Nano Sensors

PhD/ MTech/ BTech

Course No.: EEL7450

L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL

ELECTRICAL ENGINEERING

IIT JODHPUR

Lecture 01 dated 03rd January 2025

Course Title	*Nano-Sensors*	Course No.	EEL7450			
Department	Electrical Engineering	Structure (LTPC)	3	0	0	3
Offered for	B.Tech. (IV year), M. Tech., and Ph.D.	Status	Program Elective			

Class: Slot J (4 PM TO 4.50PM)

TUE THU FRI

TA: Ms. PRACHI SONI

Objective

1. Make the students understand the **importance of nanoscale materials** for **sensing applications**.
2. Explain the **approaches** used for **characterizing sensors based nanomaterials**.
3. Teach the **approaches** used for **tailoring nanomaterials** for a **specific sensing application**.

Contents

1. **Nanomaterials and Properties**: Nanoscale physics for quantum dot, nanowire and quantum wells; Properties of nanomaterials; nanomechanical oscillators, nano(bio)electronics, nanoscale heat transfer; fluids at nanoscale (8 lectures)
2. **Nanoscale Characterization**: Examination of nanoscale characterization approaches including imaging, scattering, and spectroscopic techniques and their physical operating mechanisms. Microscopy (optical and electron: SEM, TEM); scattering & diffraction; spectroscopies (EDX, SIMS, Mass spec, Raman, XPS, XAS); scanning probe microscopes (SPM, AFM); particle size analysis (8 lectures)
3. **Nanofabrication**: Basic engineering principles of nanofabrication. Topics include: photo-, electron beam and nanoimprint lithography, block of copolymers and self-assembled monolayers, colloidal assembly, biological nanofabrication (8 lectures)
4. **Nanosensors**: Nanosensors based on metal nanoparticles, semi-conductor nanowires and nanocrystals and carbon nanotubes etc. (10 lectures)
5. **Case Studies of Nanosensors**: Optical, mechanical and chemical sensors based on nanomaterials, Hybrid nanomaterial-based sensors, Quantum wells based IR sensors (8 lectures)

Course Evaluation

1. Continuous evaluation: 40%
    i. Quizzes
    ii. Assignments
    iii. Minor projects

2. Minor examination: 20%
3. Major/ final examination: 40 %

Textbooks

1. Mindy Adams, (2016) Engineered Nanomaterials: Modeling, Methodologies and Applications, Wellford Press
2. John Hutchison, Angus Kirkland, (2007) Nano characterisation, RSC
3. Roger George Jackson, (2004) Novel Sensors and Sensing, CRC Press

Preparatory Course Material:

Research articles from journals such as ACS Nano Letters, ACS Sensors, ACS Nano, Sensors & actuators B, etc.

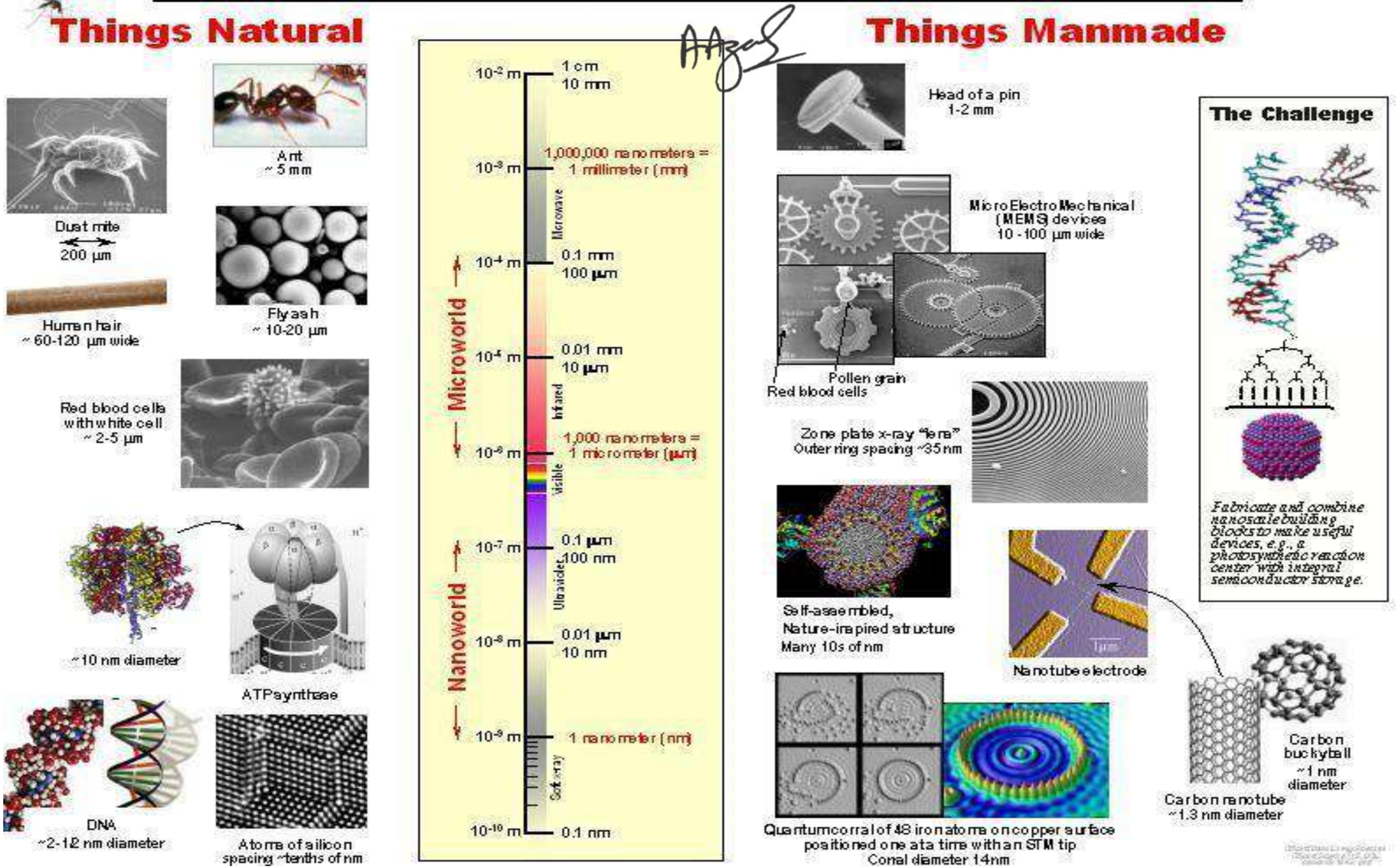
Introduction

What is Nano Sensor?

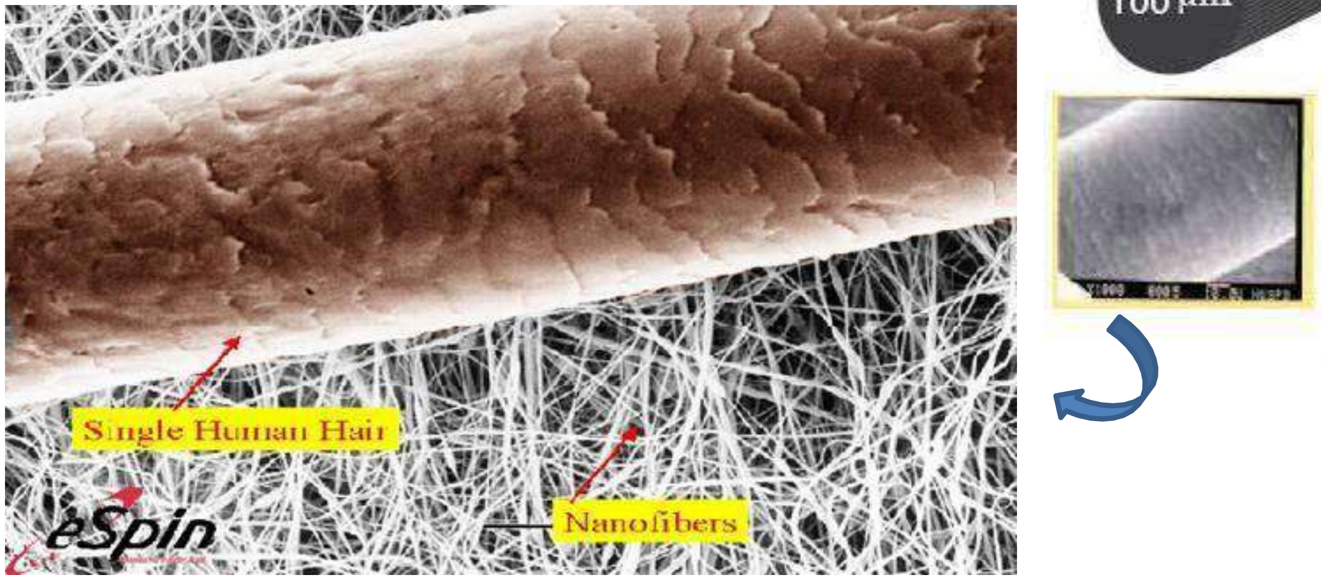
- Nano
  - Nano is a **unit prefix** meaning "one billionth". Used primarily with the metric system, this prefix denotes a factor of $\mathbf{10^{-9}}$ or **0.000000001**

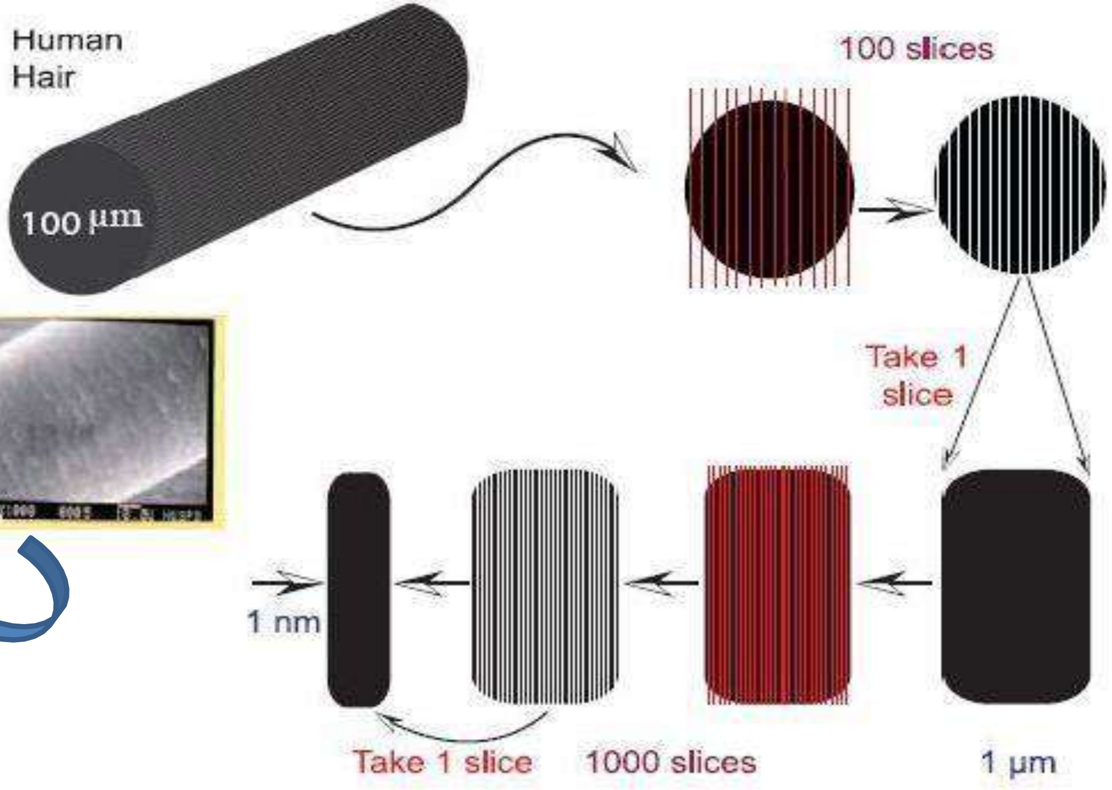
- Sensor
  - a **device** which **detects or measures** a physical property and records, indicates, or otherwise responds to it

The Scale of Things – Nanometers and More



Compared to Human Hair





A Human Hair is about 100,000nm in diameter

Nano Sensors

PhD/ MTech/ BTech

Course No.: EEL7450

L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL

ELECTRICAL ENGINEERING

IIT JODHPUR

Lecture 02 dated 07th January 2025

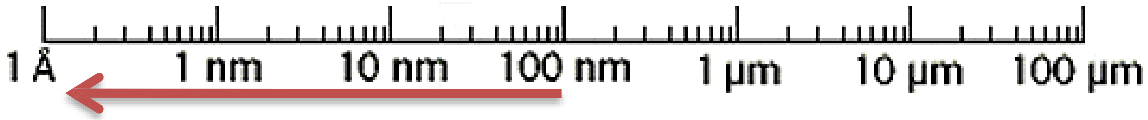
What are Nanomaterials?

Nanoscience- deals with the science of very small objects

Nanomaterials

Particle sizes less than 100 nm at least one dimension

(1 nanometer (nm) = 10^{-9} m, 1 nm is 1 billionth of a meter)



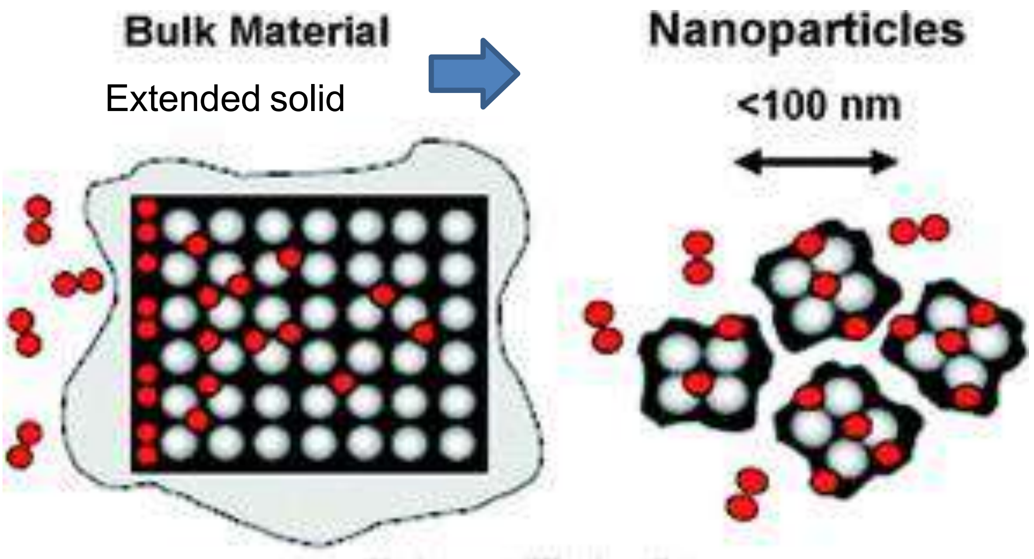
A **nanostructured material (or nanomaterial) is defined as a solid material** characterized by at least one dimension in the nanometer range

Nanotechnology- Engineering nano-materials for functional usage.

Synthesize, characterize, and manipulate materials at less than 100 nm length scale.

Developing new materials for practical applications

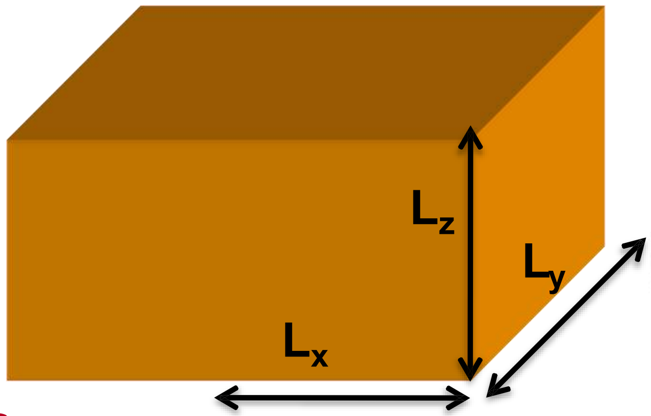
Size/ Dimension Reduction



Sub-atomic	Atomic	Microscopic	Bulk
< 0.2 nm	0.2-10 nm	1-1000 µm	> 1 mm

Classification of Nanomaterials

Bulk (3D) Material



L_x , L_y , L_z ~ mm or cm

Low-Dimensional Systems

2D Systems:

Systems confined in 1 dimensions

L_z<<100nm

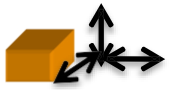
1D Systems:

Systems confined in 2 dimensions

L_z and L_y<<100nm

0D Systems:

Systems confined in 3 dimensions



L_z , L_y and L_x <<100nm

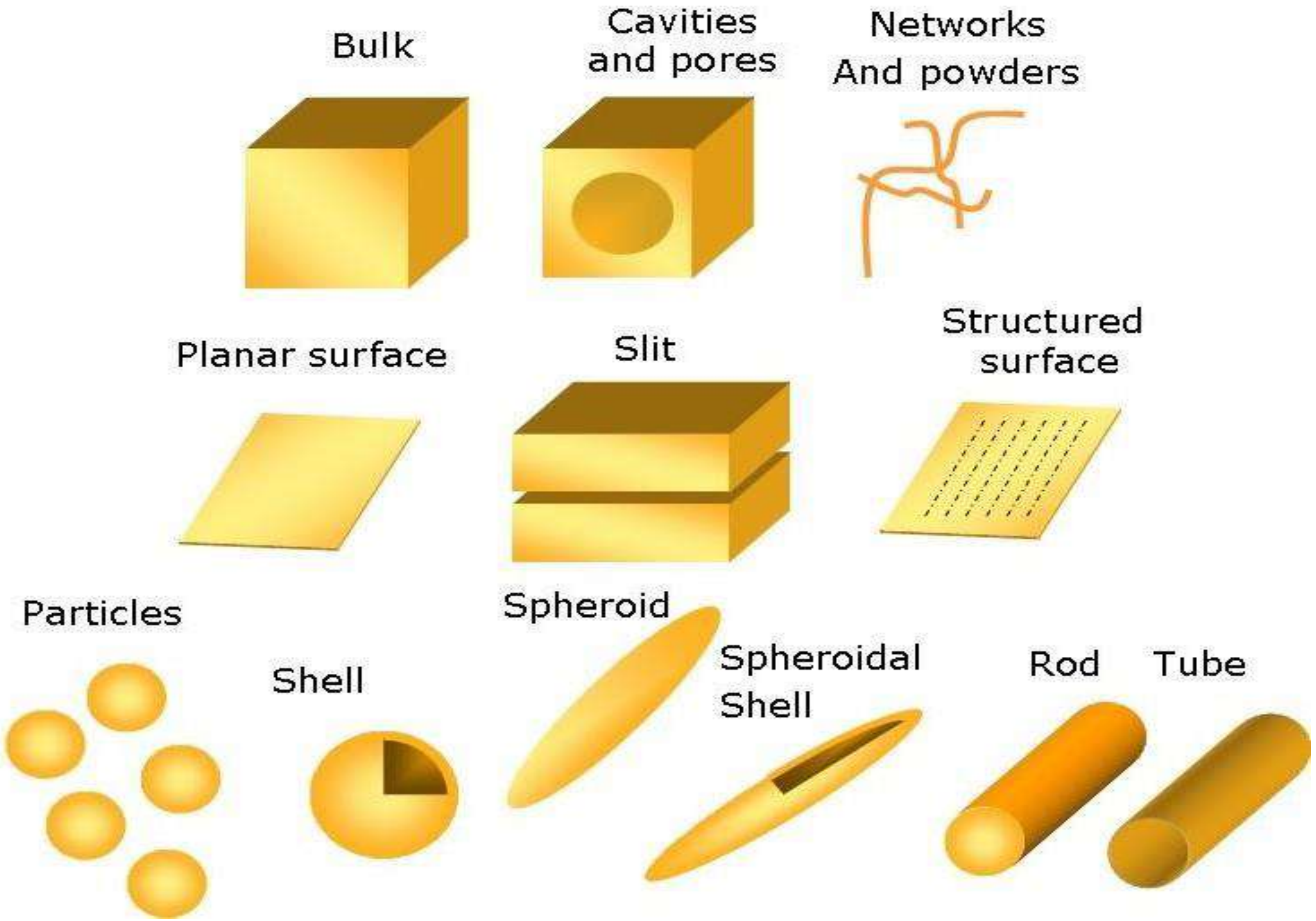
Nanomaterials can be metals, semiconductors, oxides, ceramics, polymers, or composite materials

MOLECULES

	Size (approx.)	*Materials*
Nanocrystals and clusters (quantum dots)	1 – 10 nm (diam.)	Metals, semiconductors, magnetic materials
Other nanoparticles	1 – 100 nm (diam.)	Ceramic oxides
Nanowires	1 – 100 nm (diam.)	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	1 – 100 nm (diam.)	Carbon, layered metal chalcogenides
Nanoporous solids	0.5 – 10 nm (pore diam.)	Zeolites, phosphates, etc.
2-D arrays (of nanoparticles)	Several nm^2 – μm^2	Metals, semiconductors, magnetic mater.
Surfaces and thin films	1 – 1000 nm (thickness)	A variety of materials
3-D structures (superlattices)	Several nm in the three dimensions	Metals, semiconductors, magnetic materials

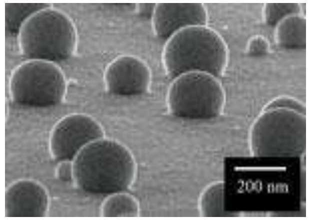
BULK MATERIALS

Nanostructure Geometries

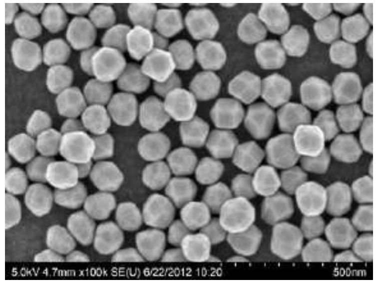


Structures of engineered nanomaterials

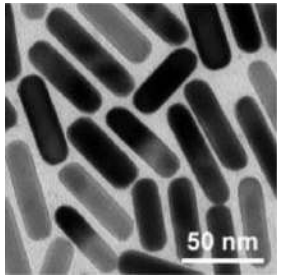
- Particles



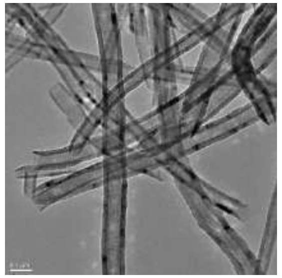
Au nano-particles



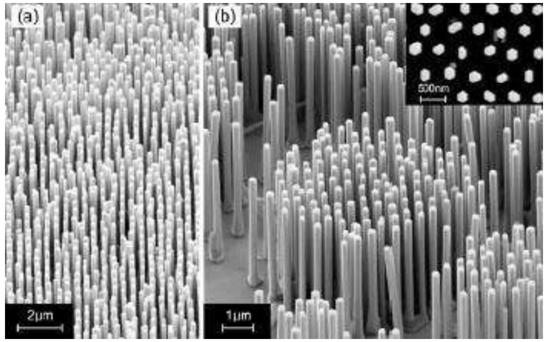
- Rods, fibres and tubes



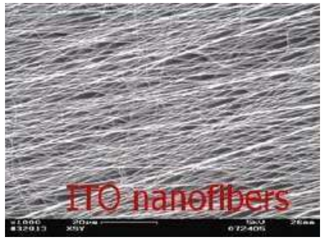
Au nanorods



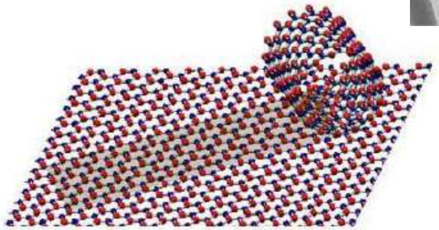
Carbon nanotubes



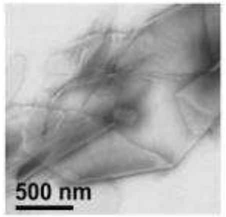
ZnO nanotubes



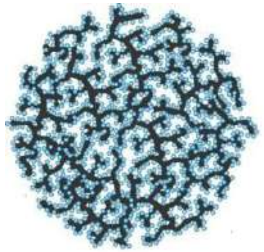
- Sheet



BN nanosheets

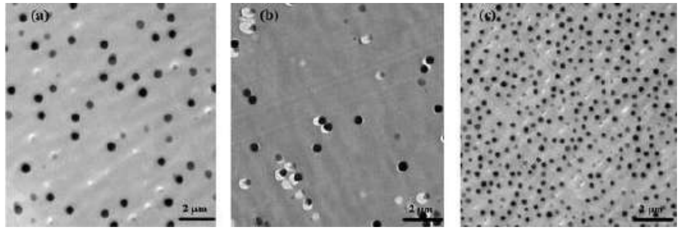


- Composites



silicon-carbon nanocomposite

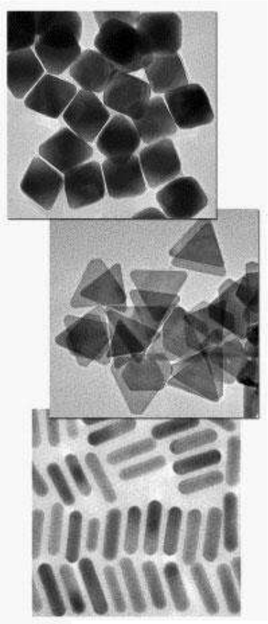
- Embedded in non-nanostructures



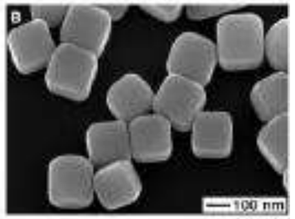
PMMA/silica nanocomposites

Spherical and other Shaped Nanomaterials

They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes

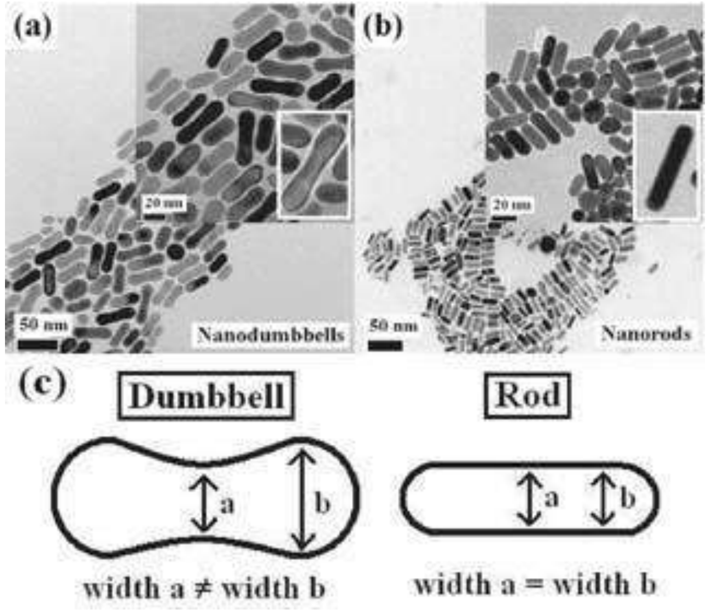


Ag nanocubes

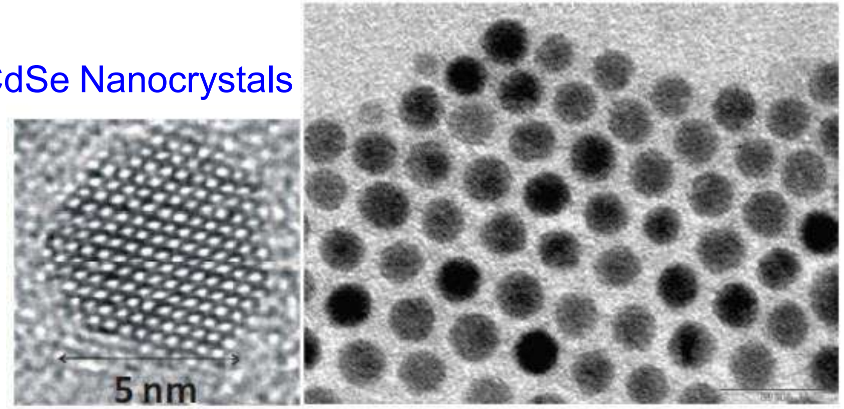


Different shapes of Silver Nanoparticles

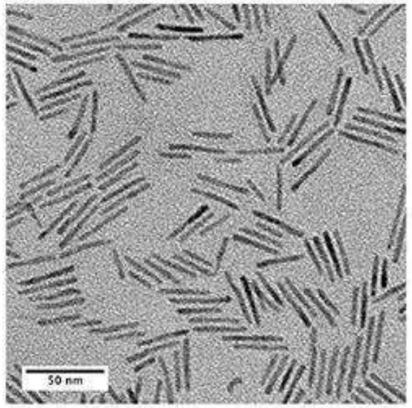
Different shapes of Gold Nanoparticles



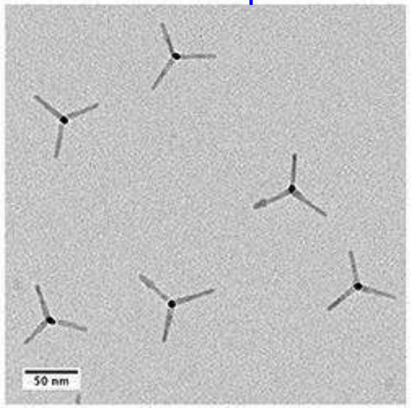
CdSe Nanocrystals



CdSe Nanorods

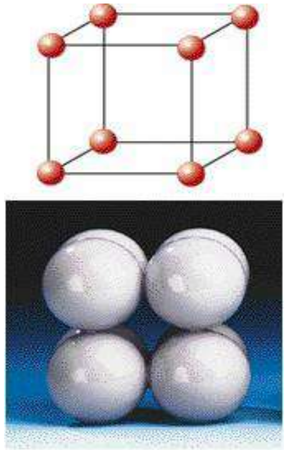


CdSe Tetrapods

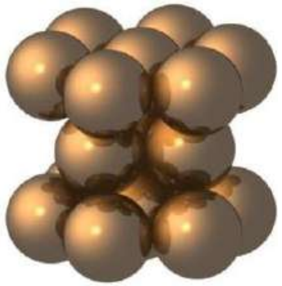


Atomic Arrangement: Ordered vs. Disordered

Crystalline:
atoms are arranged in a 3D, periodic array giving the material "*long range order*"

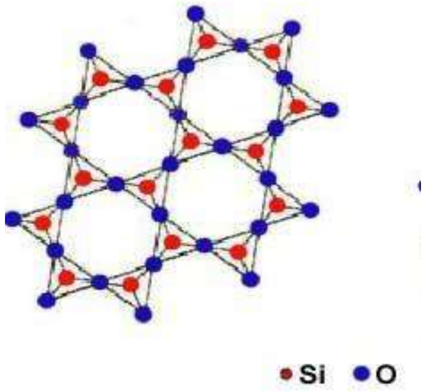


simple cubic

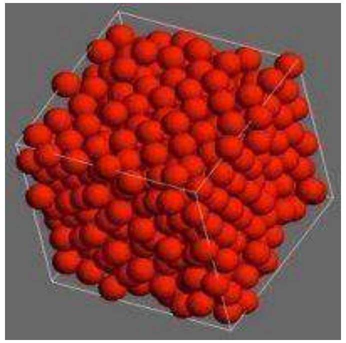


hexagonal close-packed

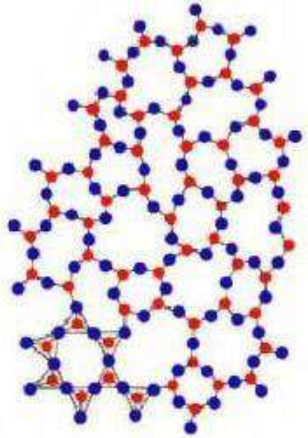
• anisotropic materials



Non-crystalline or amorphous:
atoms only have short-range, *nearest neighbor order*



• isotropic materials



Isotropic vs. Anisotropic materials

S. No	Isotropic Material	Anisotropic Material
1	Isotropic materials show the same properties in all directions.	Anisotropic materials show different properties in different directions.
2	Glass, crystals with cubic symmetry, diamonds, metals are examples of isotropic materials.	Wood, composite materials, all crystals (except cubic crystal) are examples of anisotropic materials.
3	These materials are direction-independent.	These materials are direction-dependent.
4	These materials have a single refractive index.	These materials have many refractive indices.
5	These materials have consistent chemical bonding.	These materials have inconsistent chemical bonding.
6	Isotropic minerals generally appear dark.	Anisotropic minerals generally appear light.
7	These materials don't show characteristics such as optical activity, dichroism, etc.	Optical activity, dichroism, dispersion in presence of different refractive indices are a few characteristics of anisotropic materials.
8	These materials are used in windows and lenses.	These materials are used for wedges, optical waveplates, polarizers, etc.
9	These materials show the same velocity of light in all directions.	These show different velocities of light in different directions.
10	Unpolarized light does not split (double refraction) into two in an isotropic medium.	Anisotropic medium splits unpolarized light into two when it enters the medium.

Questions

Nano Sensors

PhD/ MTech/ BTech

Course No.: EEL7450

L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL

ELECTRICAL ENGINEERING

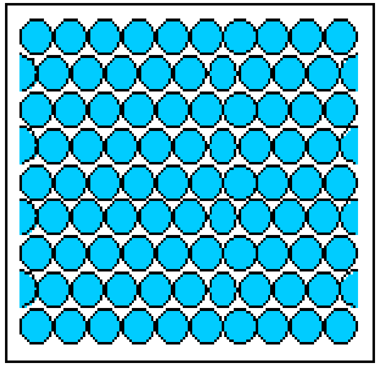
IIT JODHPUR

Lecture 03 dated 09th January 2025

Types of Solids

Crystalline material

Single crystal

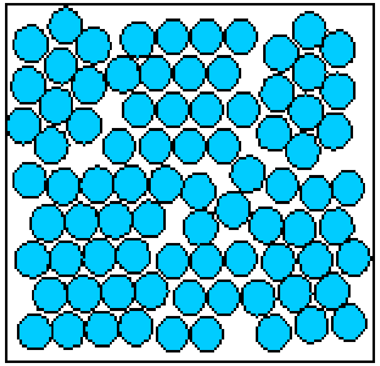


Single crystal

Periodic across the whole volume.

periodic array over the entire extent of the material

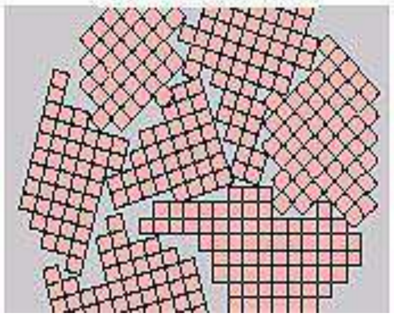
Polycrystalline material

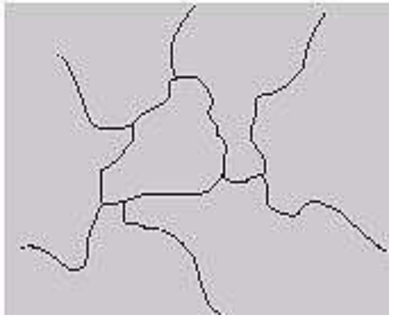


Polycrystal

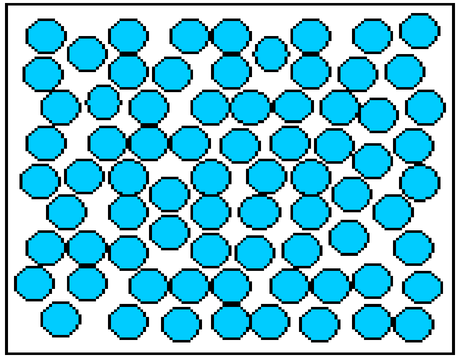
Periodic across each grain.

many small crystals or grains





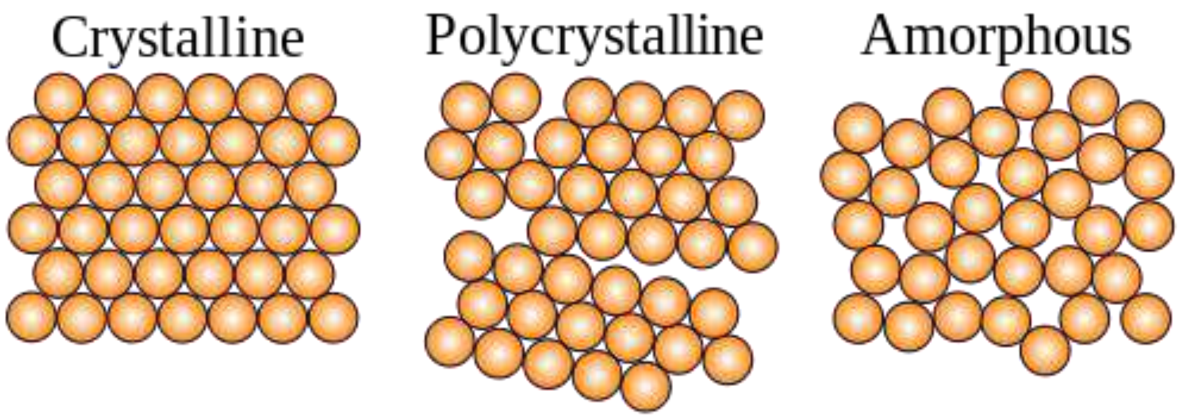
Amorphous



Amorphous solid

Not periodic.

Crystalline vs. Non-crystalline



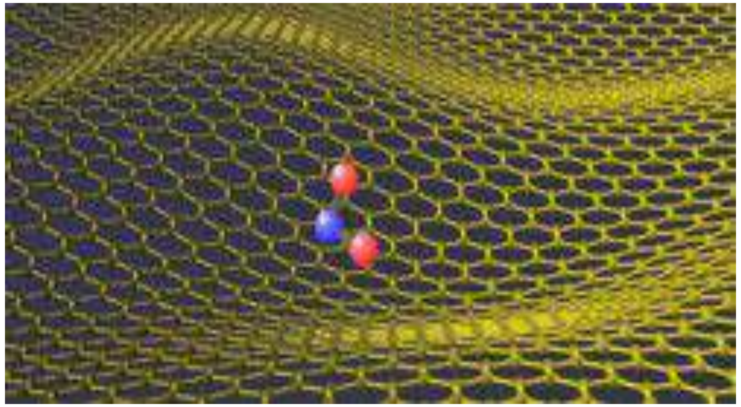
Crystalline vs Noncrystalline Solids

More Information Online WWW.DIFFERENCEBETWEEN.COM

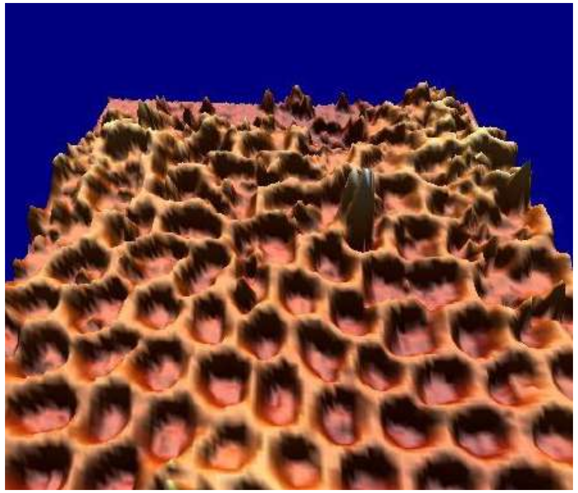
	Crystalline Solids	Noncrystalline Solids
DEFINITION	In crystalline solids, constituent particles (atoms, molecules or ions) arrange in a three-dimensional periodic manner.	Non-crystalline solids do not have a consistent arrangement of particles.
GEOMETRY	Have a well-defined geometrical shape due to the regular arrangement of unit cells.	Do not have well-defined geometrical shape.
RANGE OF ORDER	Have a long-range order.	Have a short range order.
MELTING POINT	Have a definite melting point.	Melt over a range
HEAT OF FUSION	Have a high fixed value for the heat of fusion.	Do not have a fixed value for the heat of fusion.
PROPERTIES	These solids are true solids, so they show all the properties of solids.	These solids do not show all the properties of solids. Therefore, they are called "pseudo solids".
ENERGY	Energy in crystalline solids is lower than that of non-crystalline solids.	Energy in non-crystalline solids is higher than that of crystalline solids.

Nano-structures/ Nano-materials

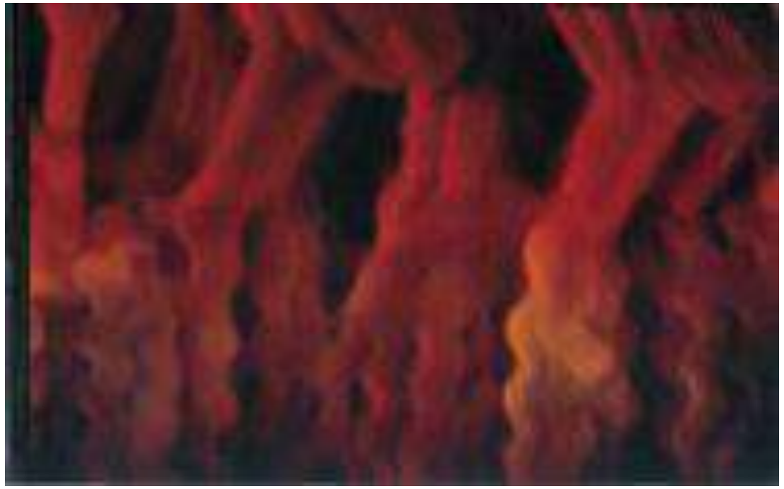
2- D structures



Graphene sheet: can detect single molecule - the ultimate sensitivity. F Schedin *et al*, *Nature Materials*, 2007, DOI: 10.1038/nmat1967



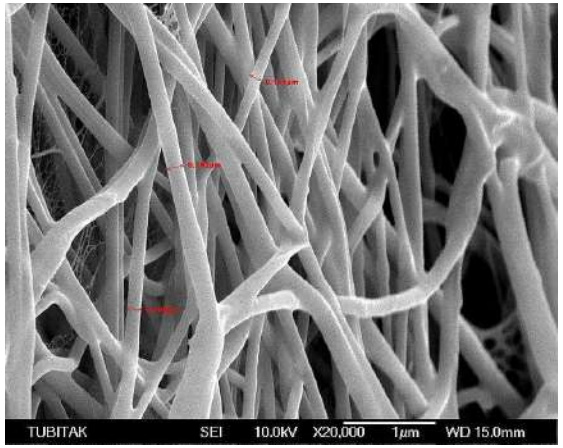
Nanomesh: The distance between two pore centers is 3.2nm, & the pores are 0.05nm deep. M. Corso et al., Boron Nitride Nanomesh, Science 303, doi:10.1126/science.1091979



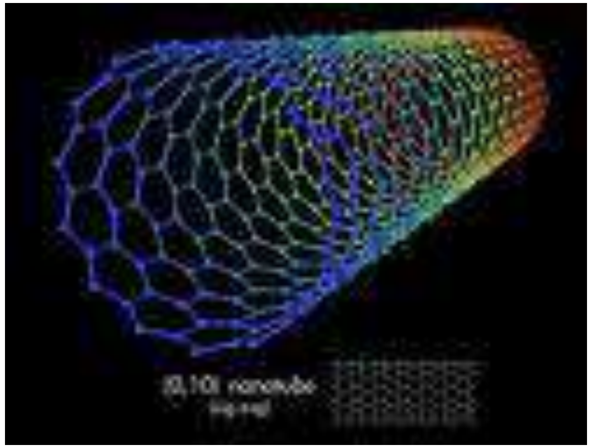
Sculptured thin films are nanostructured materials with varying properties that can be designed & realized in a controllable manner. A. Lakhtakia and R. Messier, Sculptured Thin Films: Nanoengineered Morphology & Optics, SPIE Press, Bellingham, USA, 2005

Nano-structures/ Nano-materials

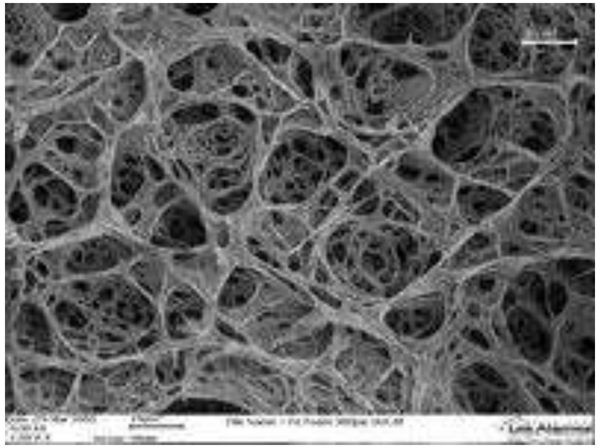
1- D structures



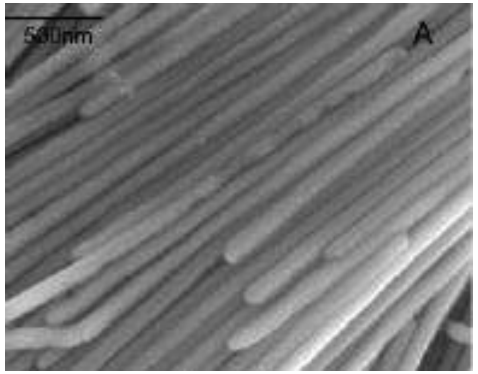
Nano-fibers: dia. ~100nm; produced by polymerization & electro-spinning; catalytic synthesis (carbon nano-fibers). Source: Nano FMG



Carbon nanotubes, CNTs: cylindrical nanostructure with length-to-diameter ratio of up to 28,000,000:1 Zheng et al., Nature Materials 3, 2004 673, doi:10.1038/nmat1216



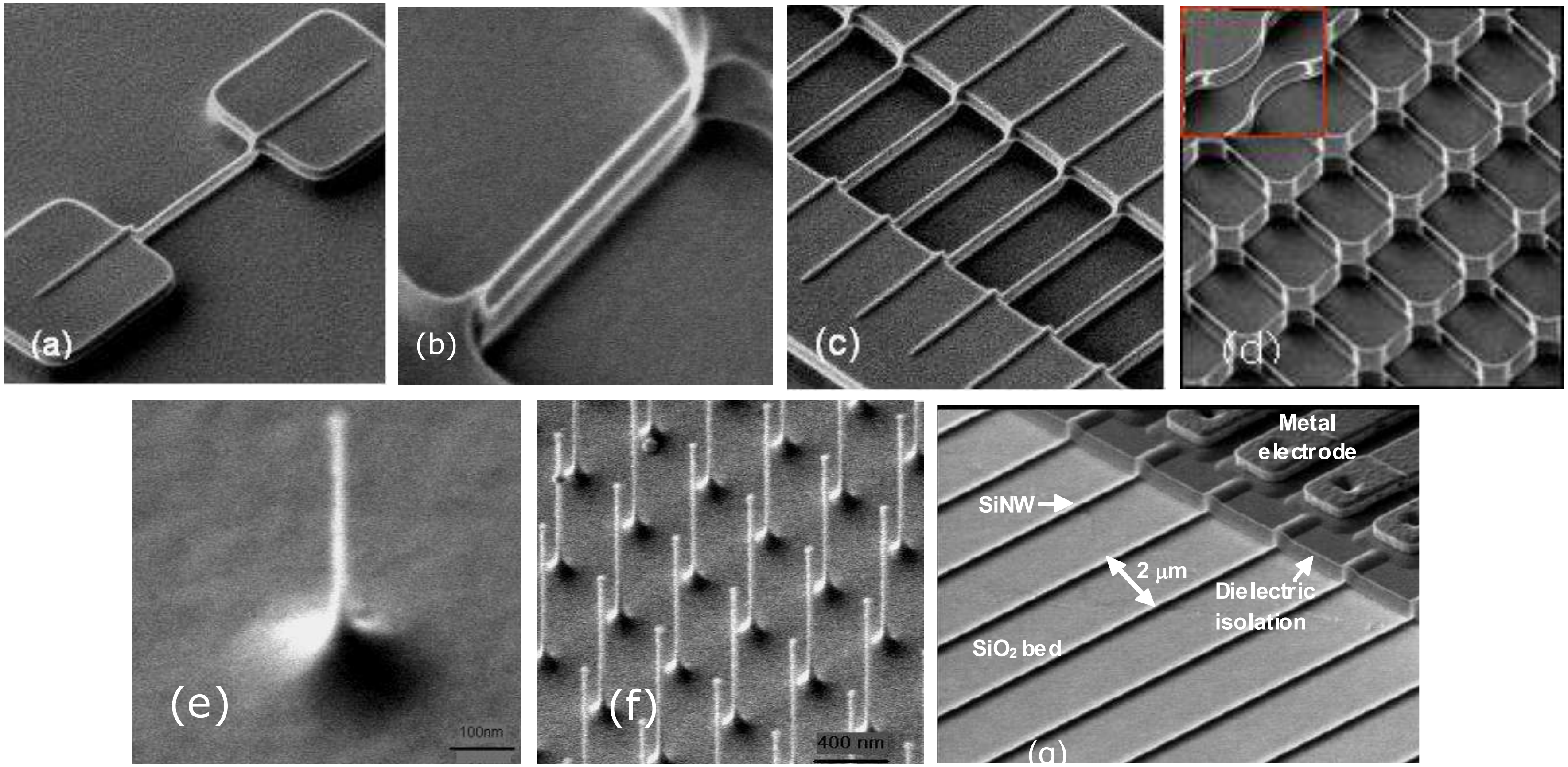
Nanofoam: porous material, contains significant population of pores with dia <100nm; e.g. aero-gels. R&D magazine 100 Awards, access date Aug. 26, 2008



Nanorods: Self-assembled nano-rods on a substrate. Zhang et al., J. Phys. Chem. B 109, 2005, 12544

Nano-structures/ Nano-materials

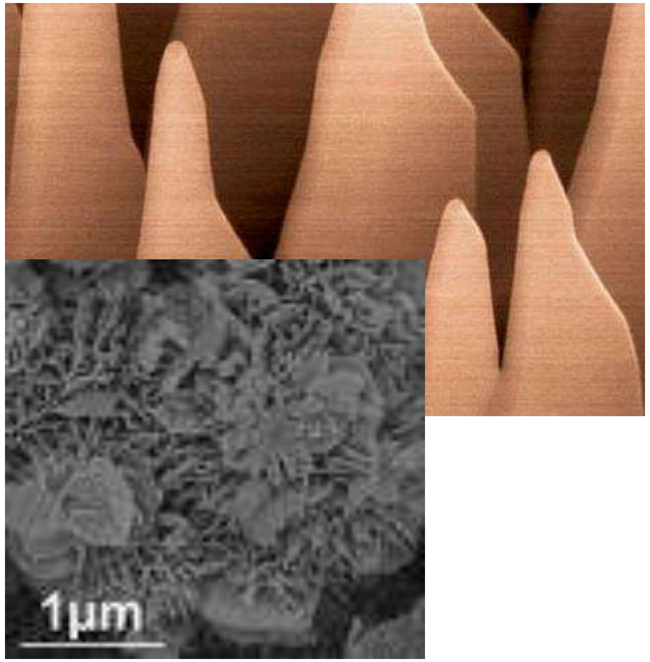
1- D structures



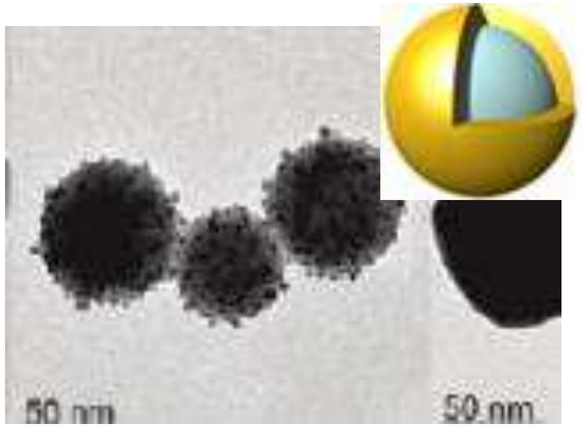
Silicon nanowire: (a) Single SiNW, (b) vertically stacked twin SiNWs (c) An array of SiNW (d) large area regular mesh of nanowires. The inset: curved SiNW (e) & (f) 1.0 μm tall isolated & dense-array of vertical SiNW of dia ~ 20 nm (g) **SiNW array for bio-chemical sensors**; length-to-cross section ratio up to 40,000:1.

Nano-structures/ Nano-materials

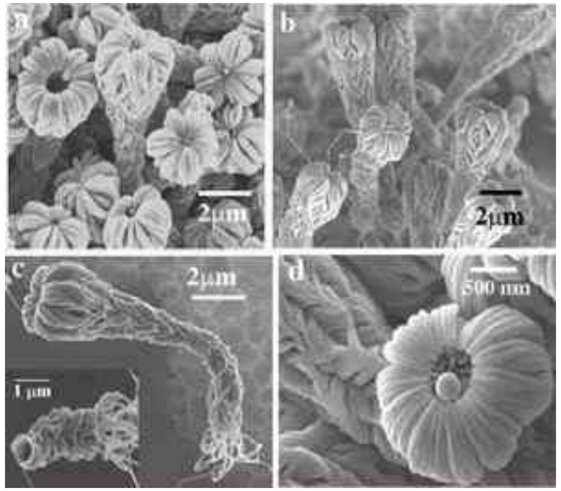
0-D nanostructures



Nanoflake: perfect crystalline structure that absorb all light; have potential to convert up to 30 % of the solar energy into electricity. Nano-Science Center at the University of Copenhagen



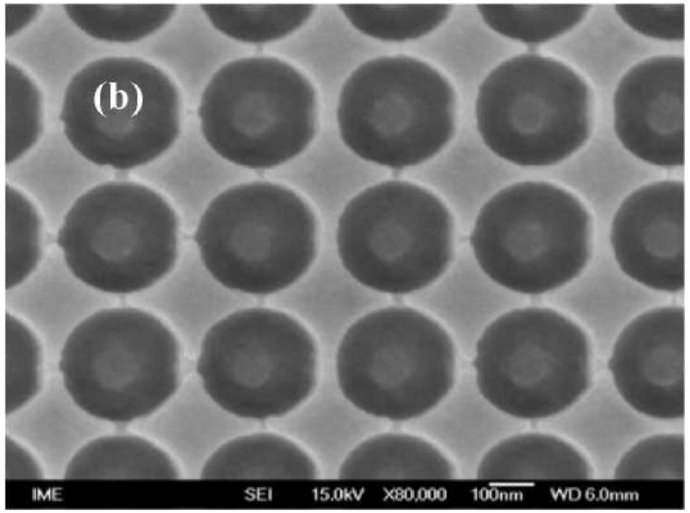
Nanoshell: a typical spherical nanoparticle consisting of a dielectric core covered by a thin metallic shell (usually gold). Discovered by Naomi Halas at Rice University



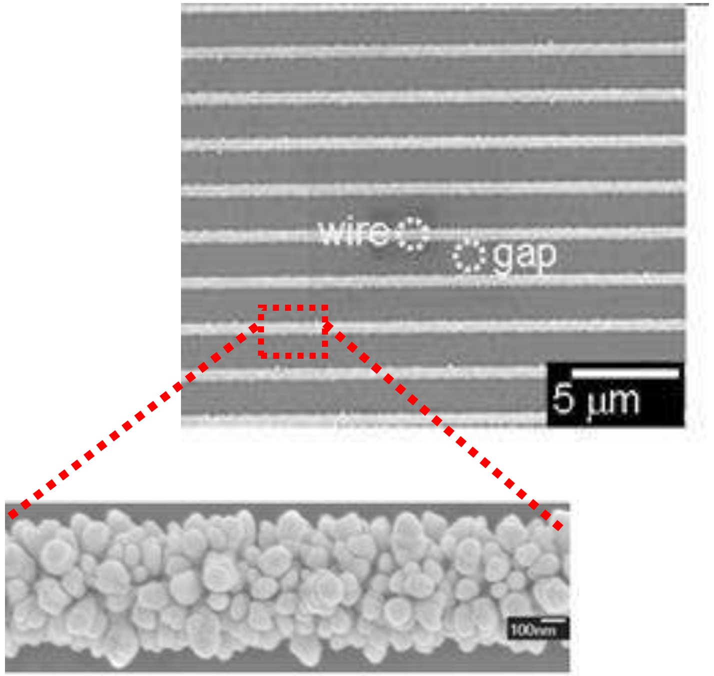
Nanoflowers & nanotrees: nano-scale wires of silicon carbide are grown from tiny droplets of liquid Gallium on silicon. Ghim Wei Ho, Cambridge University.

Nano-structures/ Nano-materials

0-D structures



3-D sub-micron structures with regular array of **nano-gaps** as SERS.



Silver nanoparticles deposited on silicon nanowires as SERS active substrate

Why should we use
Nano-technologies/ Nano sensors
for Sensing applications?

Nanotechnology / Nano-material important for the sensors

- Improves sensitivity & performance
- New signal transduction technologies in biosensors
- Submicron dimensions in nano sensors/ probes/ systems allow simple & rapid in vivo analysis
- Portable instruments for multi-components analysis realized

Why Nanomaterials are interesting?

Novel Properties: Size dependent Properties

At the nanometer scale, properties become size-dependent.

For example,

(1) Chemical properties – reactivity, catalysis
(2) Thermal properties – melting temperature
(3) Mechanical properties – adhesion, capillary forces
(4) Optical properties – absorption and scattering of light
(5) Electrical properties – tunneling current
(6) Magnetic properties – superparamagnetic effect

New properties enable new applications

Property	Influence of size reduction on properties of nanoparticle
Structural	Decrease or increase of lattice parameter
	Structure transformations
Mechanical	Enhancement of hardness, strength, fracture ductility
	Arise of superplasticity
	Raising of wear resistance
Thermal	Decrease of melting point
	Decrease of phase transition temperatures
	Decrease of melting entropy
	Softening of phonon spectra
Thermo-dynamical	Increase of heat capacity
	Increase of thermal expansion
	Decrease of Debye temperature
	Stabilization of high temperature phases
Kinetic	Increase of diffusion coefficient
	Sharp drop of thermal conductance under some critical size d*
	Oscillation of kinetic coefficients
Electrical	Increase of conductivity for nanometals
	Arise of conductivity for nanodielectrics
	Increase of dielectric inductivity for ferroelectrics at d*
Electronic	Increase of band gap
	Arise of phonon generation
	Raising of conductivity under low temperatures in semimetallic Bi

Magnetic	Increase or decrease of coercive force at d* Decrease of Curie temperature Rise of paramegnetism in ferromagnetics at some d* Rise of gaint magnetoresistance Rise of maximal temperature of magnetoresistance Increase of magnetic permeability in ferromagnetics at d*
Optical	Diffraction and interference Increase of absorption in ultraviolet range (blue shift) Oscillation of optical absorption Arise of nonlinear optical properties
Chemical	Increase of catalytic activity Increase of velocity of physico-chemical interactions Swap of solubility

Questions?

Assignment 1

Write a short note on any 03 properties of Nano-sized materials.

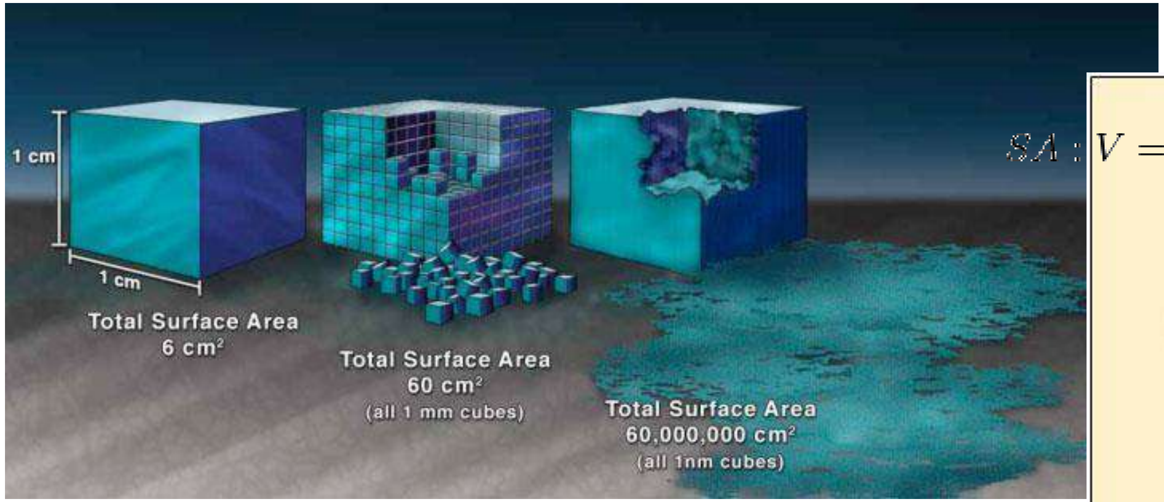
Last date of submission: 14th Jan 2025

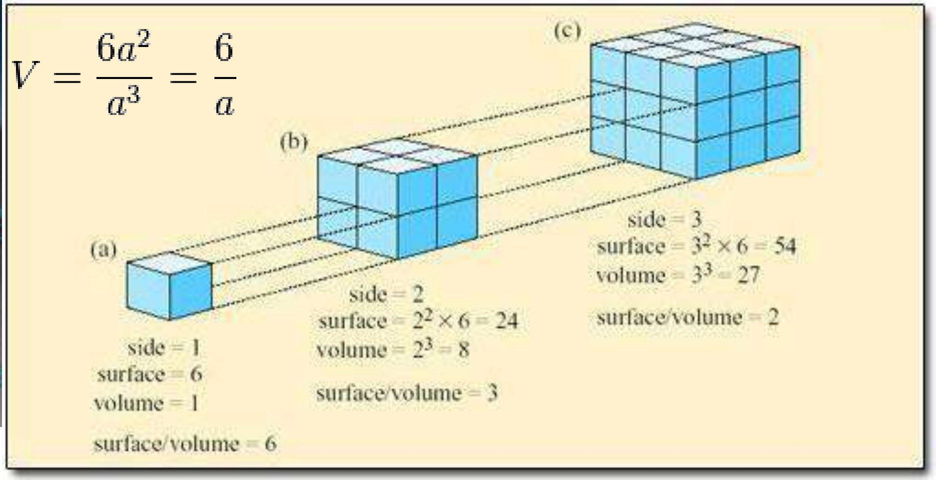
Size dependent Properties of nanoscale materials

Two principle factors causes the properties of nm differ significantly from bulk material

1. Large Surface effect - Increase in surface area to volume ratio

If a bulk material is divided in smaller particles, the **total volume of material** remains the **same**, whereas the collective surface area is greatly increased. In other words, the so called surface-to-volume ratio is significantly increased.





As the particle/ grain size reduces the proportion of atoms exposed on its surface increases

5% for 30 nm particles

20% for 10 nm particles

50% for 3 nm particles

✦ *<u>This leads to high chemical reactivity of the nanomaterials</u>*

Nano Sensors

PhD/ MTech/ BTech

Course No.: EEL7450

L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL

ELECTRICAL ENGINEERING

IIT JODHPUR

Lecture 04 dated 10th January 2025

Physical Properties of Nanomaterials

- **Known origins that cause physical properties to change:**
  1. large fraction of surface atoms,
  2. Large surface energy,
  3. Spatial confinement, and
  4. Reduced imperfections

Physical Properties of Nanomaterials

1. **Reduced melting point:** Nanomaterial may have a significantly lower melting point or phase transition temperature and appreciably **reduced lattice constants (spacing between atoms is reduced), due to huge fraction of surface atoms** in the total amount of atoms.
2. **Ultra Hard**: Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply **due to the reduced probability of defects**

Physical Properties of Nanomaterials

3. **Optical properties** of Nanomaterials can be significantly different from bulk crystal.
   - Semiconductor Blue shift in adsorption and emission due to an increased band gap – Quantum size effects, Particle in box
   - Metallic Nanoparticles colour changes in spectra due to Surface Plasmons Resonances – Lorentz Oscillator Model
4. Electrical conductivity decreases with a reduced dimension due to increased surface scattering

   Electrical conductivity increases due to the better ordering and ballistic transport

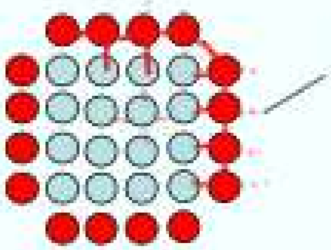
Physical Properties of Nanomaterials

5. Magnetic properties of nanomaterials are distinctly different from the bulk materials.
   - Ferromagnetism disappears and transfers to superparamagnetism in the nanometer scale due to the huge surface energy
6. Self purification is an intrinsic thermodynamic property of nanostructures and nanomaterials due to enhanced diffusion of impurities/ defects/ dislocations in the nearby surfaces
   - Increased perfection enhances chemical stability

Physical Properties of Nanomaterials

1. Reduced melting point:

Melting points and lattice constants



Nanoparticles of metals,

semiconductors and

molecular crystals

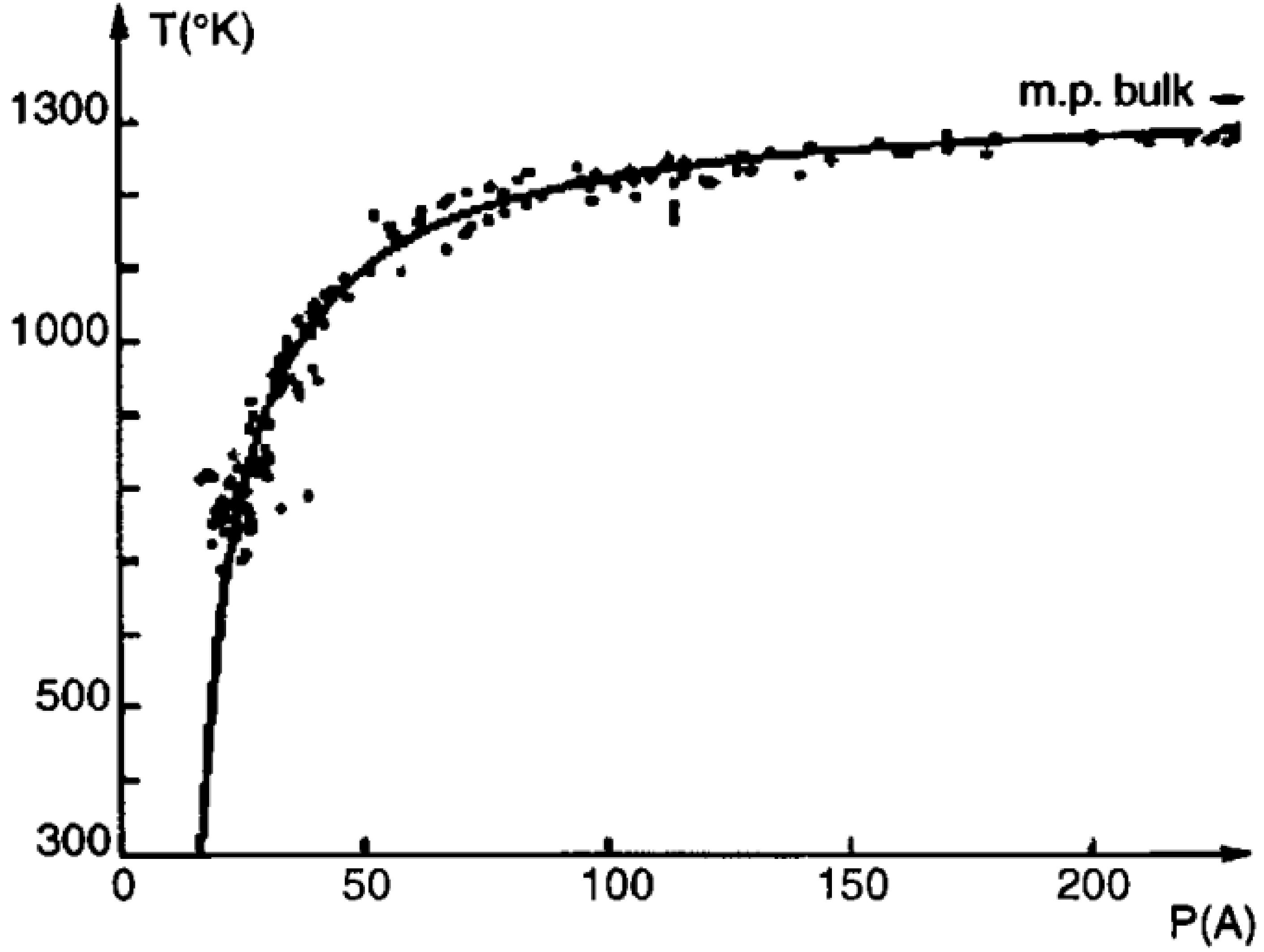
if < 100 nm have a

a lower melting point (the difference can be as large as 1000 deg C) and reduced lattice constant.

Reason:

surface energy to volume energy ratio changes dramatically.

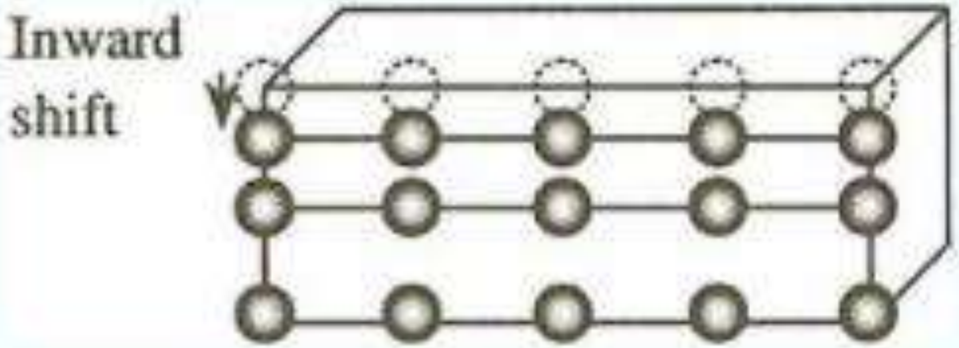
what is easier to get off? surface atom or volume atom.



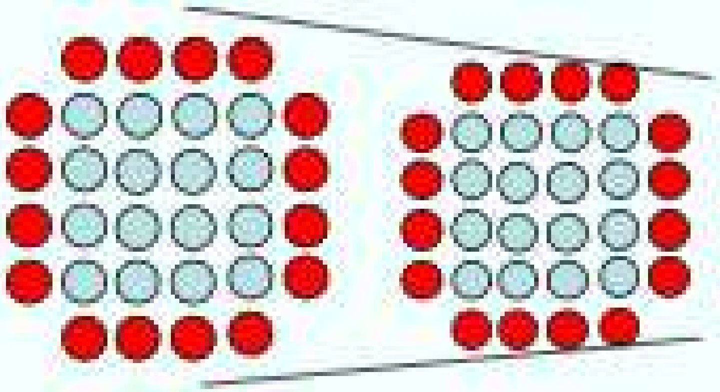
The melting point of bulk gold is of 1337 K and decreases rapidly for nanoparticles with diameters below 5nm. Both experimental data (the dots) and the results theoretical points (the solid line)

Melting points and lattice constants

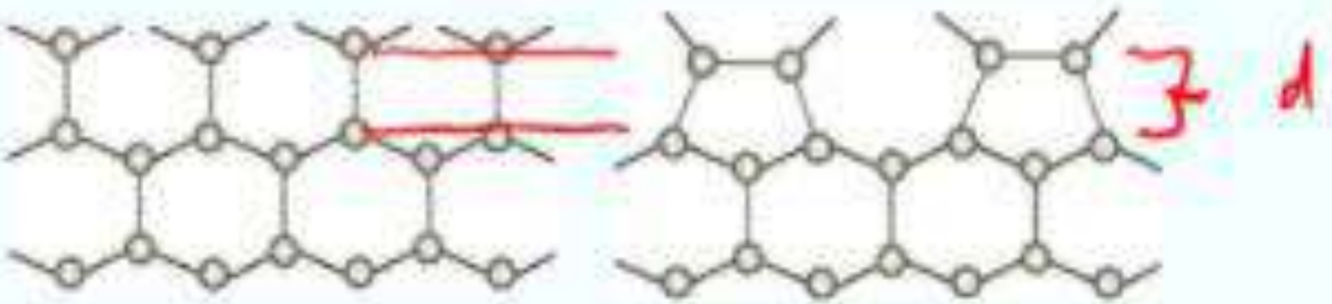
Atoms or molecules on a solid surface possess fewer nearest neighbors or coordination numbers, and thus have dangling or unsatisfied bonds exposed to the surface. Because of the dangling bonds on the surface, surface atoms or molecules are under an inwardly directed force and the bond distance between the surface atoms or molecules and the subsurface atoms or molecules, is smaller than that between interior atoms or molecules.



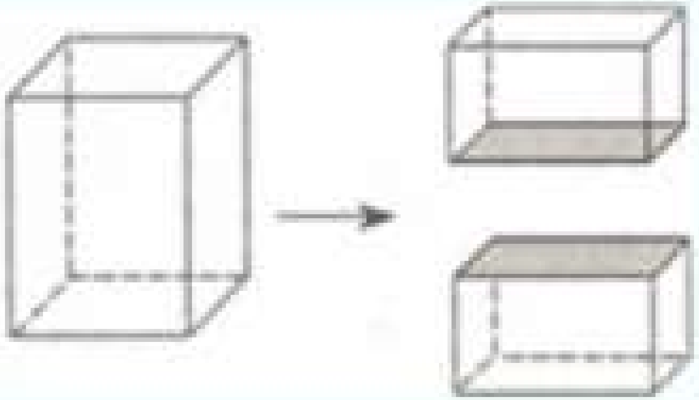
When solid particles are very small, such a decrease in bond length between the surface atoms and interior atoms becomes significant and the lattice constants of the entire solid particles show an appreciable reduction.



surface free energy triggers reconstruction (Example Silicon 100 reconstructs to (2x1)) surface lattice



The extra energy possessed by the surface atoms is described as surface energy, surface free energy or surface tension. Surface energy, γ, by definition, is the energy required to create a unit area of "new" surface:



What is the source of surface free energy?

Concepts of thermodynamics are used to calculate the surface energy of a material.

$$\gamma = \left(\frac{\partial GibbsfreeEnergy}{\partial Area} \right) \Bigg|_{@\,constpressure,\ temp,number}$$

Gibbs free Energy is defined as the energy portion of a thermodynamic system available to do work.

$$G = H - TS$$

H is enthalpy, S is entropy and T is the temperature in Kelvin

Enthalpy: a thermodynamic quantity equivalent to the total heat content of a system

Entropy: the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system

Mechanical Properties of Nanomaterials

- they typically improve

<u>The calculated strength of perfect crystals exceeds that of real ones by two or three orders of magnitudes.</u>

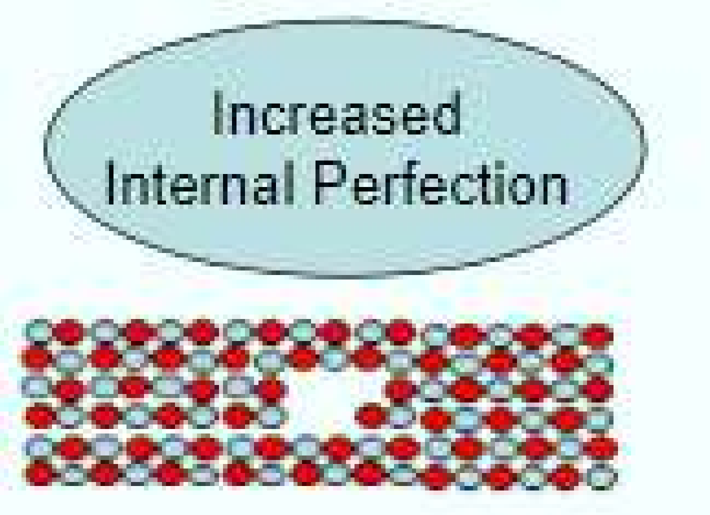
A lot of work has been done on whiskers that approach the theoretical limit first demonstrated by Herring and Galt in 1952 if diameter are less than 10 um.

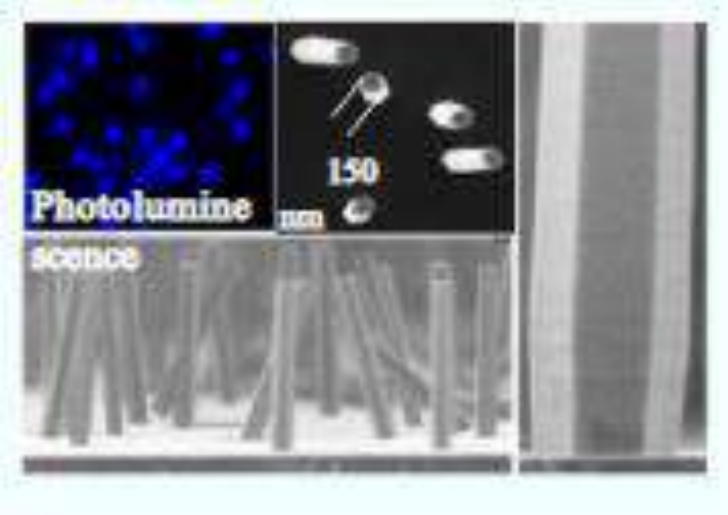
Note: The enhancement starts in the micrometer scale which is different from other size dependent properties.

Two possible mechanisms have been proposed to explain the enhanced strength of nanowires or nanorods (in reality with diameters less than 10 microns).

Increased Internal Perfection

Increased Surface Perfection



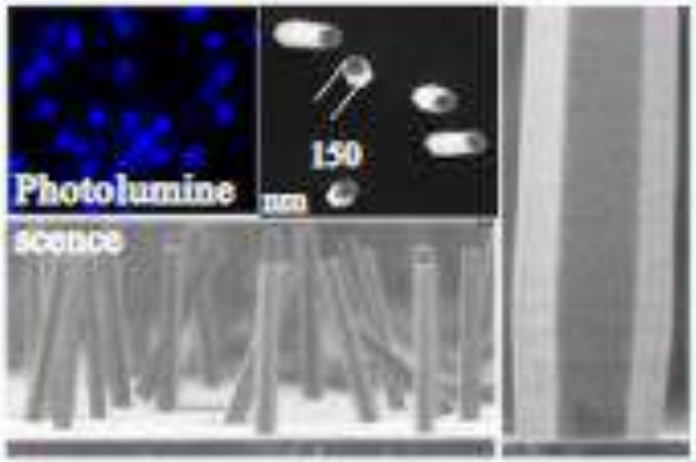


The smaller the cross-section of a whisker or nanowires, the less is the probability of finding in it any imperfections such as dislocations, micro-twins, impurity precipitates, etc

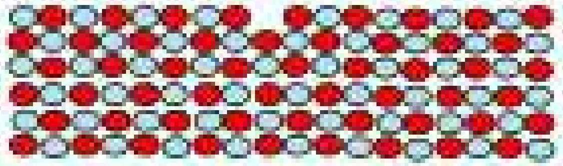
Thermodynamically, imperfections in crystals are highly energetic and can be eliminated -- small sizes makes such elimination of imperfections possible

Imperfections in bulk materials, such as dislocations are often created to accommodate stresses generated in the synthesis and processing of bulk materials due to temperature gradient and other inhomogeneities.

Such stresses can not be excluded but are generally not as likely to exist in small structures, particularly in nanomaterials



Increased Surface Perfection



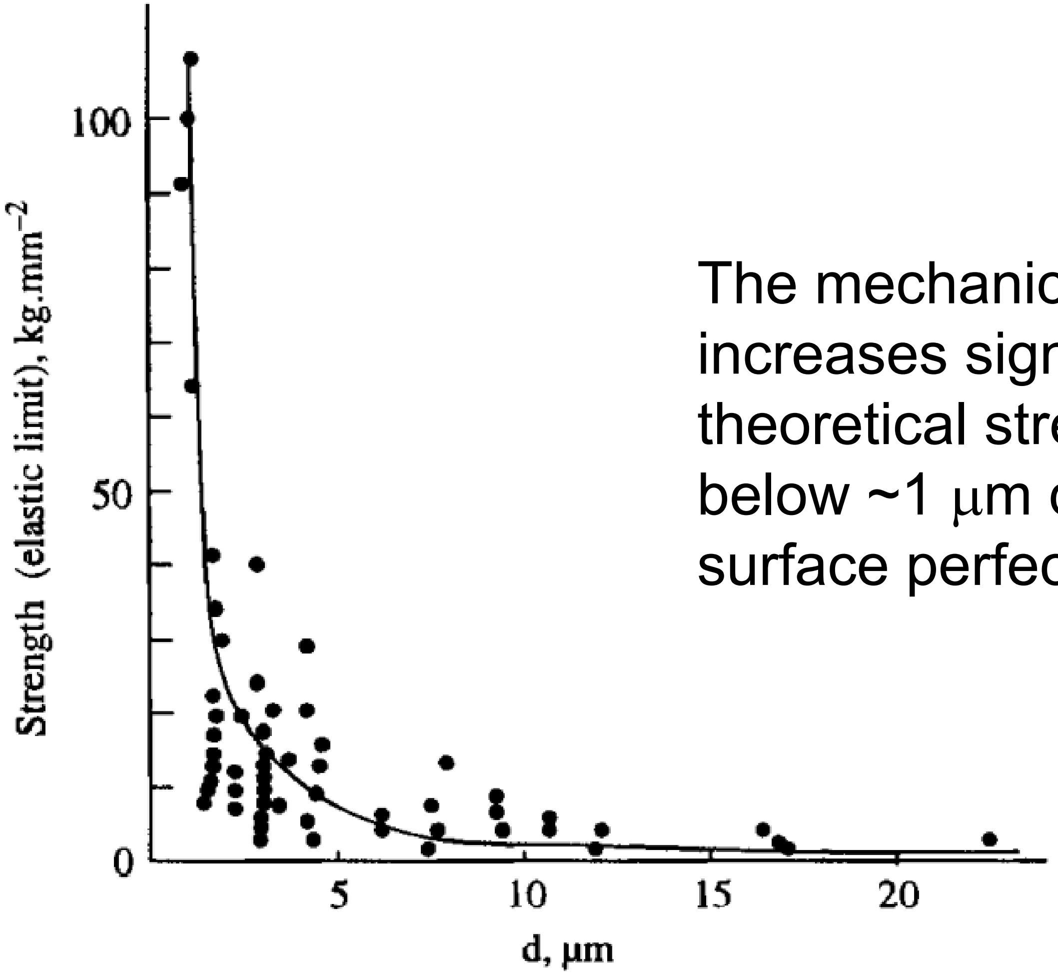
In general, smaller structures have less surface defects. It is particularly true when the materials are made through a bottom-up approach.

Vapor grown whiskers with diameters of 10 microns or less had no detectable steps on their surfaces by electron microscopy, whereas irregular growth steps were revealed on whiskers with diameters above 10 microns.

In the last few years, AFM and TEM have been applied for measuring the mechanical property of nanowires or nanorods.

Both AFM and TEM promise some direct evidence for the mechanical behavior of nanostructures and nanomaterials.

The Applied force per unit area before plastic deformation occurs



The mechanical strength of NaCl whiskers increases significantly and approaches the theoretical strength as the diameters decrease below ~1 μm due to an increased bulk and surface perfections

End of Class