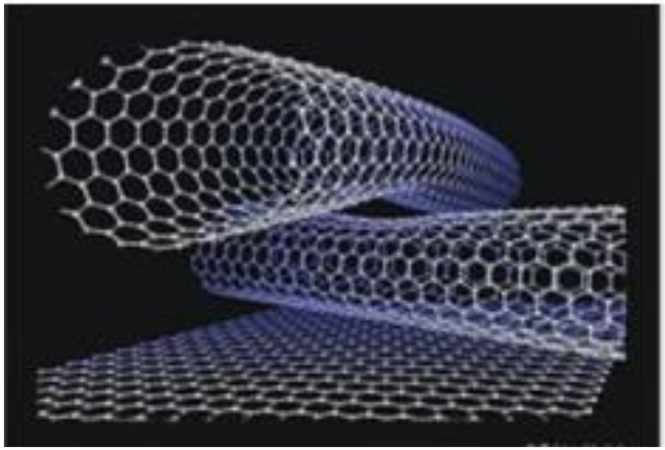
- Physics - solids essentially of infinite array of bound atoms or molecules >100 nm
- Significant gap exist between regimes of Chem. & Phy.

Nanomaterials…….

- **Natural nanomaterials**—A nanomaterial made by nature through (bio)geochemical or mechanical processes, without direct or indirect connection to a human activity or anthropogenic process.
- **Incidental nanomaterials**—A nanomaterial unintentionally produced as a result of any form of direct or indirect human influence or anthropogenic process.
- **Engineered nanomaterials**—A nanomaterial conceived, designed, and intentionally produced by humans.
- **Anthropogenic nanomaterials**—Both incidental and engineered nanomaterials.

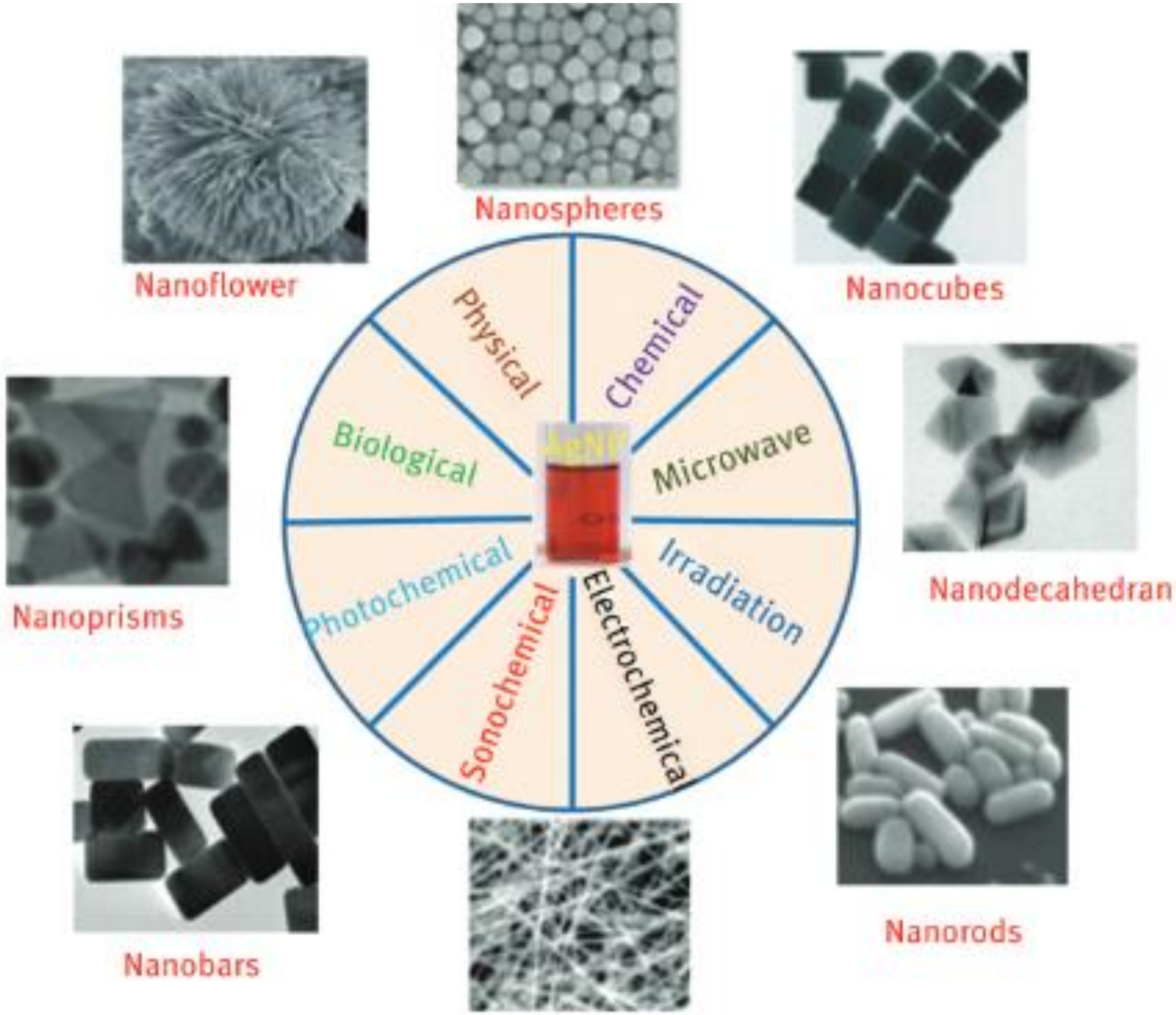
Shapes of Nanoparticles





- Nanosheets or nanofilms have one dimension in this size range; (e.g., clay minerals)
- Nanorods have two dimensions in this size range
- Nanoparticles have three dimensions in this size range
- Nanotubes are nanoscale materials that have a tube-like structure; e.g., carbon nanotubes in the accompanying figure.

Shapes of Nanoparticles



Size is a Material Property?

<u>The gold we know:</u>

Material properties don't change with size
- resistivity
- melting point
- optical absorption

<u>The gold we are discovering:</u>

Material properties (such as optical Absorption, shown here) change with the size of the gold nanoparticle.

Unique Characteristics of Nanoparticles

- Large surface to volume ratio
- High percentage of atoms/molecules on the surface
- Surface forces are very important, while bulk forces are not as important.
- Metal nanoparticles have unique light scattering properties and exhibit plasmon resonance.
- Semiconductor nanoparticles may exhibit confined energy states in their electronic band structure (e.g. quantum dots)
- Can have unique chemical and physical properties
- Same size scale as many biological structures

Examples of Unusual Properties

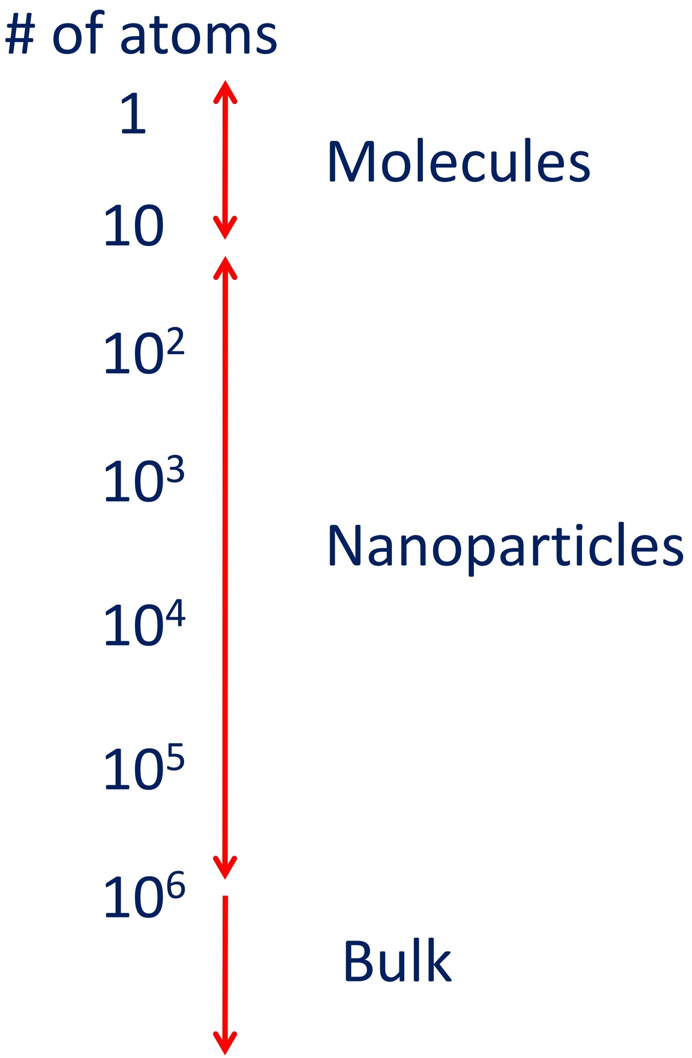
- Lowered phase transition temps
- Increased mechanical strength
- Different optical properties
- Altered electrical conductivity
- Magnetic properties
- Self-purification and self-perfection

Physical Properties of Nanoparticles

- Physical properties of nanoparticles are dependent on:
  - Size
  - Shape (spheres, rods, platelets, etc.)
  - Composition
  - Crystal Structure (FCC, BCC, etc.)
  - Surface ligands or capping agents
  - Medium in which they are dispersed

Size of Nanoparticles

- Molecules, nanoparticles, and bulk materials can be distinguished by the number of atoms comprising each type of material.
- *__Note:__* these are very approximate numbers!



Size of Nanoparticles

- Nanoparticles exhibit unique properties due to their high surface area to volume ratio.
- A spherical particle has a diameter (D) of 100nm.
  - Calculate the volume (V) and surface area (SA)

$$V = \frac{4}{3}\pi r^3 = \frac{\pi D^3}{6}$$

$$V = \frac{\pi(100 \times 10^{-9})^3}{6}$$

$$V = 5.24x10^{-22} m^3$$

$$SA = 4\pi r^2 = \pi D^2$$

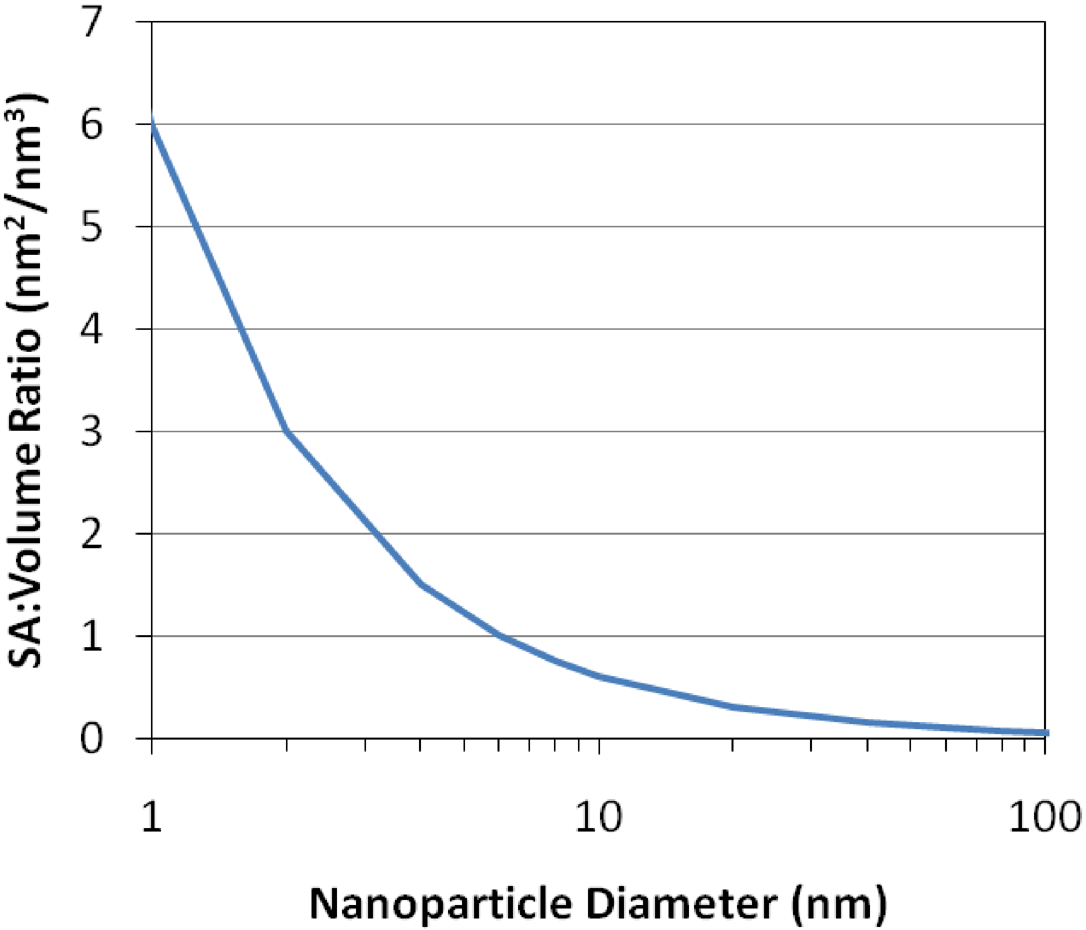
$$SA = \pi(100 \times 10^{-9})^2$$

$$SA = 3.141 \times 10^{-14} m^2$$

Surface Area: Volume Ratio

- Approximate surface area to volume ratio of $>10^7:1$
  - significantly larger than a macro sized particle.
- Increased surface area to volume ratio- increased percentage of atoms at the surface and surface forces become more dominant.
- Generally accepted material properties are derived from bulk, where the percentage of atoms at surface is miniscule.
- These properties change at the nanoscale.

Surface Area: Volume Ratio



<u>In this graph:</u>

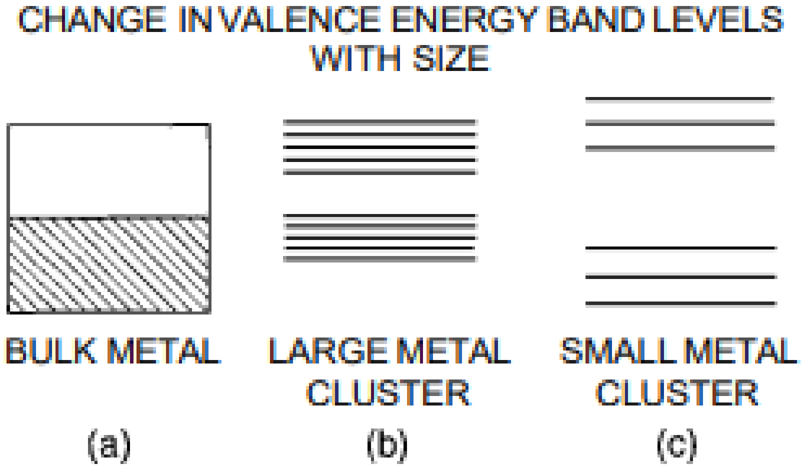
SA = nm^2

Vol = nm^3

SA:Vol Ratio = nm^2/nm^3

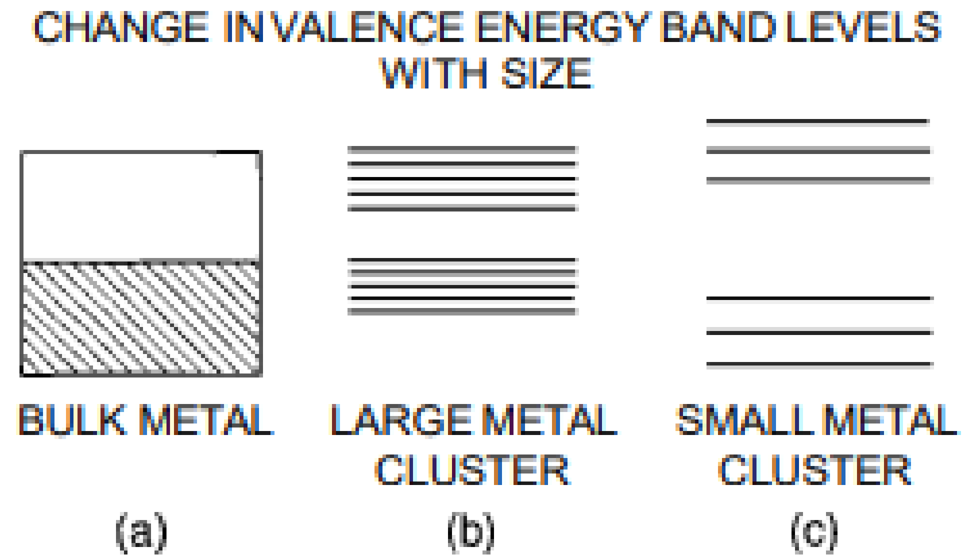
Ratio increases dramatically when nanoparticle diameter drops below about 100 nm

Electronic Structure



- When atoms form a lattice, the discrete energy levels of the atoms are smudged out into energy bands.
- **Density of states** refers to *number of energy levels in a given interval of energy*.
- When a **metal particle** having bulk properties is reduced in size to a few hundred atoms, the density of states in the conduction band containing electrons, changes dramatically.
- Continuous density of states in the band is replaced by a set of discrete energy levels, which may have energy level spacings larger than thermal energy $k_B T$, and a gap opens up.

Electronic Structure



- Small cluster is analogous to a molecule having discrete energy levels with bonding and antibonding orbitals.
- Eventually a size is reached where the surfaces of the particles are separated by distances, which are in the order of the wavelengths of the electrons.
- Energy levels can be modeled by the quantum-mechanical treatment of a particle in a box. This is referred to as the *quantum size effect*.

Electronic Structure

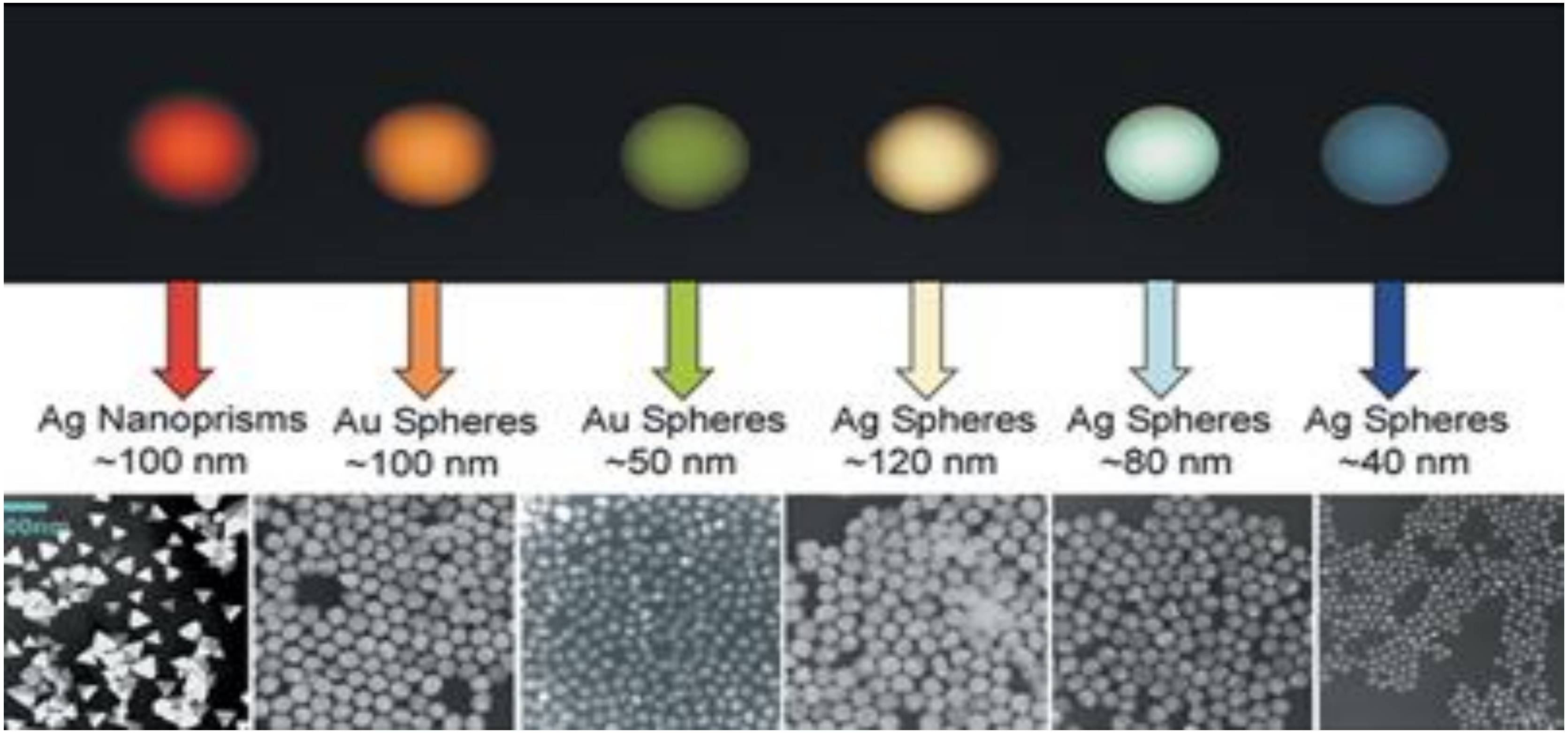
- The quantum size effect occurs in semiconductors at larger sizes because of the longer wavelength of conduction electrons and holes in semiconductors due the larger effective mass.
- In a semiconductor the wavelength can approach one micrometer, whereas in a metal it is in the order of 0.5nm.

Electronic Structure

- Color of a material is determined by wavelength of light that is absorbed by it.
- Absorption occurs because electrons are induced by photons of the incident light to make transitions between lower-lying occupied levels and higher unoccupied energy levels of materials.
- Clusters of different sizes will have different electronic structures, and different energy-level separations.
- Light-induced transitions between these levels determines the color of the materials.
- Clusters of different sizes can have different colors, and the size of the cluster can be used to engineer the color of a material.

Size of Nanoparticles

- Increased percentage of atoms at surface change mechanical, optical, electrical, chemical, and magnetic properties.
  - Ex. optical properties (color) of gold and silver change, when spatial dimensions are reduced, and concentration is changed.



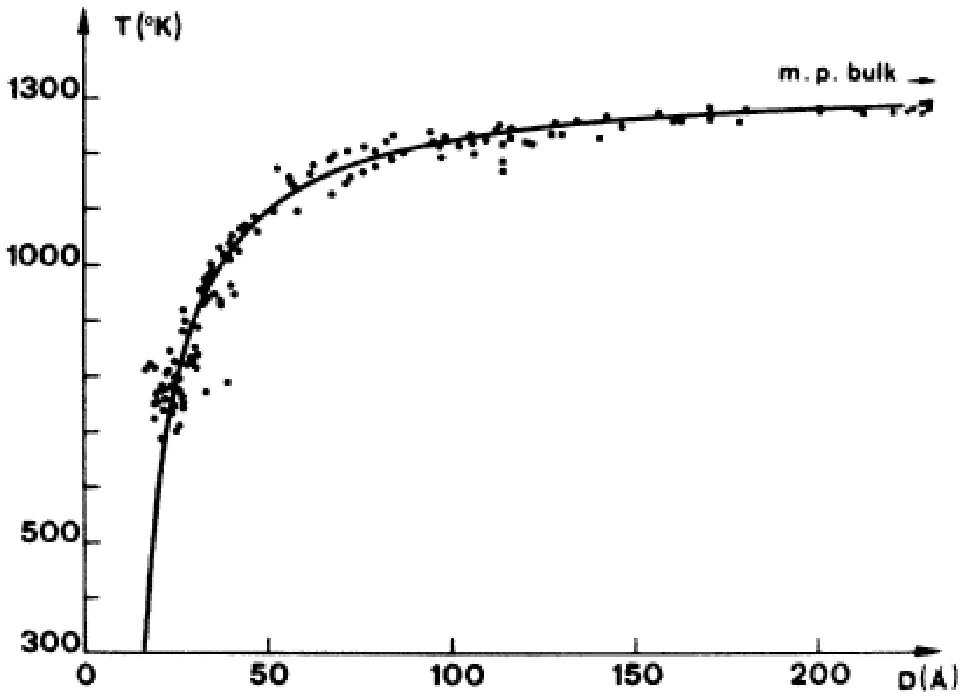
Bulk to nano transition

- In a cluster with less than 100 atoms, amount of energy needed to ionize it, that is, to remove an electron from the cluster, differs from the work function.
- *Work function is the amount of energy needed to remove an electron from the bulk solid*.
- Clusters of gold have been found to have same melting point of bulk gold only when they contain 1000 atoms or more.
- Different physical properties of clusters reach the characteristic values of solid at different cluster sizes.
- Size of the cluster where the transition to bulk behavior occurs appears to depend on the property being measured.

Size of Nanoparticles

Melting point versus particle size

- Nanoparticles have a lower melting point than their bulk counterparts



Melting point of gold nanoparticles as a function of size.

Size of Nanoparticles

Melting point versus shape

- **Particles**: May sinter together at lower-than-expected temperature.
- **Rods**: Can melt and form spherical droplets if heated too high.
- **Films**: Thin films can form pin-holes. Continued heating can lead to de-wetting behavior and island formation.

Crystal Structure

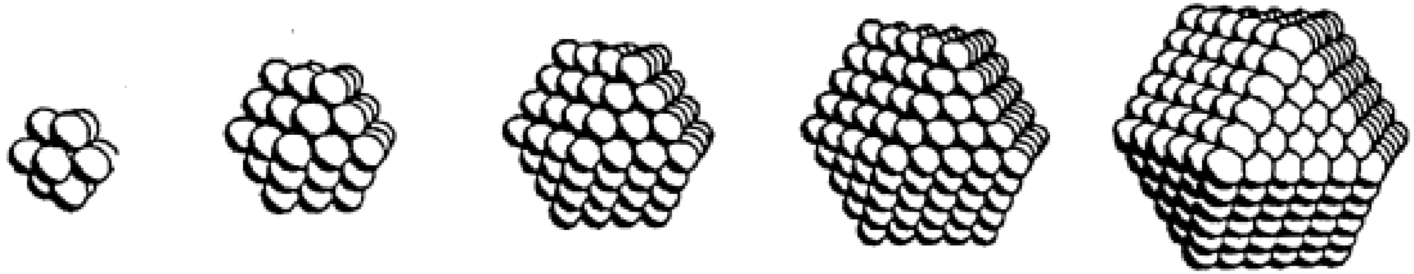
- Most solids are crystalline with their atoms arranged in a regular manner.
  - Impacts the functionality of the material.
- Some solids have this order presented over a long range as in a crystal.
- Amorphous materials such as glass and wax lack long range order, but they can have a limited short-range order, defined as the local environment that each atom experiences.

Size & Crystal Structure

- How does crystal structure impact nanoparticles?
- Nanoparticles have a "**structural magic number**", that is, the optimum number of atoms that leads to a stable configuration while maintaining a specific structure.
- **Structural magic number** = minimum volume and maximum density configuration
- If the crystal structure is known, then the number of atoms per particle can be calculated.

Close-Packed Magic Number Clusters

Full-shell "magic number" clusters



Number of shells	1	2	3	4	5
Number of atoms in cluster	13	55	147	309	561
Percentage of surface atoms	92	76	63	52	45

- Magic Number = Cluster has a complete, regular outer geometry
- Formed by successively packing layers around a single metal atom.
- Number of atoms (y) in shell (n): $y = 10n^2 + 2$ $(n = 1,2,3...)$
- Maximum number of nearest neighbors (metal-metal hcp packing)
- Decreasing percentage of surface atoms as cluster grows

Size & Crystal Structure

- For n layers, the number of atoms N in an approximately spherical FCC nanoparticle is given by :

  $N = 1/3[10n^3 – 15n^2 + 11n - 3]$

- The number of atoms on the surface N_{surf}

  $N_{Surf} = 10n^2 – 20n + 12$

Size & Crystal Structure

Number of atoms (structural magic numbers) in rare gas or metallic nanoparticles with face-centered cubic close-packed structure[a]

Shell Number	Diameter	Number of FCC Nanoparticle Atoms: Total	On Surface	% Surface
1	1*d*	1	1	100
2	3*d*	13	12	92.3
3	5*d*	55	42	76.4
4	7*d*	147	92	62.6
5	9*d*	309	162	52.4
6	11*d*	561	252	44.9
7	13*d*	923	362	39.2
8	15*d*	1415	492	34.8
9	17*d*	2057	642	31.2
10	19*d*	2869	812	28.3
11	21*d*	3871	1002	25.9
12	23*d*	5083	1212	23.8
25	49*d*	4.90×10^4	5.76×10^3	11.7
50	99*d*	4.04×10^5	2.40×10^4	5.9
75	149*d*	1.38×10^6	5.48×10^4	4.0
100	199*d*	3.28×10^6	9.80×10^4	3.0

[a]The diameters *d* in nanometers for some representative FCC atoms are Al 0.286, Ar 0.376, Au 0.288, Cu 0.256, Fe 0.248, Kr 0.400, Pb 0.350, and Pd 0.275.

Example Calculations:

How many atoms (N) are in idealized Au NP's with the following diameters?

5 nm Au NP:

With 9 shells, $n = 9$ and

NP diameter = 17d = 4.896 nm

$N = 1/3[10n^3 - 15n^2 + 11n - 3]$ N = 2057

Other Approximate Values

10 nm = 17,900

20 nm = 137,000

30 nm = 482,000

40 nm = 1.1 million

50 nm = 2.2 million

Optical Properties

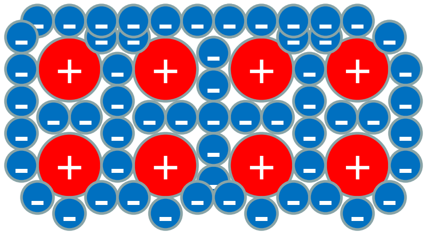
- The size dependence on the optical properties of nanoparticles is the result of two distinct phenomena:
  - Surface plasmon resonance for metals
  - Increased energy level spacing due to the confinement of delocalized energy states. Most prominent in semiconductors

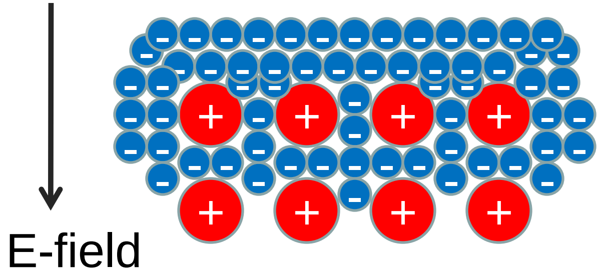
Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

Optical Properties

Surface Plasmons

- Recall that metals can be modeled as an arrangement of positive ions surrounded by a sea of *free electrons*.
- The sea of electrons behaves like a fluid and will move under the influence of an electric field

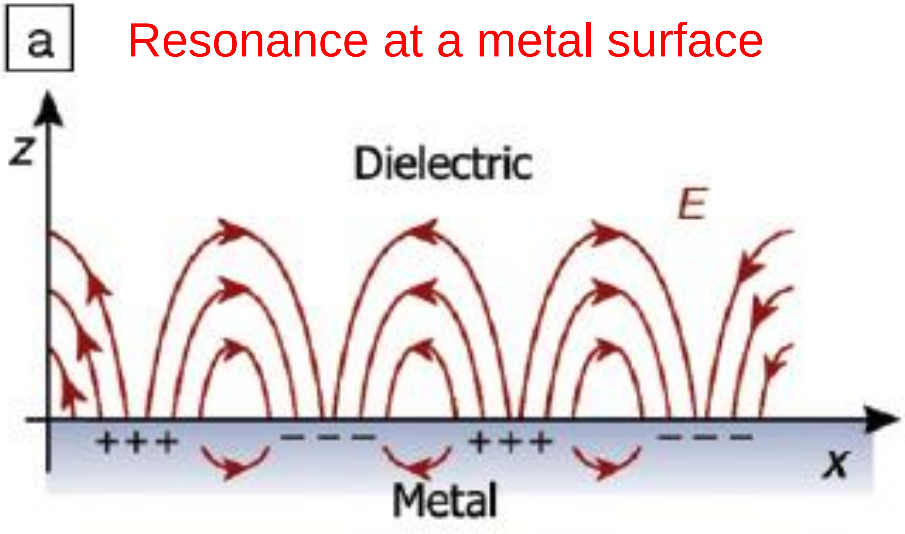


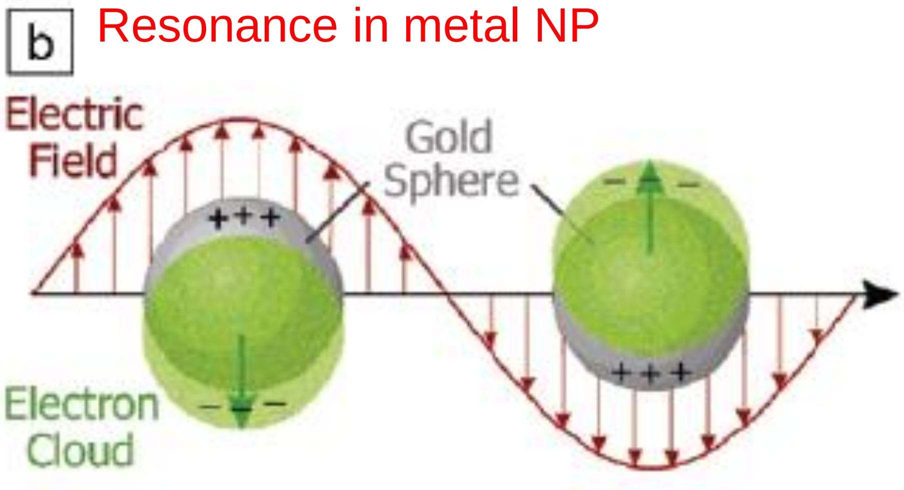


Optical Properties

Surface Plasmons

- If the electric field is oscillating (like a photon), then the sea of electrons will oscillate too.
- These oscillations are quantized and resonate at a specific frequency. Such oscillations are called **plasmons**.





Source: MRS Bulletin 2005, 30(5), 338.

Optical Properties

Surface Plasmons

- Formal definition: Plasmons are the coherent excitation of *free electrons* in a metal.
- The plasmon resonance frequency (f) depends on particle size, shape, and material type.
- It is related to the plasmon energy (E) by Planck's constant. $E = h*f$
- Surface plasmons are confined to the surface of the material.
- *Optical properties of metal nanoparticles are dominated by the interaction of surface plasmons with incident photons.*

Optical Properties

Surface Plasmons

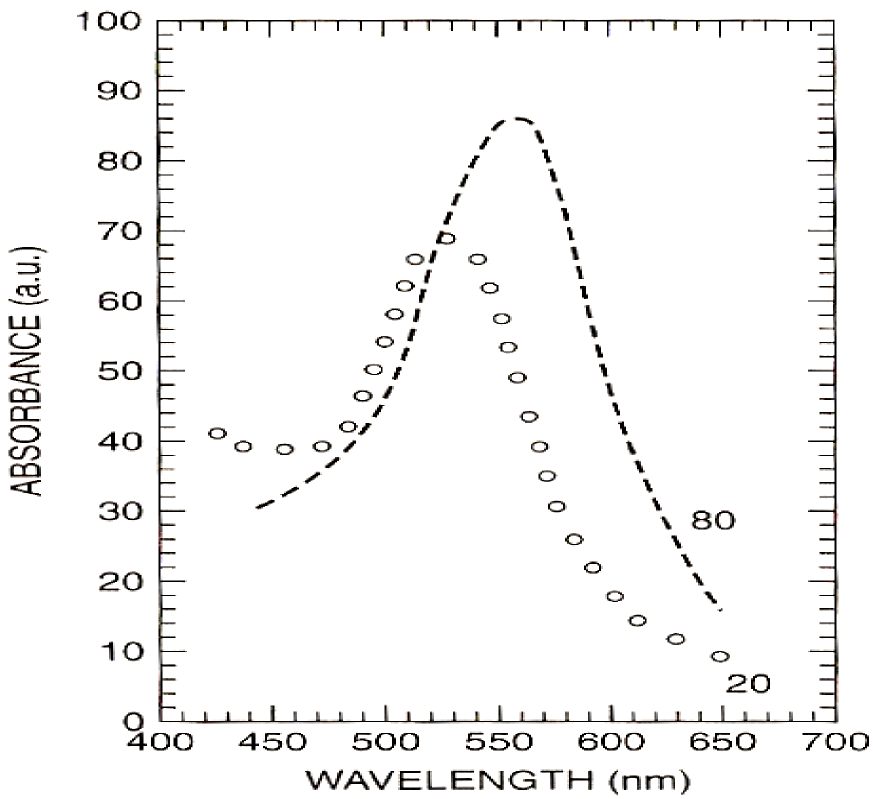
- Metal nanoparticles like gold and silver have plasmon frequencies in the visible range.

- When white light impinges on metal nanoparticles the wavelength corresponding to the plasmon frequency is absorbed.

- *The spectral locations, strengths, and number of plasmon resonances for a given particle depend on the particle's shape and size.*

Optical Properties

- Absorption spectra of spherical Au nanoparticles

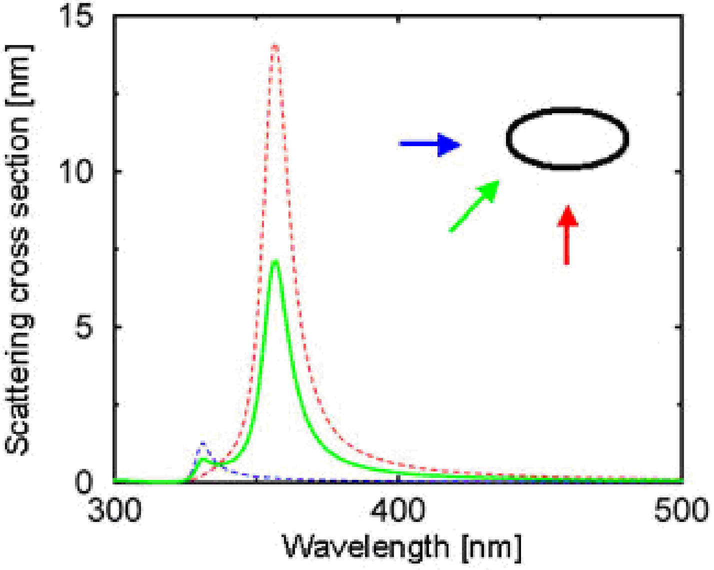


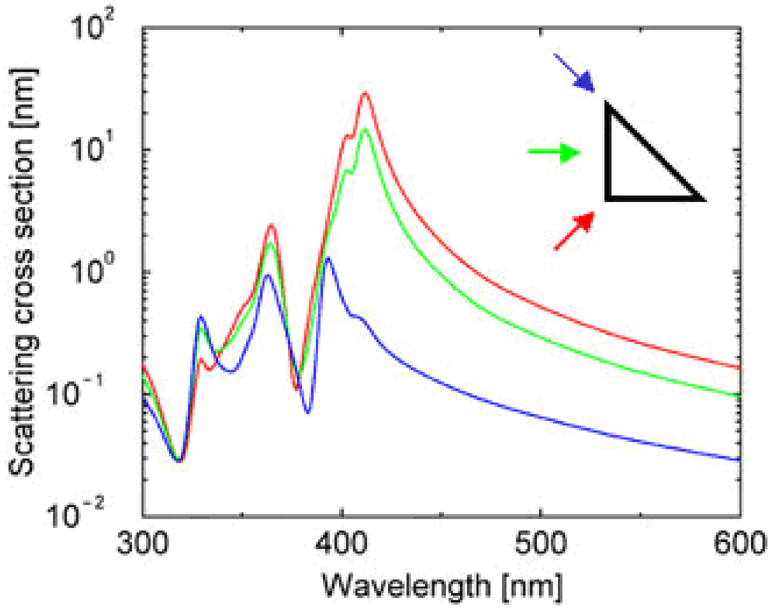
Optical absorption spectrum of 20- and 80-nm gold nanoparticles embedded in glass.
[Adapted from F. Gonella et al., in *Handbook of Nanostructured Material and Nanotechnology*, H. S. Nalwa, ed., Academic Press, San Diego, 2000, Vol. 4, Chapter 2, p.85.]

Optical Properties

Surface Plasmons: Shape dependence of absorption spectra

- Amount of light that is scattered into the far field is described by the *scattering cross section (SCS).*
- SCS is plotted against wavelength of light used to illuminate a particle from a specific angle.
- Arrows indicate the illumination angle, and their colors correspond to the different plot lines.

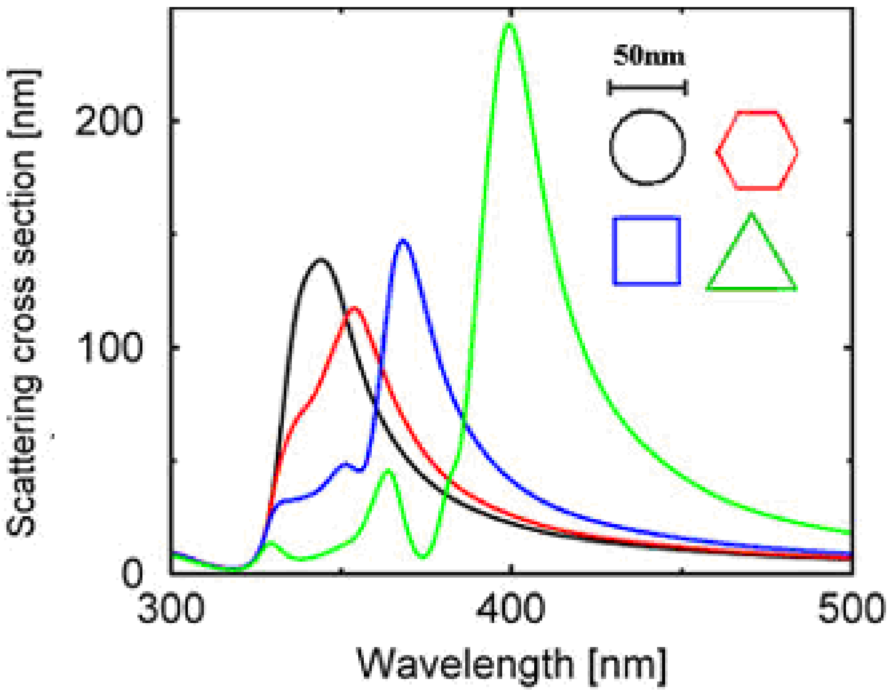




Martin, Olivier J.F. "Spectral response of plasmon resonant nanoparticles with non-regular shape". Optics Express Col. 6. No. 11 May 2000

Optical Properties

Surface Plasmons: Shape dependence of absorption spectra



Martin, Olivier J.F. "Plasmons". Plasmons. 22 Mar. 2006. Ecole Polytechnique Fédérale de Lausanne. 26 Jan. 2003.

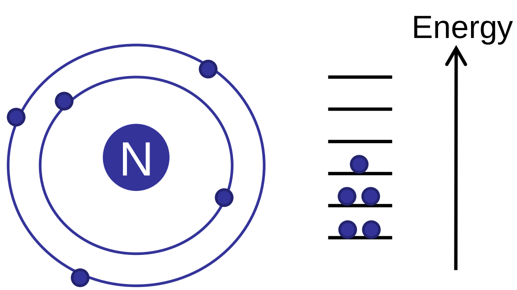
- Triangular shaped nanoparticles produce plasmons with altered frequency and magnitude

Optical Properties

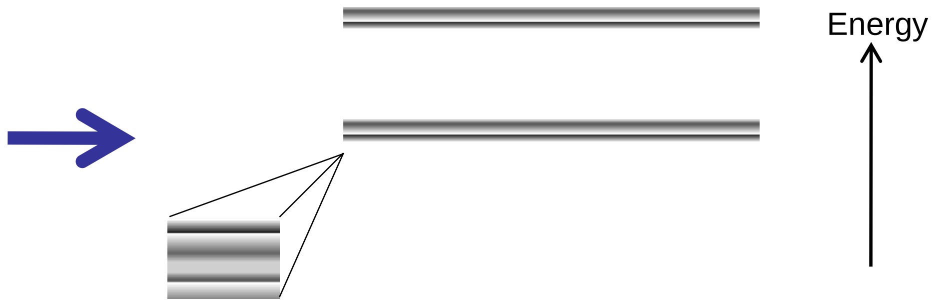
Energy levels: from atoms to bulk materials…

- The Pauli Exclusion Principle states that electrons can only exist in unique, discrete energy states.
- In an atom the energy states couple together through spin-orbit interactions to form the energy levels.
- When atoms are brought together in a bulk material, the energy states form nearly continuous bands of states, or in semiconductors and insulators, nearly continuous bands separated by an energy gap.

Atoms: Discrete Energy Levels



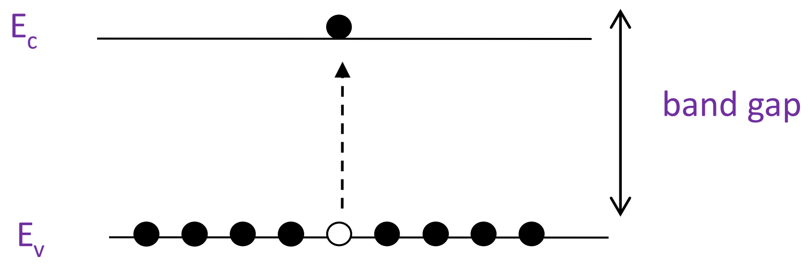
Bulk Materials: Band Structures



Optical Properties

Energy levels

- In semiconductors and insulators, the **valance band** corresponds to the ground states of the valance electrons.
- In semiconductors and insulators, the **conduction band** corresponds to excited states where electrons are a free to move about in the material and participate in conduction.
- In order for conduction to take place in a semiconductor, electrons must be excited out of the valance band, across the **band gap** into the conduction band. This process is called **carrier generation**.
- Conduction takes place due to the empty states in the valence band (holes) and electrons in the conduction band.



Electron excited into conduction band

Optical Properties

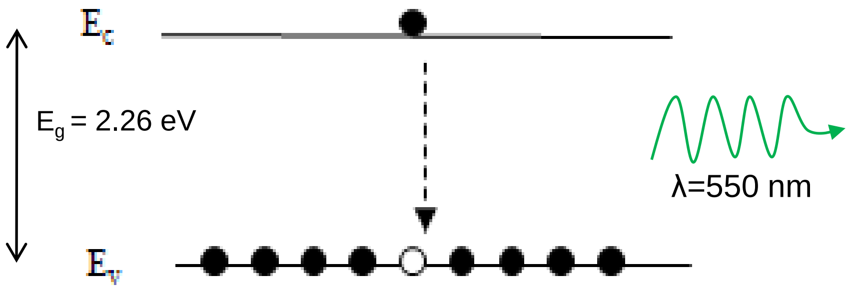
Energy level spacing

- In semiconductors and insulators, a photon with an energy equal to the band gap energy is emitted when an electron in the conduction band recombines with a hole in the valance band.
- The electronic band structure of a semiconductor dictates its optical properties.
- GaP, a material commonly used for green LEDs, has an intrinsic band gap of 2.26 eV. Carrier recombination across the gap results in the emission of 550 nm light.

$$E = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{E}$$

$$\lambda = \frac{(4.136 * 10^{-15}\ \text{eV} \cdot \text{s})(2.998 * 10^{8}\ \text{m/s})}{2.26\ \text{eV}}$$

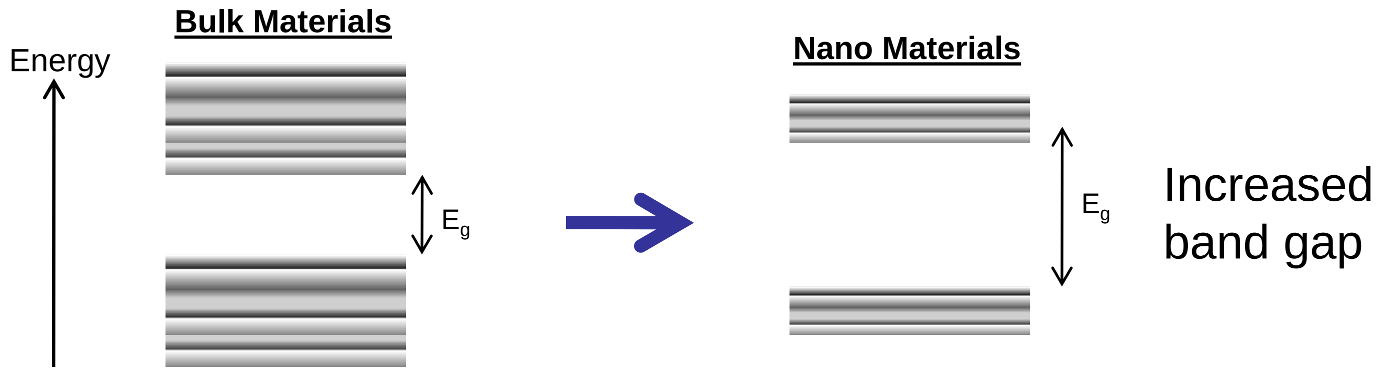
$$\lambda \cong 550\ \text{nm}$$



Optical Properties

Energy level spacing and quantum confinement

- The reduction in the number of atoms in a material results in the confinement of normally delocalized energy states.
- Electron-hole pairs become spatially confined when the dimensions of a nanoparticle approach the de Broglie wavelength of electrons in the conduction band.
- As a result the spacing between energy bands of semiconductor or insulator is **increased** (Similar to the *particle in a box* scenario, of introductory quantum mechanics.)



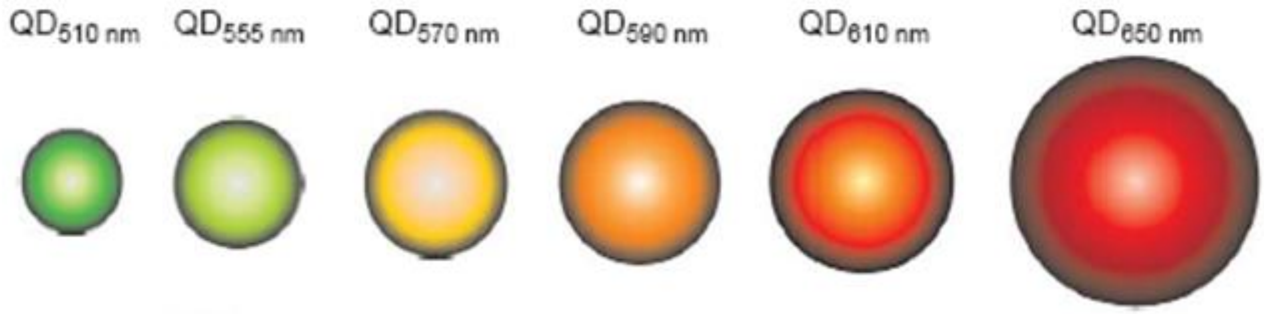
Optical Properties

Energy level spacing and quantum confinement

- Semiconductor nanoparticles that exhibit 3 dimensional confinement in their electronic band structure are called **quantum dots.**
- What does this all mean?
    - **Quantum dots are band gap tunable.**
    - We can engineer their optical properties by controlling their size.
    - For this reason quantum dots are highly desirable for biological tagging.

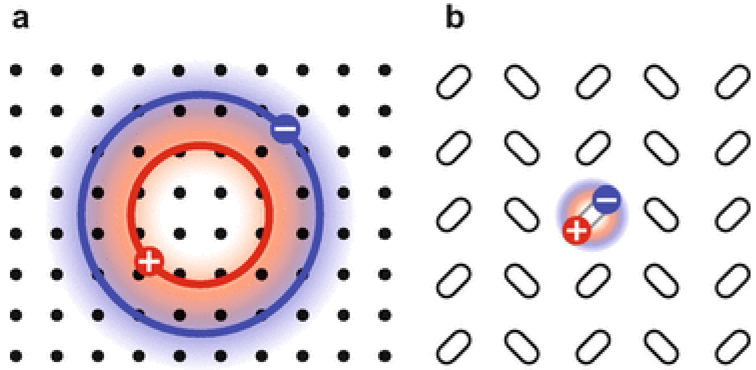
Optical Properties

- Energy level spacing and quantum confinement
  - As semiconductor particle size is reduced the band gap is increased.
  - Absorbance and luminescence spectra are blue shifted with decreasing particle size.



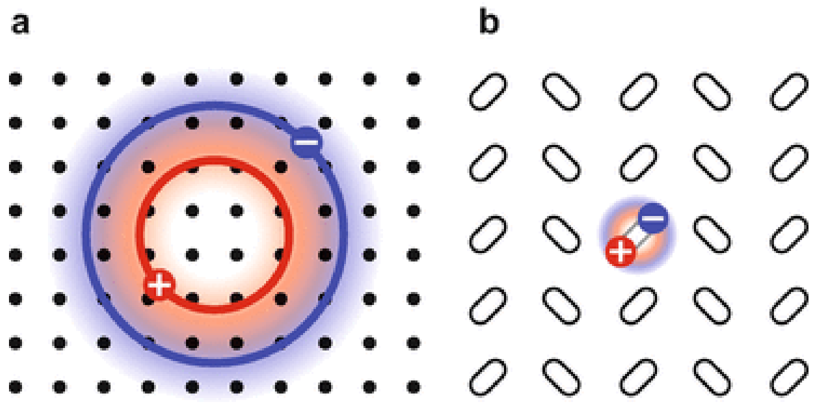
Jyoti K. Jaiswal and Sanford M. Simon. **Potentials and pitfalls of fluorescent quantum dots for biological imaging.** TRENDS in Cell Biology Vol.14 No.9 September 2004

Semiconducting nanoparticle-optical properties



- In a bulk semiconductor *a bound electron-hole pair, called an exciton*, can be produced by a photon having an energy greater than that of the band gap of the material.
- Photon excites an electron from filled band to unfilled band above.
- Result is a hole in filled valence band, which corresponds to an electron with an effective positive charge.
- Because of the Coulomb attraction between hole and electron, a bound pair, called an exciton, is formed that can move through lattice.
- Separation between hole and electron is many lattice parameters.
- Existence of exciton has a strong influence on the electronic properties of the semiconductor and its optical absorption.

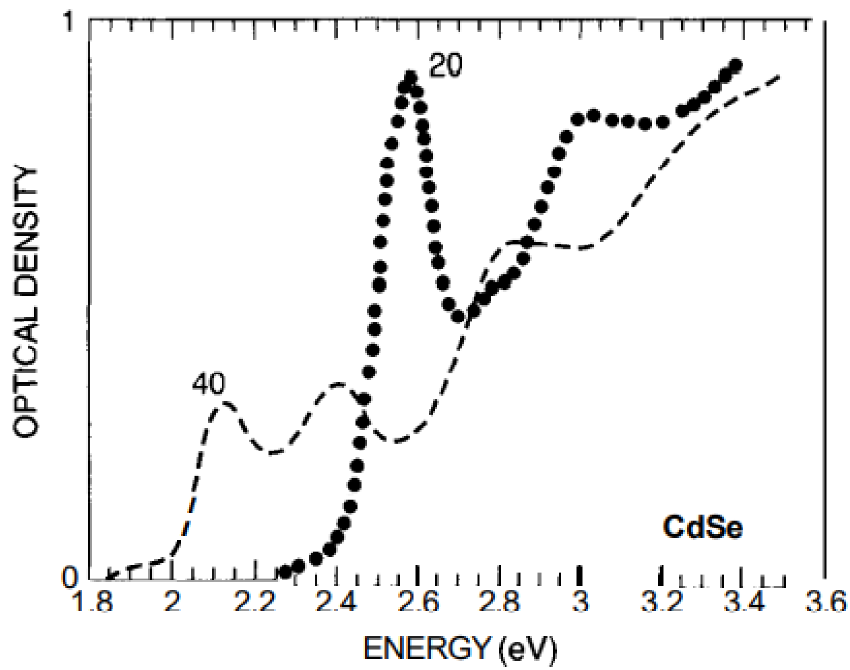
Semiconducting nanoparticle-optical properties



- When nanoparticle becomes smaller than or comparable to the radius of orbit of the electron-hole pair, there are two situations, called the ***weak-confinement and strong-confinement regimes***.
- In weak regime, particle radius is **larger** than radius of electron-hole pair, however range of motion of the exciton is limited, which causes a blue shift of the absorption spectrum.
- When the radius of the particle is **smaller** than the orbital radius of the electron-hole pair, the motion of the electron and the hole become independent, and the exciton does not exist.
- The hole and electron have their own set of energy levels.
- There is also a blue shift, and the emergence of a new set of absorption lines.

Semiconducting nanoparticle-optical properties

- Lowest energy absorption region, absorption edge, is shifted to higher energy as the particle size decreases.
- Since the absorption edge is due to the band gap, the band gap increases as particle size decreases.
- Intensity of absorption increases as particle size is reduced.
- Higher energy peaks are associated with the exciton, and they shift to higher energies with the decrease in particle size.



Optical absorption spectrum of CdSe for two nanoparticles having sizes 20A and 40A, respectively. [D. M. Mittleman, Phys. Rev. B49, 14435 (1994).]

As the particle size is reduced, hole and electron are forced closer together, and separation between the energy levels changes.

Nanoparticles: Synthesis

Approaches – Physical and Chemical

- **Physical**
- Bottom up - Controlling aggregation
  - Vaporize metals or oxides
    - Resistive heating from crucible
    - Electron beam heating
    - Laser pulses
- Top down – Deformation of coarser materials
  - High energy ball-mill
  - High-energy shear process
  - Very useful in generating commercial quantities of material
  - suffers from the disadvantage of contamination

Nanoparticles: Synthesis

Thin film deposition techniques can be put as follows:

1. Physical Methods (Bottom up)

Physical Vapor Deposition (using different heating techniques)

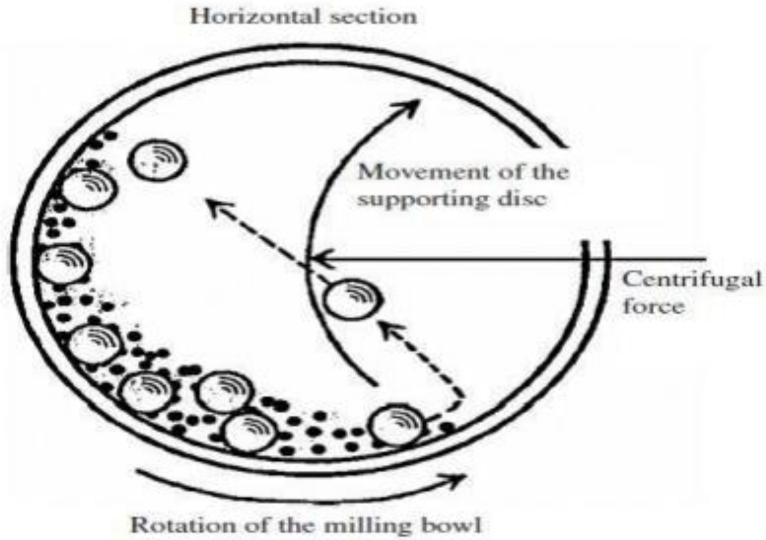
- Resistive heating
- Laser heating
- Electron beam heating
- Induction heating

2. Chemical Methods

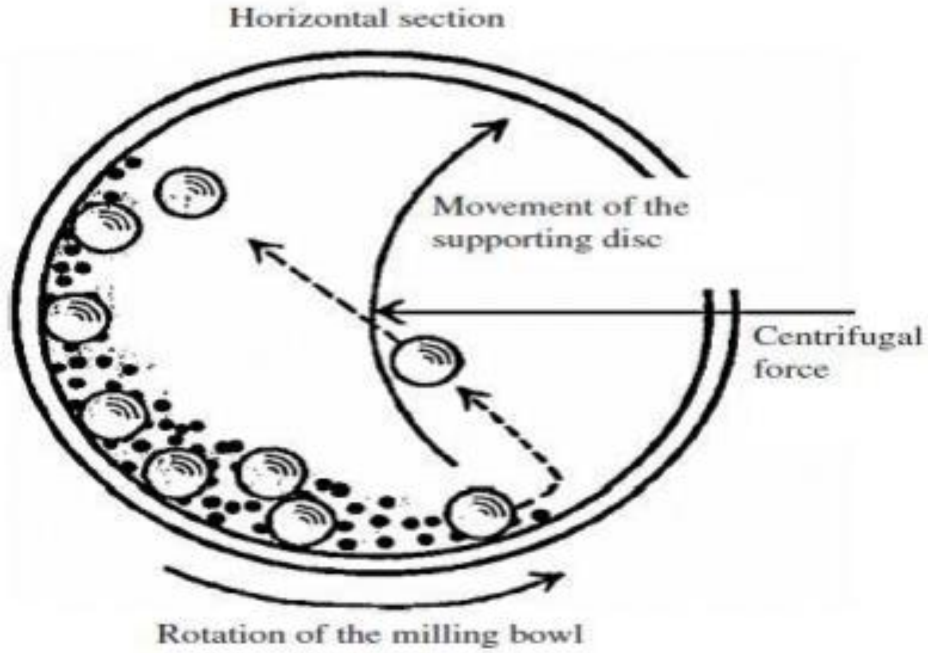
- Screen printing
- Chemical Vapour deposition (CVD)
- Solution Growth or electroless deposition.
- Electrochemical deposition.

Top-Down Approach: Mechanical Milling (Ball milling)

- Mechanical Milling (Ball milling): A Top-Down Approach for synthesis of Nanomaterials and Nanocomposites
- A simple, low cost and in high yield method of synthesis of nanoparticles has been a great challenge.
- High energy ball milling, has been widely exploited for synthesis of various nanomaterials, nanograins, nanoalloy, and nanocomposites materials.



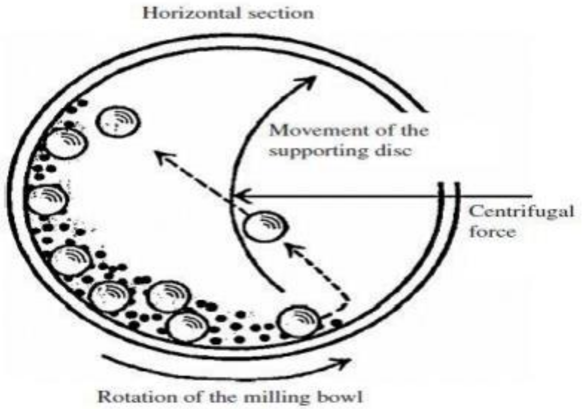
Ball milling



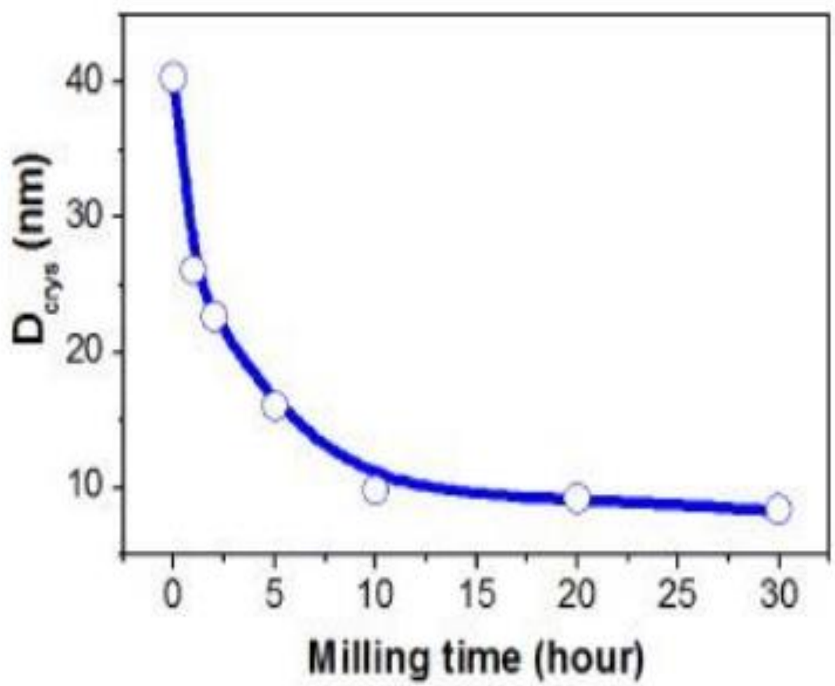
- In high-energy ball milling, plastic deformation, cold-welding and fracture are predominant factors.
  - Deformation leads to a change in particle shape
  - Cold-welding leads to an increase in particle size
  - Fracture leads to decrease in particle size
- Resulting in formation of fine dispersed alloying particles in the grain-refined soft matrix

Ball milling

- More economical process for large scale production .
- Reduces particle size and blends into new phases.
- Balls impact upon powder changes with different ball sizes.
- Kinetics of mechanical milling depends on energy transferred to the powder from balls during milling.
- Energy transfer is governed by type of mill, powder, milling speed, size and size distribution of balls, dry or wet milling, temperature and duration of milling.



Ball milling



- Size and size distribution of balls should be optimized.
- Temperature during milling depends on kinetic energy of balls and material characteristics of powder and milling media (**process control agent**).
- Temperature of powder influences diffusivity and defect concentration in powder influencing phase transformations induced by milling.

Cluster Beam Evaporation

- Solid metal material is heated by electron bombardment.
- During deposition, temperature of crucible is kept as high as Melting point of solid material.
- Chamber is evacuated with high vacuum (10^{-6} torr) to minimize impurities and increase mean free path for getting good quality film.
- Substrate temperature: Either Room or liquid nitrogen temperature (low as –196°C).

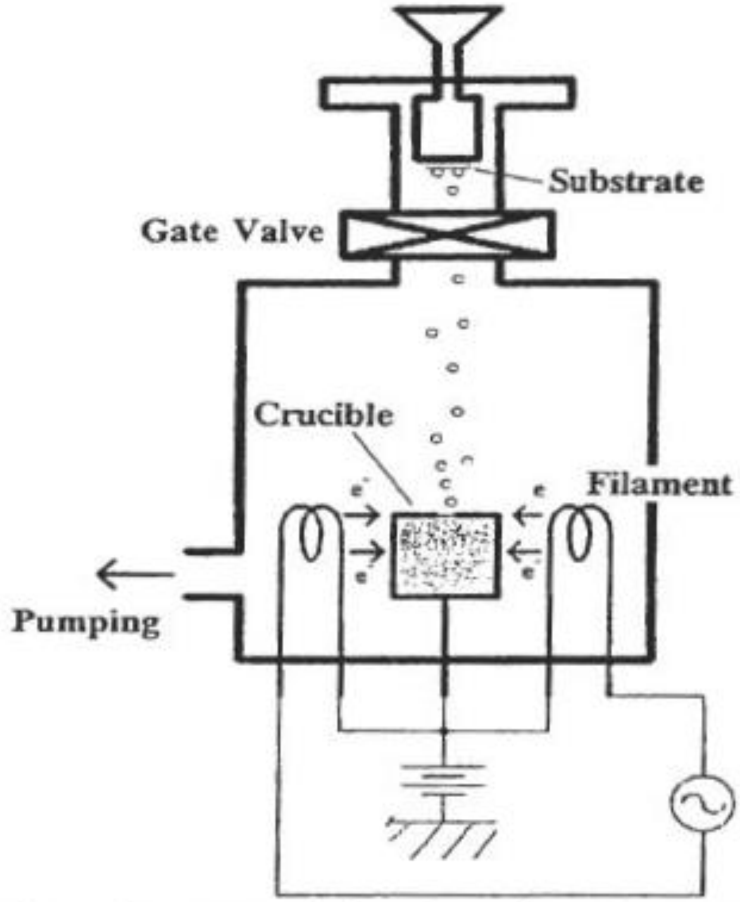
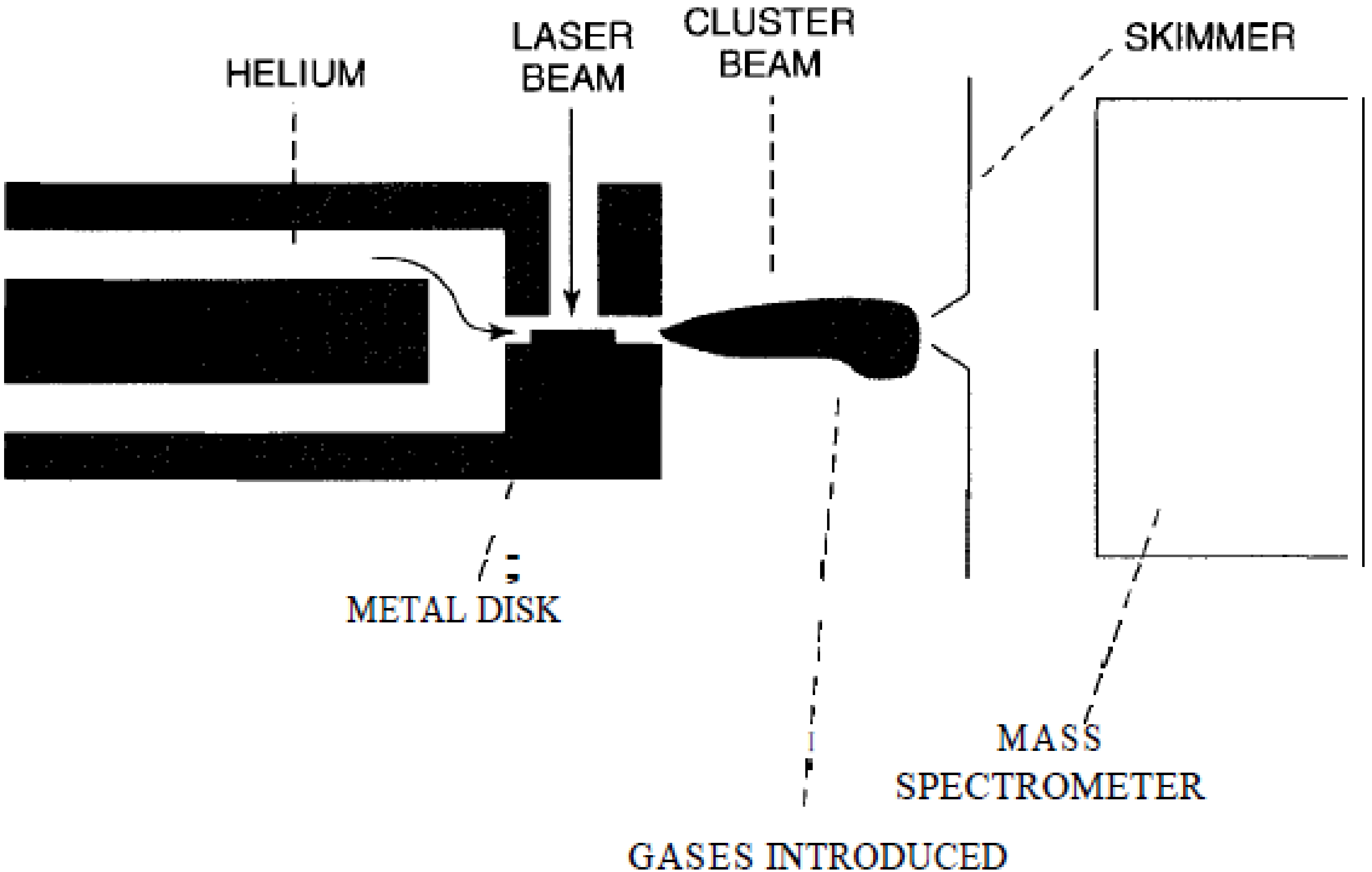


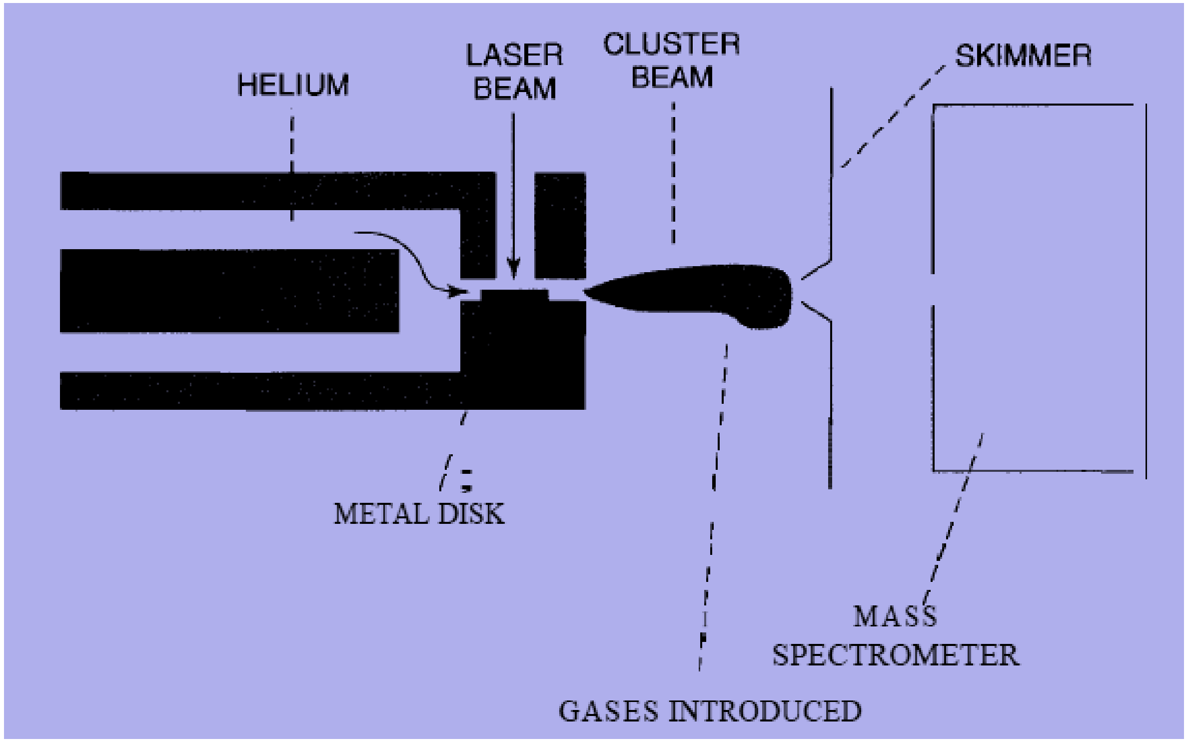
Fig.1 Apparatus of the cluster-beam evaporation technique.

- Classical nucleation theory predicts that size of nanostructures formed by cluster beam evaporation would be much smaller than those by conventional thermal vacuum evaporation technique.

Laser induced evaporation of atoms from surface of a metal.

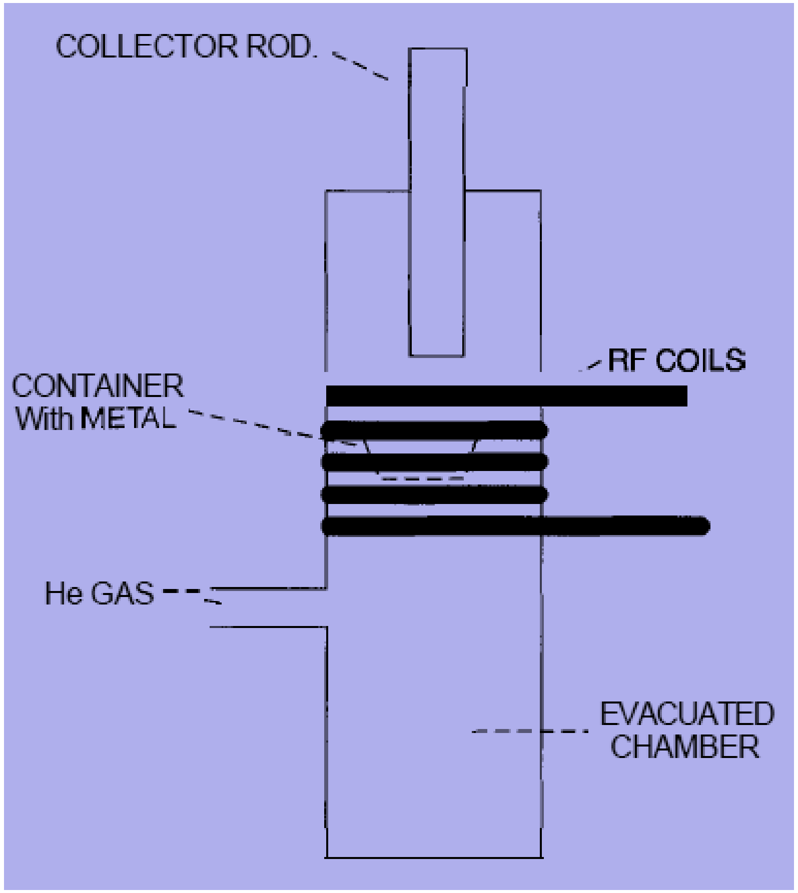


Laser evaporation



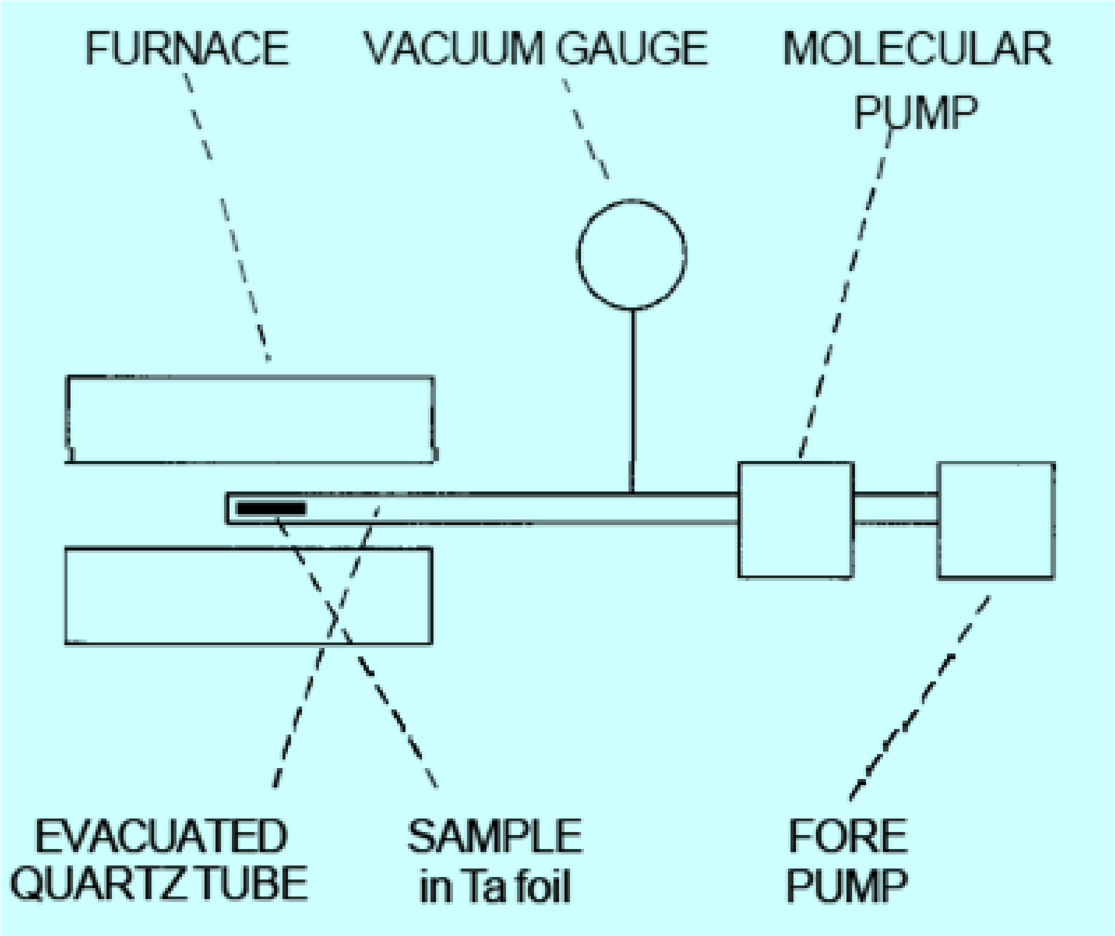
- A high intensity laser beam is incident on a metal rod, causing evaporation of atoms from the surface of metal.
- Atoms are then swept away by a burst of helium and passed through an orifice into a vacuum where the expansion of the gas causes cooling and formation of clusters of the metal atoms.
- These clusters are then ionized by UV radiation and passed into a mass spectrometer that measures their mass : charge ratio.

RF Plasma



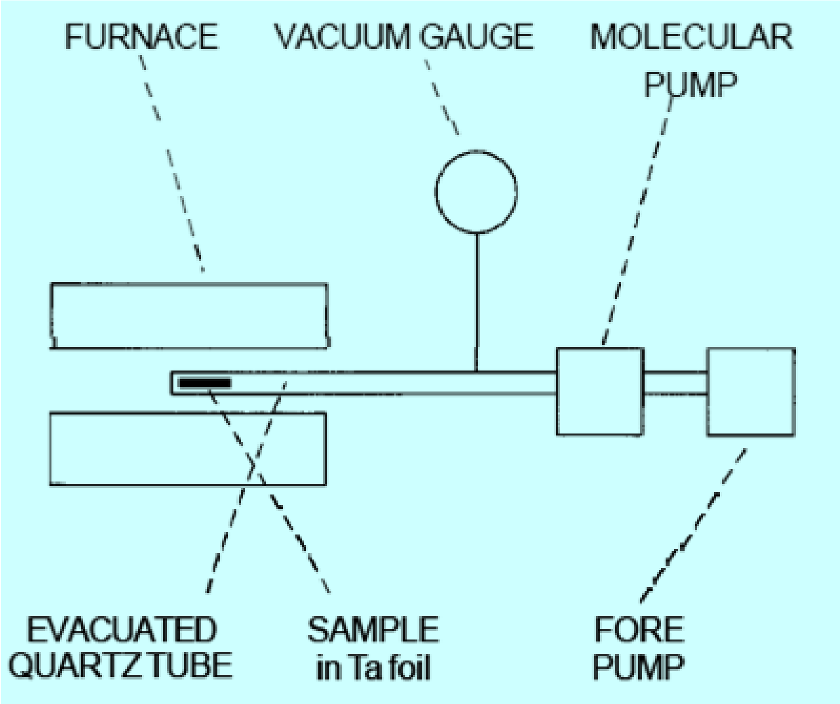
- Starting metal is contained in a pestle in an evacuated chamber.
- Metal is heated above its evaporation point using high voltage RF coils wrapped around evacuated system in the vicinity of pestle.
- Helium gas is then allowed to enter the system, forming a high temperature plasma in the region of the coils.
- Metal vapor nucleates on He gas atoms and diffuses up to a colder collector rod where nanoparticles are formed.
- The particles are generally passivated by the introduction of some gas such as oxygen.
- In the case of aluminum nanoparticles, oxygen forms a layer of aluminum oxide about the particle.

Thermolysis



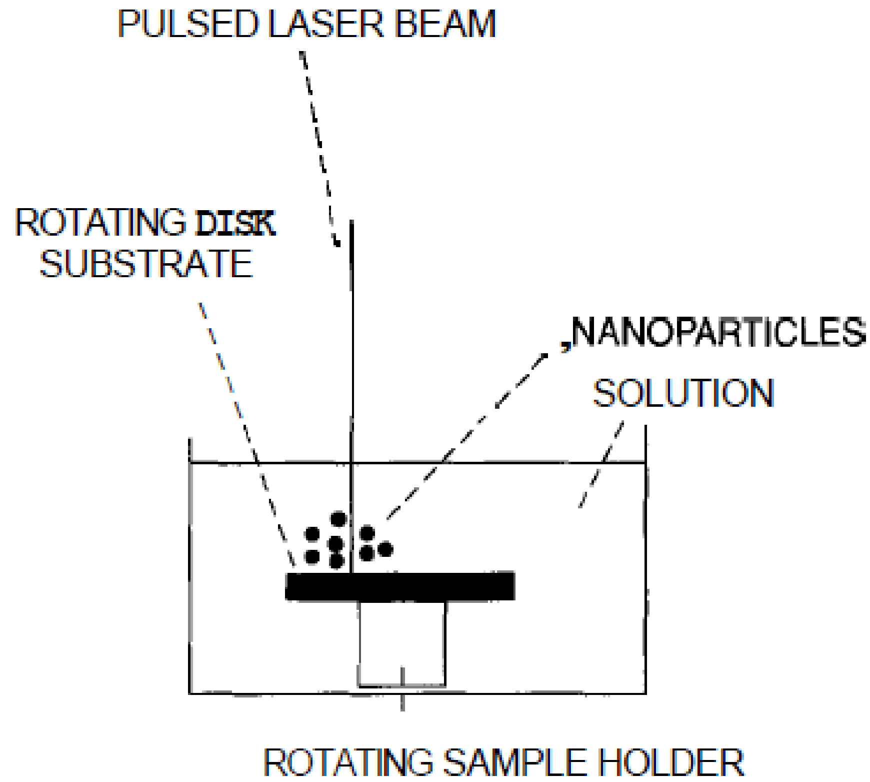
Synthesis of metal nanoparticles by thermally decomposing solids consisting of metal cations and molecular anions, or metal organic solids called thermolysis.

Thermolysis



- Material is placed in an evacuated quartz tube and heated to 400°C.
- At about 370°C LiN_3 decomposes, releasing N_2 gas
- Indicates increased pressure on vacuum gauge.
- In a few minutes pressure drops back to its original low value, indicating removal of N_2.
- Remaining Li atoms coalesce to form small colloidal metal particles.
- Particles less than 5 nm can be made by this method.
- Passivation achieved by introducing an appropriate gas.
- Ex., small Li particles made by decomposing lithium azide, LiN_3.

Pulsed Laser Method



- Metal nitrate solution and a reducing agent are flowed through a blender like device.
- Solid disk in blender rotates in solution.
- Solid disk is subjected to pulses from a laser beam creating hot spots on surface of disk.
- Metal nitrate and reducing agent react at these hot spots, resulting in formation of small metal particles.
- Metal particles are then separated from solution using a centrifuge.
- *Particle size is controlled by energy of laser and rotation speed of disk*.
- This method is capable of a high rate of production of 2-3 g/min.

Nanoparticles: Synthesis

Chemical

- Chemistry plays vital role in developing new materials with novel and technologically important properties.
- Advantage
  - Versatility in designing and synthesizing new materials that can be refined into final product.
  - Good chemical homogeneity
    - Chemical synthesis offers mixing at molecular level.
  - Molecular chemistry can be designed to prepare new materials by
    - Understanding how matter is assembled on atomic and molecular level
    - Consequent effects on desired macroscopic properties.

Nanoparticles: Synthesis

Chemical: Advantages

- Basic understanding of principles of
  - Crystal chemistry
  - Thermodynamics
  - Phase equilibrium
  - Reaction kinetics

Important to take advantage of many benefits that chemical processing has to offer.

Nanoparticles: Synthesis

Chemical: Disadvantages

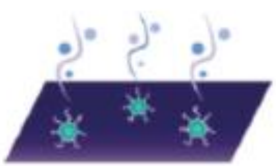
- In some preparations
  - Chemistry is complex and hazardous.
  - Contamination can result from
    - Byproducts being generated or
    - Side reactions in chemical process.
      - Should be minimized or avoided to obtain desirable properties in final product.
  - Agglomeration major concern any stage in synthetic process
    - Can dramatically alter the properties of the materials.
    - Example
      - Agglomeration frequently makes it more difficult to consolidate nanoparticles to a fully dense compact.
  - Although many chemical processes are scalable for economical production, it is not always straightforward for all systems

Nanoparticles: Synthesis

Chemical

Step one: colloidal synthesis of nanoparticles stabilized in liquid solutions.

Step two: drop casting of colloidal solution on substrate



Step three: "Calcination of the catalyst material to evaporate solvent and decompose surfactant.

Result: nanoparticles on substrate, contaminated due to the solvent and surfactant.

Nanoparticles: Synthesis

Chemical: Solution Chemistry

- Used sometimes to prepare precursor
- Subsequently converted to nanophase particles by
  - Non-liquid phase chemical reactions.
- Precipitation from solution is common technique for synthesis of fine particles.
  - Generally, involves reactions in aqueous or nonaqueous solutions containing soluble or suspended salts.
  - Solution becomes supersaturated with product
  - Precipitate formed by either homogeneous or heterogeneous nucleation.
- Formation of stable material with or without presence of foreign species by
  - Heterogeneous or
  - Homogeneous nucleation.

Nanoparticles: Synthesis

Chemical: Solution Chemistry

- Growth of nuclei after formation usually proceeds by diffusion
  - Growth rate of particles determined by
    - Concentration gradients
    - Reaction temperatures
- For instance
  - Prepare un-agglomerated particles with very narrow size distribution
    - All nuclei must form at nearly same time
    - Subsequent growth must occur without further nucleation or agglomeration of particles.

Nanoparticles: Synthesis

Chemical: Solution Chemistry

- Importance of reaction kinetics
  - Particle size and particle size distribution
  - Physical properties such as
    - Crystallinity
    - Crystal structure
    - Degree of dispersion
- Additional factors
  - Concentration of reactants
  - Reaction temperature
  - pH
  - Order of addition of reactants to solution

Nanoparticles: Synthesis

Chemical: Solution Chemistry

- Multi-element materials often made by coprecipitation of batched ions
- It is not always easy to coprecipitate all desired ions simultaneously
  - Different species may only precipitate at different pH.
- Control of chemical homogeneity and stoichiometry requires very careful control of reaction conditions.
- Problem of agglomeration may be avoided by
  - Spray drying
  - Freeze drying.

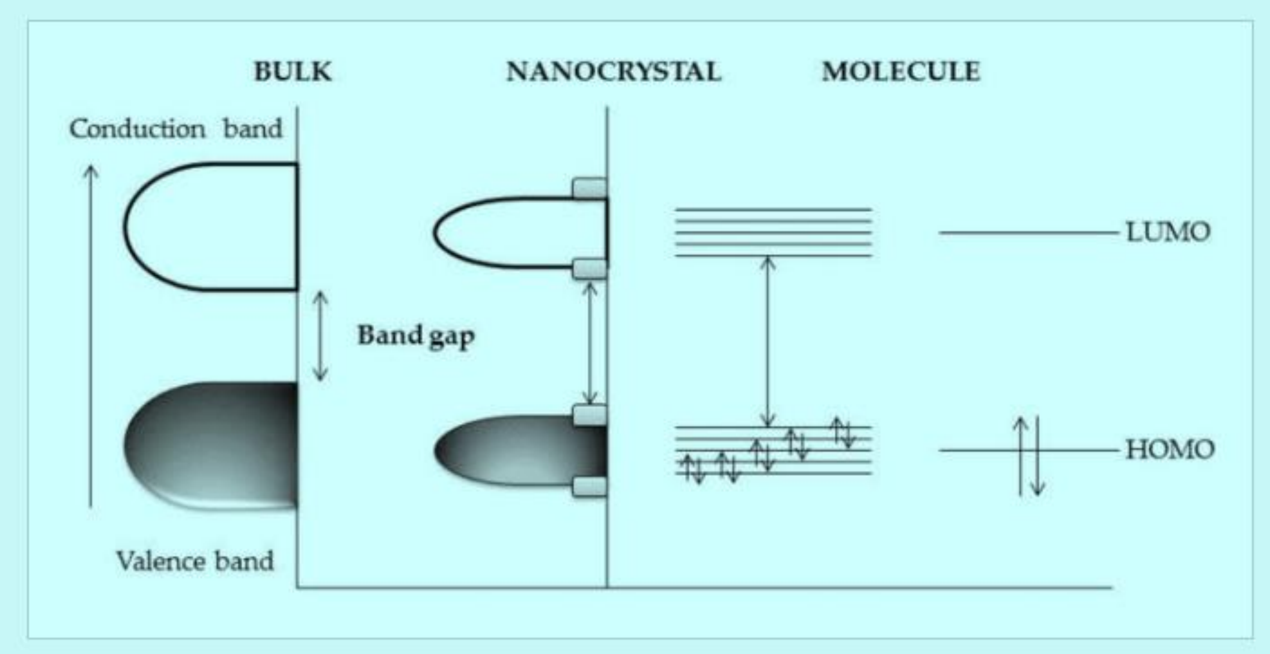
Nanoparticles: Electronic Structure

- When atoms form a lattice, discrete energy levels of atoms are smudged out into energy bands.
- Density of states refers to number of energy levels in a given interval of energy.
- For a metal, top band is not totally filled.
- In semiconductor top occupied band, called the valence band, is filled.
- Small energy separation, band gap, between it and next higher unfilled band.

Nanoparticles: Electronic Structure

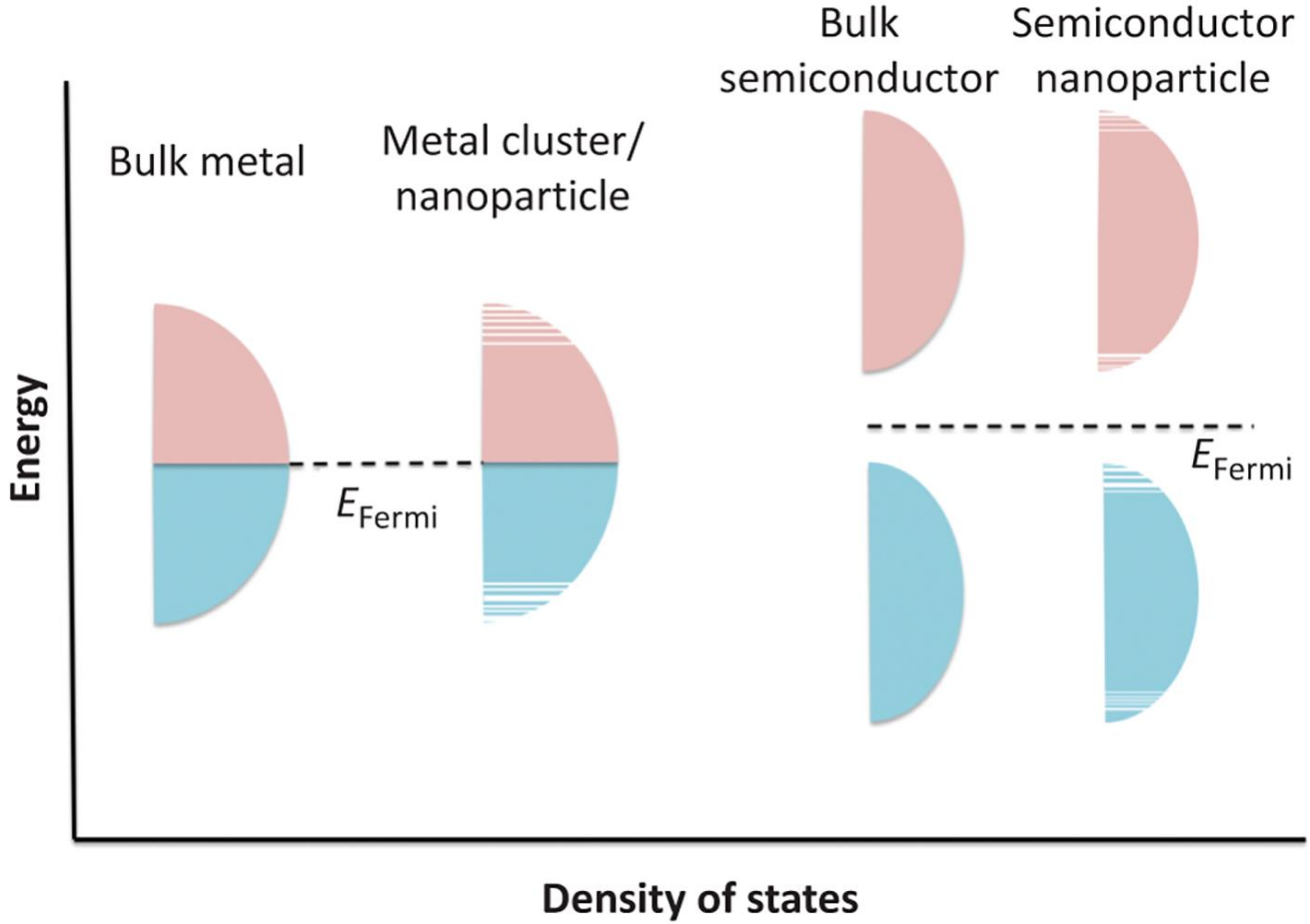
- Electronic, optical and magnetic properties become size-and shape-dependent at nano range.
- Optical behaviour is very sensitive to quantum effects otherwise called ‘quantum confinement’.
- Significance of quantum mechanical effects depends on temperature and distance between neighbouring energy levels or bands.
  - Has to be large compared to thermal energy, $k_B T$, in order to avoid a smear-out of effect by thermal fluctuations.

Nanoparticles: Electronic Structure



- Density of states in conduction band containing electrons, changes dramatically with reduction in size.
- Continuous density of states in the band is replaced by a set of discrete energy levels.
- May have energy level spacings larger than thermal energy kT, and a gap opens up.

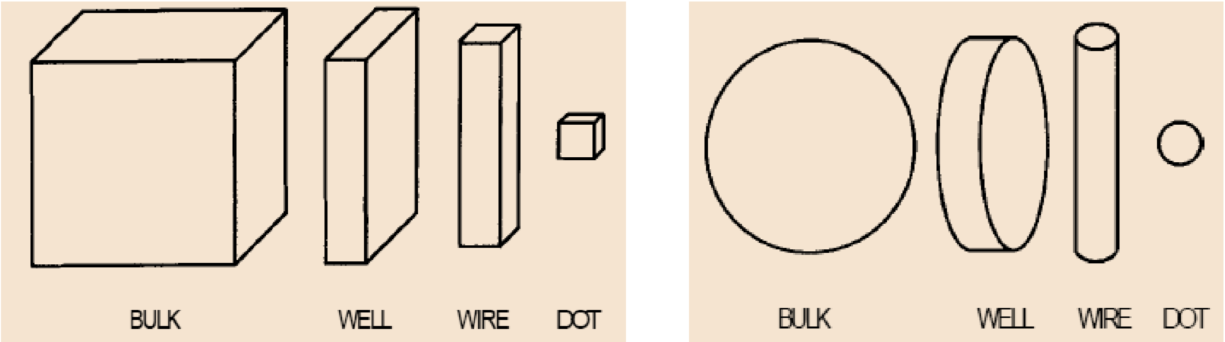
Nanoparticles: Electronic Structure



Nanoparticles: Electronic Structure

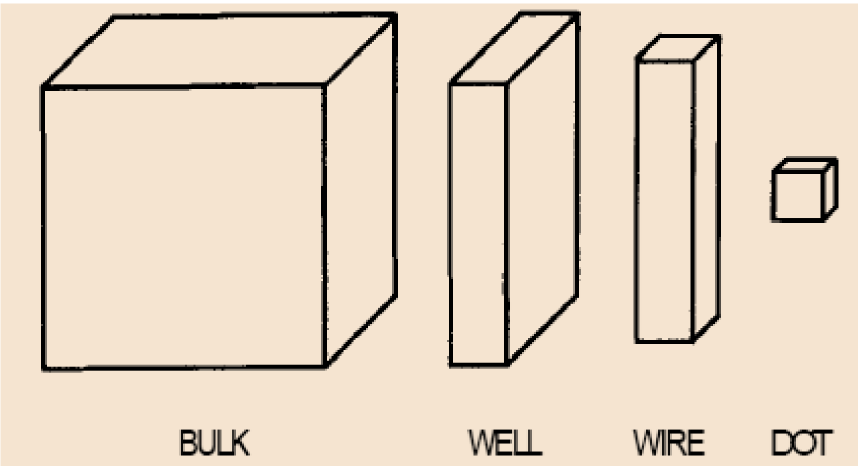
- Spacing of electronic levels and bandgap increases with decreasing particle size.
  - Because electron-hole pairs are now much closer together and Coulombic interaction between them can no longer be neglected giving an overall higher kinetic energy.
- Increase in bandgap can be observed experimentally by blue-shift in the absorption spectrum or sometimes even visually by colour of samples.
- A larger bandgap means more energy is required to excite an electron from valance band to conduction band.
  - hence light of a higher frequency and lower wavelength would be absorbed.

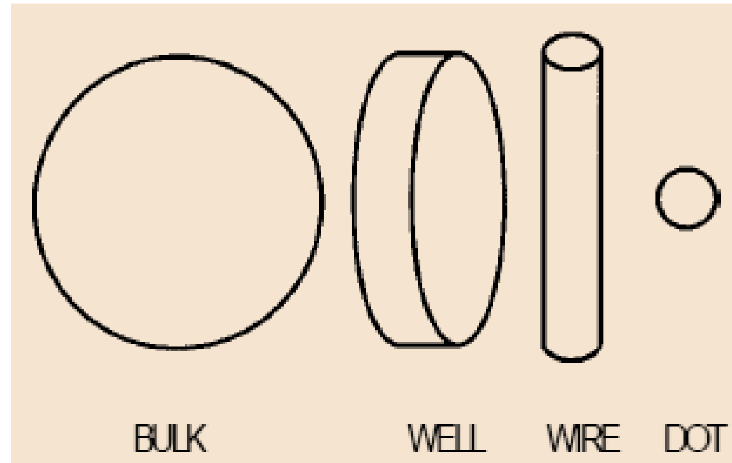
Nanoparticles: Quantum Wells, Wires and Dots



- Word **quantum** is associated with three types of nanostructures
  - changes in properties arise from quantum-mechanical nature of physics in the domain of the ultrasmall.
- If one dimension is reduced to nano-range while other two dimensions remain large, then structure known as a **quantum well**.
- If two dimensions are so reduced and one remains large, structure is referred to as a **quantum wire**.
- Size reduction in all three dimensions is called **quantum dot**.

Nanoparticles: Quantum Wells, Wires and Dots



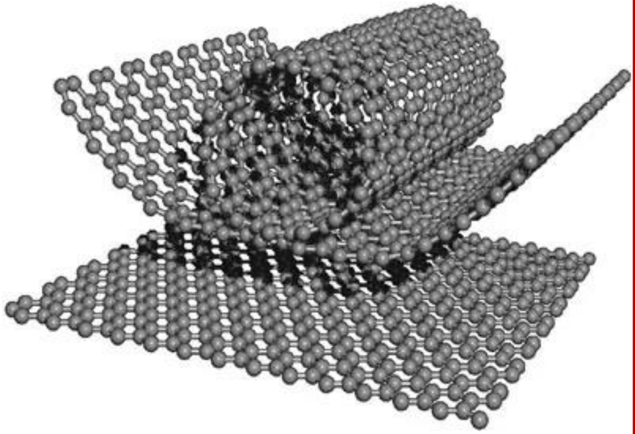


- Dimensionality effects that occur when one, two, or all three dimensions becomes small.
- How electronic properties are altered by these changes?

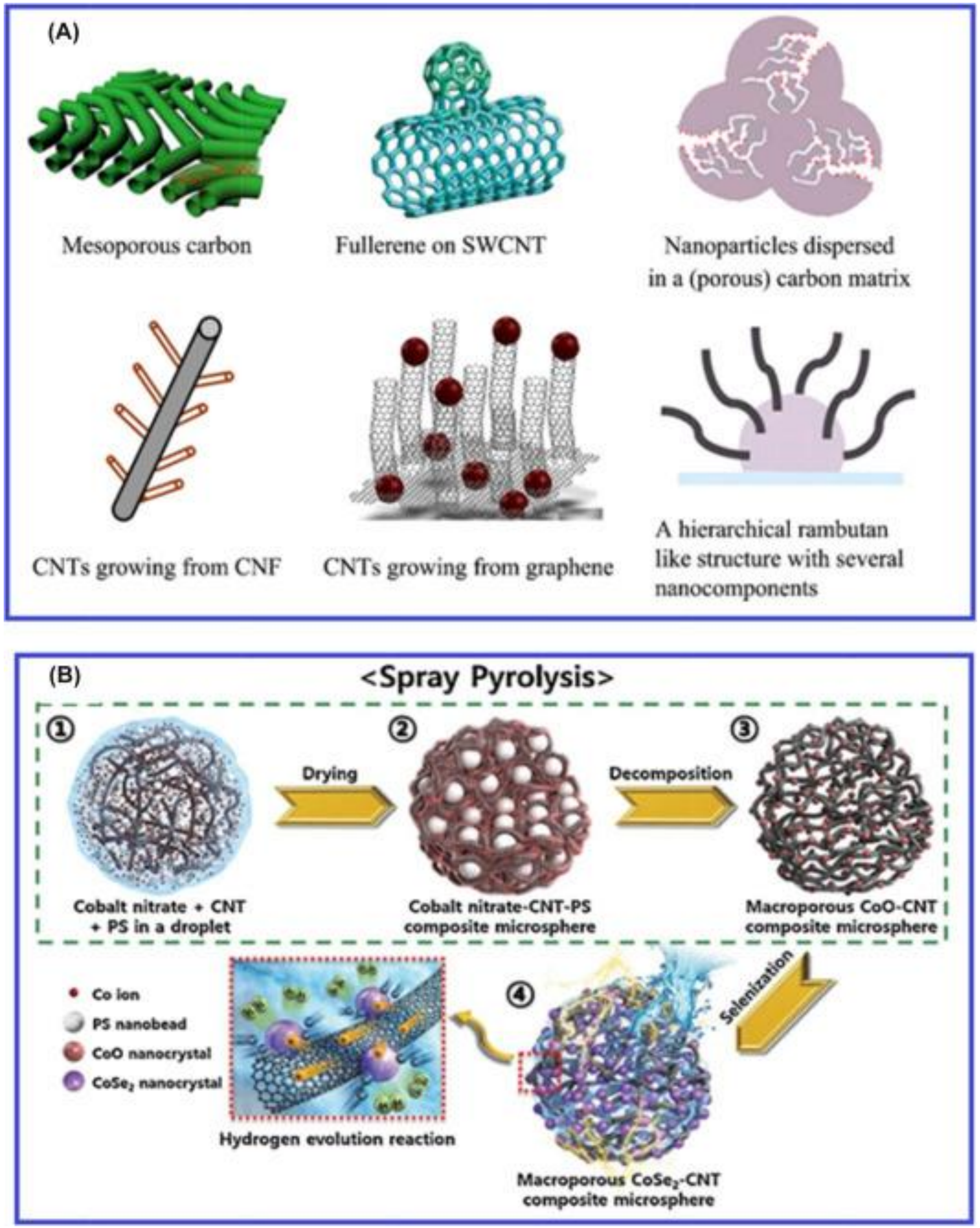
Nanoparticles: Quantum Confinement

- Particle behaves as if it was free when confining dimension is large compared to wavelength of particle.
- During this state, bandgap remains at its original energy due to a continuous energy state.
- As confining dimension decreases typically in nanoscale, energy spectrum becomes discrete.
- As a result, bandgap becomes size-dependent.
- As size of particles decreases, electrons and electron holes come closer, and energy required to activate them increases,
- Results in a blueshift in light emission.

Nanoparticles: Carbon nanotubes (CNT)



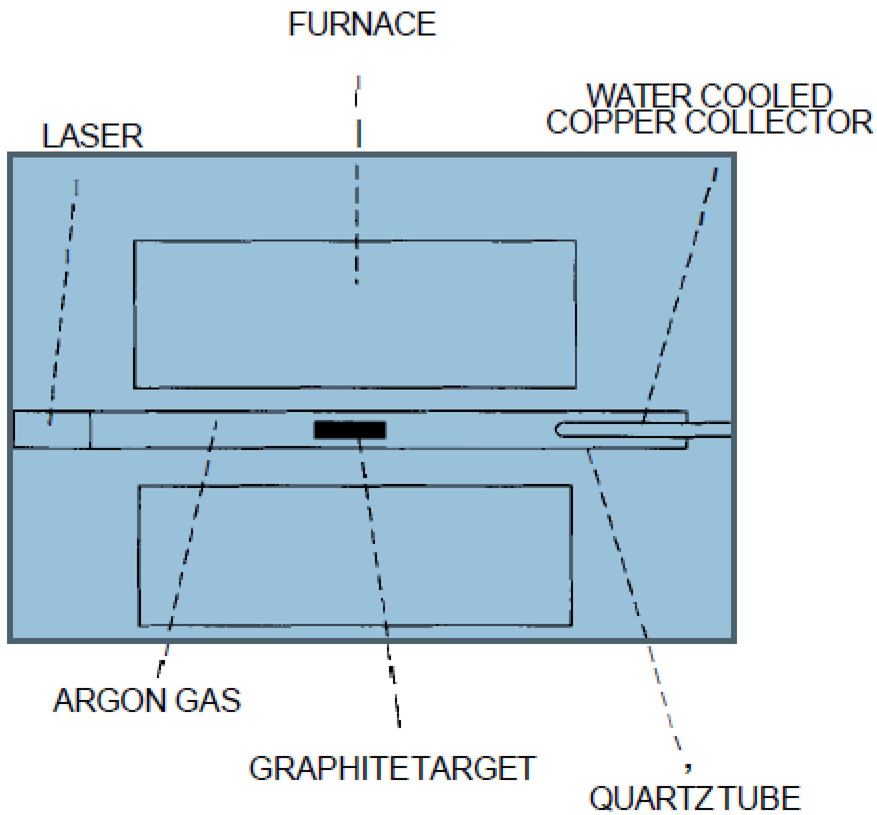
- Cylindrical molecules consist of rolled-up sheets of single-layer carbon atoms (graphene).
- CNT can be
  - single-walled with a diameter of less than 1 nm or
  - multi-walled, consisting of several concentrically interlinked nanotubes, with diameters >100 nm.
- Their length can reach several μm or even mm.
- Ultra-high strength, low-weight materials that possess highly conductive electrical and thermal properties



(A)
Mesoporous carbon
Fullerene on SWCNT
Nanoparticles dispersed in a (porous) carbon matrix
CNTs growing from CNF
CNTs growing from graphene
A hierarchical rambutan like structure with several nanocomponents
(B)
<Spray Pyrolysis>
①
Drying
②
Decomposition
③
Cobalt nitrate + CNT + PS in a droplet
Cobalt nitrate-CNT-PS composite microsphere
Macroporous CoO-CNT composite microsphere
Selenization
Co ion
PS nanobead
CoO nanocrystal
$CoSe_2$ nanocrystal
Hydrogen evolution reaction
④
Macroporous $CoSe_2$-CNT composite microsphere

Carbon nanotubes (CNT): Synthesis

Carbon nanotubes can be made by laser evaporation, carbon arc methods, and chemical vapor deposition.



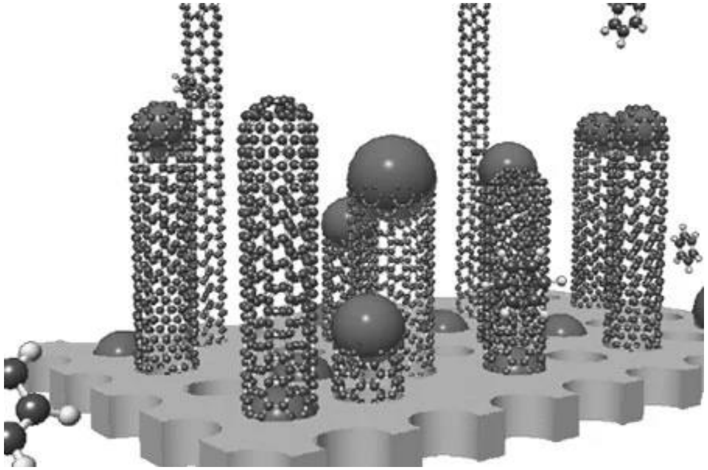
Carbon nanotubes (CNT): Synthesis- laser evaporation

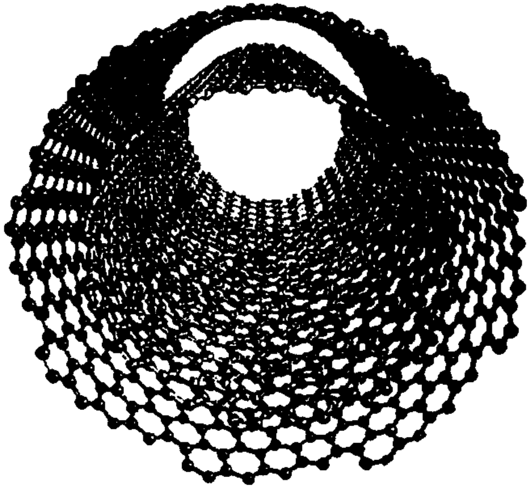
- Quartz tube containing argon gas and a graphite target are heated to 1200°C.
- A water-cooled copper collector is placed in the same tube but outside furnace.
- Graphite target contains small amounts of cobalt and nickel that act as nucleation sites for the formation of carbon nano tubes.
- An intense pulsed laser beam is incident on the target, evaporating carbon from the graphite.
- Argon then sweeps the carbon atoms from high temperature zone to colder copper collector on which they condense into nanotubes.
- ***Tubes 10-20 nm in diameter and 100 μm long can be made by this method.***

Carbon nanotubes (CNT): Synthesis-Carbon Arc

- A potential of 20-25 V is applied across carbon electrodes of 5-20 μm diameter and separated by 1 mm at 500 torr pressure of flowing helium.
- Carbon atoms are ejected from positive electrode and form nanotubes on the negative electrode.
- As the tubes form, length of positive electrode decreases, and a carbon deposit forms on negative electrode.
- To produce single-walled nanotubes, a small amount of cobalt, nickel, or iron is incorporated as a catalyst in the central region of the positive electrode.
- If no catalysts are used, the tubes are nested or multiwalled types (MWNT), which are nanotubes within nanotubes.
- ***Carbon arc method can produce SWCNT of diameters 1-5 nm with a length of 1 μm.***

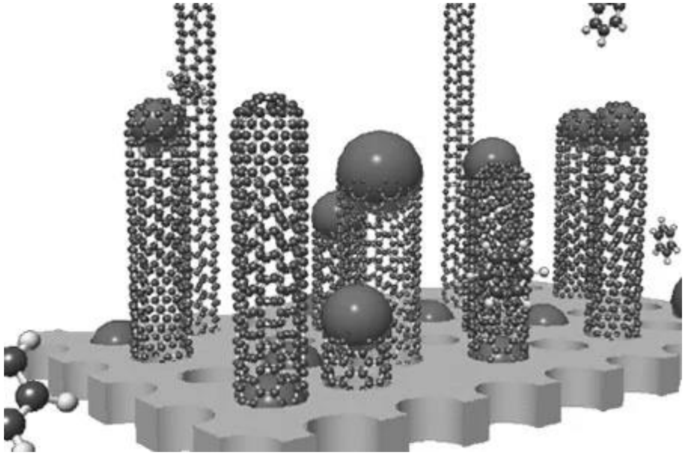
Carbon nanotubes (CNT)- Synthesis- CVD





- CVD involves decomposing a hydrocarbon gas such as methane (CH_4) at 1100°C.
- As the gas decomposes, carbon atoms condense on a cooler substrate that may contain catalysts such as iron.
- CVD produces tubes with open ends, which does not occur when other methods are used.
- CVD allows continuous fabrication and may be the most favorable method for scaleup and production.

Carbon nanotubes (CNT)- Synthesis- CVD



- A metal catalyst combined with carbon-containing reaction gases (hydrogen or carbon monoxide) to form carbon nanotubes on catalyst inside a high-temperature furnace.
- First, small secondary catalyst particles of size of a CNT diameter develop on which nanotubes start growing.
- Catalyst particle is either at top or at bottom of emerging nanotube.
- Growth will stop if catalyst particle is deactivated through development of a carbon envelope.

Carbon nanotubes (CNT)

- As the metal catalyst is necessary for the growth of SWNTs, mechanism must involve the role of the Co or Ni atoms.
- As per “scootter mechanism”
  - atoms of metal catalyst attach to the dangling bonds at the open end of the tubes,
  - these atoms scoot around the rim of the tube, absorbing carbon atoms as they arrive.

Carbon nanotubes (CNT)- Synthesis- CVD

- Generally when nanotubes are synthesized, result is a mix of different kinds, some metallic and some semiconducting.
- Separation was accomplished by depositing bundles of nanotubes, some of which are metallic and some semiconducting, on a silicon wafer.
- Metal electrodes were then deposited over the bundle.
- Using the silicon wafer as an electrode, a small bias voltage was applied that prevents the semiconducting tubes from conducting, effectively making them insulators.
- A high voltage is then applied across the metal electrodes, thereby sending a high current through the metallic tubes but not the insulating tubes.
- This causes the metallic tubes to vaporize, leaving behind only semiconducting tubes.

Carbon nanotubes (CNT)

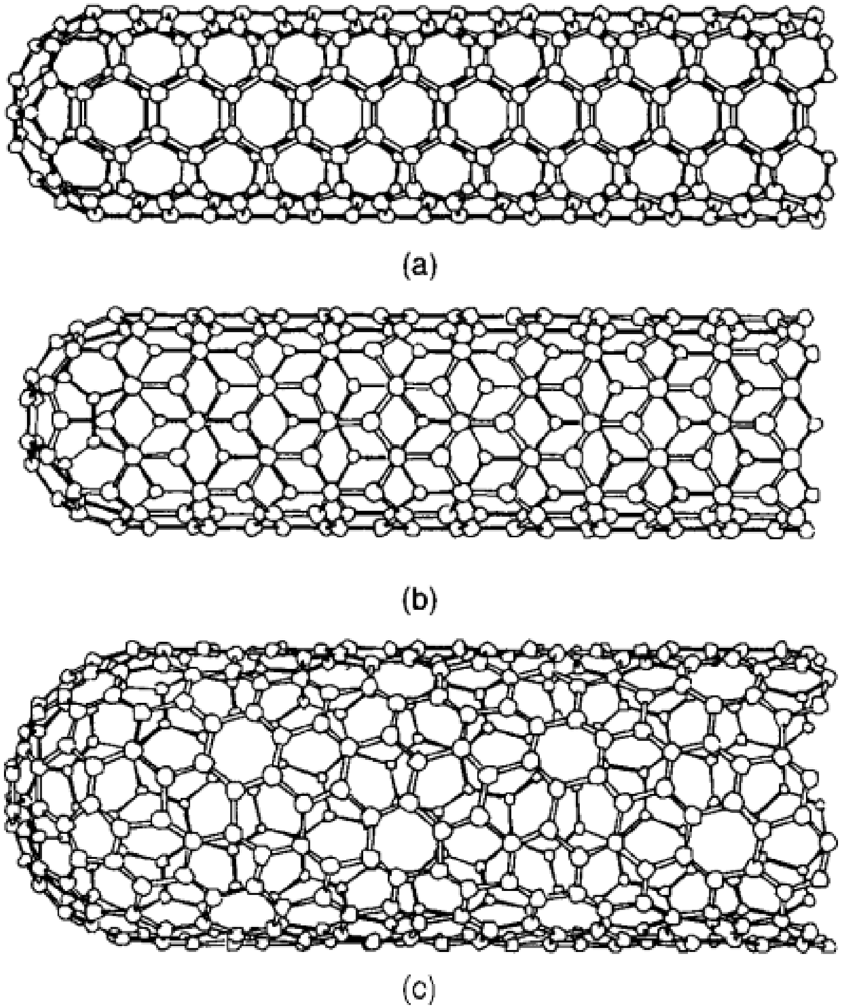
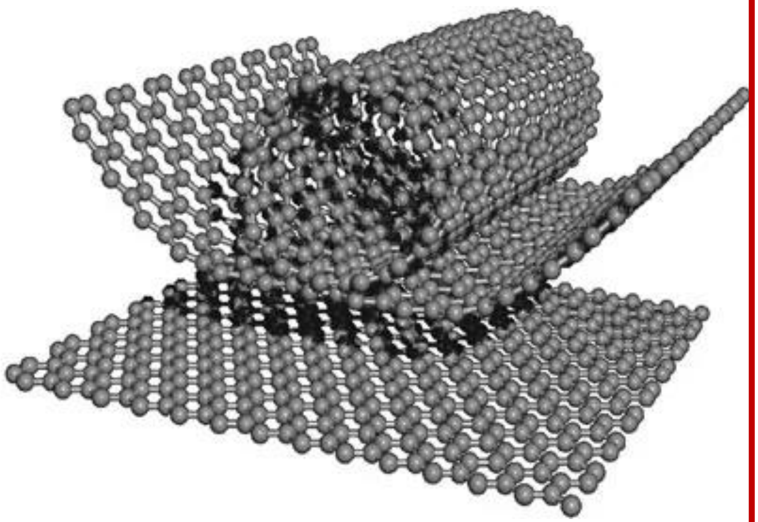


Illustration of some possible structures of carbon nanotubes, depending on how graphite sheets are rolled: (a) armchair structure; (b) zigzag structure; (c) chiral structure.

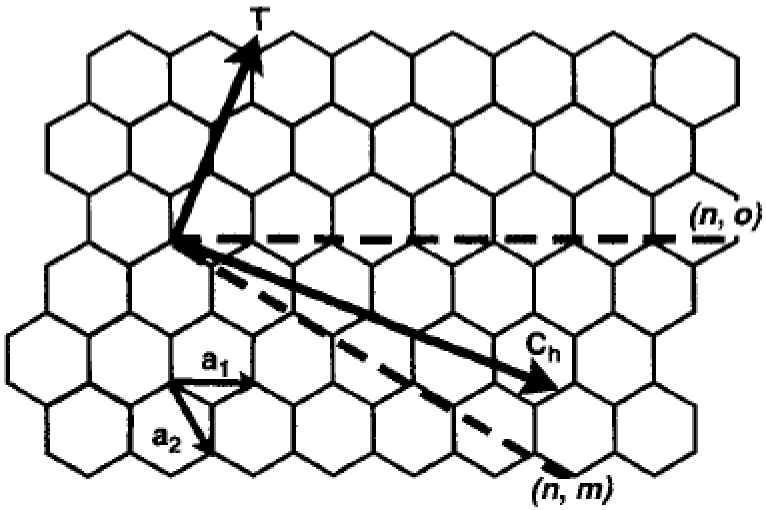
Carbon nanotubes (CNT)



- Rolling-up direction (rolling-up or *chiral* vector) of graphene layers determines electrical properties of nanotubes.
- Chirality describes angle of nanotube's hexagonal carbon-atom lattice.
- MWCNTs are always conducting and achieve at least same level of conductivity as metals.
- SWCNTs' conductivity depends on their chiral vector:
- They can behave like a metal and be electrically conducting; display the properties of a semi-conductor; or be non-conducting.
- Ex, a slight change in pitch of the helicity can transform the tube from a metal into a large-gap semiconductor.

Nanoparticles: Carbon nanotubes properties

- Carbon nanotubes have the most interesting property that they are metallic or semiconducting, depending on the diameter and chirality of the tube.
- Chirality refers to how tubes are rolled with respect to direction of the *T* vector



Graphitic sheet showing the basis vectors a, and a2 of the two-dimensional unit cell, the axis vector T about which the sheet is rolled.

Nanoparticles: Carbon nanotubes properties

- High mechanical tensile strength 400 times that of steel.
- Light-weight –density is one sixth of that of steel.
- Thermal conductivity is better than that of diamond.
- Very high aspect ratio greater than 1000,
  - in relation to their length they are extremely thin;
- A tip-surface area near the theoretical limit
  - Smaller the tip-surface area, more concentrated the electric field, and the greater field enhancement factor.

Nanoparticles: Carbon nanotubes properties

- Highly chemically stable and resist virtually any chemical impact unless they are simultaneously exposed to high temperatures and oxygen
  - Extremely resistant to corrosion;
- Hollow interior can be filled with various nanomaterials, separating and shielding them from the surrounding environment
  - Extremely useful for nanomedicine applications like drug delivery.

Nanoparticles: Carbon nanotubes synthesis

- Three main methods currently available for the production of CNTs: Arc discharge, Laser ablation of graphite, and chemical vapor deposition (CVD).
- In first two processes, graphite is combusted electrically or by means of a laser, and CNTs developing in gaseous phase are separated.
- All three methods require use of metals (e.g. iron, cobalt, nickel) as catalysts.

Nanotechnology applications

Field Emission and Shielding

- When a small electric field is applied parallel to the axis of a nanotube, electrons are emitted at a very high rate from the ends of the tube. This is called field emission.
- Samsung in Korea is developing a flat-panel display using the electron emission of carbon nanotubes.
- A thin film of nanotubes is placed over control electronics with a phosphor-coated glass plate on top.
- A Japanese company is using this electron emission effect to make vacuum tube lamps that are as bright as conventional light bulbs, and longer-lived and more efficient.

Nanotechnology applications

Field Emission and Shielding

- High electrical conductivity of carbon nanotubes means that they will be poor transmitters of electromagnetic energy.
- A plastic composite of carbon nanotubes could provide lightweight shielding material for electromagnetic radiation.
- This is a matter of much concern to the military, which is developing a highly digitized battlefield for command, control, and communication.
- The computers and electronic devices that are a part of this system need to be protected from weapons that emit electromagnetic pulses.

Nanotechnology applications

Field Emission and Shielding

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Nanotechnology Medical applications

- Nanomaterials show very high efficiency in destroying cancer cells and are already undergoing clinical trials.
- Allow cancer cells to be targeted specifically and enable detailed imaging of tissues, making planning further therapy much easier.
- Nanostructures may be used in both preventing and increasing the stability of atherosclerotic lesions.
- Other potential applications of nanotechnology in medicine include:

1. nano adjuvants with immune modulatory properties used to deliver vaccine antigens;
2. the nano-knife, an almost non-invasive method of destroying cancer cells with high voltage electricity;
3. carbon nanotubes, for repairing damaged tissues and might be used to regenerate nerves in the future.

Nanotechnology Medical applications

- Doctors have used nanotechnology to treat cancer for more than a decade.
- Two approved treatments -- **Abraxane and Doxil** -- help chemotherapy drugs work better.
- **Abraxane** is a nanoparticle made from protein albumin attached to the chemo drug docetaxel.
- It stops cancer cells from dividing.
- **Abraxane** treats breast and pancreatic cancers that have spread, and non-small-cell lung cancer.
- **Doxil** is the chemo drug doxorubicin wrapped inside a liposome, a fatty sac.
- It disrupts cancer genes so the cancer cells can't divide.
- Doxil treats ovarian cancers, multiple myeloma, and Kaposi's sarcoma.