NANOSTRUCTURES

Zero-Dimensional Nanomaterials

One-Dimensional Nanomaterials

Two-Dimensional Nanomaterials

Three-Dimensional Nanomaterials

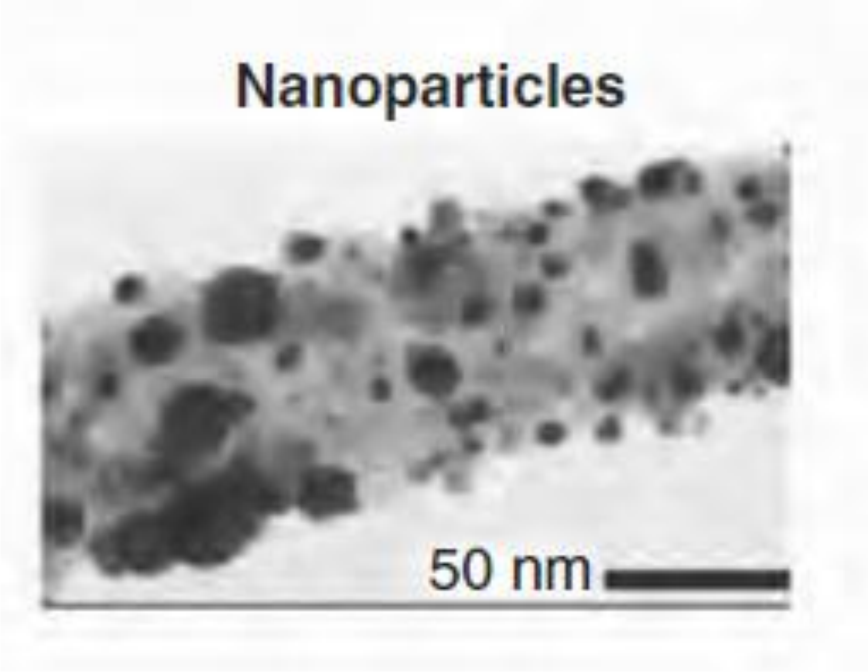
Zero-Dimensional Nanomaterials

These materials have diameters <100 nm, and are denoted by nanoparticles, nanoclusters, or nanocrystals

Nanoparticle

The term *nanoparticle* is generally used to encompass all 0 D nanosized building blocks (regardless of size and morphology), or those that are amorphous and possess a relatively irregular shape

Herein, we will define nanoparticles as amorphous or semicrystalline or single 0 D nanostructures crystal with dimensions larger than 10 nm, and a relatively large *(*≥15%*)* size dispersion.



Properties of Nanomaterials

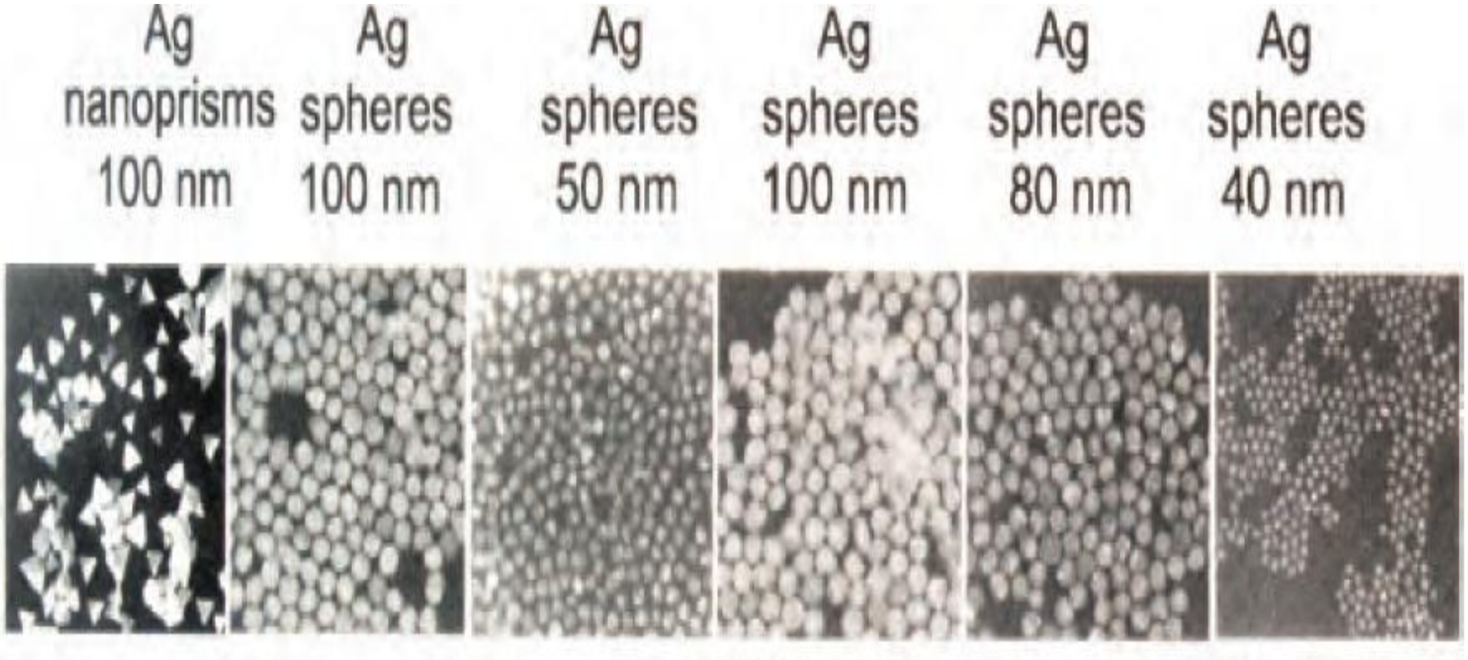
For the fabrication of nanoparticles, a small size is not the only requirement.

For any practical application, the processing conditions need to be controlled in such a way that resulting nanoparticles have the following characteristics:

(i) identical size of all particles (also called monosized or with uniform size distribution)
(ii) identical shape or morphology,
(iii) identical chemical composition and crystal structure (iv) individually dispersed or monodispersed, i.e. no agglomeration.

If agglomeration does occur, nanoparticles should be readily redispersible

Properties of Nanomaterials

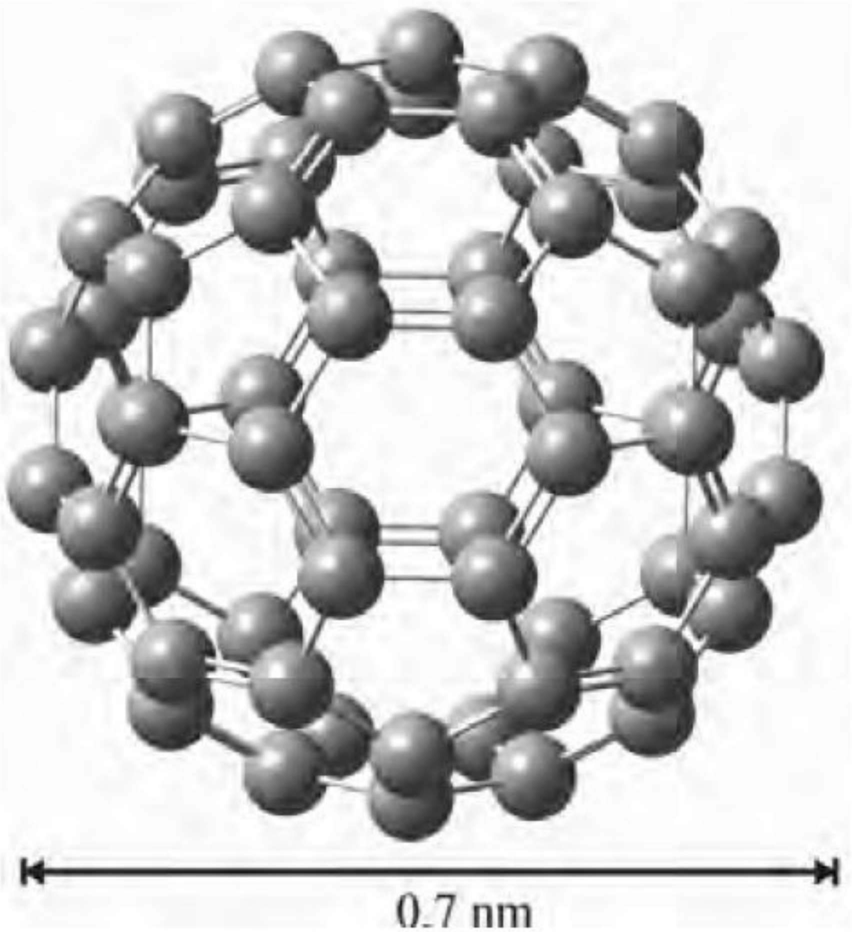


The first 0D nanoarchitecture: the fullerenes

"Nanotechnology revolution" was catalyzed by the mid-1980s discovery of carbon nanoclusters known as *fullerenes* C60

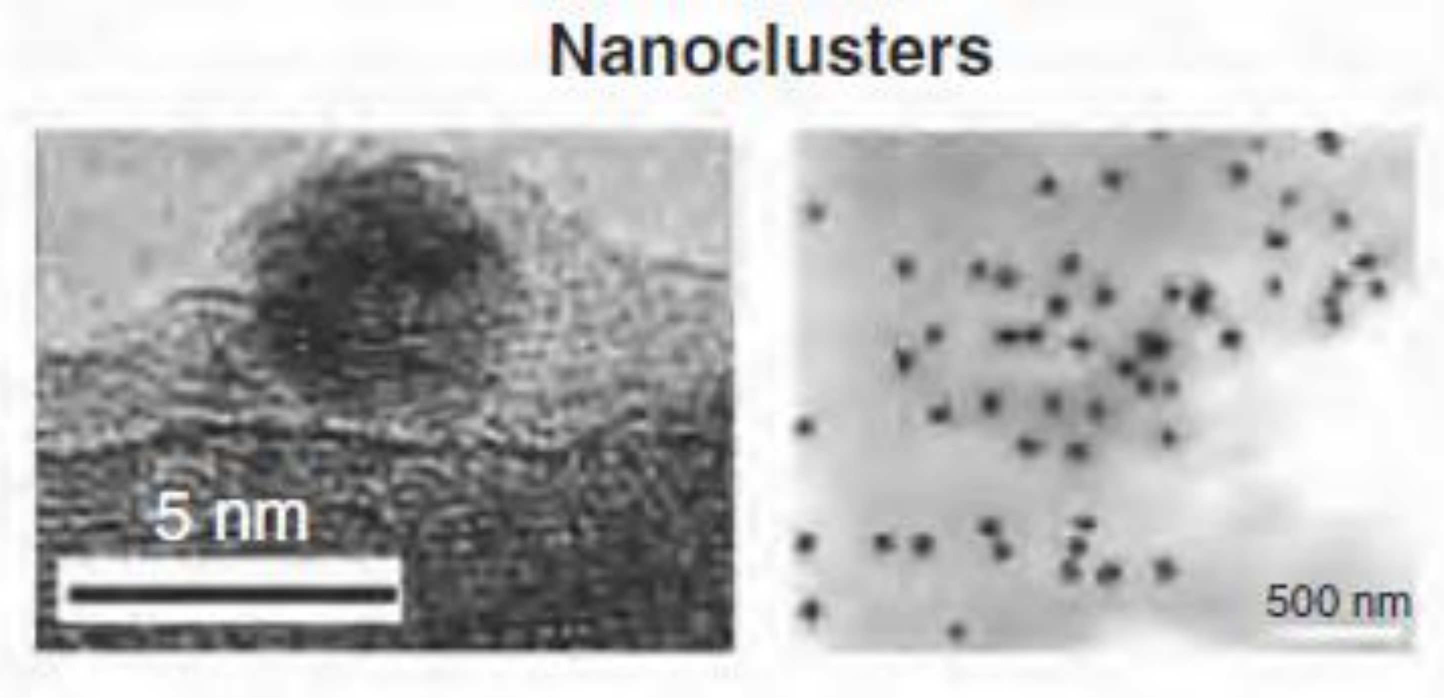
The 1996 Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl, and Sir Harold Kroto for this discovery

To date, the most common applications for fullerenes include MRI contrast agents (exploiting its container properties), drug-delivery agents (through surface functionalization), and light-activated antimicrobial Agents etc.



C60, containing alternating six- and five membered rings of sp2 hybridized carbon atoms. This is only one isomer for C60, out of a staggering total of 1,812 possible structures

For amorphous/semicrystalline nanostructures smaller in size (*i.e.*, 1–10 nm), with a narrow size distribution, the term *nanocluster* is more appropriate.



Properties of Nanomaterials

It is also important here to note the difference between nanoparticles/nanoclusters and traditional *colloids*, which date back to the early 1860s

Term colloid, which is used to describe solid/liquid and solid/gas suspensions such as milk, paints, butter, smoke, and smog.

Although both types of materials have sizes within the nanoregime, the leading difference is the control one has over composition and morphology.

In order to stabilize metal nanostructures, a stabilizing agent must be used to prevent agglomeration into a larger powder. This is also the case for colloids, which generally employ polydispersed organic polymers and other ionic species that may adsorb to the colloid surface.

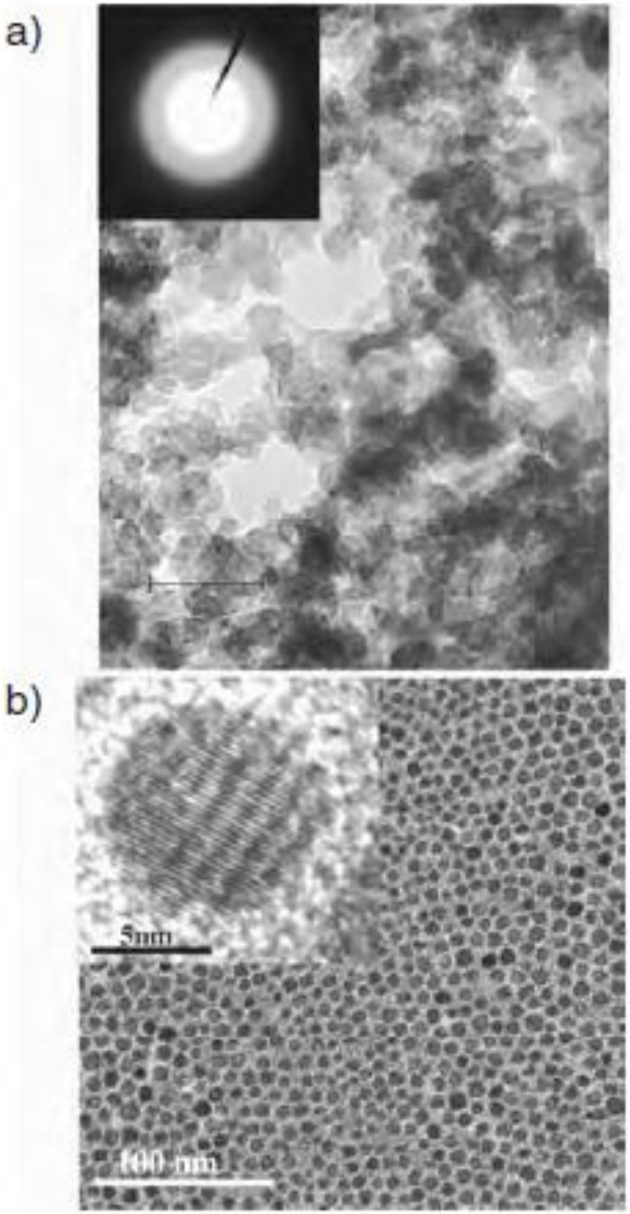
Properties of Nanomaterials

Analogous to bulk materials, any nanomaterial that is crystalline should be referred to as a *nanocrystal*. This term should be reserved for those materials that are single crystalline; if a particle exhibits only regions of crystallinity, it is better termed a nanoparticle or nanocluster depending on its dimensions.

Transmission electron microscopy, especially in tandem with electron diffraction is most useful in determining the crystallinity of any nanostructure

A special case of nanocrystal that is comprised of a semiconductor is known as a ***quantum dot*****.**

Typically, the dimensions of these nanostructures lie in the range 1–30 nm, based on its composition Quantum dots currently find applications as sensors, lasers, and LEDs. In fact, new high-density disks (*e.g.*, HD-DVD and Blu-ray high-definition DVD formats) may only be read *via* blue lasers, which are fabricated from quantum dots. Long-term applications for these structures will likely include optical computing and high-efficiency solar cells.



TEM images of amorphous nanoclusters (a), and nanocrystals, (b). The inset of (a) shows selected area electron diffraction (SAED); the absence of a pattern indicates an amorphous structure. The scale bar is 20 nm. The high-resolution TEM image inset in (b) shows lattice spacings of an individual nanocrystal.

Quantum dot

when an electron is promoted from the valence to conduction bands, an electron–hole pair known as an *exciton* is created in the bulk lattice. The physical separation between the electron and hole is referred to as the *exciton Bohr radius* (r_B) that varies depending on the semiconductor composition.

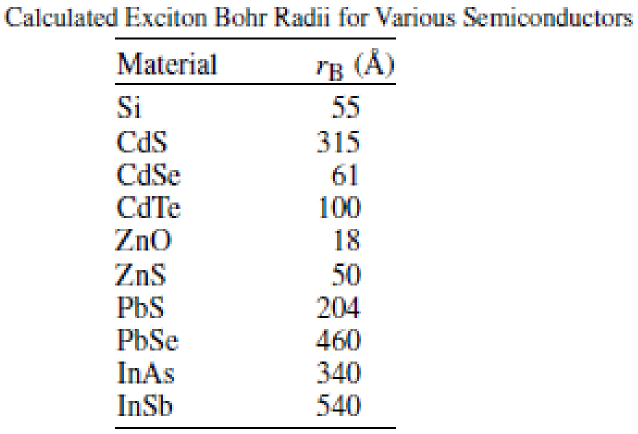
In a bulk semiconductor crystal, r_B is significantly smaller than the overall size of the crystal; hence, the exciton is free to migrate throughout the lattice

However, in a quantum dot, r_B is of the same order of magnitude as the diameter (D) of the nanocrystal, giving rise to *quantum confinement* of the exciton. Empirically, this translates to the strongest exciton confinement when $D \leq 2r_B$.

Properties of Nanomaterials

Analogous to the “particle-in-a-box” model from introductory physical chemistry, exciton quantum confinement results in discrete energy levels rather than the continuous bands of a bulk semiconductor crystal. Since the gap between adjacent energy levels is infinitesimally small for a bulk semiconductor, the bandgap is considered as a fixed value. In contrast, since the dimensions of a quantum dot are extremely small, the addition/subtraction of a single atom will significantly change the nanocrystal dimensions and bandgap.

Table lists the *r*B values for common semiconductor crystals whose bandgap may be easily fine-tuned by simply changing the diameter
of the quantum dot, as long as the dimensions are smaller than *r*B.



Calculated Exciton Bohr Radii for Various Semiconductors

Material	r_B (Å)
Si	55
CdS	315
CdSe	61
CdTe	100
ZnO	18
ZnS	50
PbS	204
PbSe	460
InAs	340
InSb	540

Properties of Nanomaterials

In the early 1980s, Efros described the size-dependent electronic properties of quantum dots, first delineating that the bandgap, En, will increase from the bulk value based on a $1/R2$ confinement energy term (Eq. 1). According to quantum confinement theory, electrons in the conduction band and holes in the valence band are spatially confined by the potential barrier of the surface. Due to confinement of both electrons and holes, the lowest energy optical transition from the valence to conduction band will increase in energy, effectively increasing the bandgap.

$$(1) \qquad E_{\mathrm{n}} = E_{\mathrm{g}} + \frac{h^2\pi^2}{2\mu R^2},$$

where Eg is the bandgap of the bulk semiconductor; h, Planck’s constant; R, the radius of the quantum dot; and μ is mass of the exciton given by $m_e m_h/(m_e + m_h)$. Here me and m_h are masses of the electron and hole, respectively

$$(2) \qquad E_{\mathrm{n}} = E_{\mathrm{g}} + \frac{h^2\pi^2}{2\mu R^2} - \frac{1.786\,\mathrm{e}^2}{\varepsilon R} + 0.284\,E_{\mathrm{R}},$$

where E_R is the Rydberg (spatial correlation) energy of bulk semiconductor:

$$E_{\mathrm{R}} = \frac{\mu\,\mathrm{e}^4}{2\varepsilon^2\varepsilon_0^2 h^2} = 13.56\frac{\mu}{\varepsilon^2 m_{\mathrm{e}}},$$

where ε_0 is the permittivity of free space; ε, the dielectric constant of the bulk semiconductor; and m_e is the mass of the electron. Hence, the absorption energy of quantum dots will shift to higher frequency with decreasing diameter of the dots, with a dependence of $1/R^2$.

Synthesis of metallic and oxide nanoparticles

Reduction of metal complexes in dilute solutions is the general method in the synthesis of metal colloidal dispersions, and a variety of methods have been developed to initiate and control the reduction reactions.

In the synthesis of metallic nanoparticles, or more specifically speaking, metallic colloidal dispersion, various types of precursors, reduction reagents, other chemicals, and methods were used to promote or control the reduction reactions

$$\mathrm{RhCl_3} + \frac{3}{2}\mathrm{CH_3OH} \rightarrow \mathrm{Rh} + \frac{3}{2}\mathrm{HCHO} + 3\mathrm{HCl}$$

Colloidal dispersion of rhodium by refluxing a solution of rhodium chloride and **PVA** in a mixture of methanol and water at *79° C. Here*, methanol was used as a reduction reagent

Commonly oxide particles in colloidal dispersions are synthesized by sol-gel processing.

One-Dimensional Nanostructures

Nanotube, Nanofiber, Nanowire, and Nanorod

Referred to as 1D nanostructures, is reserved for those materials that have nanoscale dimensions that are equivalent in all but one direction.

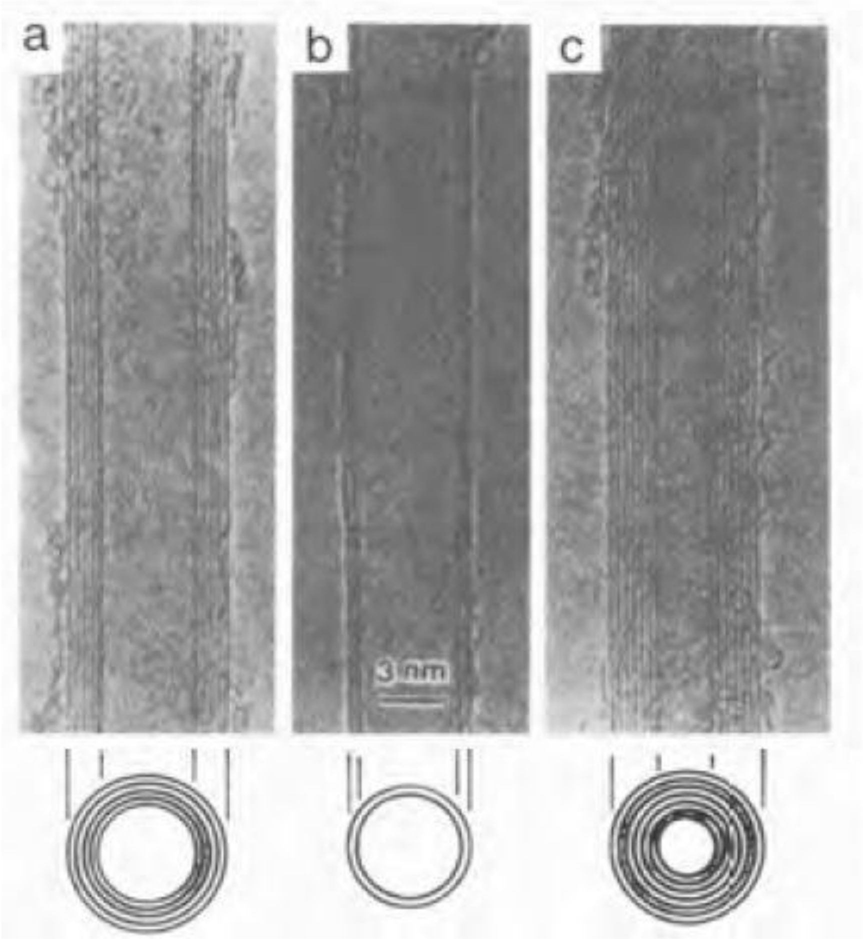
The common thread among all of these structures is that their diameters must be within the 1–100 nm range; typically, their lengths are within the micron (or larger) regime.

Carbon nanotubes

The most widely studied 1D nanomaterial is the *carbon nanotube* (CNT).

These structures were first discovered by Iijima in 1991, and consist of a graphitic sheet(s) rolled into a tubular array.

Based on the layers of graphene sheets that comprise the CNT, the structures are designated as single-walled, double-walled, or multiwalled nanotubes (SWNTs, DWNTs, or MWNTs respectively)



TEM images of MWNTs, formed from the folding (a) 5-, (b) 2- (*i.e.*, DWNT), and (c) 7- stacked graphene sheets.

Properties of Nanomaterials

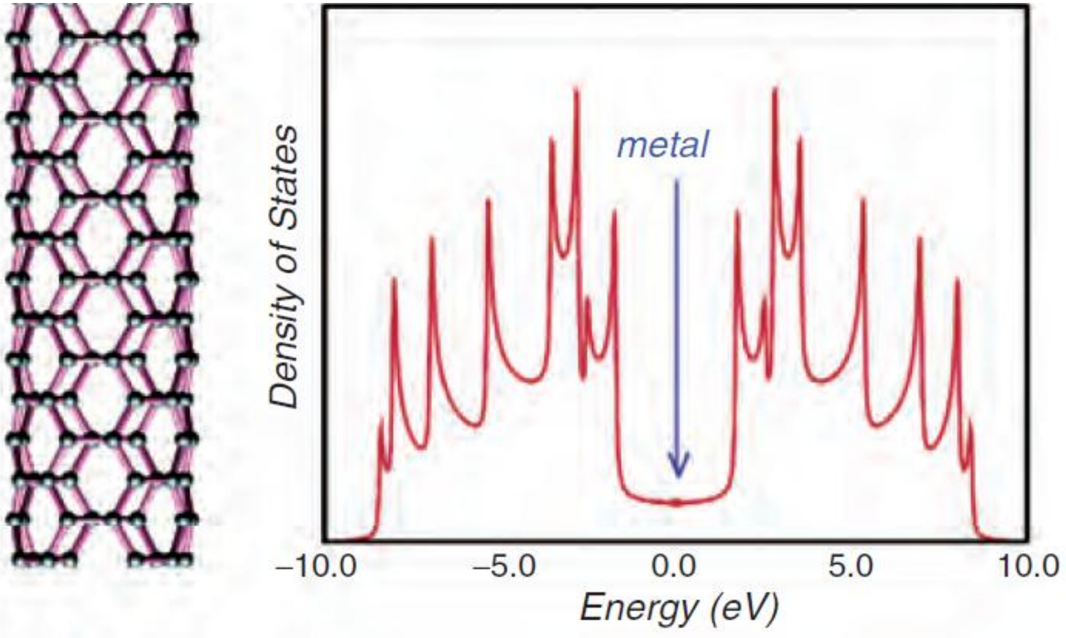
The diameters of CNTs range from 1 nm (SWNTs) to >30 nm (MWNTs), with aspect ratios (length:width) ranging from 100 to greater than 1×10^6.

Even though the diameters of CNTs are orders of magnitude smaller than a human hair, their tensile strength is *ca.* 20 times greater than steel – a property attributed to extremely strong sp^2 bonding between neighboring hexagonal units.

The electrical conductivity of SWNTs may vary from metallic to semiconducting, depending on the way a graphene sheet is folded

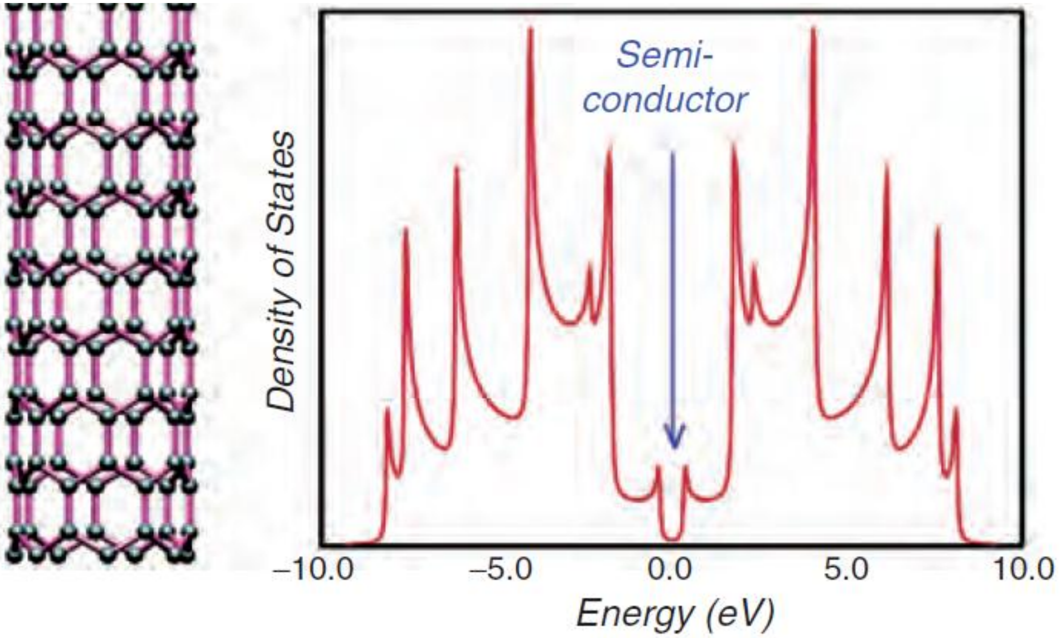
For metallic SWNTs, the electrical conductance may exceed silver or copper by three orders of magnitude.

Properties of Nanomaterials



metallic

semiconducting



Since **CNTs** have a high electrical conductivity and contain sharp tips, these **nanomaterials are the best-known field emitter.**

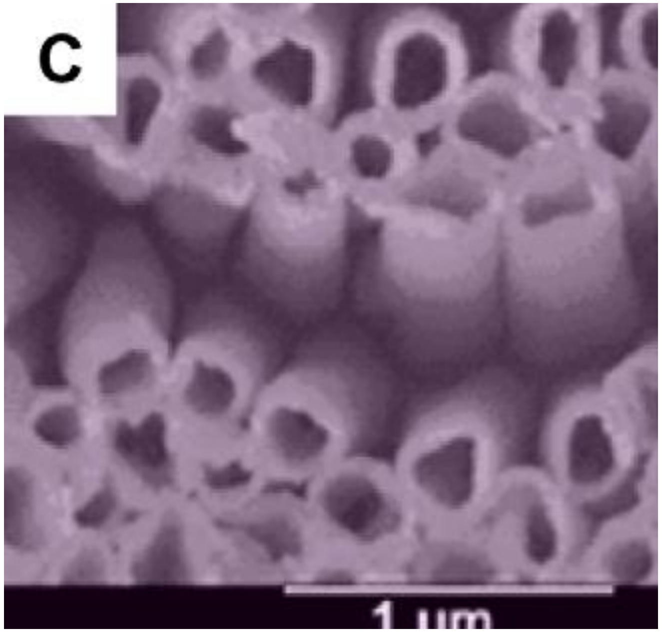
In general, the smaller the radius of curvature of the tip, the more concentrated the electric field will be, which corresponds to increased field emission at low required voltages. This property is currently being exploited for the design of flat-panel field emission displays.

Though plasma and LCD displays are hot ticket items at electronics stores, they both possess inherent disadvantages. Plasma displays are extremely heavy, consume a significant amount of energy, and are prone to "burn-in," which permanently degrades the screen. On the other hand, LCD screens are expensive to produce and often lack the response time required to view fast-paced sporting events/movies without blur.

Properties of Nanomaterials

Hence, as far as picture quality is concerned, traditional CRT displays are still among the finest quality. The replacement of this technology with CNTs is a logical step in the evolution of display panels. Rather than a single electron gun, CNT-based screens will contain a separate nanotube electron gun for each individual pixel in the display – dramatically enhancing the resolution and clarity of the picture. Further, in contrast to current large flat-panel televisions, the overall weight of CNT-based analogues will be significantly lower, and they will consume far less power.

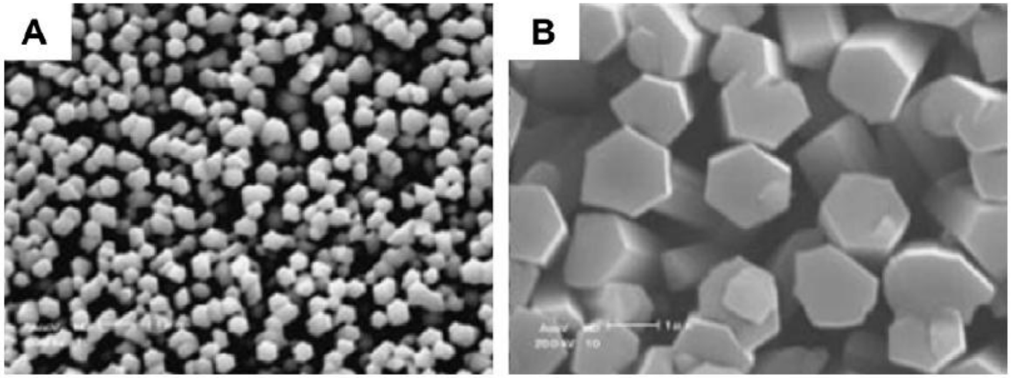
A *nanotube* is a 1D structure that contains a hollow core, whereas the other three nanoarchitectures are solid throughout.



MnO$_2$ nanotube arrays

Nanorods

A *nanorod* is typically a crystalline 1D nanostructure, with an overall length comparable to its width (*i.e.*, both dimensions are <100 nm). As their name implies, another feature of nanorods is their rigid sidewall structures. The term “nanocrystal” is probably more appropriate for these structures (or, more explicitly: “rod-like nanocrystals”).

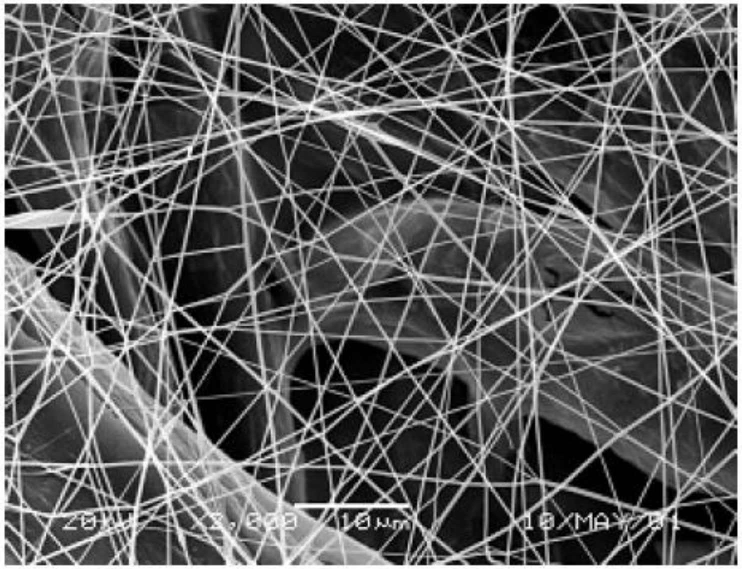


SEM pictures of ZnO nanorods on sapphire substrate (A) and SiO_2 substrate (B)

Whereas nanowires, nanofibers, and nanotubes exhibit an interwoven array, nanorods are completely linear in morphology. As such, nanorods are capable of stacking onto each other to yield interesting 2D and 3D arrays

Nanofibers

The term ***nanofiber*** should be reserved for 1D nanostructures that are amorphous (and usually nonconductive) such as polymers and other nongraphitized carbonaceous structures



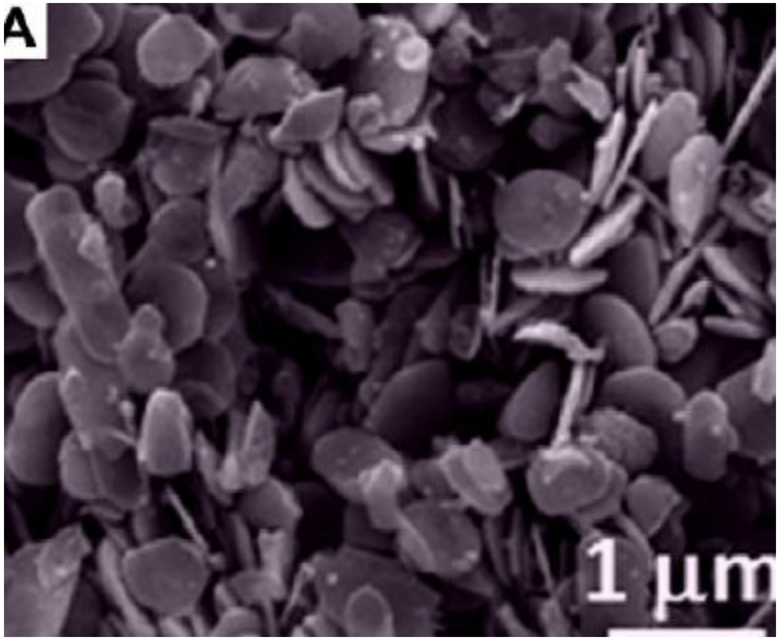
Polymeric nanofibers can be made using the electrospinning process. Elecotrospun nanofibers, with fiber diameters of 0.25 microns have been used in industrial, consumer and defense filtration applications for more than twenty years.

Nanofibers provide dramatic increases in filtration efficiency

2Dimentional Nano Structured Materials

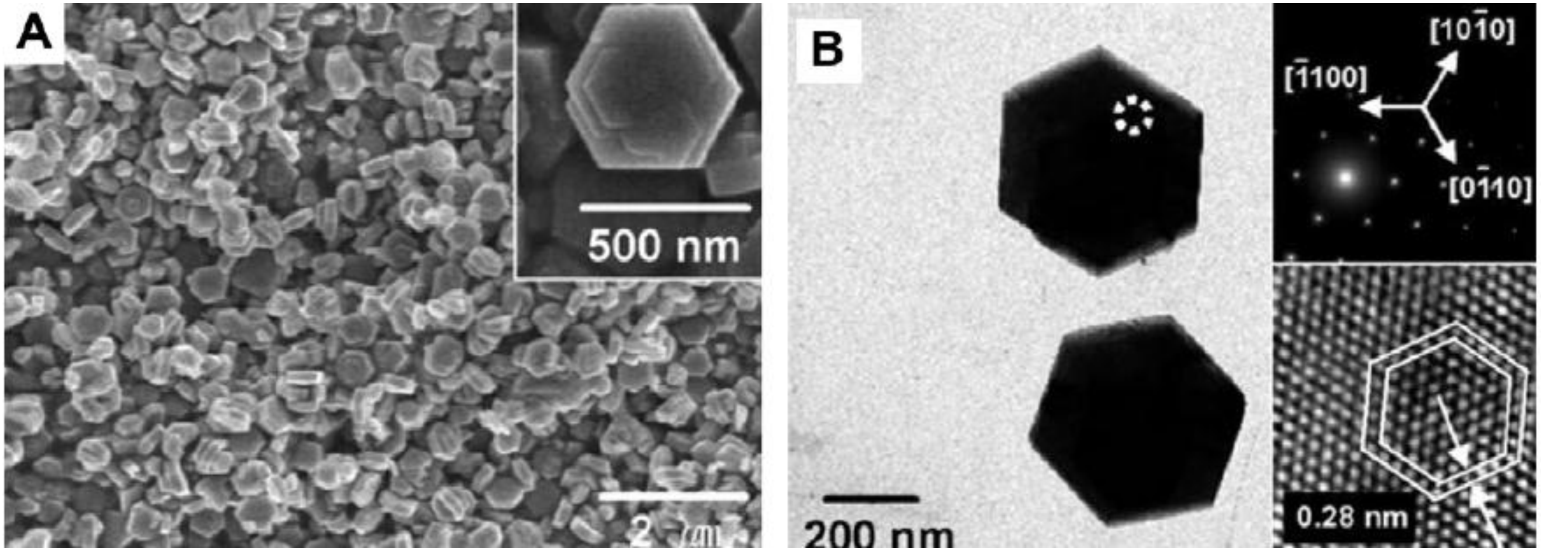
2D nanostructures have two dimensions outside of the nanometric size range. In recent years, a synthesis 2D NSMs have become a focal area in materials research, owing to their many low dimensional characteristics different from the bulk properties. In the quest of 2D NSMs, considerable research attention has been focused over the past few years on the development of 2D NSMs. 2D NSMs with certain geometries exhibit unique shape-dependent characteristics and subsequent utilization as building blocks for the key components of nanodevices

Properties of Nanomaterials



SEM image of Bi_2WO_6 nanoplates

Properties of Nanomaterials



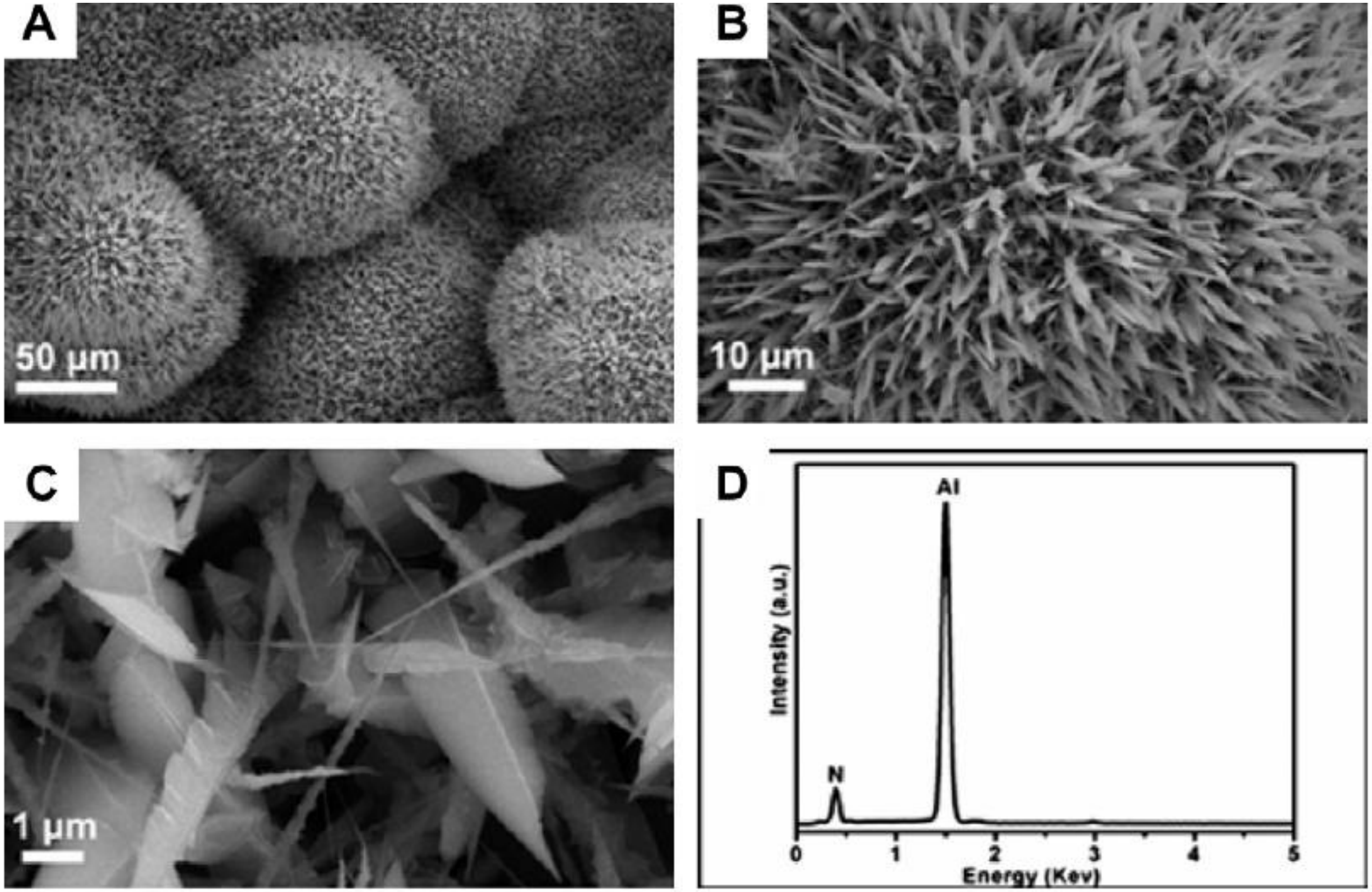
SEM and TEM images of ZnO nanodisks

3 Dimentional Nano Structured Materials

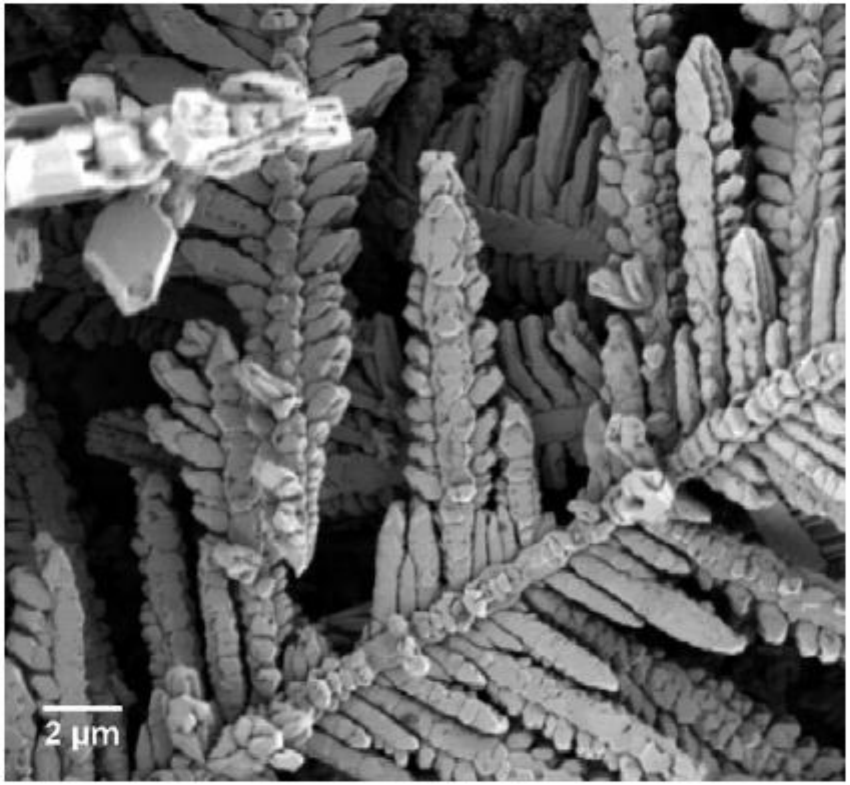
It is of great interest to synthesize 3D NSMs with a controlled structure and morphology. In addition, 3D nanostructures are an important material due to its wide range of applications in the area of catalysis, magnetic material and electrode material

for batteries. Moreover, the 3D NSMs have recently attracted intensive research interests because the nanostructures have higher surface area and supply enough absorption sites for all involved molecules in a small space . On the other hand, such materials with porosity in three dimensions could lead to a better transport of the molecules

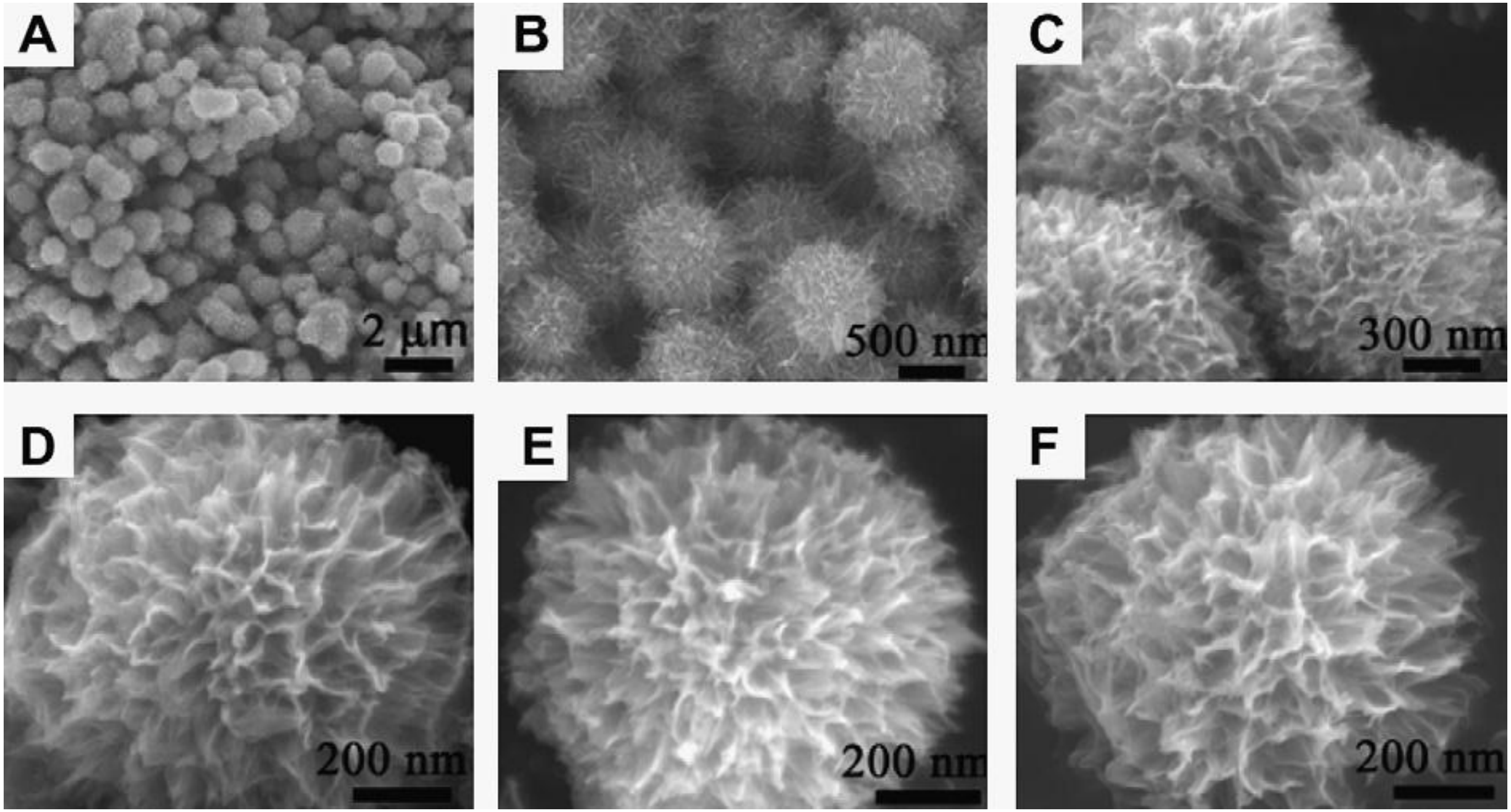
nanoballs (dendritic structures),
nanocoils, nanocones, nanopillers
and nanoflowers



3D urchin-like nanostructured AlN



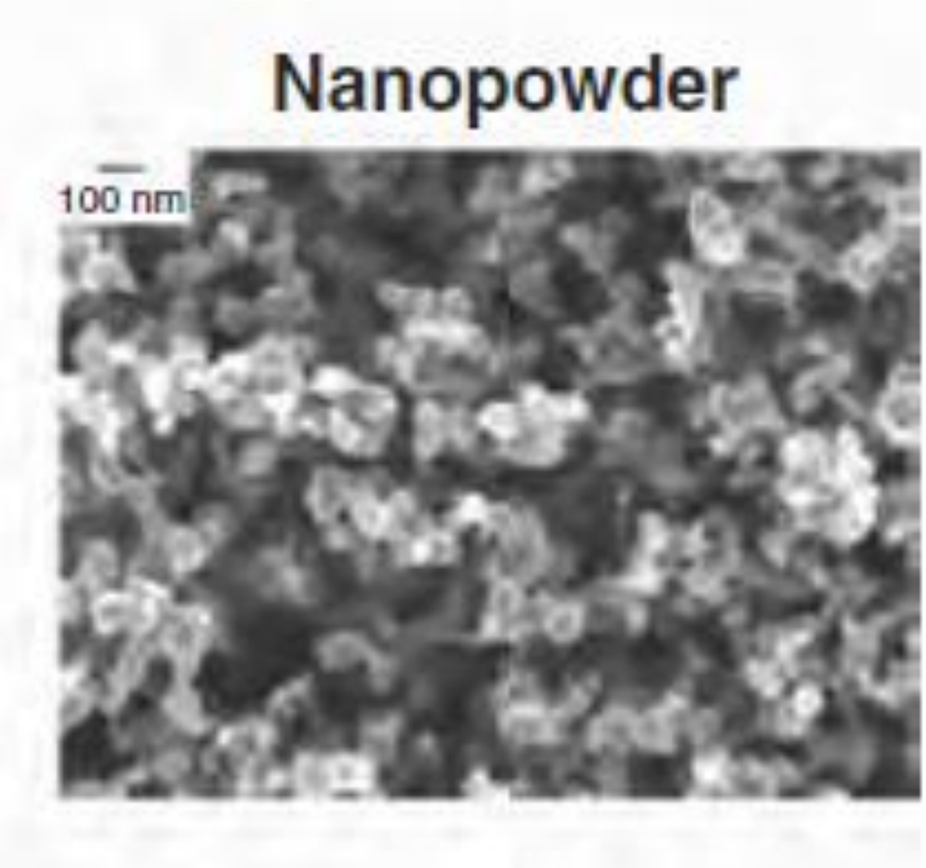
SEM image of Ag dendrites formed on the surface of Al foil



Low-magnification SEM images of 3D crystalline TiO2 nanostructures

Nanopowder

Analogous to bulk materials, the agglomeration of noncrystalline nanostructural subunits should best be termed a ***nanopowder***



Many techniques have been developed in the **synthesis and formation of one-dimensional nanostructured materials**

These techniques can be generally grouped into four

(1) Spontaneous growth:
(a) Evaporation-condensation
(b) Vapor (or solution)–liquid–solid (VLS or SLS) growth

(2) Template-based synthesis:
(a) Electroplating
(b) Colloid dispersion, melt, or solution filling

(3) Electrospinning
(4) Lithography

Spontaneous growth and template-based synthesis are considered as a bottom-up approach, whereas lithography is a top-down technique.

Spontaneous growth commonly results in the formation of single crystal nanowires or nanorods along a preferential crystal growth direction depending on the crystal structures and surface properties of the nanowire
materials.

Template-based synthesis mostly produces polycrystalline or
even amorphous products

Evaporation (dissolution)-condensation growth

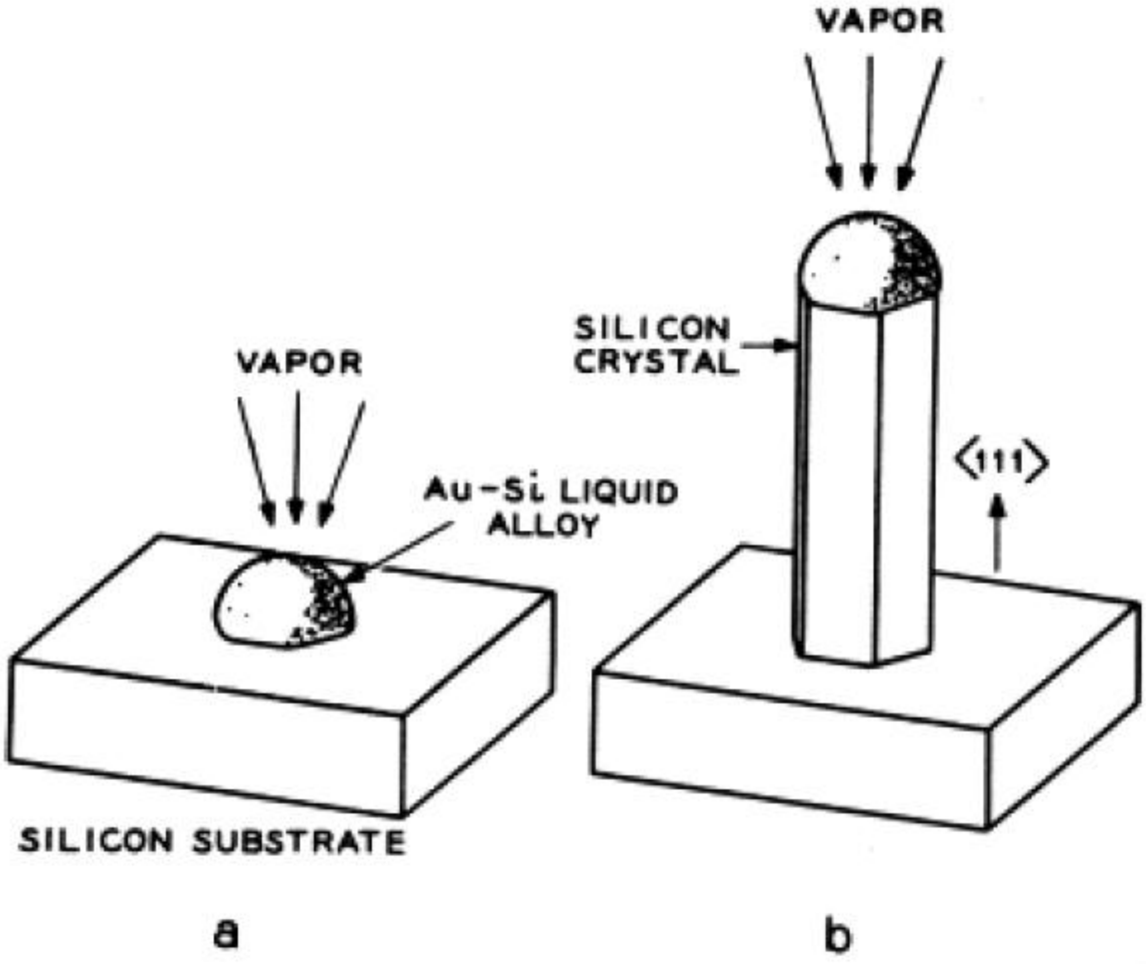
Evaporation-condensation process is also referred to as a vapor–solid (VS) process

Nanowires and nanorods grown by evaporation-condensation methods are commonly single crystals with fewer imperfections. The formation of nanowires, nanorods or nanotubules through evaporation (or dissolution)-condensation is due to the anisotropic growth.

In a VLS growth, the process can be simply described as following

The growth species is evaporated first, and then diffuses and dissolves into a liquid droplet. The surface of the liquid has a large accommodation coefficient, and is therefore a preferred site for deposition. Saturated growth species in the liquid droplet will diffuse to and precipitate at the interface between the substrate and the liquid. The precipitation will follow first nucleation and then crystal growth.

Continued precipitation or growth will separate the substrate and the liquid droplet, resulting in the growth of nanowires.



Schematic showing the principal steps of the vapor–liquid–solid growth technique: (a) initial nucleation and (b) continued growth

Example the VLS growth

A thin layer of gold is sputtered on a silicon substrate and annealed at an elevated temperature (above the eutectic point of 385 C of the silicon–gold system), which is typically the same as the growth temperature.

During the annealing, silicon and gold react and form a liquid mixture, which forms a droplet on the silicon substrate surface.

When silicon species is evaporated from the source and preferentially condensed at the surface of the liquid droplet, the liquid droplet will become supersaturated with silicon.

Subsequently, the supersaturated silicon will diffuse from the liquid–vapor interface to and precipitate at the solid–liquid interface

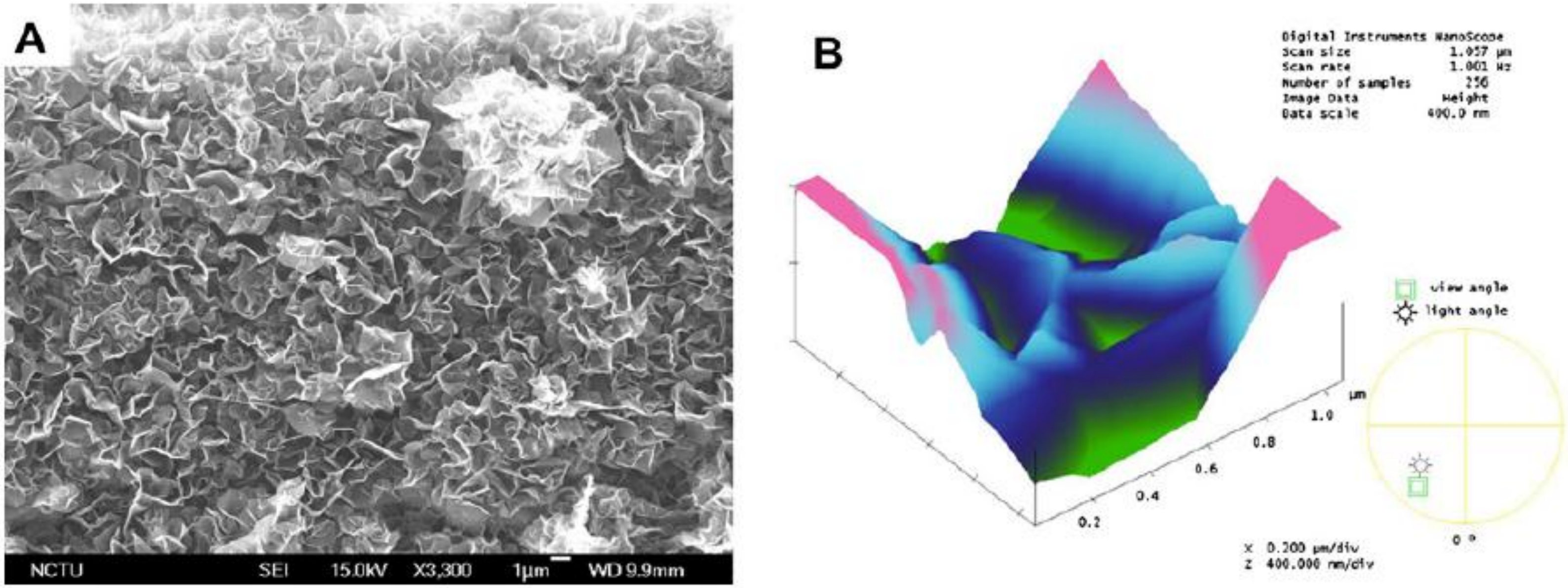
Control of the size of nanowires

The size of nanowires grown by VLS method is solely **determined by the size of the liquid catalyst droplets**. To grow thinner nanowires, **one can simply reduce the size of the liquid droplets.** Typical method used to form small liquid catalyst droplets is to coat a thin layer of catalyst on the growth substrate and to anneal at elevated temperatures

Synthesis of 3D NSMs by physical processes In recent years, with the progress of nanotechnology, there has been increasing interest in the synthesis of 3D NSMs (for instance spring-like nanocoils, ball-like nanodendritic structures, and nanoflowers) because they are exhibit newer and/or better physical/chemical properties.

Concerning the fabrication of these nanoarchitectures, evaporation technique, sputtering technique, lithography process, hot plasma, cold plasma, spray pyrolysis, inert gas phase condensation technique,

3D graphitic nanosheets using CVD in the presence of methane gas



(A) SEM and (B) AFM images of the 3D graphitic nanosheets

Metallic nanoparticles

Metallic nanoparticles possess unique optical, electronic, chemical and magnetic properties that are strikingly different from that of the individual atoms as well as their bulk counterparts .

Various physical properties, such as, mechanical strength, ductility, thermal stability, sintering ability, diffusivity and the chemical reactivity of the particles in the nanometer regime have also been found to be dependent on particle size without a change in the chemical composition of the particles.

Properties of Nanomaterials

In a metal cluster, atoms at surfaces have fewer neighbours than atoms in the bulk. As a result, the atoms in the bulk are co-ordinatively saturated while the atoms on the surface are co-ordinatively unsaturated.

Because of this lower coordination and unsatisfied bonds, surface atoms are less stabilised than bulk atoms.

The smaller a particle, the larger the fraction of atoms at the surface and the higher the average binding energy per atom.

One distinguishing characteristic of nanometer scale structures is that unlike macroscopic materials, they typically have a high percentage of their constituent atoms at the surface.

Properties of Nanomaterials

The volume of an object ($V \alpha R^3$, where R is the characteristic length) decreases more quickly than its surface area ($S \alpha R^2$) as the size diminishes: $S/V \alpha R^{-1}$, where R has atomic or molecular dimensions.

This scaling behavior leads, in the most extreme case, to structures where nearly every atom in the structure is interfacial and in some sense, it could be assumed that nanostructures are “all surface”. The term ‘surface’ has been used to indicate the geometrical separation between two or more phases of matter whereas the term ‘interface’ implies a region of finite thickness over which the phase change occurs

Properties of Nanomaterials

Another important aspect is the electronic structure of the nanoparticles that depends critically on the size of the particles.

In metals and semiconductors, the electronic wavefunctions of conduction electrons are delocalised over the entire particle.

Electrons can, therefore, be described as ‘particles in a box’ and the densities of state and the energies of the particles depend crucially on the size of the box which, at the onset, leads to a smooth size dependence.

Properties of Nanomaterials

The HOMO– LUMO band gap of semiconductor particles and therefore, their absorption and fluorescence wavelengths become size dependent

Ionisation potentials and electron affinities are tuned between the atomic values and the work function of the bulk material by variation of the cluster size. These properties relate to the availability of electrons for forming bonds or getting involved in redox reactions and thus, the catalytic activity and selectivity also become functions of size

Properties of Nanomaterials

However, for small particles with dimension in the nanometer regime, the electronic states are not continuous, but discrete, due to confinement of the electron wavefunction.

The average spacing of successive quantum levels, δ, known as the Kubo gap, is given by,
$\delta = 4E_F /3N$

where, E_F is the Fermi energy of the bulk materials and N, the nuclearity i. e., the number of atoms in the nanocluster.

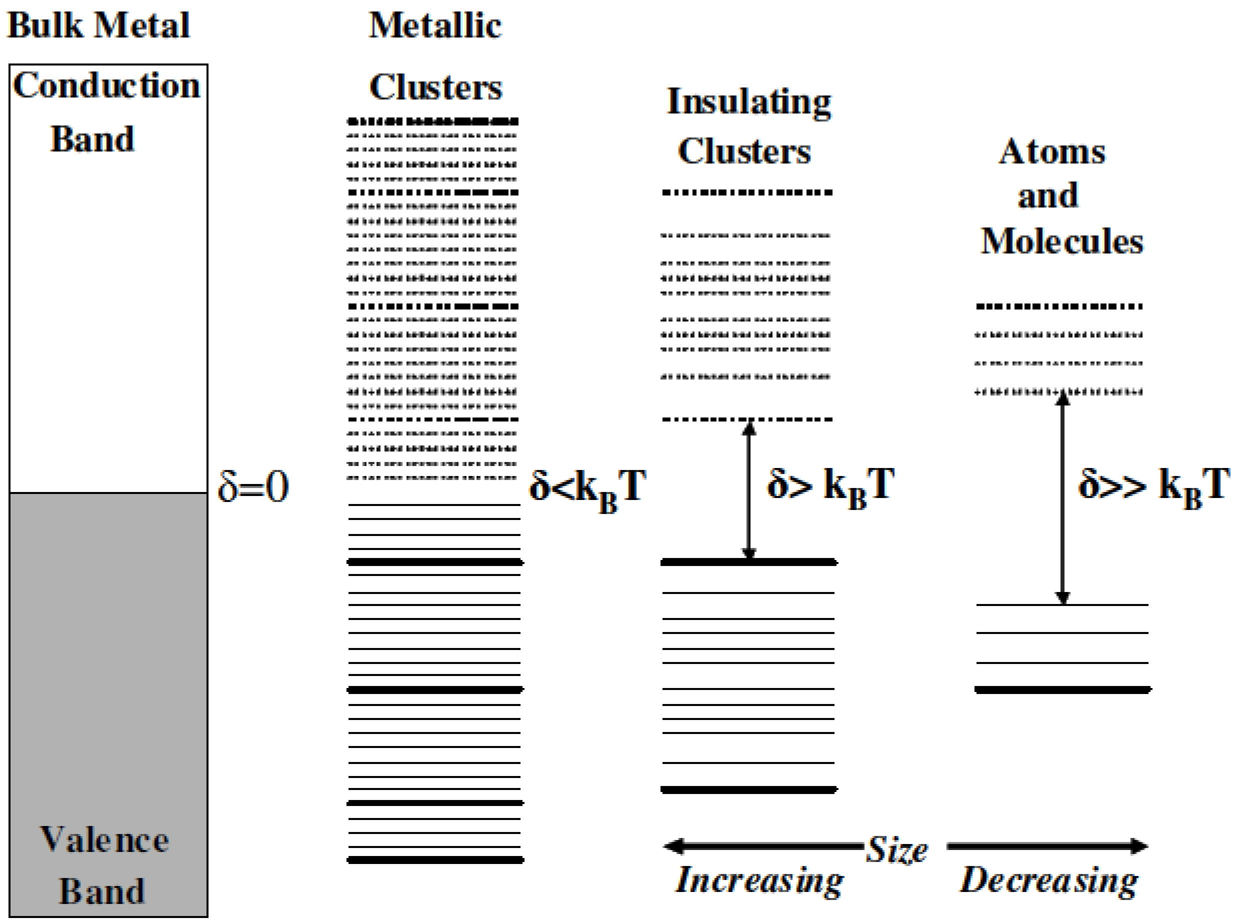
Fermi energy of the bulk metal and *n* is the number of valence electrons in the nanoparticle (usually taken as its nuclearity). Thus, for a Ag nanoparticle of 3-nm diameter containing ~103 atoms, the value of d would be 5–10 meV. Since at room temperature, *k*T @ 25 meV, the 3-nm particle would be metallic (*k*T > d). At low temperatures, the level spacings especially in small particles, may become comparable to *k*T, rendering them nonmetallic

Properties of Nanomaterials

Named after the Japanese theoretical physicist, Roygo Kubo introduced the concept in 1962.

The Kubo gap is the average spacing that exists between consecutive energy levels and measured in the units of millielectron volts (meV).

Since, the number of valence electrons in the nanoparticles is measured as a function of nuclearity, the energy level spacing varies inversely with the nuclearity of the particles



Evolution of the band gap and the density of states as the number of atoms in a system increases

In band theory, the breadth of a band is directly related to the strength of interactions among nearest neighbours.

For atoms/molecules, this interaction is weak which corresponds to a narrow band.

Additional atoms are added to the solid, stronger interactions will occur resulting in a greater density of states near the Fermi level.

Hence, the insulating properties of very small nanoclusters are due to the small number of neighboring atoms which are held together primarily by non-metallic interactions (e.g., van der Waal forces).

As size of the nanocluster increases, the atomic s/p and d orbitals from a larger number of constituent atoms will broaden into bands forming an energy continuum

Theoretical investigations of the electronic structure of metal nanoparticles gold clusters with N = 6,……,147 also throw light on the size-induced changes in the electronic structure.

The HOMO-LUMO gap decreases with particle size from 1.8 eV for Au6 to 0.3 eV for Au147.

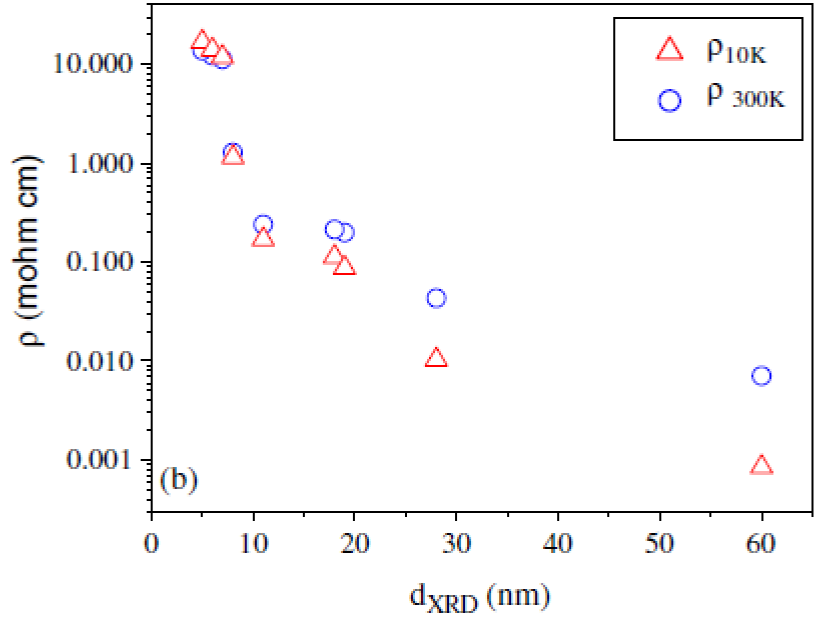
The Kubo gap has dramatic effect on the properties associated with the material. It is possible to control the Kubo gap which will, then, cause the system to become metallic or non-metallic.

Atoms have their well known atomic orbitals. Depending on the extent of overlap in a solid they remain mostly unperturbed, as in noble gases, or they combine to extended band structures, as in metals or semiconductors. The core orbitals are confined to a relatively small volume and remain localised (atom-like). Each of N atoms contributes with its atomic states to a band so that, although the width of a band increases slightly when more atoms are added, the density of states (DOS) within a band is basically proportional to the number of atoms of an ensemble with an extended band-like state.

The band width amounts typically to a few eV. Thus, the DOS is on the order of N per eV, which is very large for a bulk amount of matter (N # Avogadro’s number, NA) but low for small clusters.

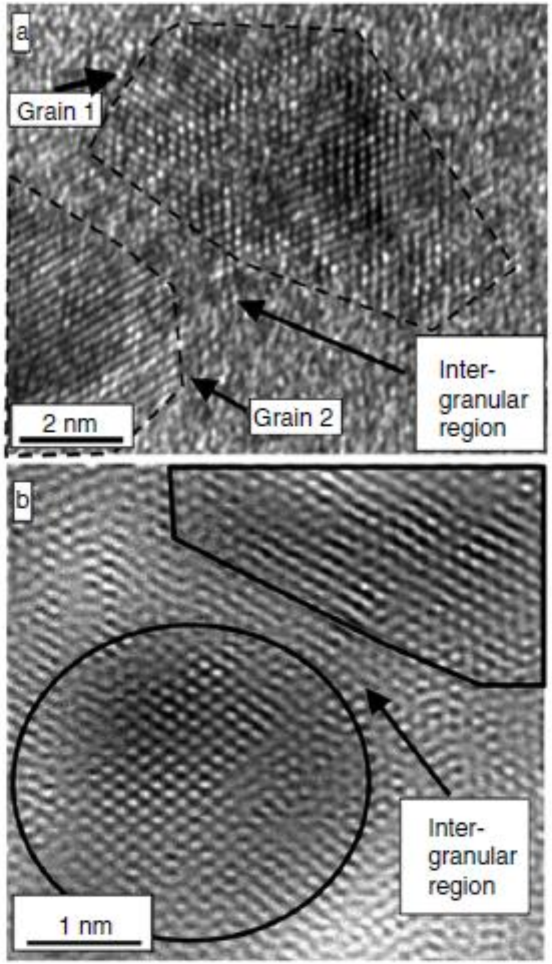
An important threshold is reached when the gap between the highest occupied and the lowest unoccupied state (called the Kubo gap d) equals thermal energy

When electrons get thermally excited across the Kubo gap, a low temperature insulator becomes a semiconductor and at higher temperatures a metal; and also magnetic properties of small clusters can change dramatically. This non-metal-to-metal transition can take place within a single incompletely filled band, or when two bands begin to overlap because of band broadening



Temperature dependence of the resistivity for nanostructured Nb films with different grain sizes (*d*XRD). The scale on the left refers to the metallic films with d_{XRD} 8 nm while the scale on the right is for the insulating films with $d_{XRD} < 8$ nm.

Particle size dependence of the resistivity at 10 and 300 K, depicted, respectively, by open triangles and circles.



High resolution transmission electron micrographs of the nanostructured Nb sample with $d_{XRD} \approx 5$ nm. The grains are defined as crystallographically ordered regions (delineated in the figure) while the disordered inter-granular regions are ≈1 nmwide.

Nanocomposites

The creation, processing, characterization, and utilization of materials, devices, and systems with dimensions on the order of 0.1–100 nm, exhibiting novel and significantly enhanced physical, chemical, and biological properties, functions, phenomena, and processes due to their nano-scale size" .

Current interests in nanotechnology encompass nano-biotechnology, nano-systems, nano-electronics, and nano-structured materials, of which nanocomposites are a significant parti

Properties of Nanomaterials

The expansion of length scales from meters (finished woven composite parts), micrometers (fiber diameter), sub-micrometers (fiber/matrix interphase) to nanometers (nanotube diameter) presents tremendous opportu-nities for innovative approaches in the processing, characterization, and analysis/modeling of this new gen-eration of composite materials.

Properties of Nanomaterials

- Constituents have at least one dimension in the nanometer scale.
  - Nanoparticles (Three nano-scale dimensions)
  - Nanofibers (Two nano-scale dimensions)
  - Nanoclays (One nano-scale dimensions)

Nanoparticle-reinforced composites

Particulate composites reinforced with micron-sized particles of various materials are perhaps the most widely utilized composites in everyday materials. Particles are typically added to enhance the matrix elastic modulus and yield strength. By scaling the particle size down to the nanometer scale, it has been shown that novel material properties can be obtained

Micron-scale particles typically scatter light making otherwise transparent matrix materials appear opaque. showed in their study of SiO_2/epoxy composites that decreasing the particle size resulted in significantly improved transmittance of visible light.

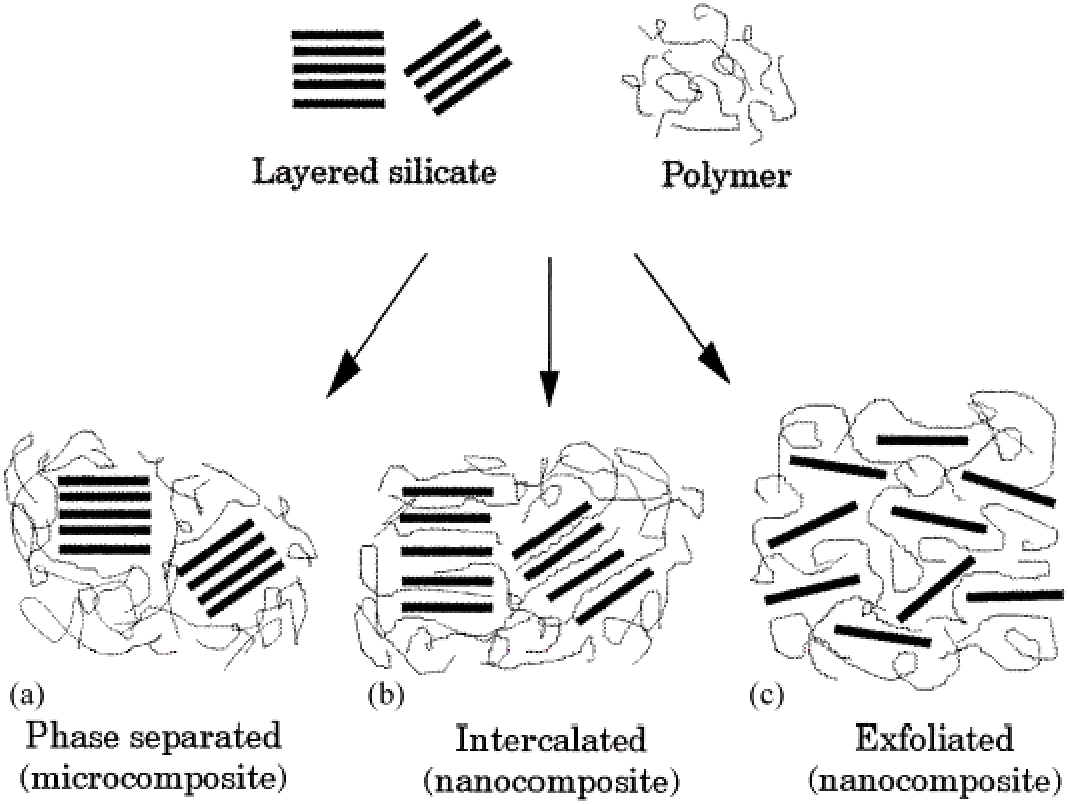
Nanoplatelet-reinforced composites

Clay and graphite. In their bulk state, both clay and graphite exist as layered materials. In order to utilize these materials most efficiently, the layers must be separated and dispersed throughout the matrix phase.

The advantages of polymer-based clay nano-composites include improved stiffness, strength, tough-ness, and thermal stability as well as reduced gas permeability and coefficient of thermal expansion

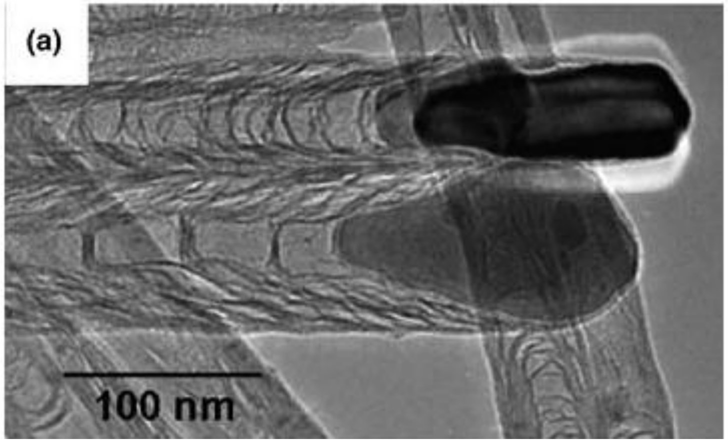
In addition to mechanical properties, the thermal sta-bility, fire resistance and gas barrier properties of poly-mer/clay nanocomposites can be enhanced through the addition of nanometer-scale reinforcement.

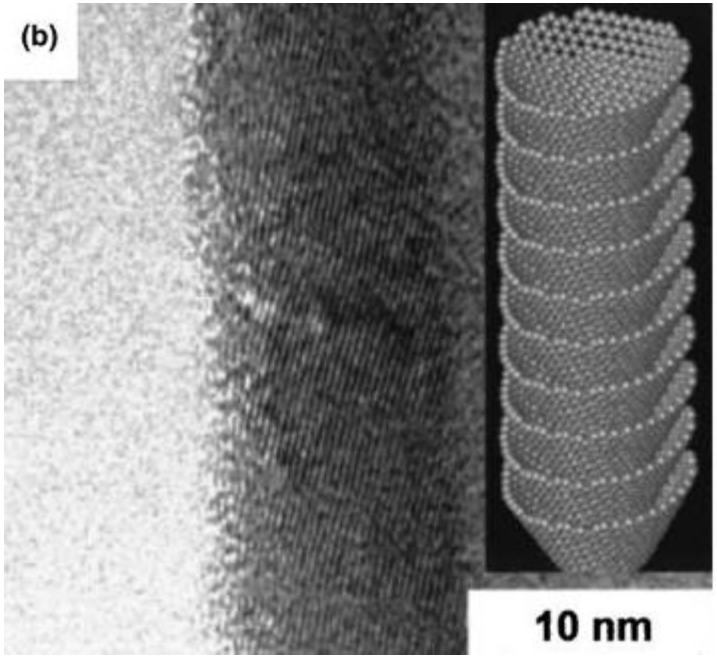
Nanoclays


Layered silicate
Polymer
(a)
Phase separated
(microcomposite)
(b)
Intercalated
(nanocomposite)
(c)
Exfoliated
(nanocomposite)

Nanofiber-reinforced composites

Vapor grown carbon nanofibers (CNF) have been used to reinforce a variety of polymers, including polypropylene, polycarbonate, nylon, and epoxy.
Carbon nanofibers are known to have wide-ranging morphologies, from structures with a disordered bamboo-like structure to highly graph-itized “cup stacked” structures





Carbon nanofibers typically have diameters on the order of 50–200 nm

Properties of Nanomaterials

Researchers utilized a variety of techniques to achieve dispersion of carbon nanofibers in a poly(ethylene terephthalate) (PET) matrix and subsequently melt-spun fibers. The compressive strength and torsional moduli of the nanocomposite fibers were considerably higher than that for the unreinforced PET fiber

Carbon nanotube-reinforced composites

The density of a SWCNT is about 1.33–1.40 g/cm3 , which is just one-half of the density of aluminum. The elastic modulus of SWCNT is comparable to that of diamond (1.2 TPa). The reported tensile strength of SWCNT is much higher than that of high-strength steel (2 GPa). The tremendous resilience of SWCNT in sustaining bending to large angles and restraightening without damage is distinctively different from the plastic defor-mation of metals and brittle fracture of carbon fibers at much lower strain when subjected to the same type of deformation.

Properties of Nanomaterials

The electric current carrying capability is estimated to be 1·10 9 amp/cm 2 , whereas copper wires burn out at about 1·10 6 amp/cm 2 . The thermal conductivity of SWCNT is predicted to be 6000 W/ m K at room temperature; this is nearly double the ther-mal conductivity of diamond of 3320 W/m K. SWCNTs are stable up to 2800□C in vacuum and 750□C in air, whereas metal wires in microchips melt at 600–1000 □C. SWCNTs have great potential in field emission applications because they can activate phosphors at 1– 3 V if electrodes are spaced 1lm apart. Traditional Mo tips require fields of 10–100 V/lm and have very limited lifetimes.

Properties of Nanomaterials

The outstanding thermal and electric properties com-bined
with their high specific stiffness and strength, and
very large aspect ratios have stimulated the development
of nanotube-reinforced composites for both structural
And functional application

Properties of Nanomaterials

Both SWCNTs and MWCNTs have been utilized for reinforcing thermoset polymers (epoxy, polyimide, and phenolic), as well as thermoplastic polymers (polypropylene, polystyrene, poly methyl methacrylate (PMMA), nylon 12 etc.

Researchers fabricated nanocomposites consisting of DWCNTs with a high degree of dispersion The resulting composites showed increase of strength, Young's modulus and strain to failure at a nanotube con-tent of only 0.1 wt%. In addition, the nanocomposites showed significantly enhanced fracture toughness as compared to the unreinforced epoxy..

Properties of Nanomaterials

In the processing of nanocomposites, carbon nano-tubes need to be separated from bundles and dispersed uniformly in a polymer matrix for maximizing their contact surface area with the matrix. Modification of nanotube surfaces, for example, the creation of cova-lent chemical bonds between nanotubes and the poly-mer matrix, enhances their interactions and gives rise to higher interfacial shear strength than van der Waals bonds.

Critical issues in nanocomposites

There is a lack of understanding of the interfacial bonding between the reinforcements and the matrix material from both analytical and experimental viewpoints

Dispersion

Uniform dispersion of nanoparticles, and nanotubes against their agglomeration due to van der Waals bond-ing is the first step in the processing of nanocomposites. Beside the problems of agglomeration of nanoparticles, exfoliation of clays and graphitic layers are essential. SWCNTs tend to cluster into ropes and MWCNTs pro-duced by chemical vapor deposition are often tangled together like spaghettis. The separation of nanotubes in a solvent or a matrix material is a prerequisite for aligning them

Alignment

Because of their small sizes, it is exceedingly difficult to align the nanotubes in a polymeric matrix material in a manner accomplished in traditional short fiber com posites. The lack of control of their orientation dimin-ishes the effectiveness of nanotube reinforcement in composites, whether for structural or functional performance.

Volume and rate

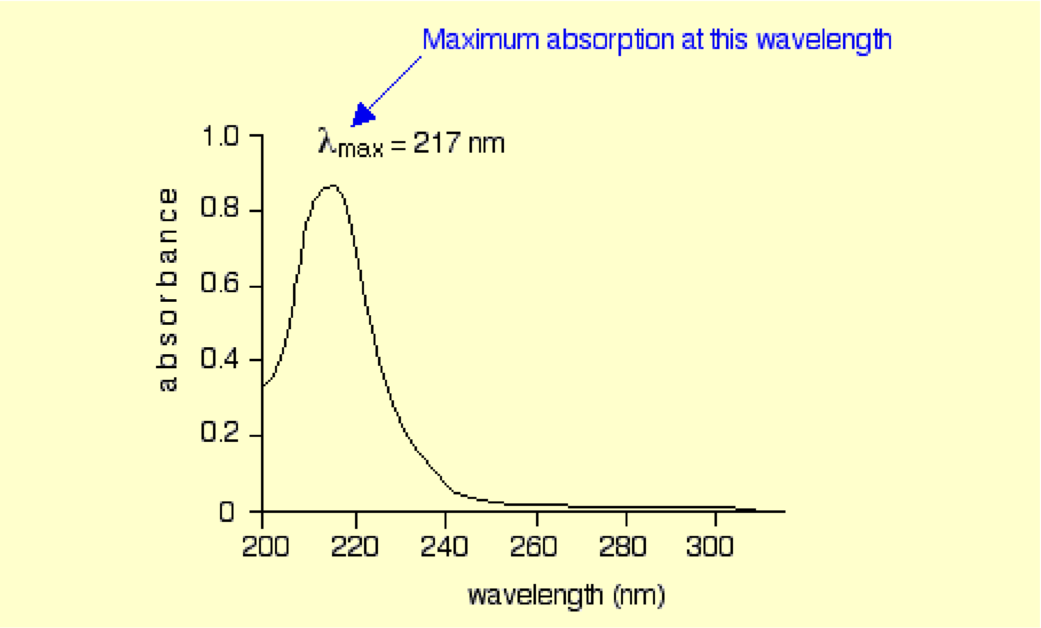
High volume and high rate fabrication is fundamental to manufacturing of nanocomposites as a commercially viable product. The lessons learned in the fabrication of traditional fiber composites have clearly demonstrated that the development of a science base for manufacturing is indispensable. Efficiency in manu-facturing is pivotal to the future development of nanocomposites

Cost effectiveness

Besides high volume andhigh rate production, the cost of nanocomposites also hinges on that of the nano-reinforcement material, particularly, nanotubes. It is anticipated that as applications for nanotubes and their composites increase the cost will be dramatically reduced

Size dependent absorption spectra

Properties of Nanomaterials



UV-visible absorption spectroscopy probes electronic transitions due to electronic excited states

Some Applications

Detection of Impurities

UV absorption spectroscopy is one of the best methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material. By also measuring the absorbance at specific wavelength, the impurities can be detected.

Structure elucidation of organic compounds.
UV spectroscopy is useful in the structure elucidation of organic molecules.

It is rarely used as a primary method for structure determination

Quantitative analysis

UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation.

Qualitative analysis

UVabsorption spectroscopy can characterize those types of compounds which absorbs UV radiation. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

Chemical kinetics

Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

Band Gap determination

Particle size determination

Transition between two electronic energy levels should give rise to a line in an absorption.

In practice, it may not be possible to distinguish individual line.

Large molecules have large number of vibrational and rotational levels. These energy levels may be close together. UV-vis radiation may rise molecules at many slightly different electronic energy levels to many slightly different higher levels.

As a result sharp lines are replaced by narrow bands

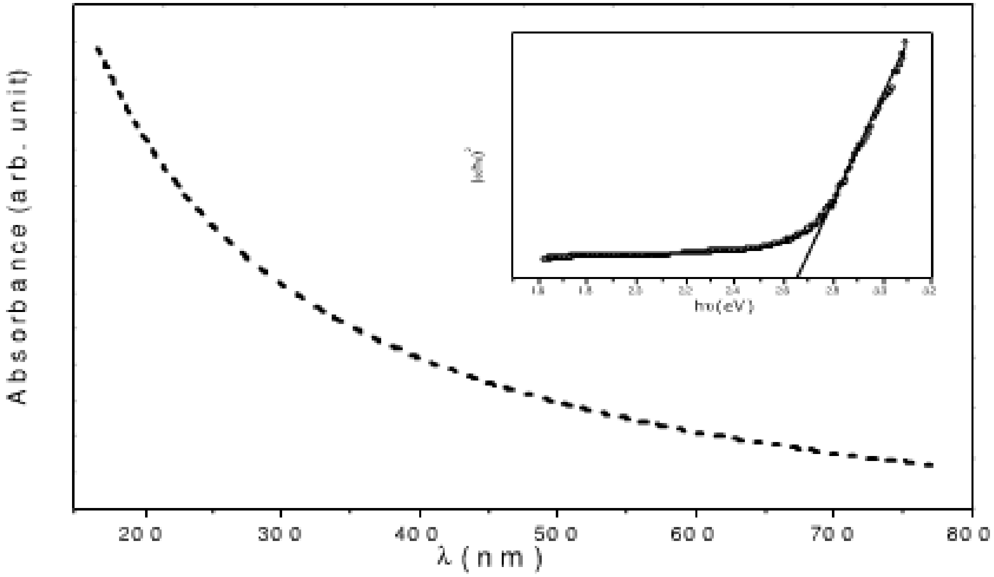
A convenient method of characterizing the size and size distribution of semiconductor nano-particles is UV/Visible absorption spectroscopy

Semiconductor nano- crystallites are know to have an absorption edge, which is shifted with respect to the bulk materials towards shorter wavelengths

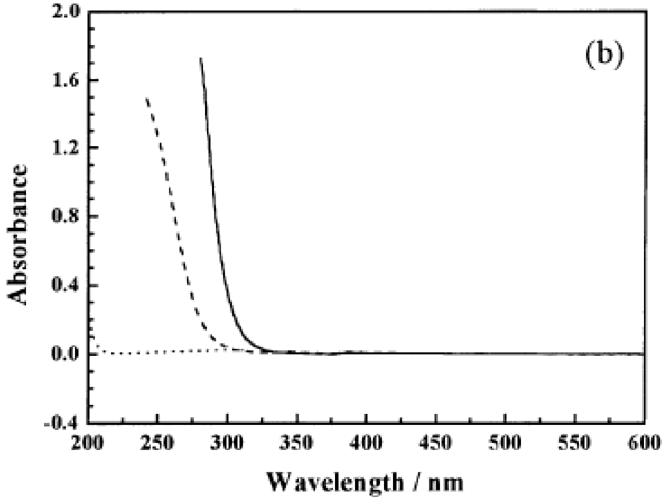
Blue Shift

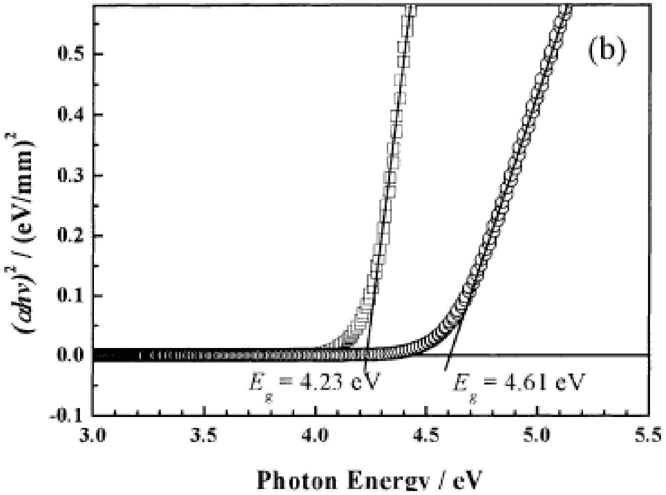
Nanosized semiconductor particles generally exhibit a threshold energy in the optical absorption measurements, due to the size specific band gap structures, which is reflected by the blue shifting of the absorption edge (from near-infrared to visible) with decreasing particle size

UV-visible absorption spectra of CdS nano-crystallites



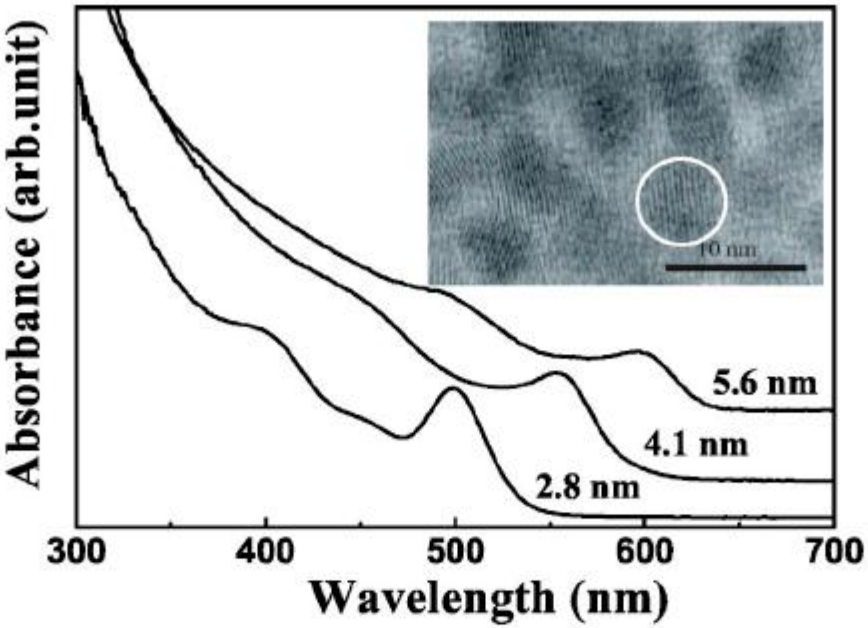
SnO_2 nanocrystalline particles less than 2 nm in mean diameter were prepared by ultra-filtration





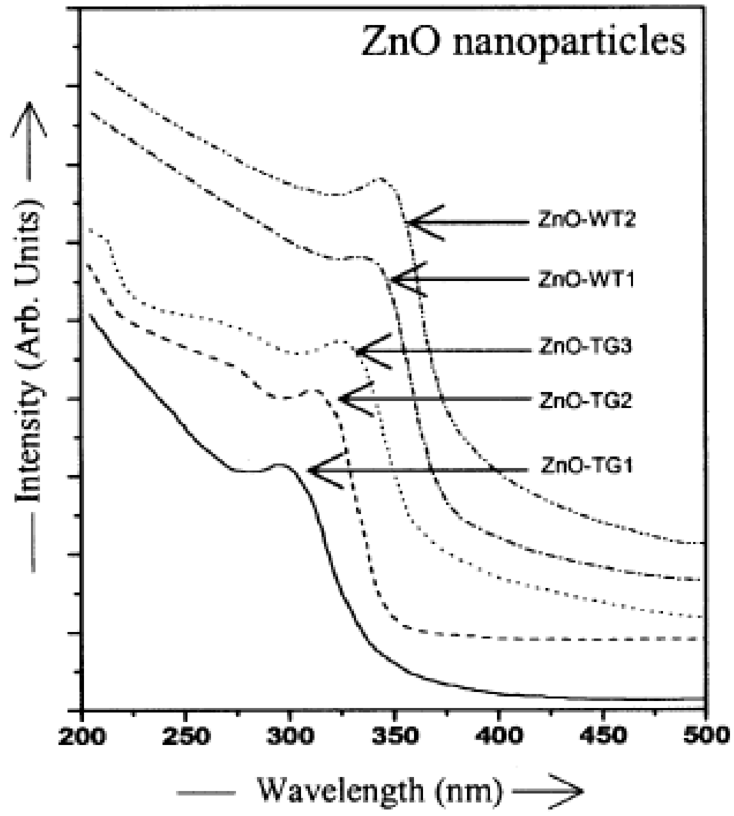
Properties of Nanomaterials

Blue shift provides an indirect way to evaluate, at least qualitatively, the variation of particle core dimensions

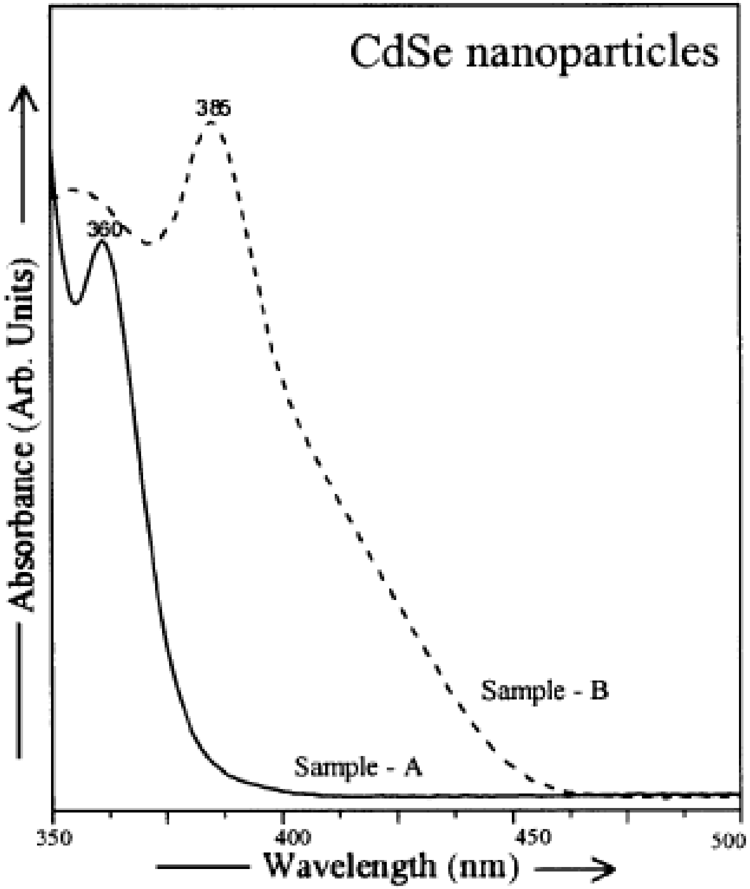


Optical absorption spectra for *d=2.8-, 4.1-, and 5.6-nm* CdSe quantum dots dispersed in chloroform

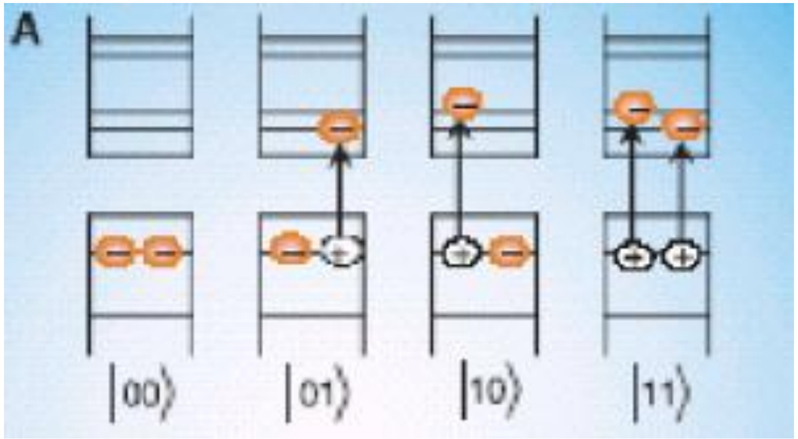
UV-Vis absorption spectra for ZnO nanoparticles.



Properties of Nanomaterials



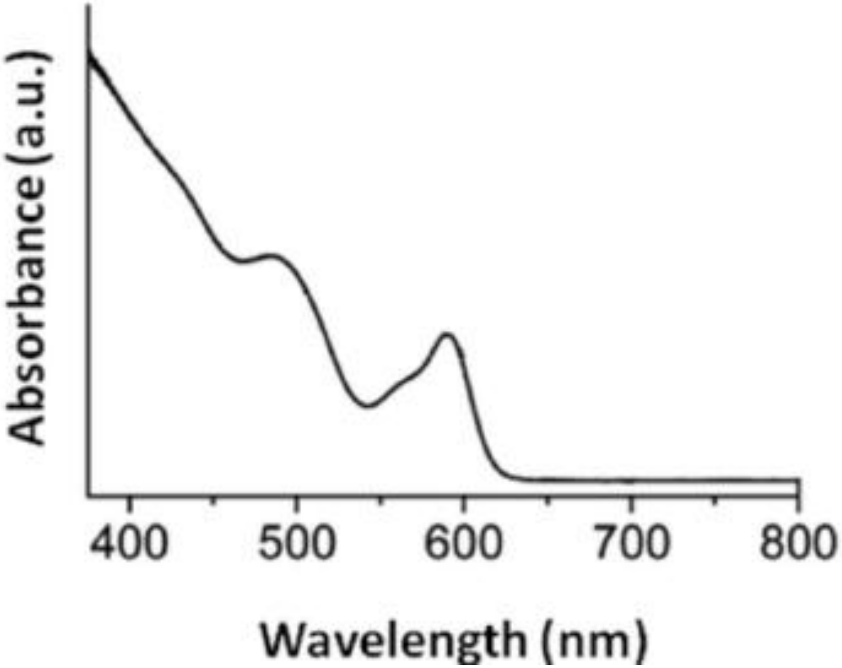
Properties of Nanomaterials



An **exciton** is a bound state of an electron and hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge

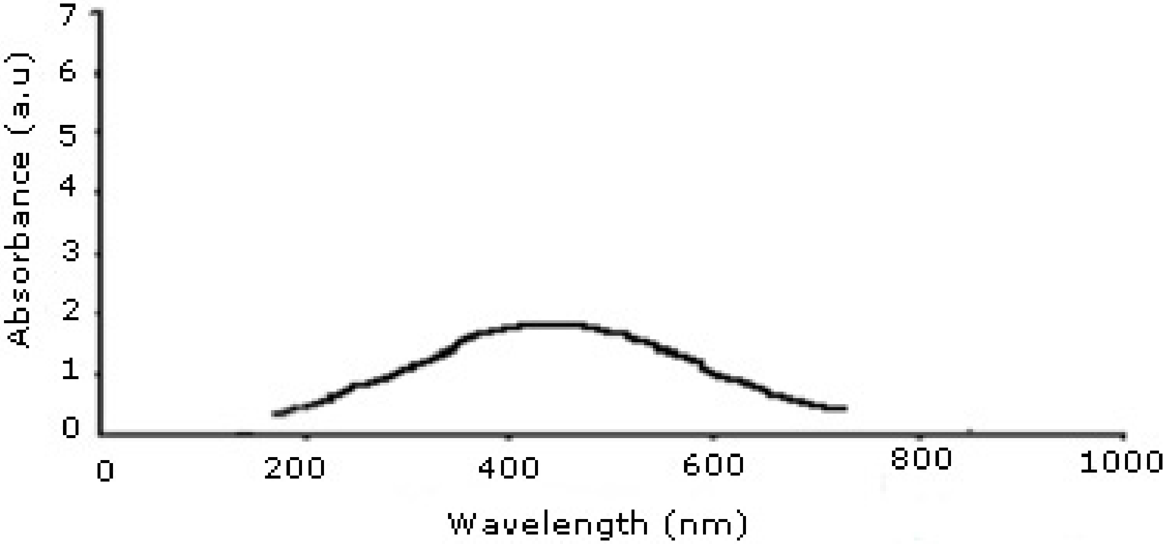
An exciton forms when a photon is absorbed by a semiconductor. This excites an electron from the valence band into the conduction band. In turn, this leaves behind a localized positively-charged hole. The electron in the conduction band is then attracted to this localized hole by the Coulomb force. This attraction provides a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound electron and hole.

Size distribution



If there is a very narrow size distribution, the first exciton peak will be very sharp. This is because due to the narrow size distribution, the differences in band gap between different sized particles will be very small and hence most of the electrons will get excited over a smaller range of wavelengths

Silver Nanoparticles



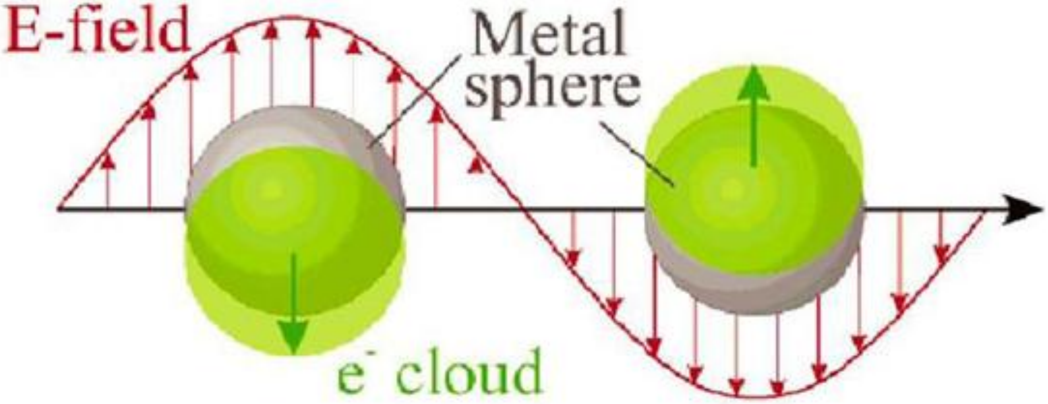
Properties of Nanomaterials

In metal nano particles such as in silver, the conduction band and valence band lie very close to each other in which electrons move freely. These free electrons give rise to a surface plasmon resonance (SPR) absorption band occurring due to the collective oscillation of electrons of silver nano particles in resonance with the light wave

Classically, the electric field of an incoming wave induces a polarization of the electrons with respect to much heavier ionic core of silver nanoparticles. As a result a net charge difference occurs which in turn acts as a restoring force. This creates a dipolar oscillation of all the electrons with the same phase.

Properties of Nanomaterials

When the frequency of the electromagnetic field becomes resonant with the coherent electron motion, a strong absorption takes place, which is the origin of the observed colour. Here the colour of the prepared silver nanoparticles is dark reddish brown. This absorption strongly depends on the particle size, dielectric medium and chemical surroundings



Oscillation of electron cloud

Small spherical nano particles (< 20nm) exhibit a single surface plasmon band . The UV/Vis absorption spectra of the silver nano particles dispersed in chloroform

UV-vis absorption spectra of 9, 22, 48, and 99 nm gold nanoparticles in water

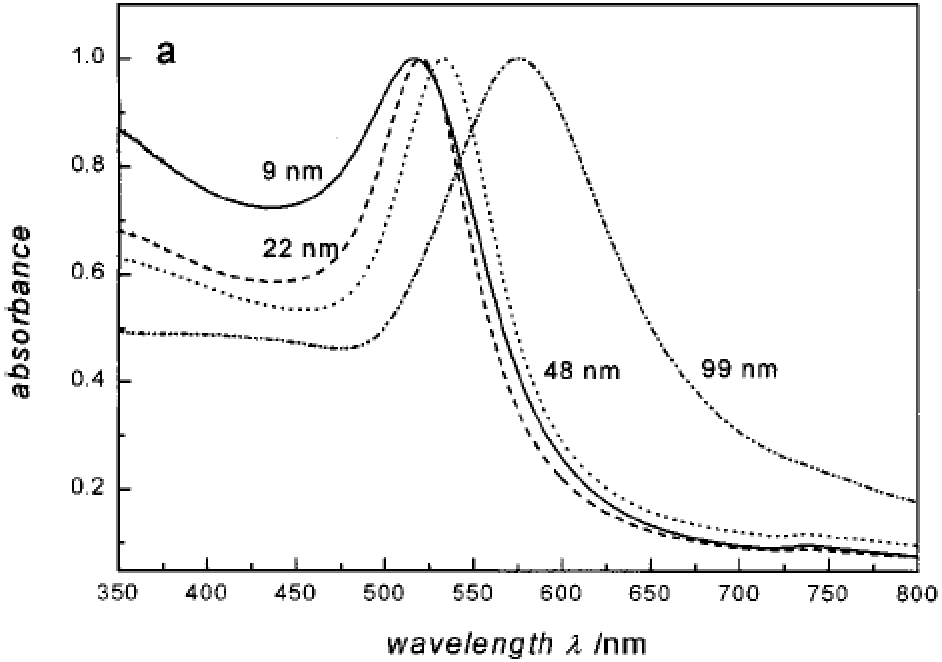
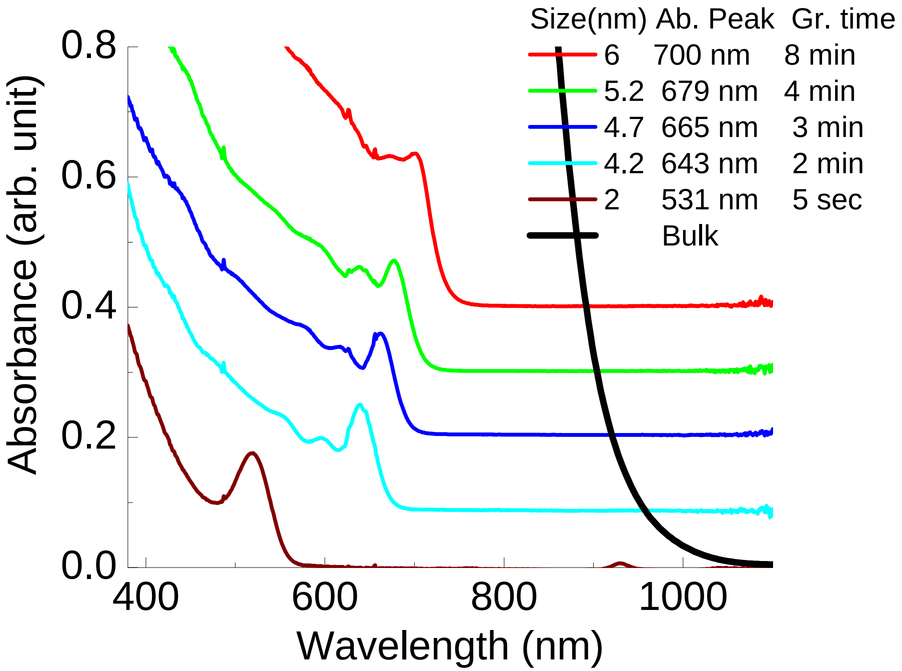


Figure shows the absorption spectra of four different size gold nanoparticles. The plasmon absorption is clearly visible and its maximum red-shifts with increasing particle diameter *517, 521, 533, and 575 nm for the 9, 22, 48, and 99* nm particles).

Absorption spectra of cadmium telluride semiconductor nanocrystals including Bulk



Phonons in Nanostructures

Phonons are the principal carriers of thermal energy in semiconductors and insulators, and they serve a vital role in dissipating heat produced by scattered electrons in semiconductor devices

Phonons are present in any material. They are the driving forces for quite a number of phenomena mentioning only the thermal expansion, heat conductivity, temperature dependence of mechanical, electric properties, phase transitions. They also enhance the diffusion. They occur in bulk crystals, surface, interfaces, multilayers, crystals with topological defects and impurities.

What are Phonons?

Just as light is a wave motion that is considered as composed of particles called photons, we can think of the normal modes of vibration in a solid as being particle-like. **Quantum of lattice vibration is called the *phonon*.**

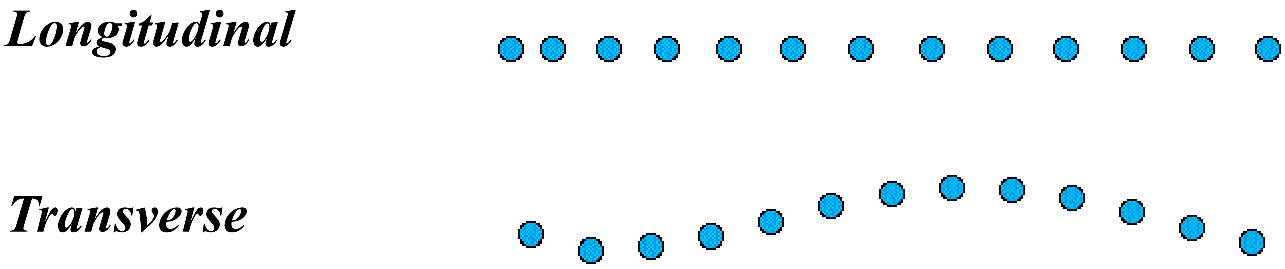
Phonon dispersion

The problem of lattice dynamics (LD) is to find the normal modes of vibration of a crystal. In other words, LD seeks to calculate the energies (or frequencies) of the phonons as a function of their wave vector's q . **The relationship between energy and q is called phonon dispersion .**

Unlike *static lattice model* , which deals with average positions of atoms in a crystal, *lattice dynamics* extends the concept of crystal lattice to an array of atoms with finite masses that are capable of motion. This motion is not random but is a superposition of vibrations of atoms around their equilibrium sites due to the interaction with neighbor atoms.

A collective vibration of atoms in the crystal forms a wave of allowed *wavelength* and *amplitude*.

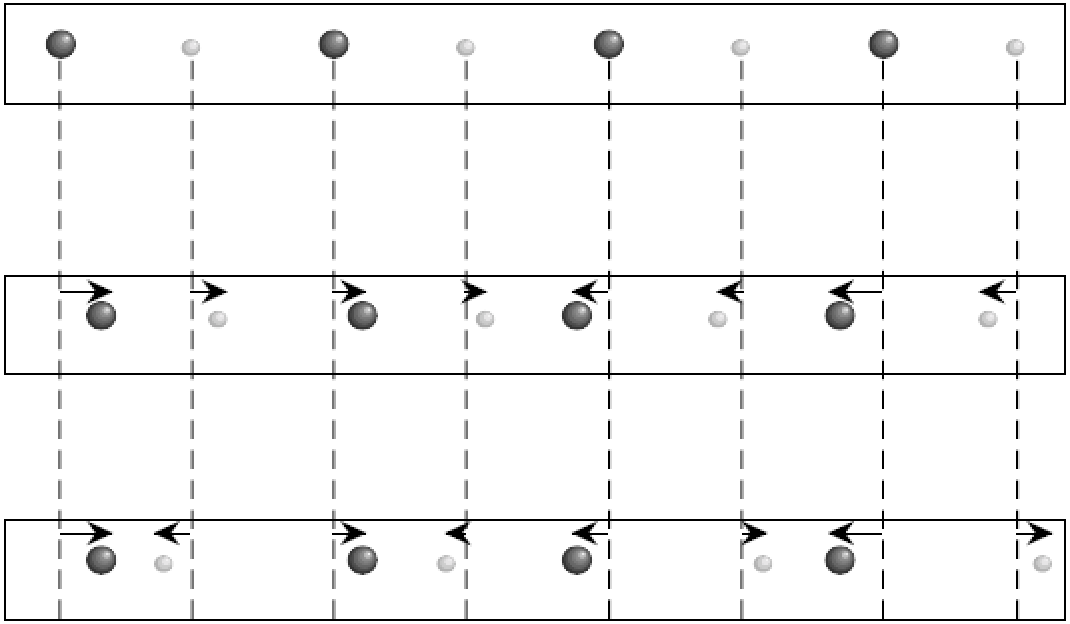
Two possible modes of vibrations of atoms in the crystal



In case of longitudinal mode the displacement of atoms from their equilibrium position coincides with the propagation direction of the wave

In the case of transverse mode, atoms move perpendicular to the propagation of the wave.

ACOUSTIC AND OPTICAL VIBRATIONS

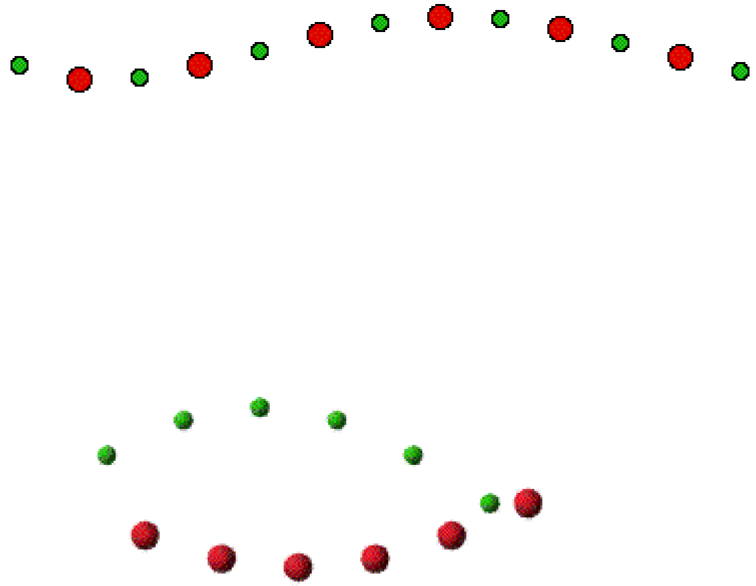


EQUILIBRIUM POSITIONS OF ATOMS

ACOUSTICAL VIBRATION: The two atoms on the unit cell vibrate along the same direction

OPTICAL VIBRATION: The two atoms on the unit cell vibrate in opposing motion.

The difference between acoustical and optical branches arises because of the more options of vibrations for atoms in the unit cell. For example, atoms A and B of diatomic cell can move together in phase (acoustical branch) or out of phase (optical branch).



ACOUSTIC AND OPTICAL BRANCHES

In a simple mono atomic solid with only one atom per primitive cell , one can have only three acoustic phonon branches corresponding to the three degrees of freedom of atomic motion.

On the other hand, for monoatomic solids with two atoms per primitive cell such as diamond, magnesium, or diatomic compounds such as GaAs, one also has three optic phonon branches in addition to the three acoustic phonons

In compounds with a greater number of atoms and complex crystal structures, the number of optic phonons is more than three.

If the crystal unit cell contains N atoms, then 3N degrees of freedom result in 3 acoustic phonons and 3N − 3 optical phonons.

These phonons can propagate in the lattice of a single crystal as a wave and exhibit dispersion depending on their wavelength or equivalently their wavevector

Phonon propagation is interrupted when a grain boundary is encountered in a polycrystalline material.

In an isolated grain the phonon can get reflected from the boundaries and remain confined within the grain.

However, from the point of view of phonons, a well-crystallized polycrystalline sample with several micrometer grain size can be treated as a bulk/infinite crystal for all practical purposes

The consequences of phonon confinement are noticeable in the vibrational spectra only when the grain size is smaller than typically 20 lattice parameters.

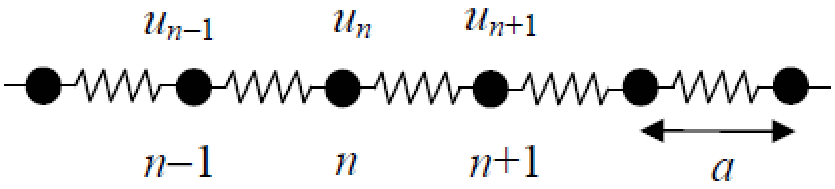
The atomic vibrational frequencies in crystalline solids range from zero to about 100 THz.

Acoustic phonons have frequencies from zero to about a few hundred wave numbers

Optic phonons have higher frequencies

Hence the vibrational spectra could be probed using infrared absorption/reflectivity or using Raman spectroscopy

One-dimensional lattice



The simplest model to study vibrations in periodic solid is known as one dimensional monoatomic chain, which consists of a chain of atoms of mass ‘m’ , equilibrium distance ‘a’ and harmonic interaction between atoms.

U_n =displacement of atom n from its equilibrium position

U_{n-1}=displacement of atom n-1 from its equilibrium position

U_{n+1}=displacement of atom n+1 from its equilibrium position

One might think about the atoms in the lattice as interconnected by elastic springs. Therefore, the force exerted on *n-th atom in the lattice is given by*

$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n),$$

where *C is the interatomic force (elastic) constant and*
$u_{n+1} - u_n$ *relative displacement*

Applying Newton's second law (F = ma) to the motion of the *n-th atom we obtain*

$$M\frac{d^2u_n}{dt^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) = -C(2u_n - u_{n+1} - u_{n-1}), \quad \text{———} \quad (1)$$

Note that we neglected here by the interaction of the *n-th atom with* all but its nearest neighbors In order to solve the above equation, travelling plans waves of amplitude A, frequency ' ω' and wave number 'q, are assumed

i. e
$$u_n = Ae^{i(qx_n - \omega t)} \quad \text{———} \quad (2)$$

where x_n *is the equilibrium position of the n-th atom so that* $x_n = na$

Now substituting Eq.(2) into Eq.(1) and canceling the common quantities (the amplitude and the time-dependent factor)

we obtain

$$M(-\omega^2)e^{iqna} = -C\left[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}\right]$$

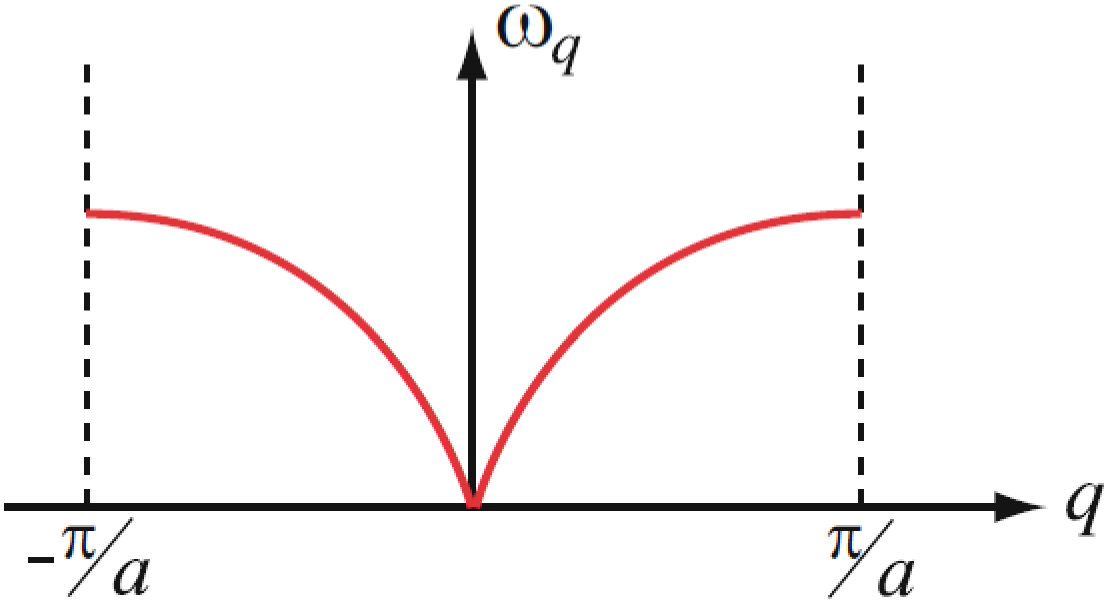
This equation can be further simplified by canceling the common factor e^{iqna}, *which leads to*

$$M\omega^2 = C\left(2 - e^{iqa} - e^{-iqa}\right) = 2C\left(1 - \cos qa\right) = 4C\sin^2\frac{qa}{2}\ .$$

We find therefore the dispersion relation for the frequency

which is the relationship between the frequency of vibrations and the wavevector q.

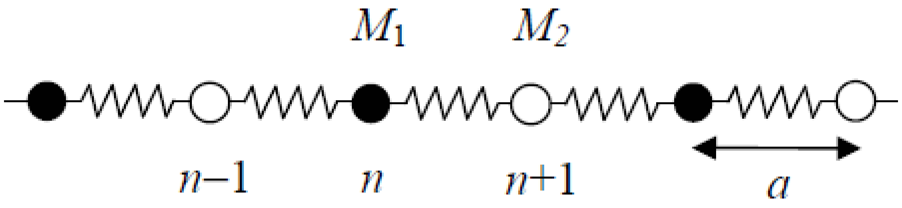
$$\omega = \sqrt{\frac{4C}{M}}\left|\sin\frac{qa}{2}\right|$$



Dispersion relation of the lattice vibration in a monatomic linear chain

Diatomic 1D lattice

Now we consider a one-dimensional lattice with two non-equivalent atoms in a unit cell



We can treat the motion of this lattice in a similar fashion as for monoatomic lattice. However, in this case because we have two different kinds of atoms, we should write two equations of motion:

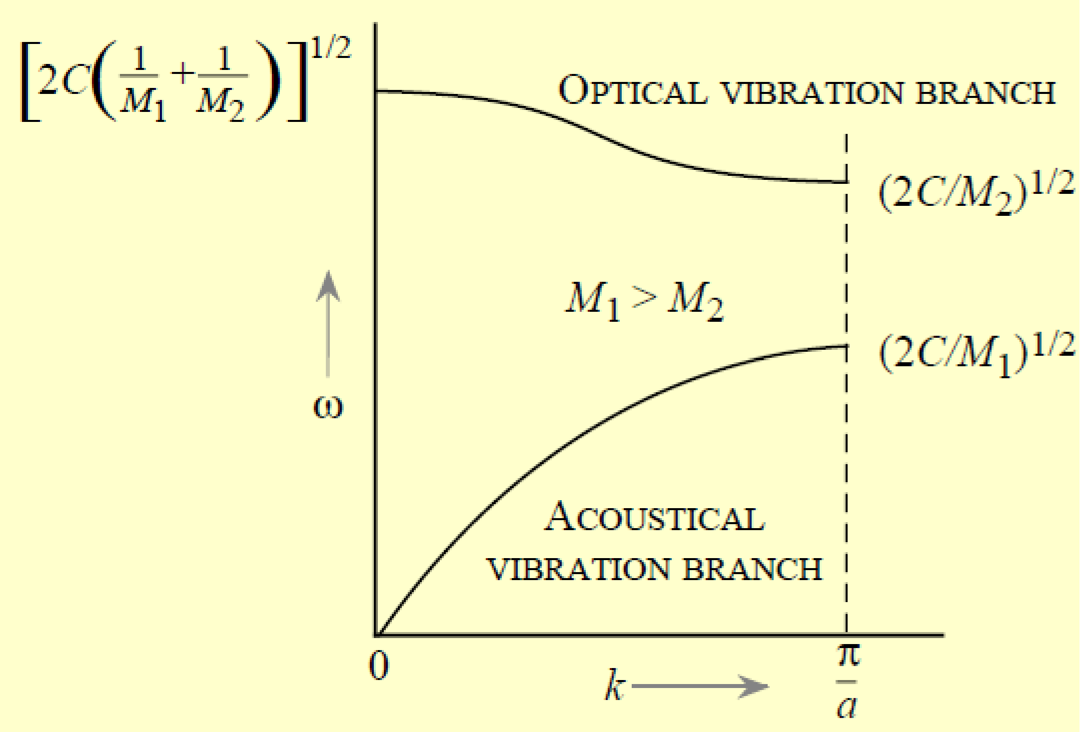
$$M_1 \frac{d^2 u_n}{dt^2} = -C(2u_n - u_{n+1} - u_{n-1})$$

$$M_2 \frac{d^2 u_{n+1}}{dt^2} = -C(2u_{n+1} - u_{n+2} - u_n)$$

Solution in the form of traveling mode for the two atoms leads to

$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2 qa}{M_1 M_2}}\,.$$

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves, as is shown in Figure



Properties of Nanomaterials

Phonons interaction are altered due to dimensional confinement in nanostructures

These effects show some similarities to those for an electron confined in a quantum well.

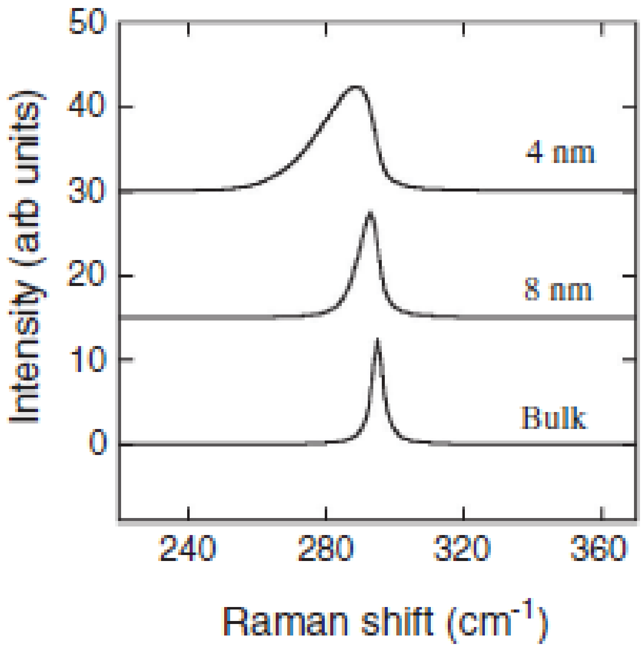
$$= \hbar^2 (k^2_x + k_y^2)/2 m_e^* + n^2\pi^2 \hbar^2/ 2m L_z^2$$

$$(n = 1, 2, 3, \ldots)$$

$$k_z = n\pi/L_z$$

The dimensional confinement of phonons also results in similar restrictions in the phonon wave vector, $q_z = n\pi/L_z$

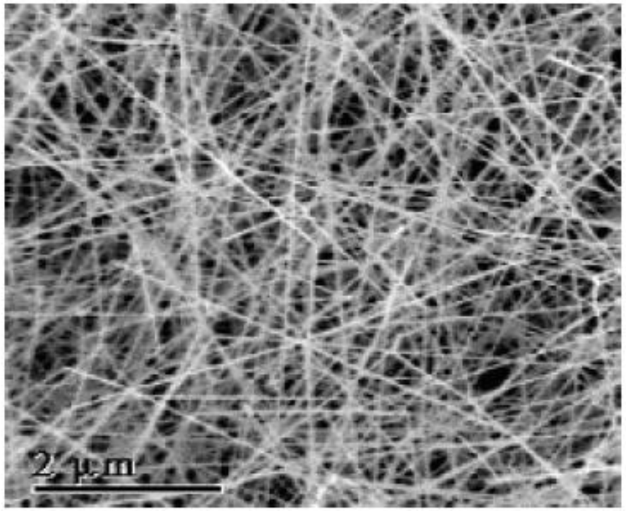
Scaling- induced phonon confinement effect in GaAs Nanoparticles



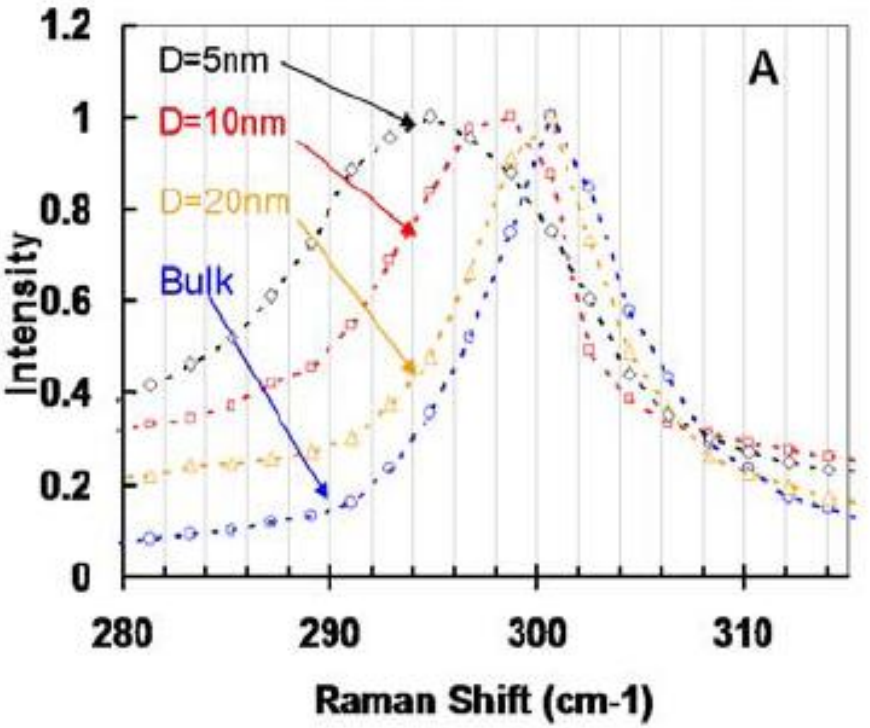
Raman spectra of confined LO phonon in GaAs nanoparticles. The bulk spectrum is also shown for comparison.

Note the asymmetric broadening of the line shape and also the shift of the peak towards the low-frequency side

Scaling- induced phonon confinement effect in Nanowire structures

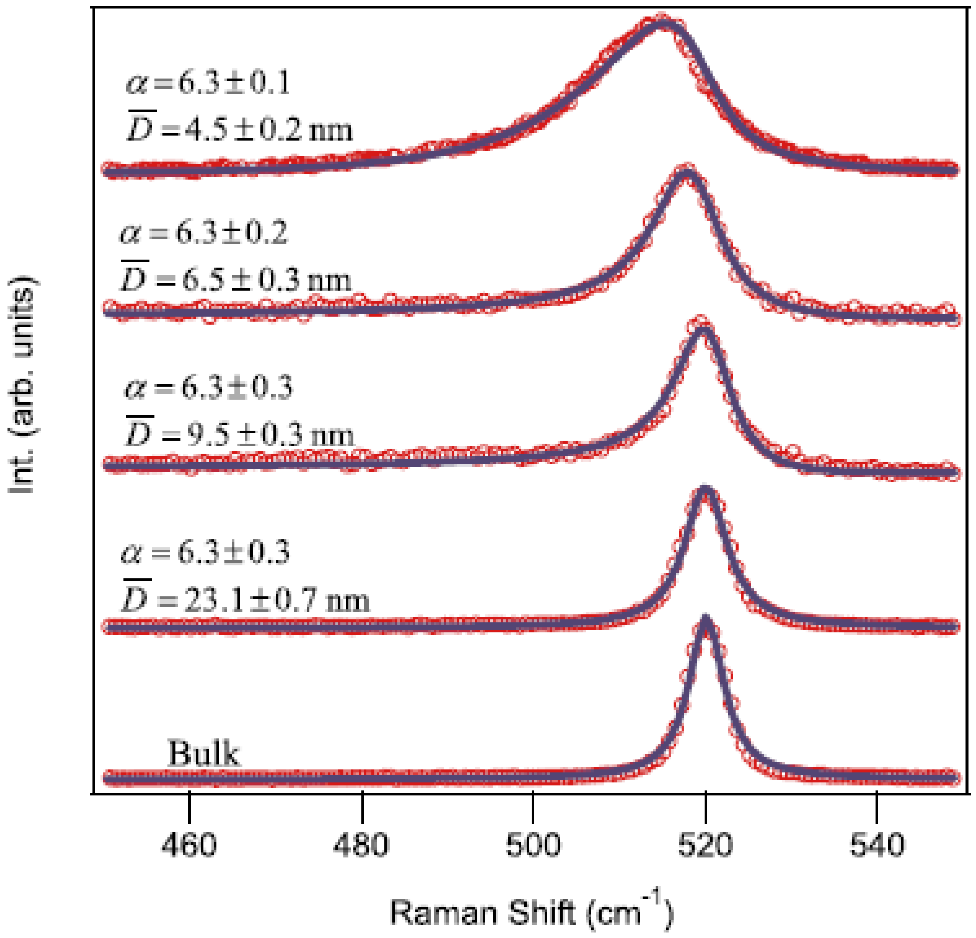


A SEM image of the as-synthesized GeNW sa



Raman spectra of 3 Ge NW samples (D=5, 10, 20nm) and bulk Ge measured at 500uW laser power with 514.523 nm wavelength.

Properties of Nanomaterials



Experimental Raman spectra four Si nanowire samples (each is a different ensemble of Si nanowires with a different core diameter distribution, as measured by TEM)

Raman spectra develop marked asymmetry towards the low frequency side and exhibit marginal shift in the peak position also towards the same side.

As the optical phonon dispersion curves in most solids have negative dispersion,

That is, phonon frequency decreases as a function of wavenumber, the increased intensity in the wing of the Raman spectra on the low-frequency side basically arises from the contribution from the phonon branch away from the zone center

Raman red shift is the consequence of the combination of the effects of size-induced phonon confinement and surface relaxation. The structural defects may also contribute to the Raman red shifts

Properties of Nanomaterials

The dependence of the peak shift and the line broadening on the particle size is shown in Figure for the longitudinal optic phonon in GaAs.

Both peak shift and the line width increase as the particle size reduces.

However, the changes are marginal if the particle size is larger than 10 nm.

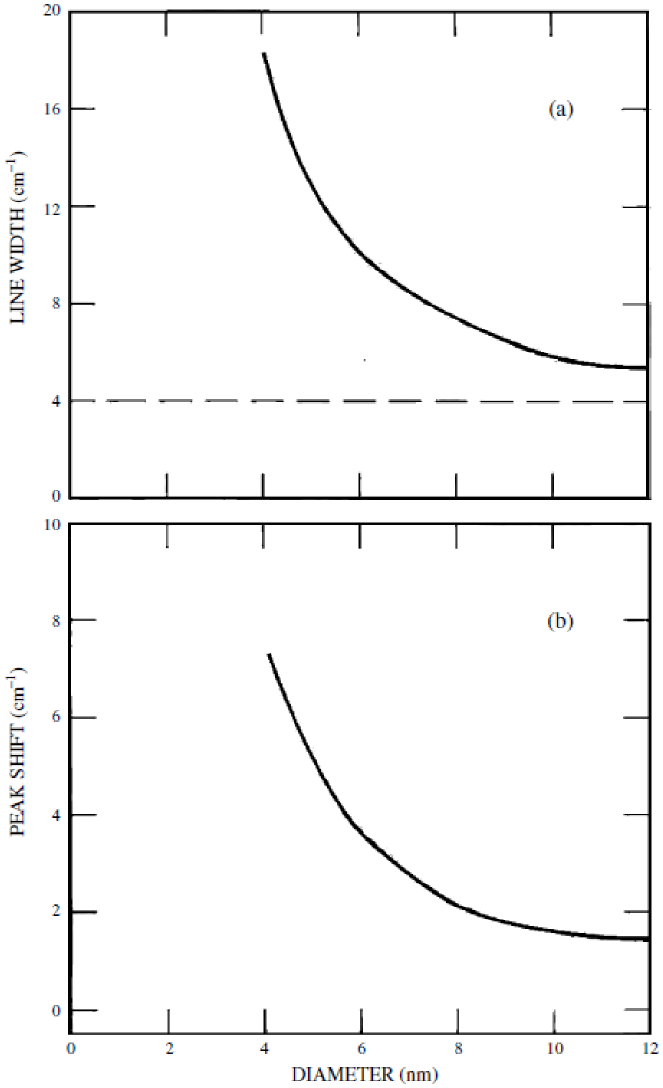


Figure 4. The dependence of linewidth (a) and peak shift (b) of the longitudinal optic phonon on the particle size for GaAs nanoparticles. Dashed line is the linewidth of the bulk phonon.

Other methods of observing the dispersion relation of lattice vibrations

- Neutron Inelastic Scattering
- Electron Energy Loss Spectroscopy (EELS)
- Inelastic Atom Scattering