College of Agricultural Technology
Theni

Dr.M.Manimaran Ph.D
Soil Science

NST 301 Fundamentals & Applications of Nanotechnology (1+0)
Syllabus

Unit 1: Basics of Nano science (4 lectures) - Introduction to nano science and technology, history, definition, classification of nanomaterials based on origin, dimension - Unique properties of nanomaterials - mechanical, magnetic, thermal, optical and electrical properties

Unit 2: Synthesis of Nanomaterials (3 Lectures): Physical, Chemical and Biological synthesis of nano-materials

***Unit 3: Properties and Characterization of Nanomaterials (4 Lectures)*:** Size (particle size analyzer), morphological (scanning electron microscope and transmission electron microscope), optical (UV-VIS and FT-IR) and structural (XRD) properties of nano-materials

Unit 4: Application of Nanotechnology (3 Lectures)
Biosensor (principle, component, types, applications) agriculture (nano-fertilizers, herbicides, nano-seed science, nano-pesticides) and food Systems (encapsulation of functional foods, nano-packaging)

Unit V - Application of Nanotechnology (2 Lectures)
Energy, Environment, Health and Nanotoxicology

Reference Books

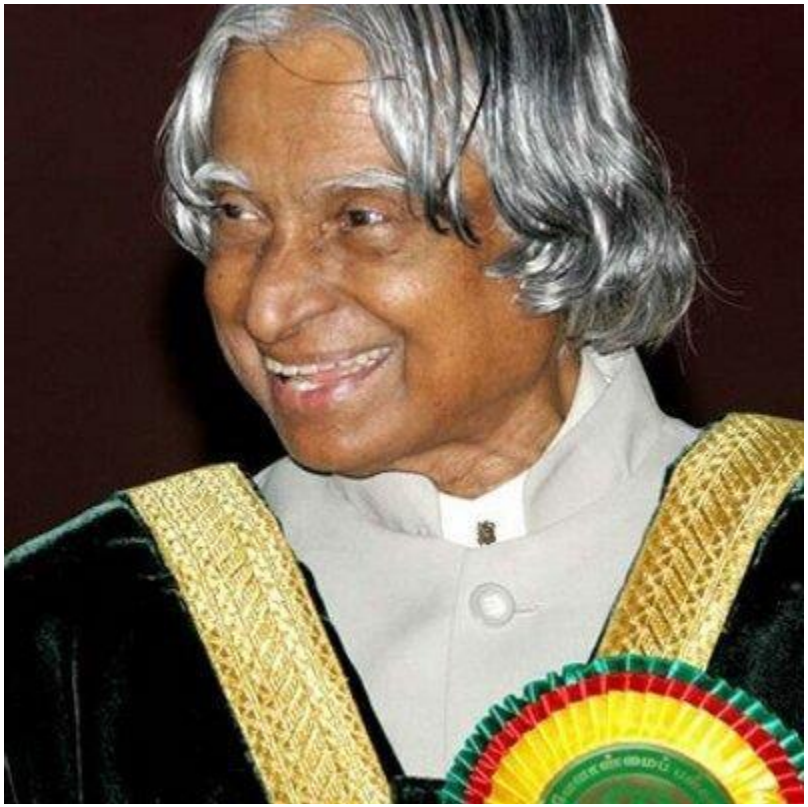
Subramanian, K.S. et al. (2018) Fundamentals and Applications of Nanotechnology, Daya Publishers, New Delhi

K.S. Subramanian, K. Gunasekaran, N. Natarajan, C.R. Chinnamuthu, A. Lakshmanan and S.K. Rajkishore. 2014. Nanotechnology in Agriculture. ISBN: 978-93-83305-20-9. New India Publishing Agency, New Delhi. Pp 1-440.

T. Pradeep, 2007. NANO: The Essentials: Understanding Nanoscience and Nanotechnology. ISBN: 9780071548298. Tata McGraw-Hill Publishing Company Limited, New Delhi. Pp 1-371.

M.A. Shah, T. Ahmad, 2010. Principles of Nanoscience and Nanotechnology. ISBN: 978-81-8487-072-5. Narosa Publishing House Pvt. Ltd., New Delhi Pp. 1-220.

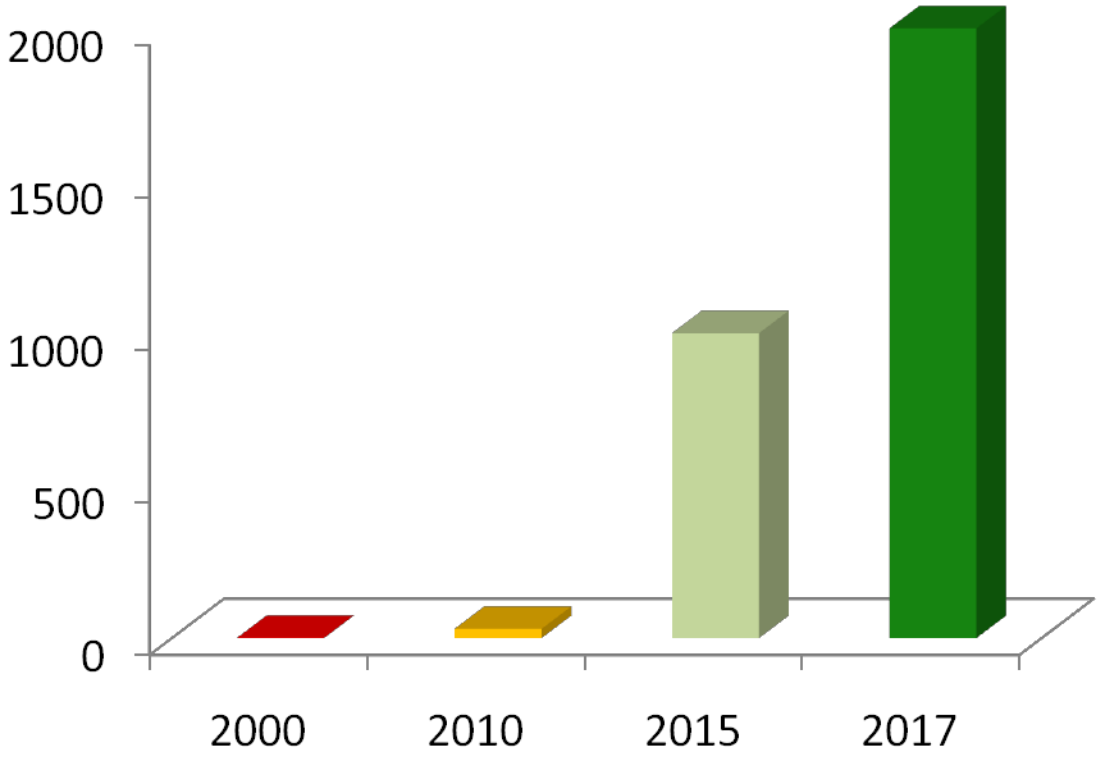
Mentor of Nanotechnology



Dr. APJ Abdul Kalam
Former President of India

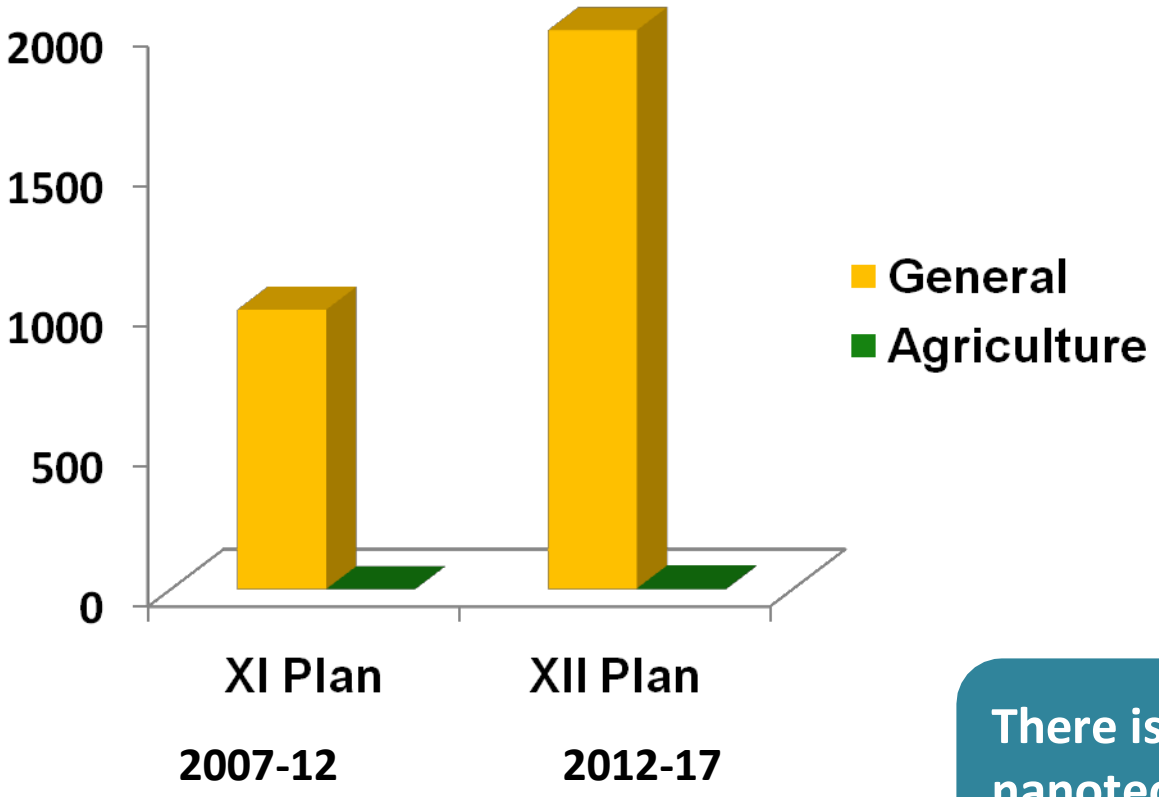
When I see children run around and cycle with the artificial limbs with lightweight prosthetics, it is sheer bliss

Global Investment in Nanotechnology
(in Billion USD)



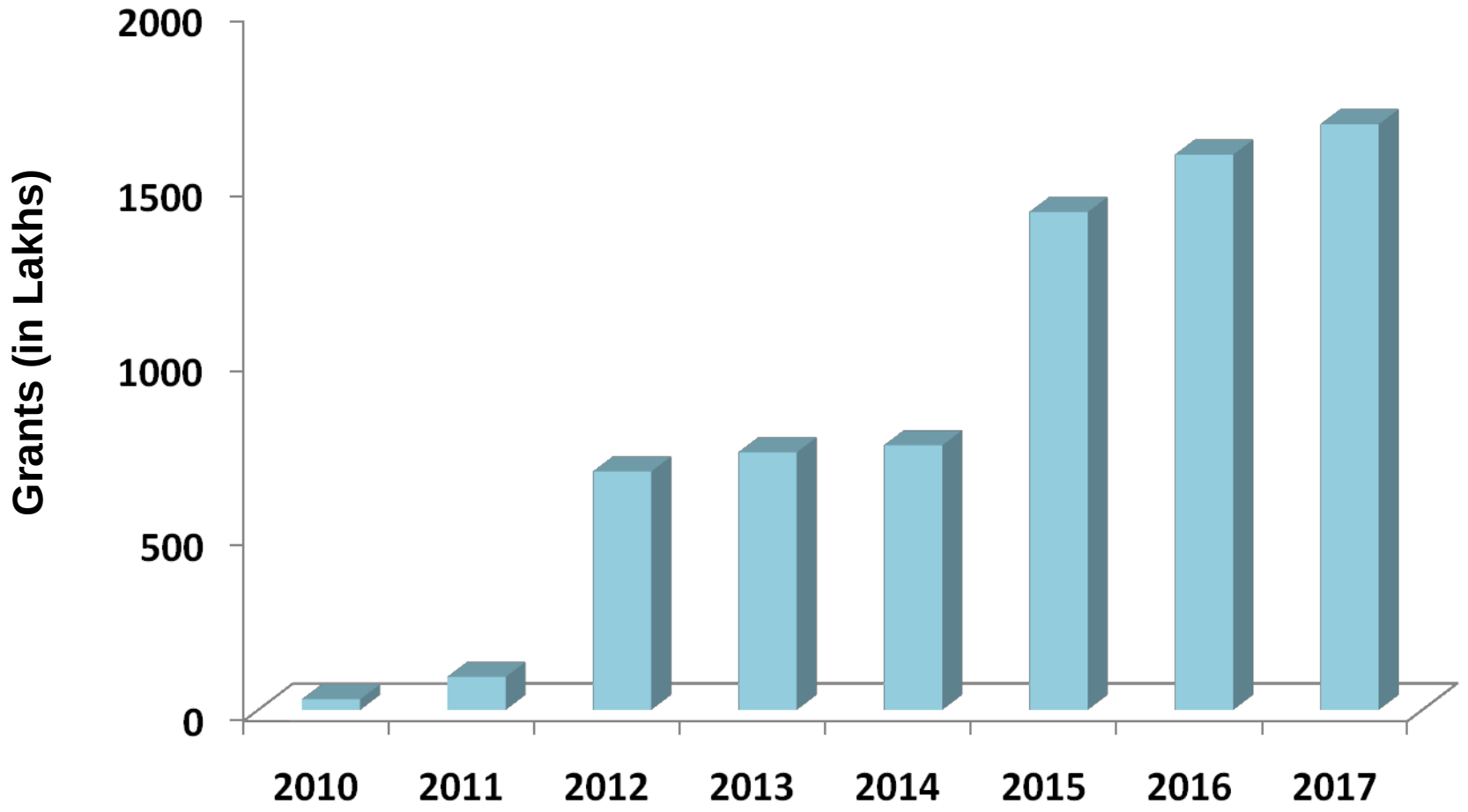
Nanotechnology investments increased by 2000-fold increase in 17 years

Nanotechnology Investments in India
(in Crores)

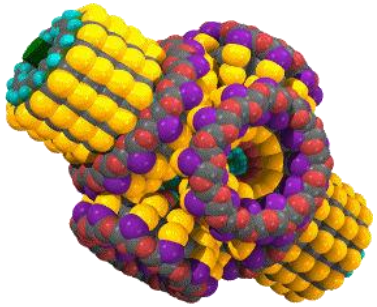


There is a great scope for nanotechnology investments in agriculture

Youngest Turned Richest



Nano Agriculture



Infuse nanotechnology concepts and principles in agricultural sciences to evolve processes and products that **precisely deliver inputs** in production systems that ensure food security and environmental safety

Shift from Green to Evergreen

Need for enhancing productivity in perpetuity without ecological harm

Solution

Tools developed by blending traditional ecological prudence and frontier technologies

"Solution to unresolved issues in agriculture"

Nanotechnology – History, Definition and Basics

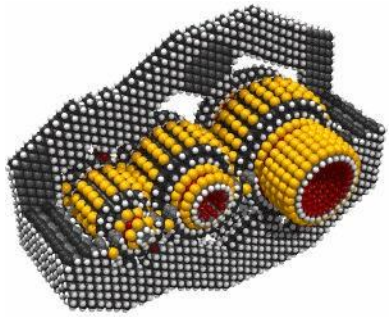
What is Nanotechnology ?

Science dealing with engineering of functional systems at the molecular scale

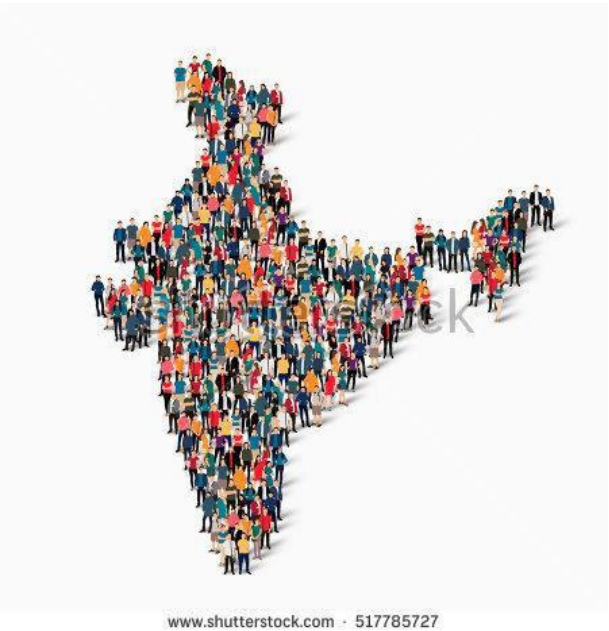
Atom by atom manipulation

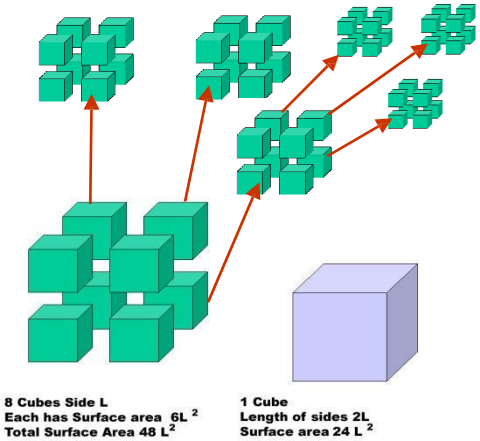
Ability to construct items *from the bottom up*, using techniques and tools to make complete, high performance products

One – billionth of a metre or One millionth of a mm



Nano = One billionth of a Metre





1,355,776,343
March 1, 2018 at 6 am

Atom-by-atom manipulation yields in précised processes and products for smart delivery of inputs

Nano Scale

Dimensions

100 µm

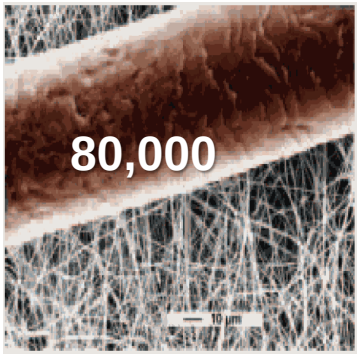
Plant, Animal Cell

10 µm

Bacteria

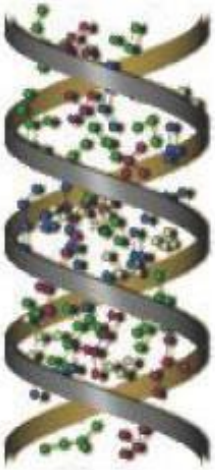
1 µm

Human hair



100 nm

Virus



Protein

10 nm

DNA "turn"

Simple Molecules

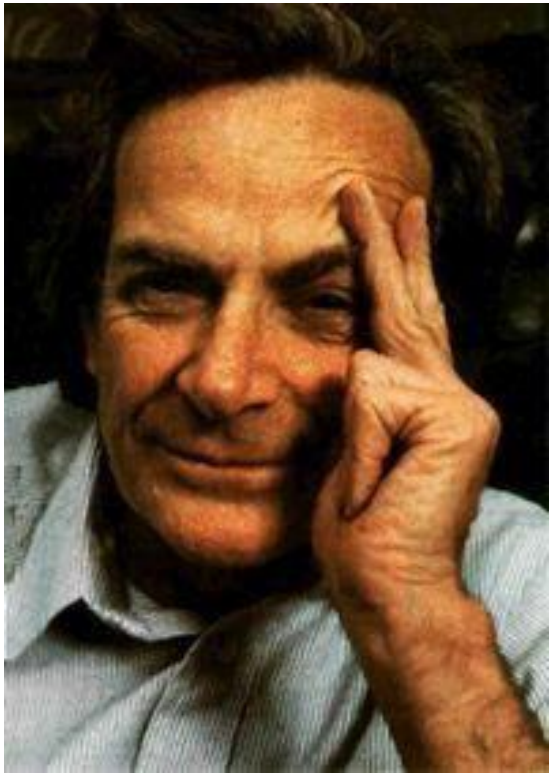
1 nm

DNA "base"

Atoms

0.1 nm

Invention of Nanotechnology



Richard P. Feynman (1986)
Particle Physicist

Eric Drexler (1981)
Molecular Machinery

Genesis of Nanotechnology

December 29, 1959: *Plenty of Room at the Bottom*
Richard Feynman proposed the “possibility of manoeuvring things atom by atom.

Mid-1970s: *Nanotechnology*
Eric Drexler proposed molecular nanotechnology

1974: *Molecular Devices*
The first molecular electronic device was patented by Aviram and Seiden of IBM.
Professor **Norio Taniguchi** of Tokyo Science University invented the term ***Nanotechnology*.**

1980: *Molecular Nanotechnology*
K. Eric Drexler wrote the first paper on advanced nanotechnology.

1986: *Engines of Creation*
K. Eric Drexler publishes “Engines of Creation.” Drexler presented his provocative ideas on molecular nanotechnology to a general audience.

1994: *Gold Particles*
Stable gold nanoparticles was made in solution

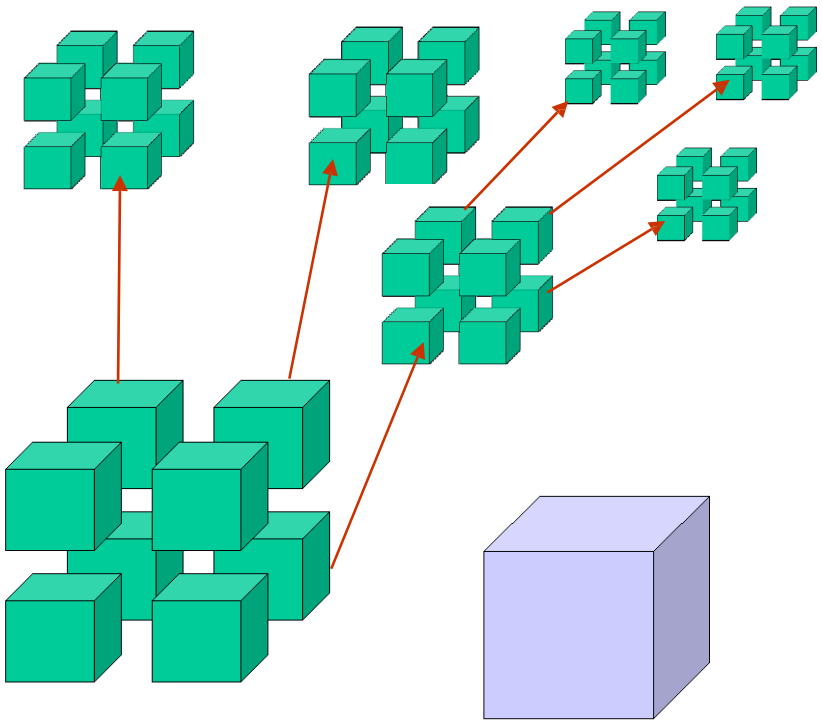
January 1996: *Assembling Molecules*
Scientists at IBM succeed in moving and precisely positioning individual molecules at room temperature.

2001: *Moore's Law Surpassed*
In June 2001, Intel Corporation created the technology needed to produce the world's sŵallest aŶd fastest silicoŶ traŶsistor ;5 trillioŶ tiŵes a sec.

September 2002: *Molecular Electronics Breakthrough*
The 64-bit memory uses molecular switches. The total area is less than one square micron, giving it a bit density that is more than ten times that of current silicon memory chips.

2008: Noble prize for Physics
The Nobel Prize in Physics 2007 was awarded jointly to Albert Fert and Peter Grünberg *"for the discovery of Giant Magnetoresistance*

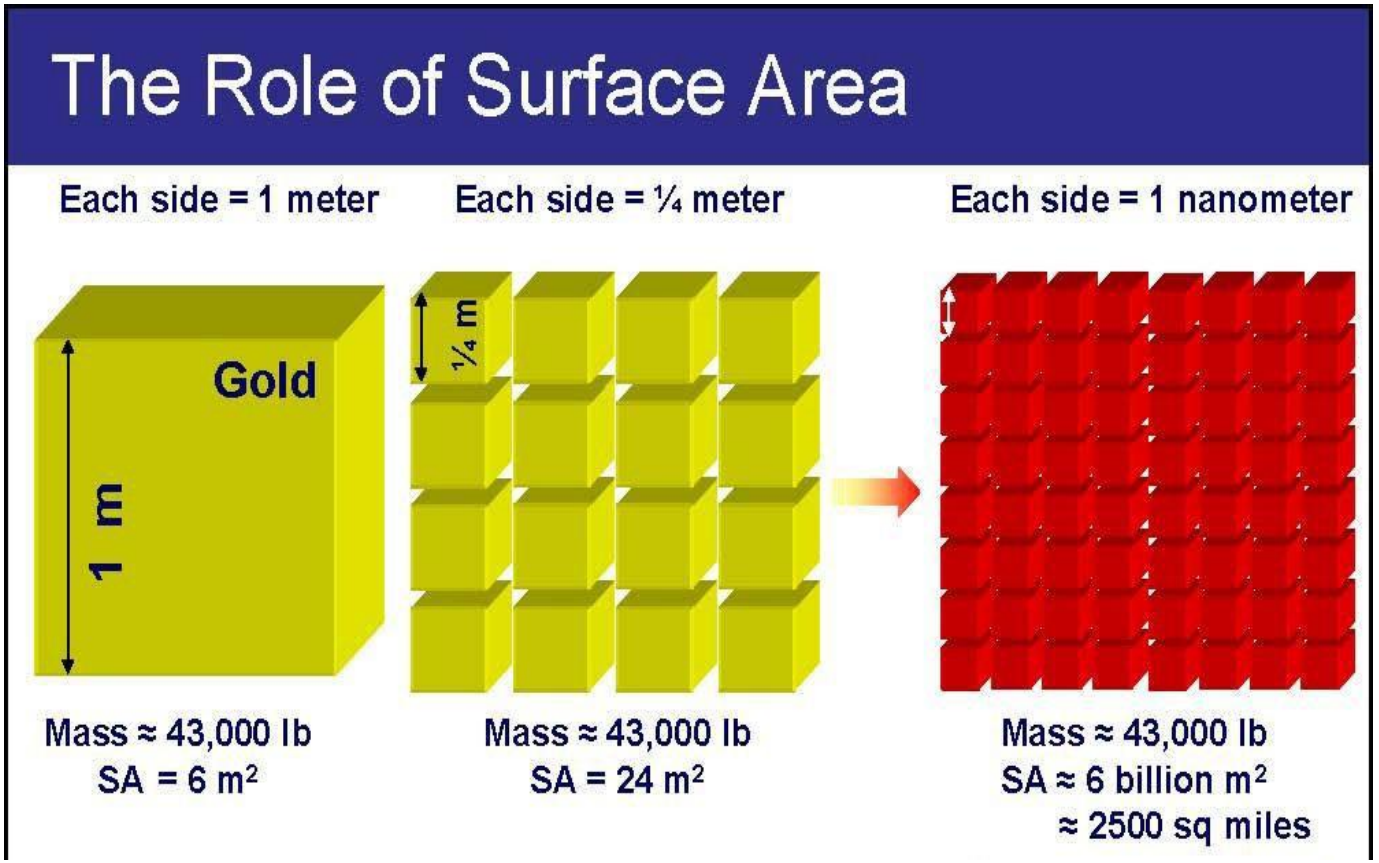
High Surface Mass Ratio – Unique Property of Nano



8 Cubes Side L
Each has Surface area $6L^2$
Total Surface Area 48 L^2

1 Cube
Length of sides 2L
Surface area 24 L^2

For example, 5 cm^3 material divided 24 times will produce 1 nanometer cubes and spread in a single layer could cover a football field



CMA (Chennai Metropolitan Area : Chennai + Thiruvallur + Kanchipuram districts)

= 1170 sq. km (~500sq miles)

Builders versus Chiselers: a Historical View

Chiseling: **Start with a relatively uniform, large piece of material -- selectively shape/remove material to define desired object.**

Building: **Start with small building blocks; combine and arrange them to form interesting assemblies**

*This slide provided by D. Janes

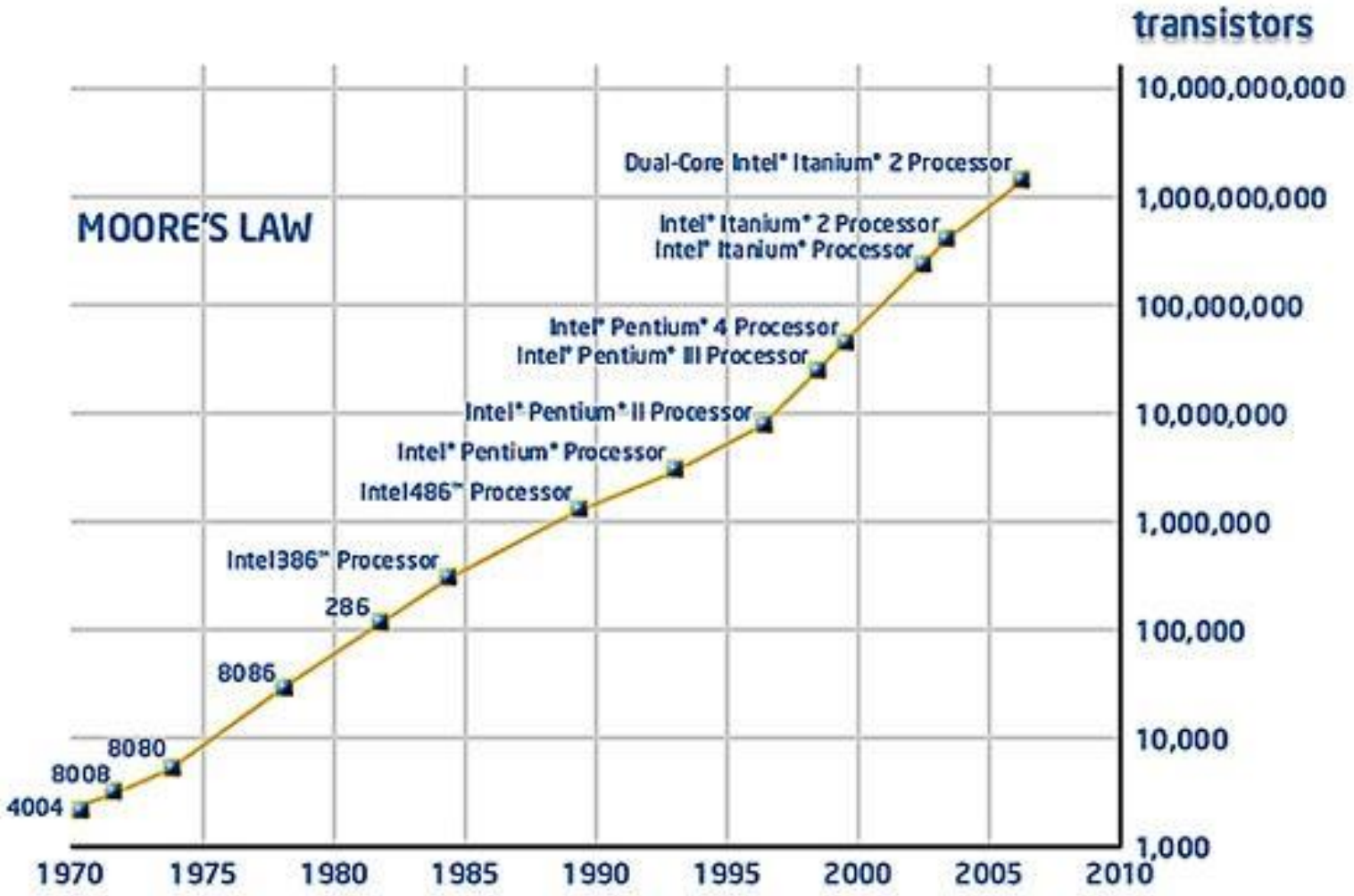
Moore’s Law (1965)

Gordon Moore, one of the founders of the Intel Corporation, came up with two empirical laws to describe the amazing advances in integrated circuit electronics

Moore's first law states that the amount of space required to install a transistor on a chip shrinks by roughly half every 18 months.

Moore's second law predicts that the cost of building a chip manufacturing plant doubles with every other chip generation, or roughly every 36 months.

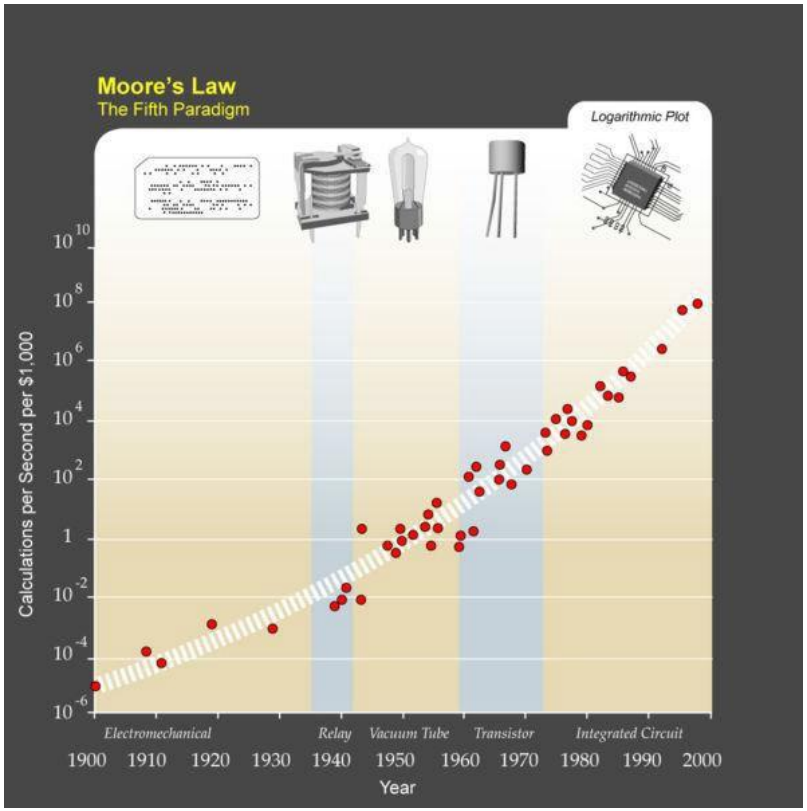
Moore's Law


transistors
10,000,000,000
1,000,000,000
100,000,000
10,000,000
1,000,000
100,000
10,000
1,000
MOORE'S LAW
Dual-Core Intel® Itanium® 2 Processor
Intel® Itanium® 2 Processor
Intel® Itanium® Processor
Intel® Pentium® 4 Processor
Intel® Pentium® III Processor
Intel® Pentium® II Processor
Intel® Pentium® Processor
Intel486™ Processor
Intel386™ Processor
286
8086
8080
8008
4004
1970
1975
1980
1985
1990
1995
2000
2005
2010

Futurists' Law

Kurzweil's extension of Moore's law from integrated circuits to earlier transistors, vacuum tubes, relays and electromechanical computers.

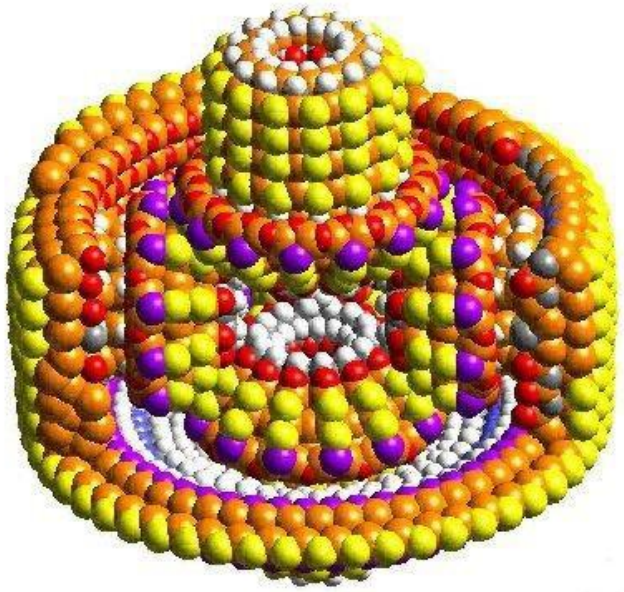
Futurists such as Ray Kurzweil, Bruce Sterling, and Vernor Vinge believe that the exponential improvement described by Moore's law will ultimately lead to a technological singularity: a period where progress in technology occurs almost instantly



Terminologies in Nanotechnology

Assembler

An all-purpose device for guiding chemical reactions by positioning molecules. The molecular machine can build any molecular structure or device from simpler chemical entities.



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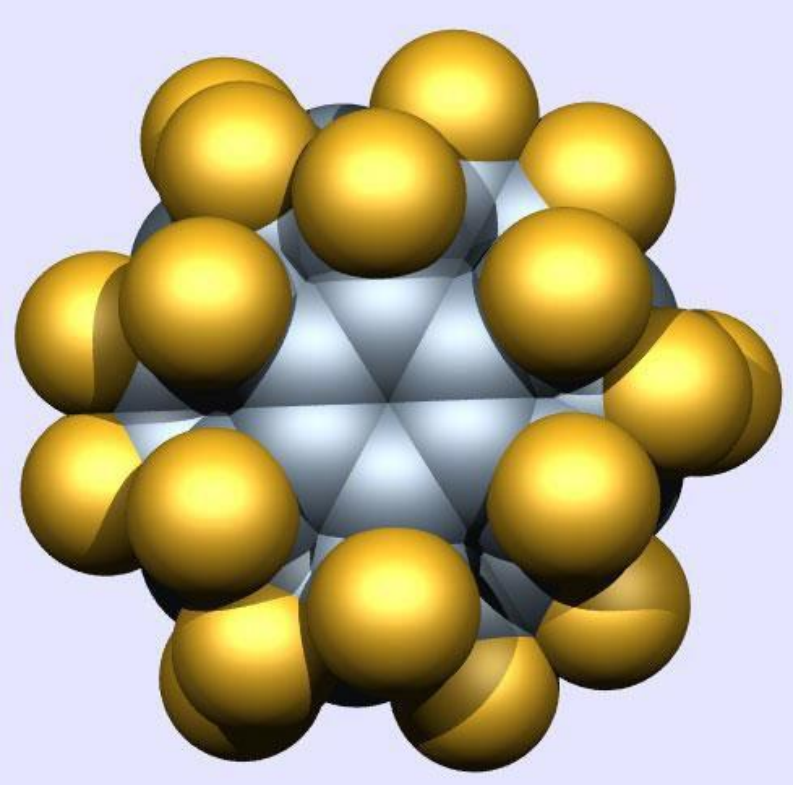
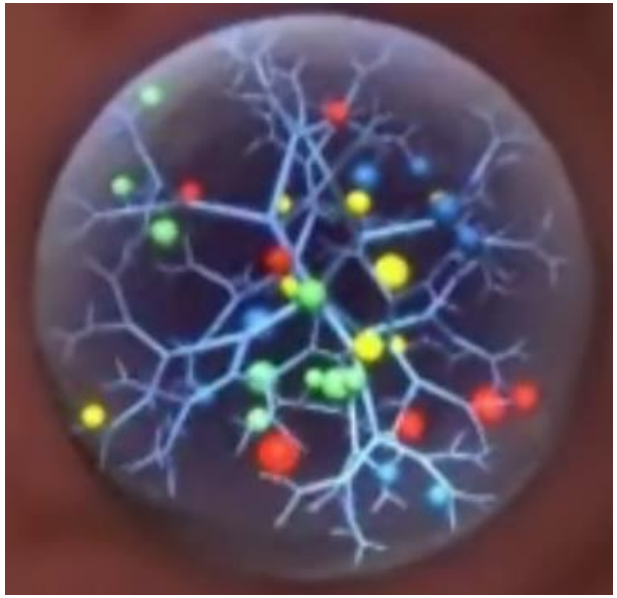
Buckminsterfullerene

Spherical cage structures of carbon containing 60 atoms, resembling a football



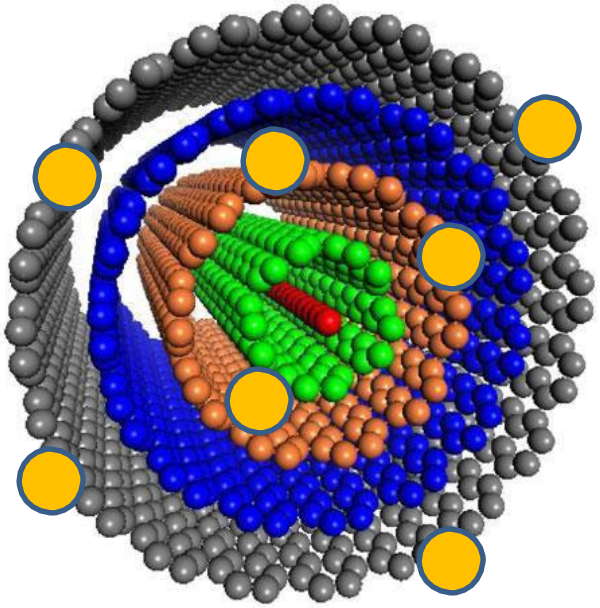
Dendrimers

The word *dendra*, tree, a dendrimer is a branching polymer. The diversity of the branches depend on generation of its growth: several of them are of nanometer dimensions. Dendrimers are used in nanoparticle synthesis.



Functionalization

The attachment of a chemically active moieties to an inert molecule/ entity.



Carbon nanotube attached with enzyme

Dry nanotechnology: Fabrication of nanostructures without biology or wet chemistry. A carbon nanotube based technology will be dry as against a technology with DNA which will be ‘wet’.

Femtotechnology: Manipulating materials on the scale of elementary particles (leptons, hadrons, and quarks). A technology after picotechnology, which is below the length scale of nanotechnology. Also used as Femtotech.

MEMS: Microelectromechanical systems: generic term to describe micron scale electrical/mechanical devices.

Mesoscale: A device or structure larger than the nanoscale (10–9 m) and smaller than the megascale. Typically in the range of 10^{-7}m. Used also as mesoscopic.

Molecular integrated microsystems (MIMS): Microsystems in which functions found in biological and nanoscale systems are integrated with materials.

Molecular mechanics: A method by which the molecular potential energy function is computed to understand and predict various properties of the system.

Molecular wire: A molecular wire, a quasi-one-dimensional molecule, which can transport charge carriers, from one end to the other.

Nanobiotechnology: Application of nanotechnology to learn biological systems and use of this knowledge for devices and methods.

Nanobot: Nanorobot or Nanomachine.

Nanobubbles: Nanosized bubbles with or without molecules or objects. We have a chapter on such objects in this volume

Quantum dots: Nanocrystals or nanoparticles. Refer to confined electrons. Electrons in them occupy discrete states as in the case of atoms and therefore, quantum dots are referred to as artificial atoms.

Quantum Hall effect: Quantised resistance observed in some semiconductors at low temperatures.

Quantum mechanics: The mechanics of subatomic, atomic and molecular objects. Motion of subatomic particles is described by this mechanics, the central aspect of it is the wavefunction which describes the system under investigation completely.

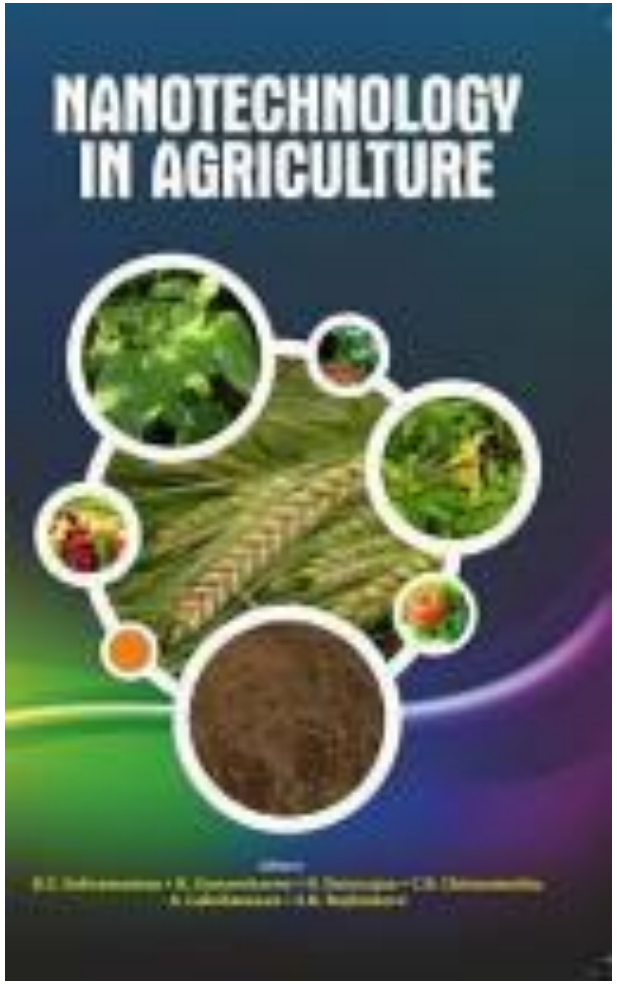
SEM: Scanning electron microscopy, imaging technique in which a focused beam of electrons is used to scan the sample and the generated secondary electrons and ions as well as deflected primary electrons are used to image the sample.

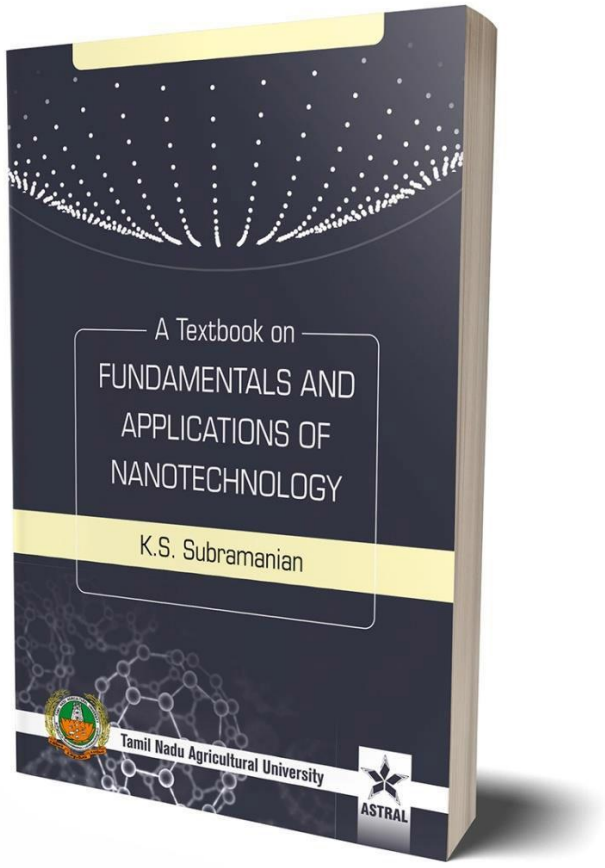
Smart materials: Products with ability to respond to the environment, such as shape transformation.

Spintronics: Electronic devices exploiting the spin of electrons, in addition to charge.

SPM: Scanning probe microscope (SPM), including AFMs and STMs, in which effect of interaction of a sharp probe with the sample is measured to infer atomic structure of the material.

STM: Scanning tunneling microscopy, also Scanning thermal microscopy, Imaging technqie using local temperature variations of the sample.


NANOTECHNOLOGY
IN AGRICULTURE


A Textbook on
FUNDAMENTALS AND
APPLICATIONS OF
NANOTECHNOLOGY
K.S. Subramanian
Tamil Nadu Agricultural University
ASTRAL

Classification of Nanomaterials based on origin and dimension Brief introduction to Quantum Dots, Buckyball, Carbon Nanotube

Compiled by

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Dept. of Nano Science and Technology, TNAU, Cbe-3

Classification based on Dimension

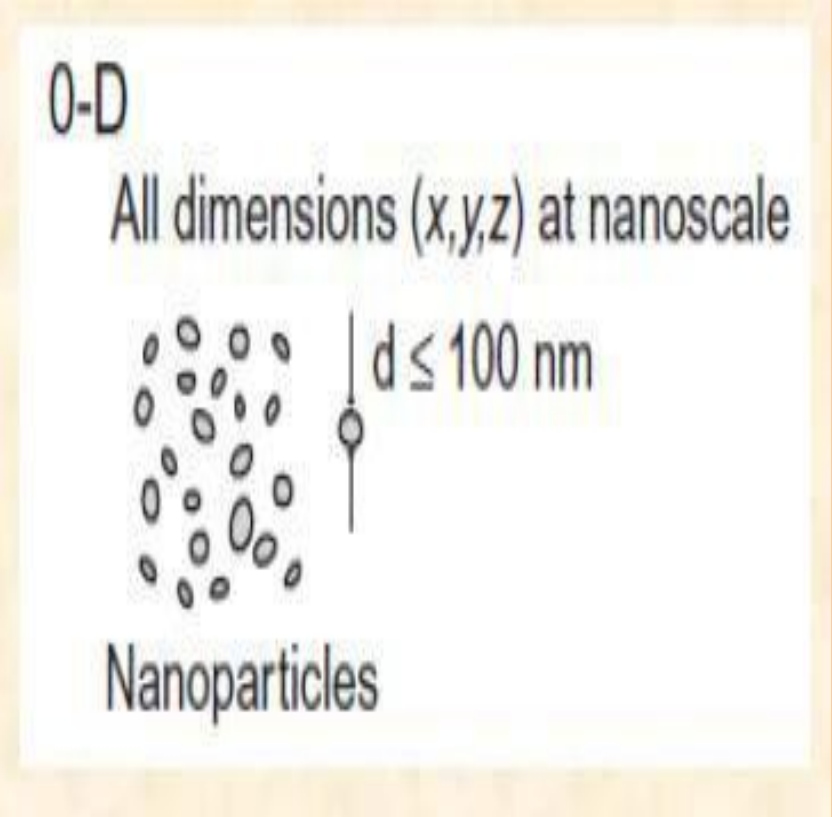
- Nanostructured materials derive their special properties from having one or more dimensions made small (<100nm)
- Nanomaterials can be classified according to the following categories i.e., Size: Any one dimension is < 100 nm across;
- Origin: Natural, Incidental or Engineered ;
- Form: Amorphous, crystalline, polymeric or composites;
- Shapes : Spheres, tubes, rods, cones and fibers etc; Non-metal (e.g., carbon), metallic (e.g., Au, Ag), semiconductor (e.g., CdSe), or a combination.
- Their physical properties are related to their size and chemical compositions.

Classification based on Dimension

- Classification based on the number of dimensions, which are not confined to the nanoscale range (<100 nm) are: zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D) (Fig. 2.1).

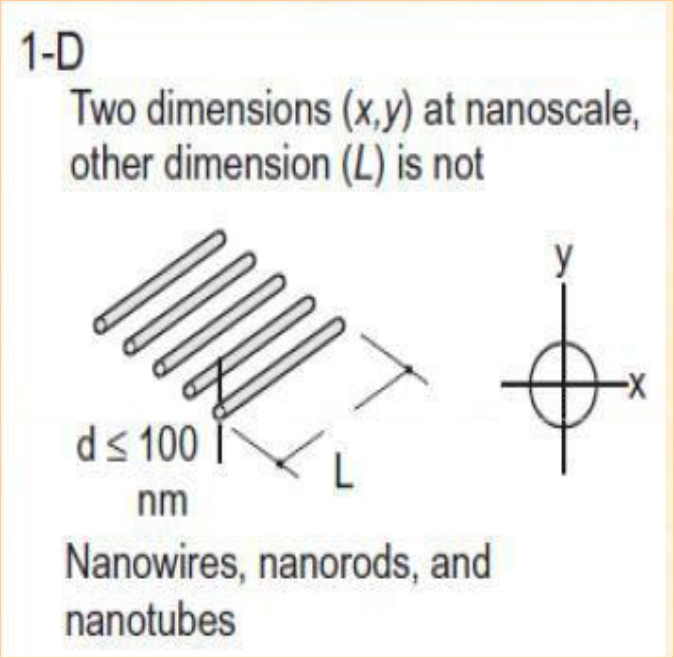
Zero-dimensional nanomaterials Materials wherein all the dimensions are measured within the nanoscale i.e., less than 100nm. (no dimensions, or 0-D, are larger than 100 nm).

The most common representation of zero-dimensional nanomaterials are nanoparticles, Quantum Dots



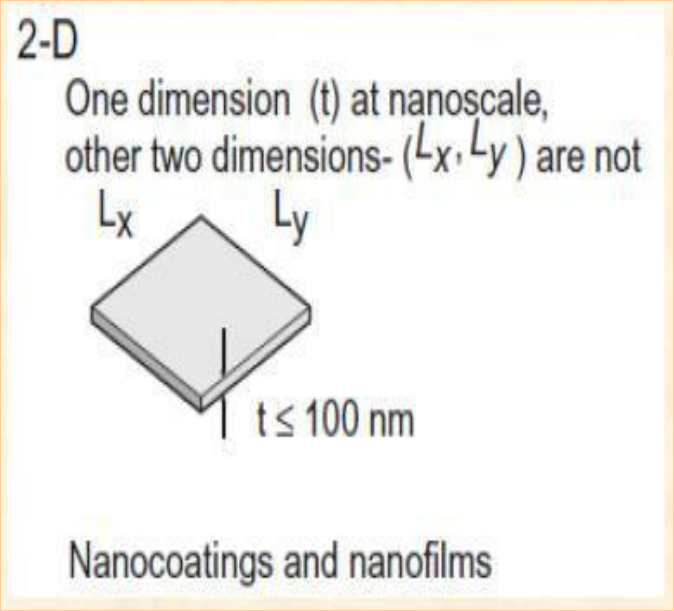
One-dimensional nanomaterials

- Only one dimension is outside the nano scale and other two dimensions are within 100nm.
- This leads to needle like-shaped nanomaterials. 1-D materials include nanotubes, nanorods and nanowires.



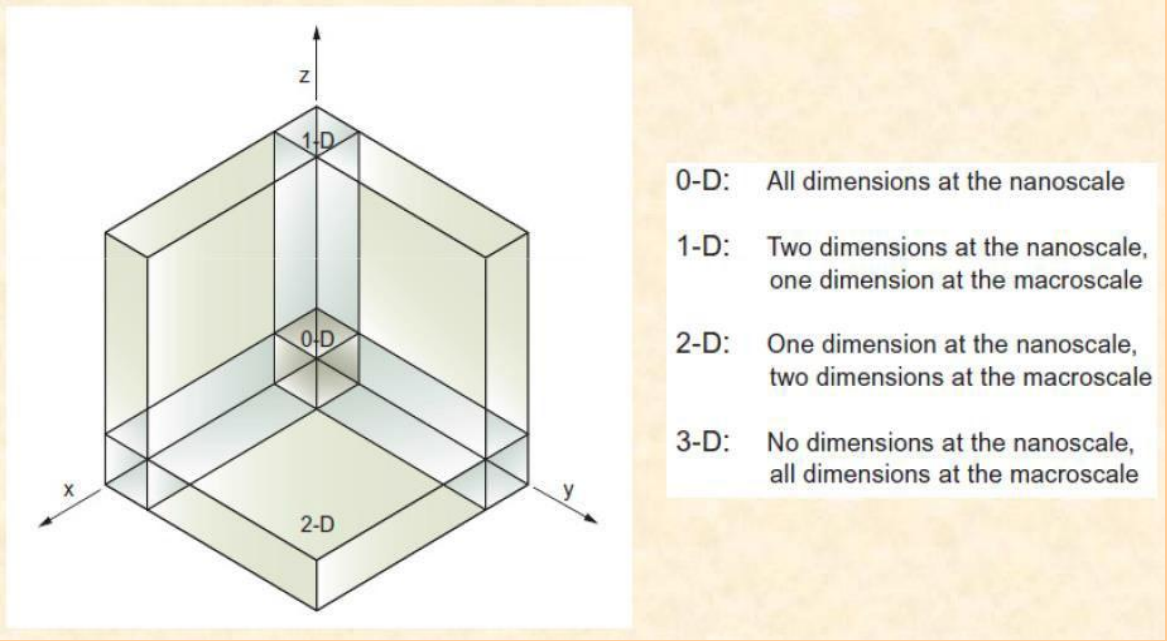
Two-dimensional nanomaterials

- Two of the dimensions are not confined to the nanoscale and only one dimension is within 100nm . 2-D nanomaterials exhibit plate-like shapes. Two-dimensional nanomaterials include nanofilms, nanolayers, and nanocoatings.



Three-dimensional materials

- Bulk materials are materials that are not confined to the nanoscale in any dimension.
- All three arbitrarily dimensions are above 100 nm.
- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations (Fig. 2.2).
- With respect to the presence of features at the nanoscale, 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers.



Nanomaterials

Characteristics

- Any one of their dimension is < 100 nm across
- Natural, Incidental or engineered
- Amorphous, crystalline, polymeric or composites
- Non-metal (e.g., carbon), metallic (e.g., Au, Ag), semiconductor (e.g., CdSe), or a combination
- Shapes : spheres, tubes, rods, cones, and fibers etc.
- Their physical properties are related to their size and chemical compositions

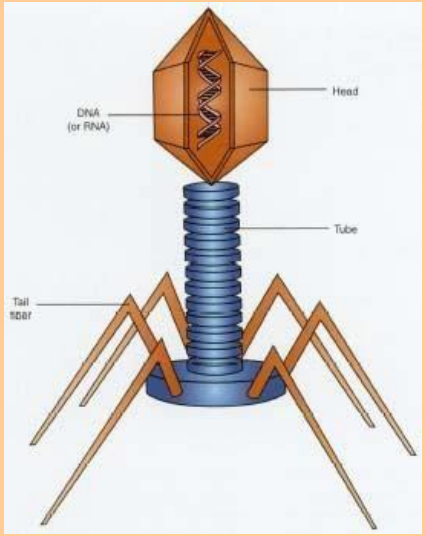
Nanoparticle Types

Nanoparticles fall into three major types:

- Naturally occurring
- Incidental
- Engineered

Naturally Occurring

1. Sea spray
2. Mineral composites
3. Volcanic ash
4. Viruses



Viruses

- Sea spray

- Volcanic ash

- Mineral composites

Incidental nanoparticles

Produced as a result of by-product of a process

- *Byproduct of combustion, industrial manufacturing, and other human activities*

Cooking smoke

Welding fumes

Diesel exhaust

Industrial effluents

Sandblasting

Engineered Nanoparticles

An Engineered Nanomaterial is any intentionally produced material that has a size in 1, 2, or 3-dimensions of typically between 1-100 nm

Examples :

- Metals
- Quantum dots
- Buckyballs/nanotubes
- Sunscreen pigments
- Nanocapsules

Nanoparticle Classifications - Composition

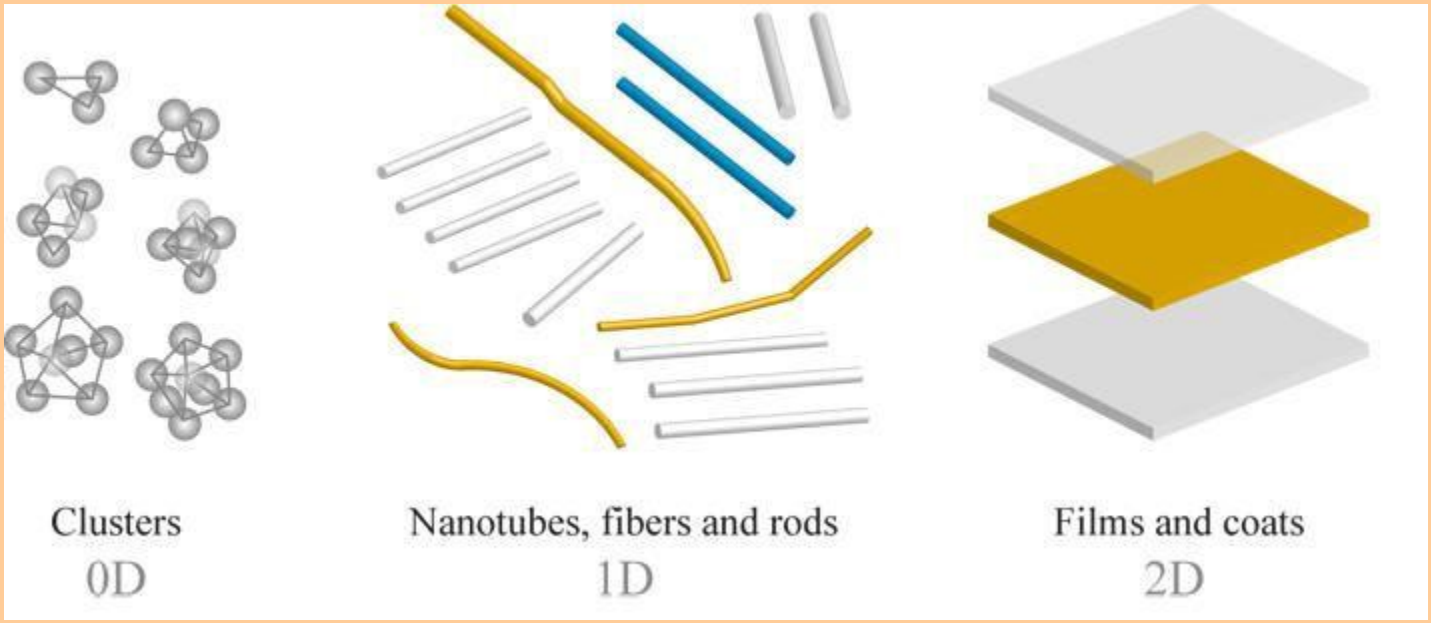
Nanoparticles can be classified into five categories:

- Fullerenes and Carbon Nanotubes
- Metals
- Ceramics
- Semiconductors (Quantum dots)
- Polymeric

Nanoparticle Classifications – Based on Size

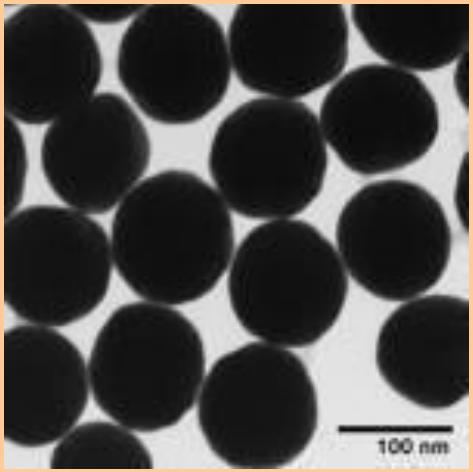
All three dimensions < 100 nm	Zero - Dimensional	Particles, quantum dots, nanoshells,microcapsules, hollow spheres
Two dimensions >100 nm	Two - Dimensional	Anti-adhesive/anti-stain coatings, applied films
One dimension >100 nm	One - Dimensional	Single-walled carbon Nanotubes, fibers, nanowires

Nanoparticle Classifications – Based on Size



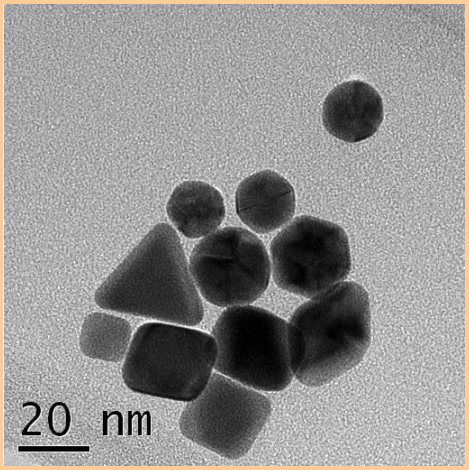
Spherical

polymer NPs



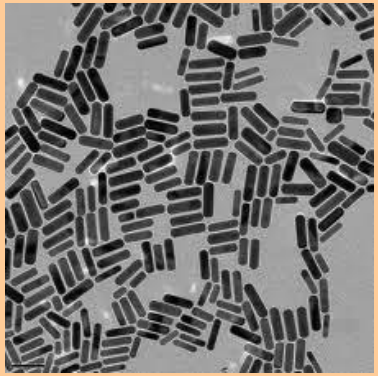
Gold NPs

Triangular

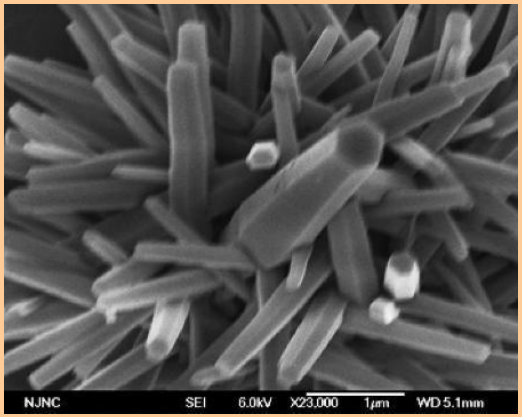


Gold NPs

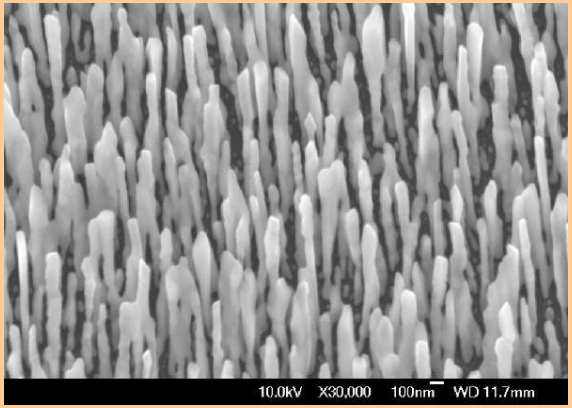
Rod



Gold Nano rods

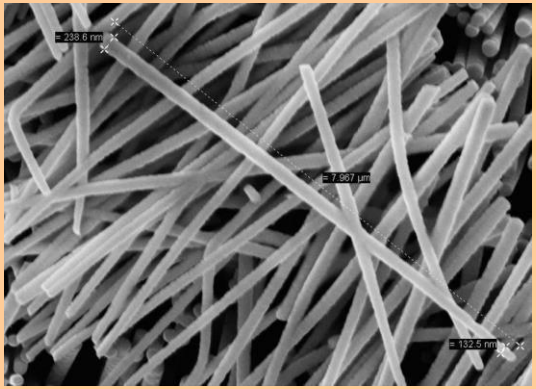


Zn Nano rods

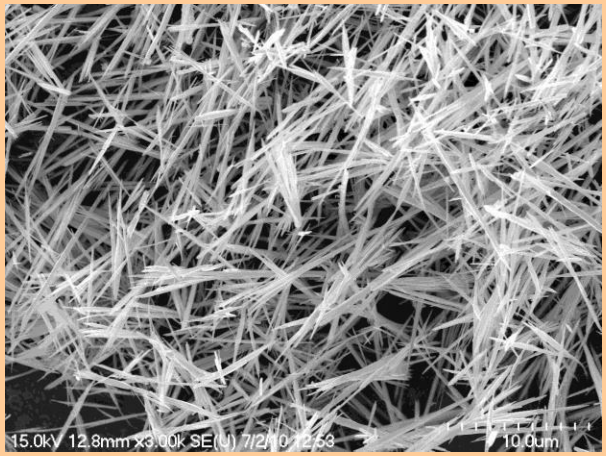


Si Nano rods

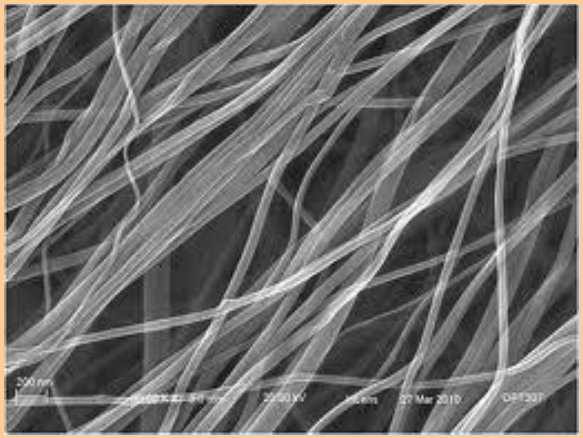
Nano wires



Ni/Fe Nano wires

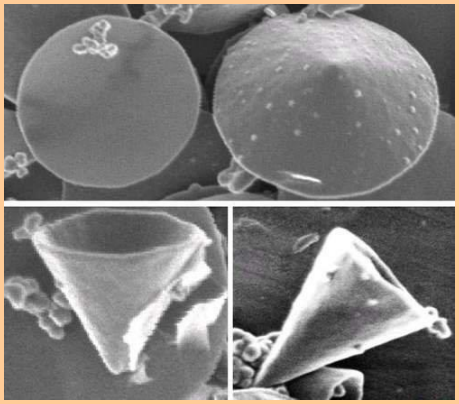


Lead Titanate



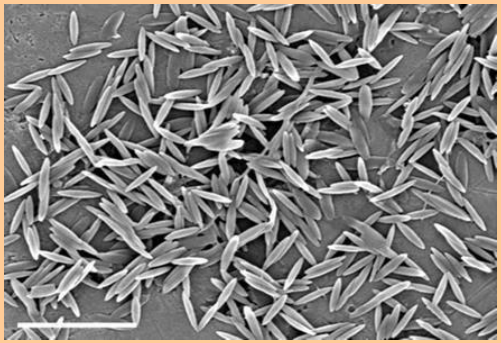
Pt-Fe nanowires

Nano cone



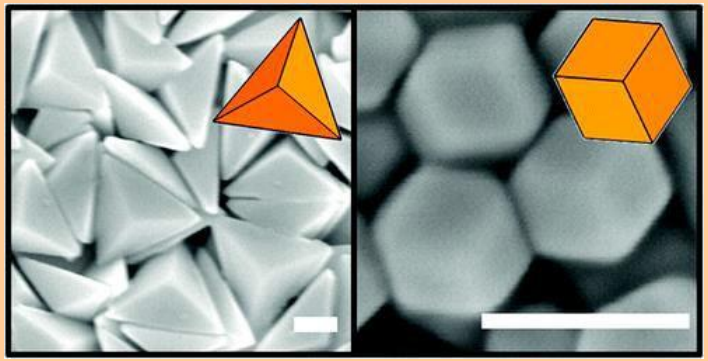
C nano cone

Elliptical



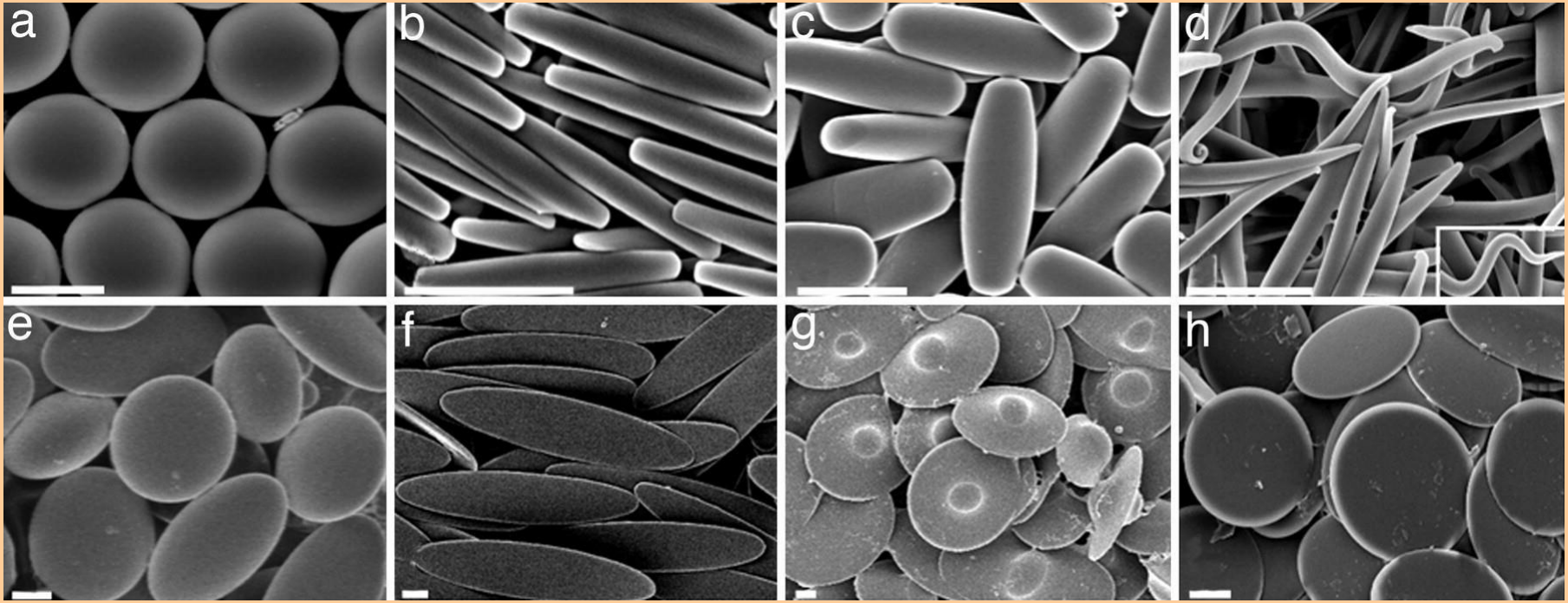
Polymeric elliptical

Triangular & cube



Gold Nps

Polymeric nanoparticles of complex shapes



(*a*) Spheres. (*b*) Rectangular disks. (*c*) Rods. (*d*) Worms. (*e*) Oblate ellipses. (*f*) Elliptical disks. (*g*) UFOs. (*h*) Circular disks.

Quantum Dots (QD)

❖ Discovered in1980 by Alexei Ekimovin & Louis Brusin and the term "Quantum Dot" was coined by Marl Reed.

❖ A semiconductor crystal of nanometre dimensions with distinctive conductive properties determined by its size.

❖ The size of Quantum Dots range from 2 to 10 nanometers in diameter (about the width of 50 atoms).

❖ They emit photons (light) under excitation, (when stimulated by an external source such as ultraviolet (UV) light) which are visible to the human eye as light.

❖ The wave length of the photon emission from Quantum Dot depends on the size of the quantum dots.

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Adv. Nat. Sci.: Nanosci. Nanotechnol. 6 (2015) 015015 (5pp) — doi:10.1088/2043-6262/6/1/015015

Synthesis and application of quantum dots-based biosensor

Ngoc Hai Nguyen, Thi Giang Duong, Van Nong Hoang, Nam Thang Pham, Tran Cao Dao and Thu Nga Pham

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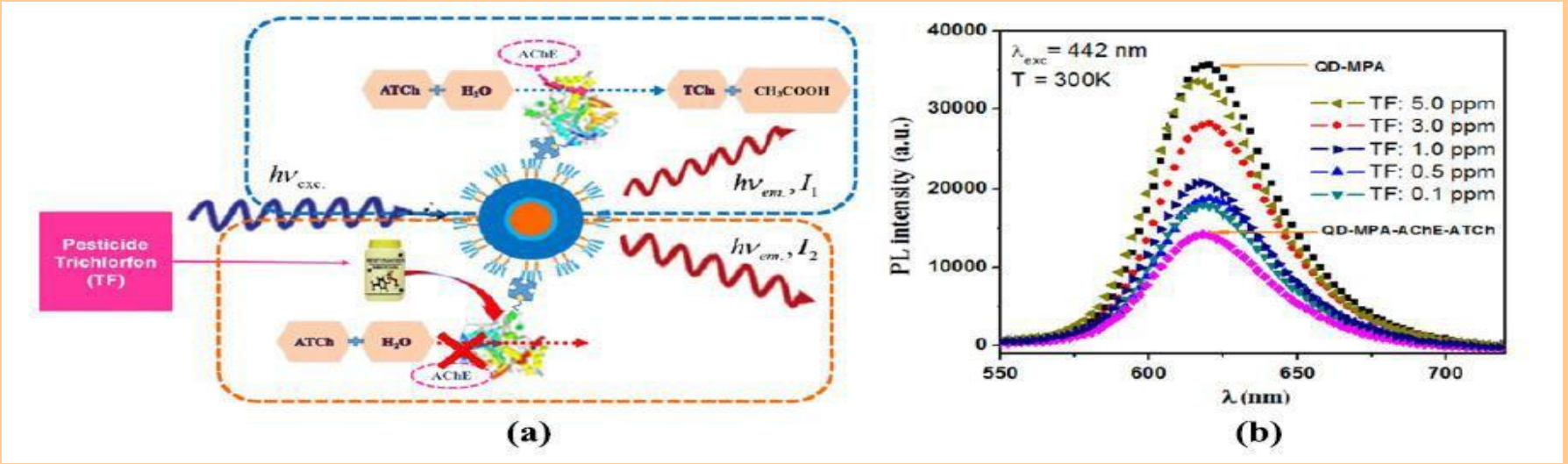
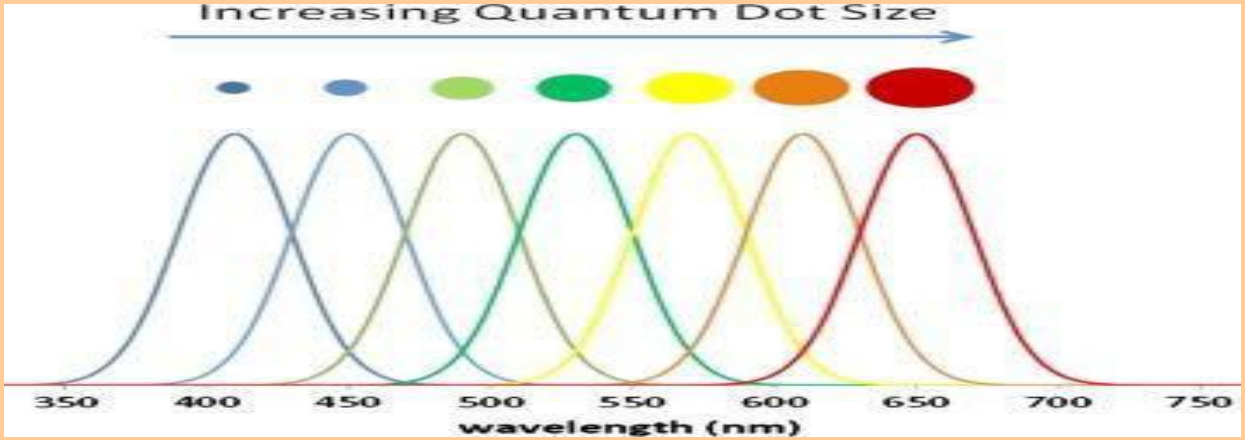
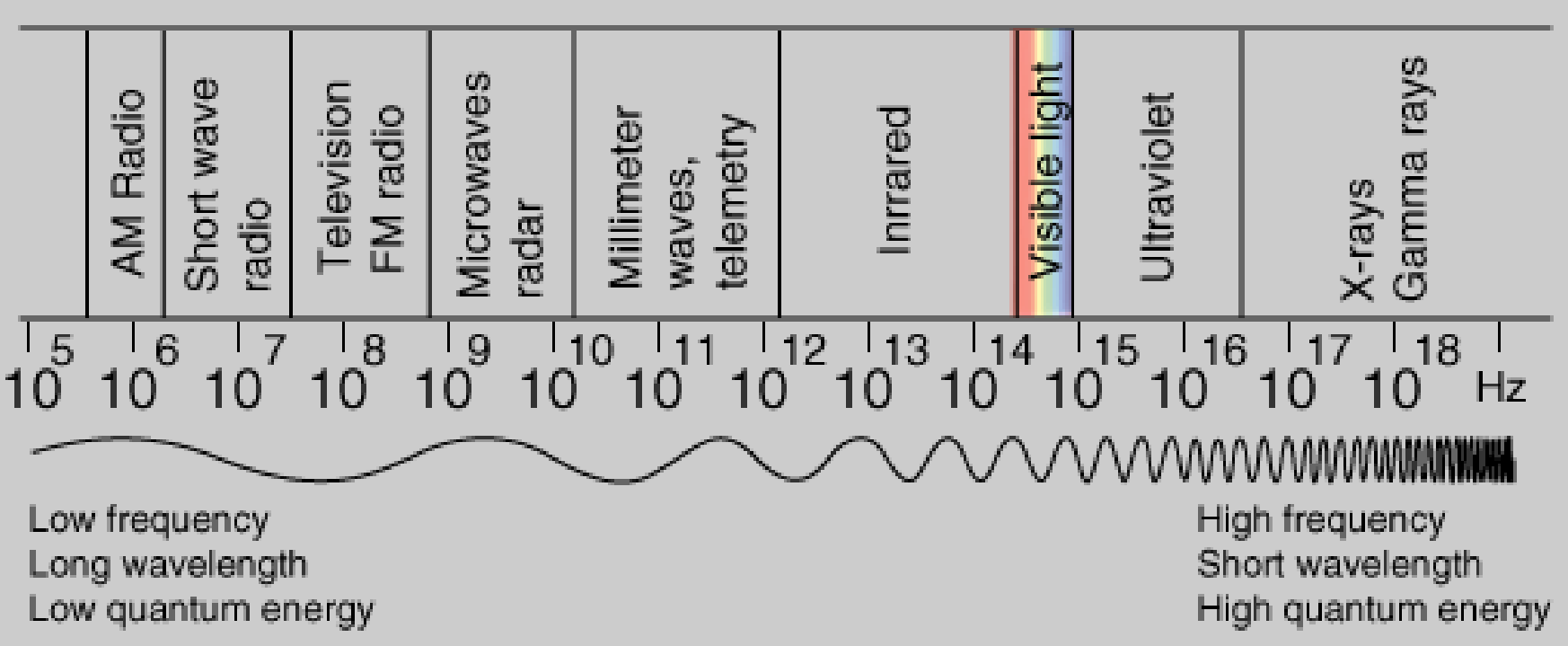


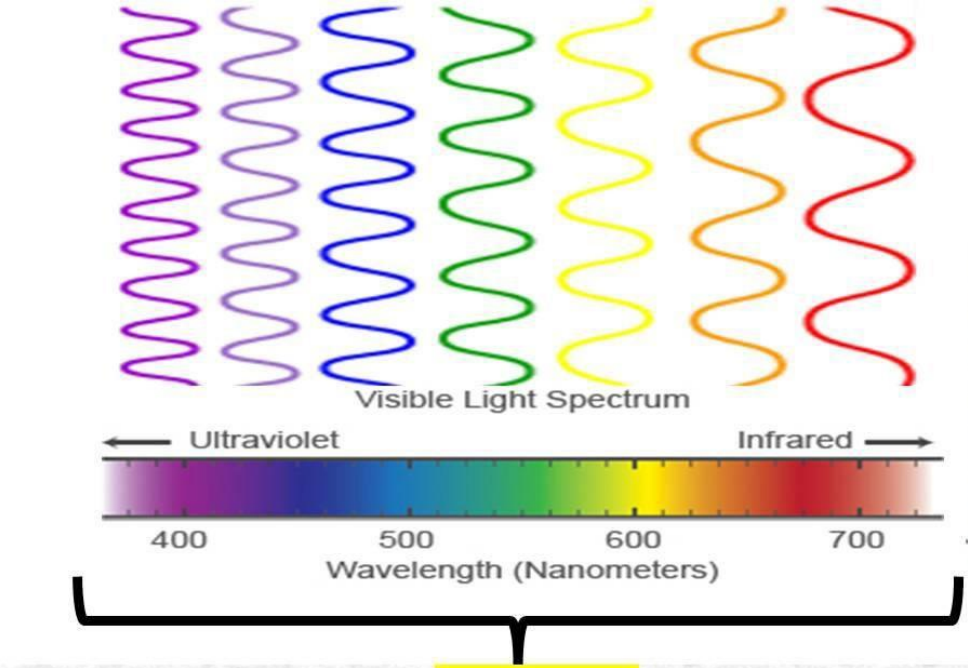
•The ability to precisely control the size of a quantum dot enables the manufacturer to determine the wavelength of the emission, which in turn determines the colour of light the human eye perceives. Quantum dots can therefore be “tuned” during production to emit any colour of light desiredThe smaller the dot, the closer it is to the blue end of the spectrum, and the larger the dot, the closer to the red end.



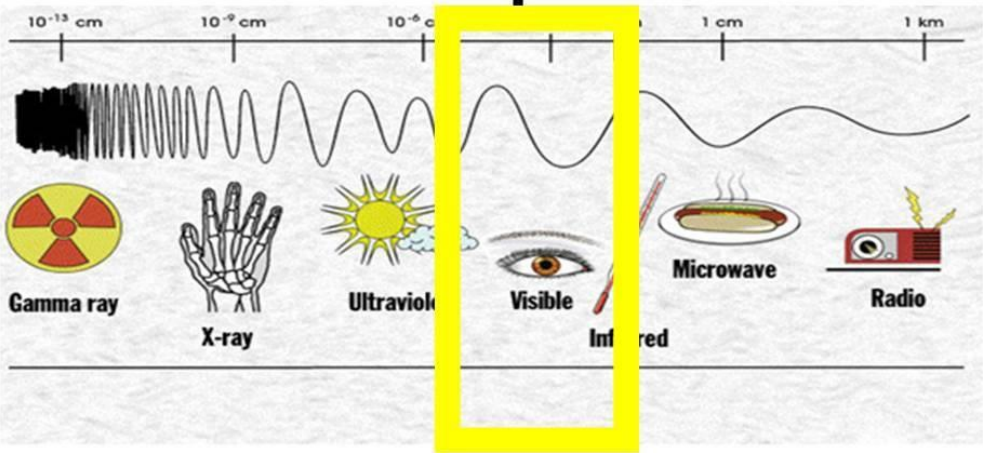
Electro Magnetic Spectrum



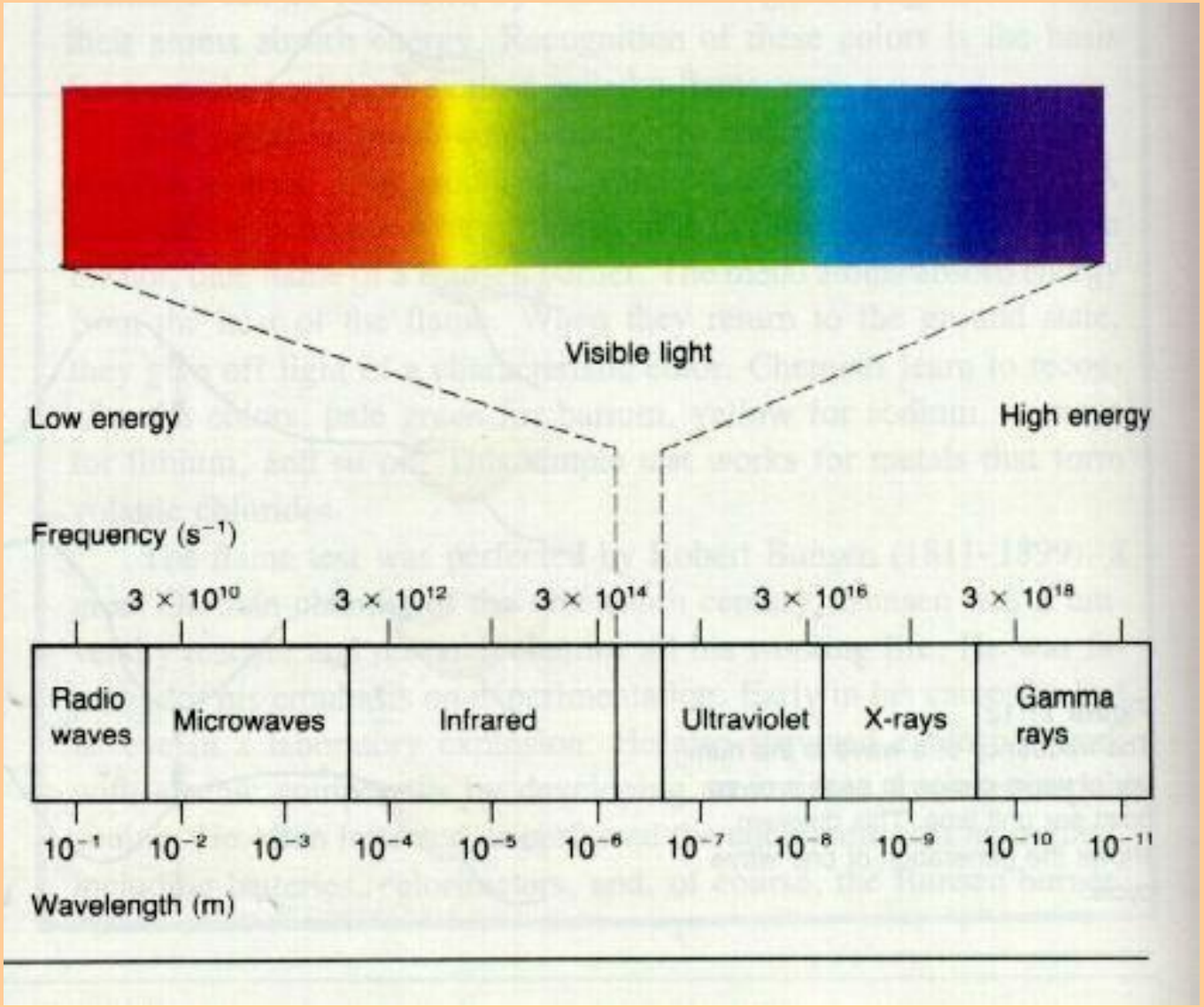
Visible Spectrum



Color	Wavelength interval
violet	~ 430 to 380 nm
blue	~ 500 to 430 nm
cyan	~ 520 to 500 nm
green	~ 565 to 520 nm
yellow	~ 590 to 565 nm
orange	~ 625 to 590 nm
red	~ 740 to 625 nm

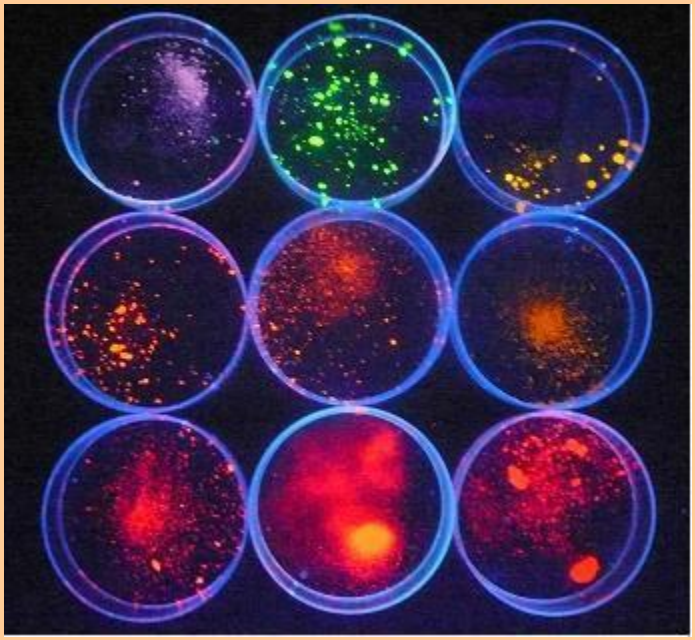


Visible Spectrum



Potential applications of Qd

- Drug discovery
- Diagnostics
- Biological reagents
- Genetic analysis
- Solid-state lighting
- Sensors
- Display screens
- Cosmetics
- Solar cells



Applications of Carbon based Nano materials (Bucky Ball, CNT) in Agriculture and Environment

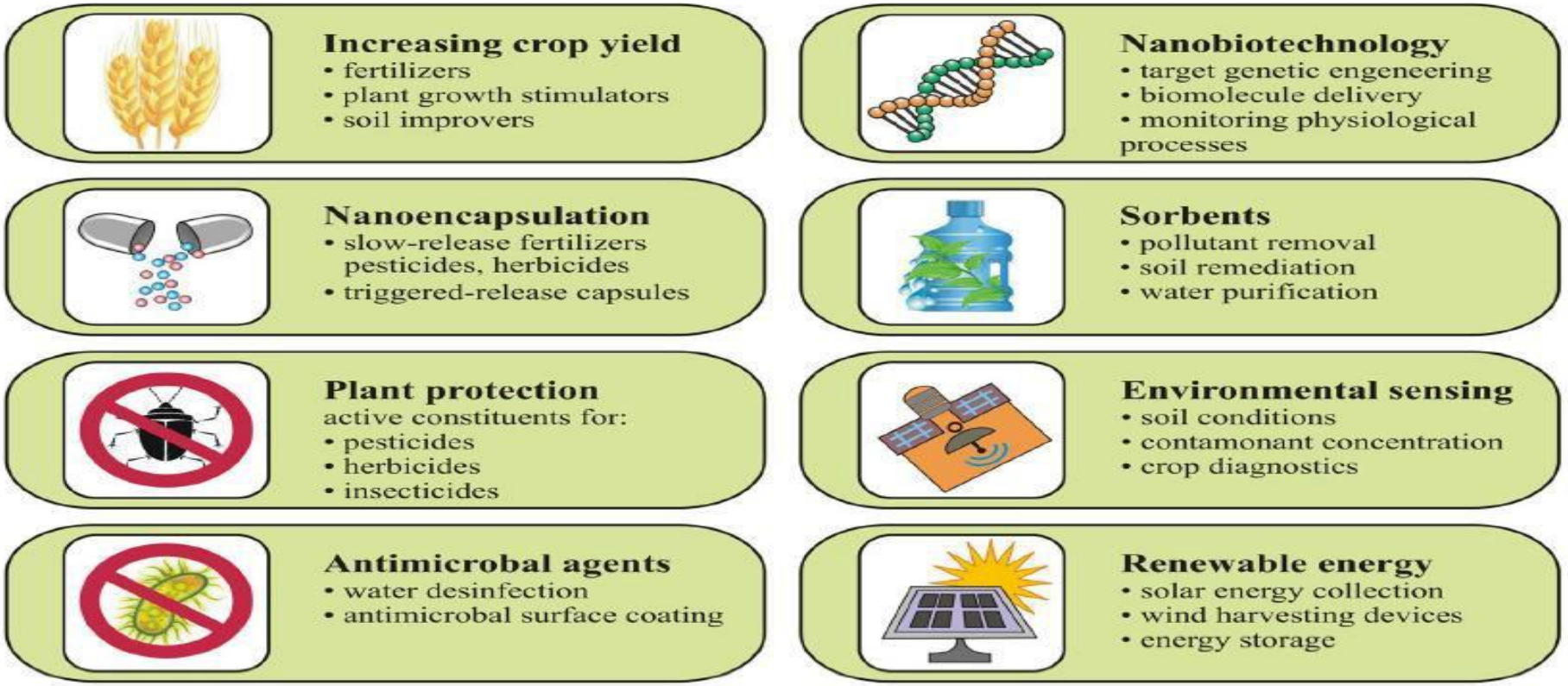
Zaytseva and Neumann *Chem. Biol. Technol. Agric.* (2016) 3:17
DOI 10.1186/s40538-016-0070-8

Chemical and Biological Technologies in Agriculture

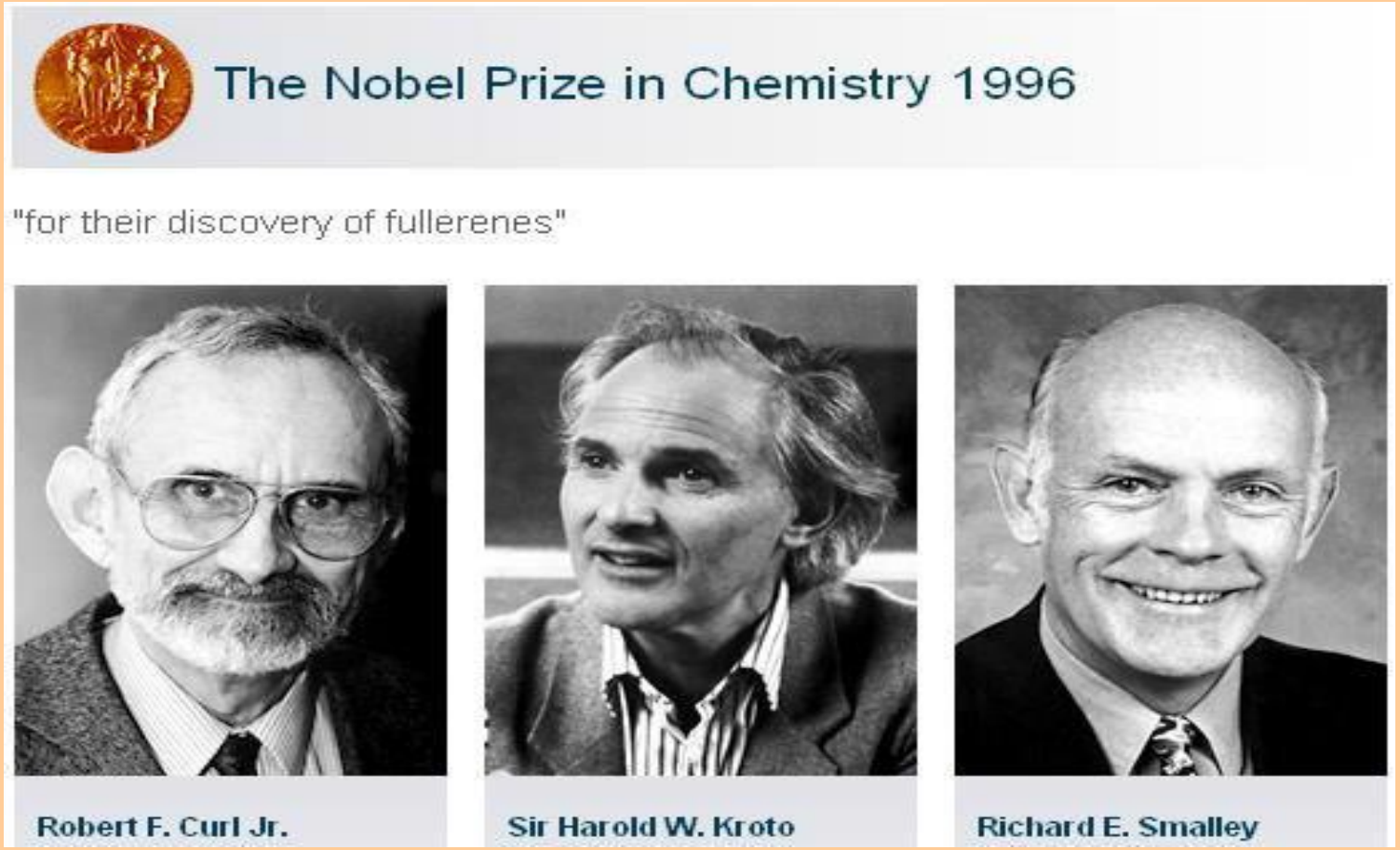
REVIEW Open Access

Carbon nanomaterials: production, impact on plant development, agricultural and environmental applications

Olga Zaytseva* and Günter Neumann



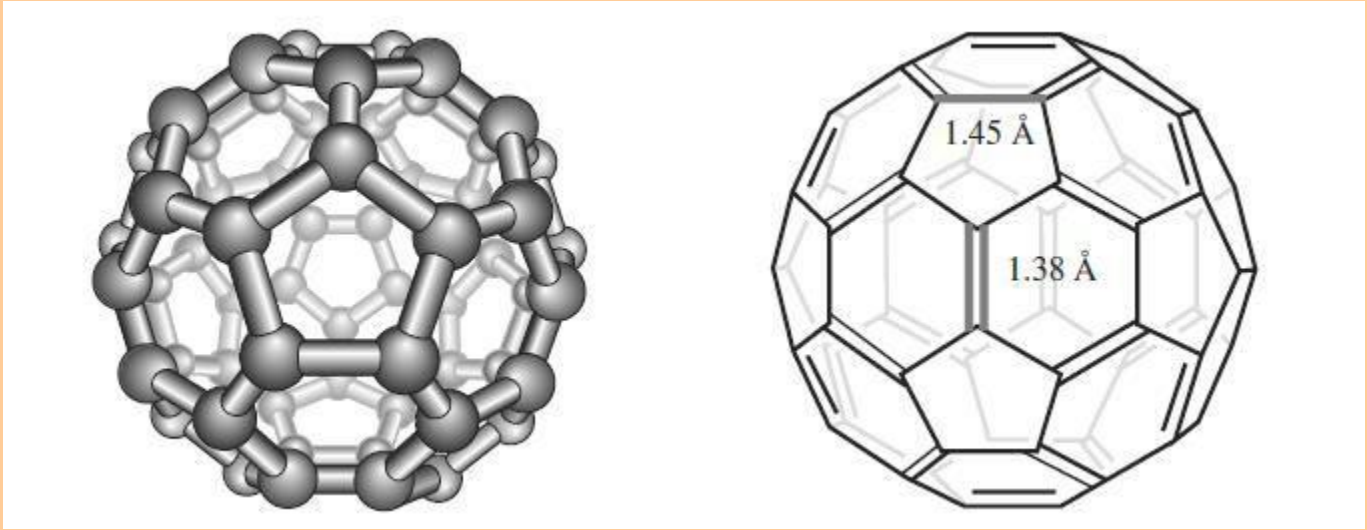
The 1996 Nobel Prize in Chemistry was awarded for the discovery of Fullerenes



Fullerene

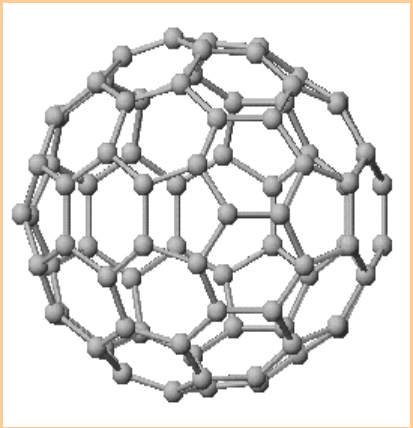
- The most common and most studies fullerene is buckminsterfullerene or buckyball
- It is the smallest stable fullerene
- Spheroidal molecule consisting of 60 carbon atoms.
- Closed cage structures & Exact replica of a football
- Formed from 12 pentagons and 20 hexagons, with each pentagon surrounded by 5 hexagons
- C60 is a highly symmetrical molecule in which all the carbon atoms are equivalent

Structure of C60

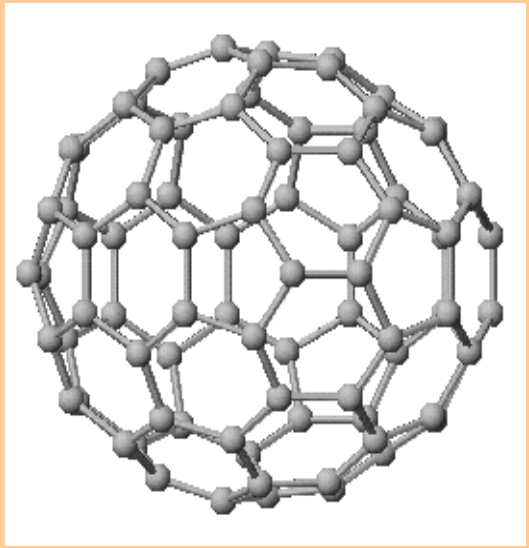


20 hexagonal faces + 12 pentagonal faces

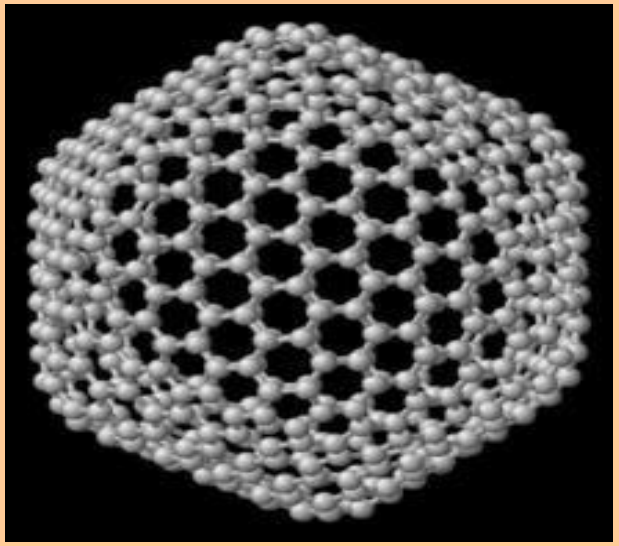
Other fullerenes that have been produced in macroscopic amounts have 70, 76, 84, 90, and 96 carbon atoms, and much larger fullerenes have been found - those that contain 180, 190, 240, and 540 carbon atoms.



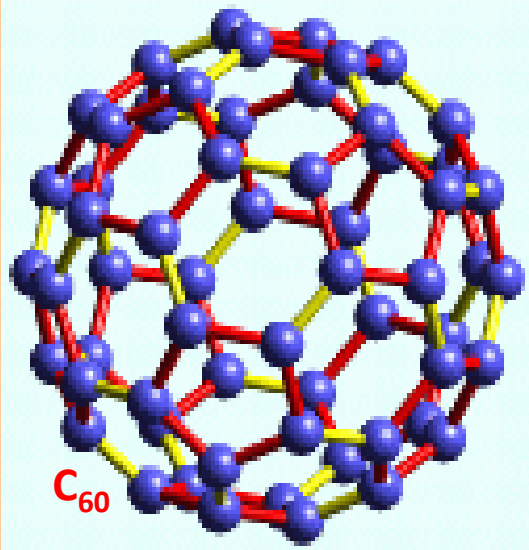
C76

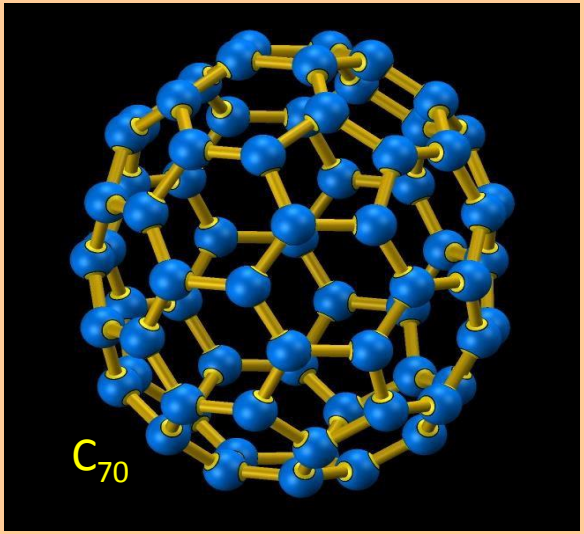


C84



C_{540}


C_{60}


C_{70}

Applications of fullerenes

- Researchers have found that water-soluble derivates of fullerenes inhibit the HIV-1 protease (enzyme responsible for the development of the virus) and are therefore useful in fighting the HIV virus that leads to AIDS
- Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death
- Elements can be bonded with C_{60} or other fullerenes to create more diverse materials, including superconductors and insulators.

Carbon Nanotubes

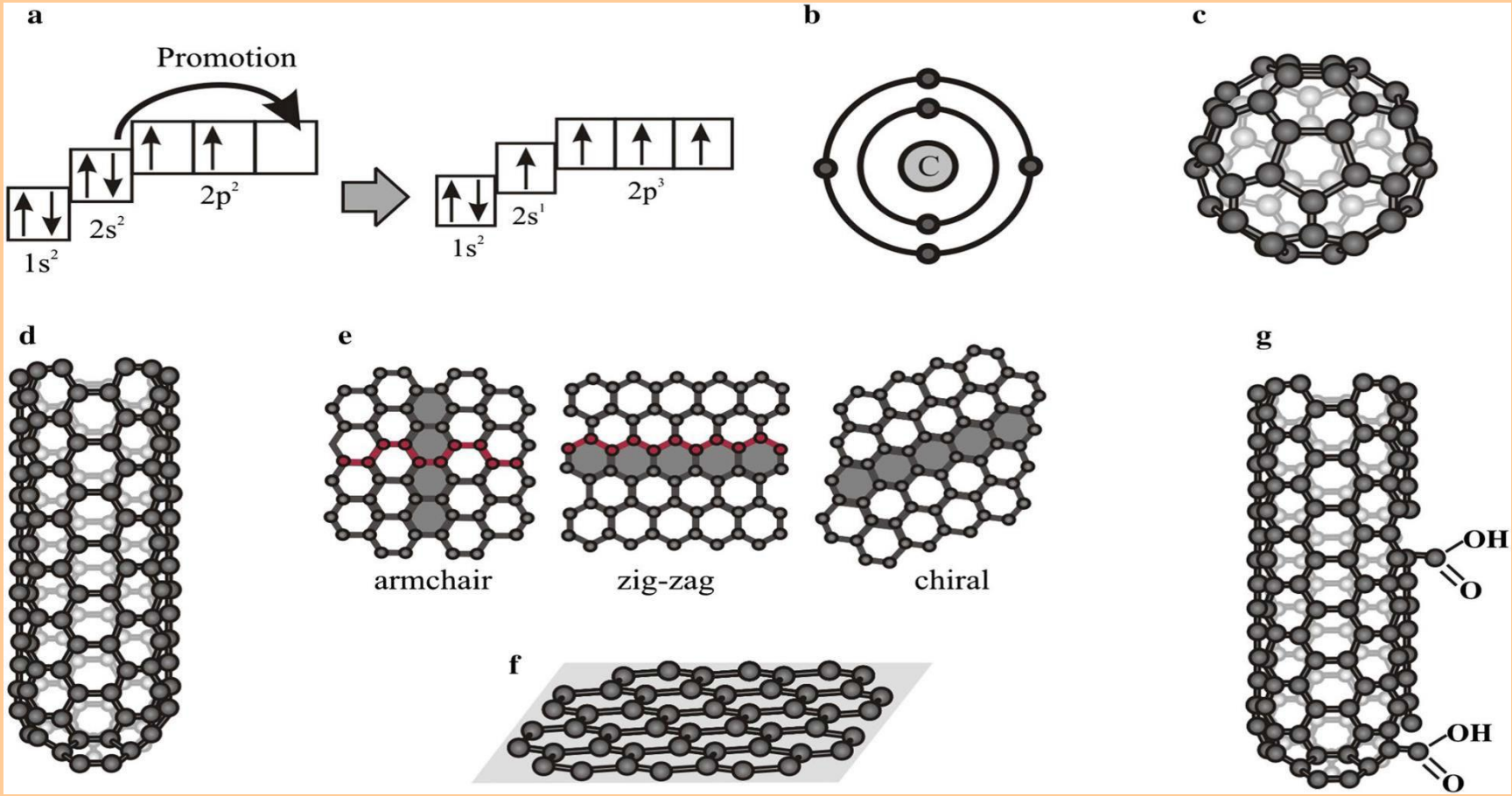
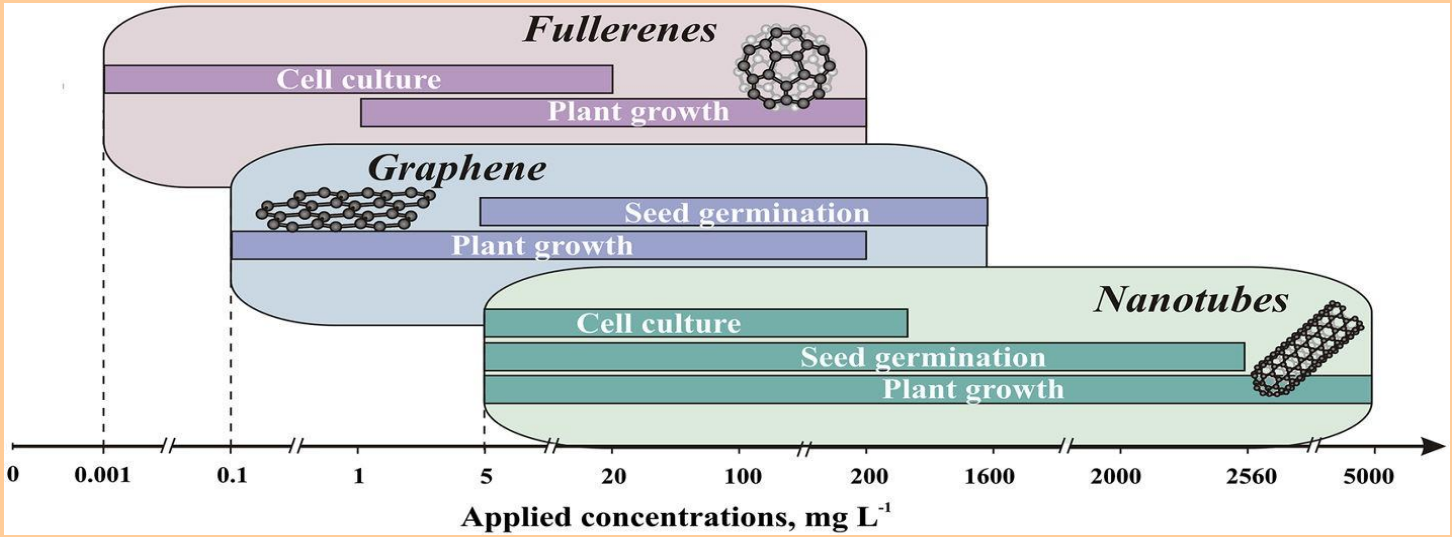


Fig. 1 Structure of a carbon atom and of carbon-based nanoparticles. **a** Electrone configuration of a carbone atom before and after promotion of one s-electrone; **b** schematic representation of a carbon atom structure with two electron orbtales arownd the nucleus and six electrones distributed on them; **c** structure of a fullerene C60; **d** structure of a single-walled nanotube; **e** different types of single-walled nanotubes: *armchair*, *zig-zag* and *chiral*; **f** structure of a graphene sheet; **g** structure of an oxidazed single-walled nanotube

Carbon nanotube (CNT)

- Discovered in 1991 by the Japanese electron microscopist Sumio Iijima
- Originally called buckytubes but now are called as Carbon nanotubes or CNT for short
- Carbon nanotubes are in the structural family of fullerene.
- Carbon nanotubes / buckytubes are allotropes of carbon with a cylindrical nanostructure
- They are molecules composed entirely of carbon atoms



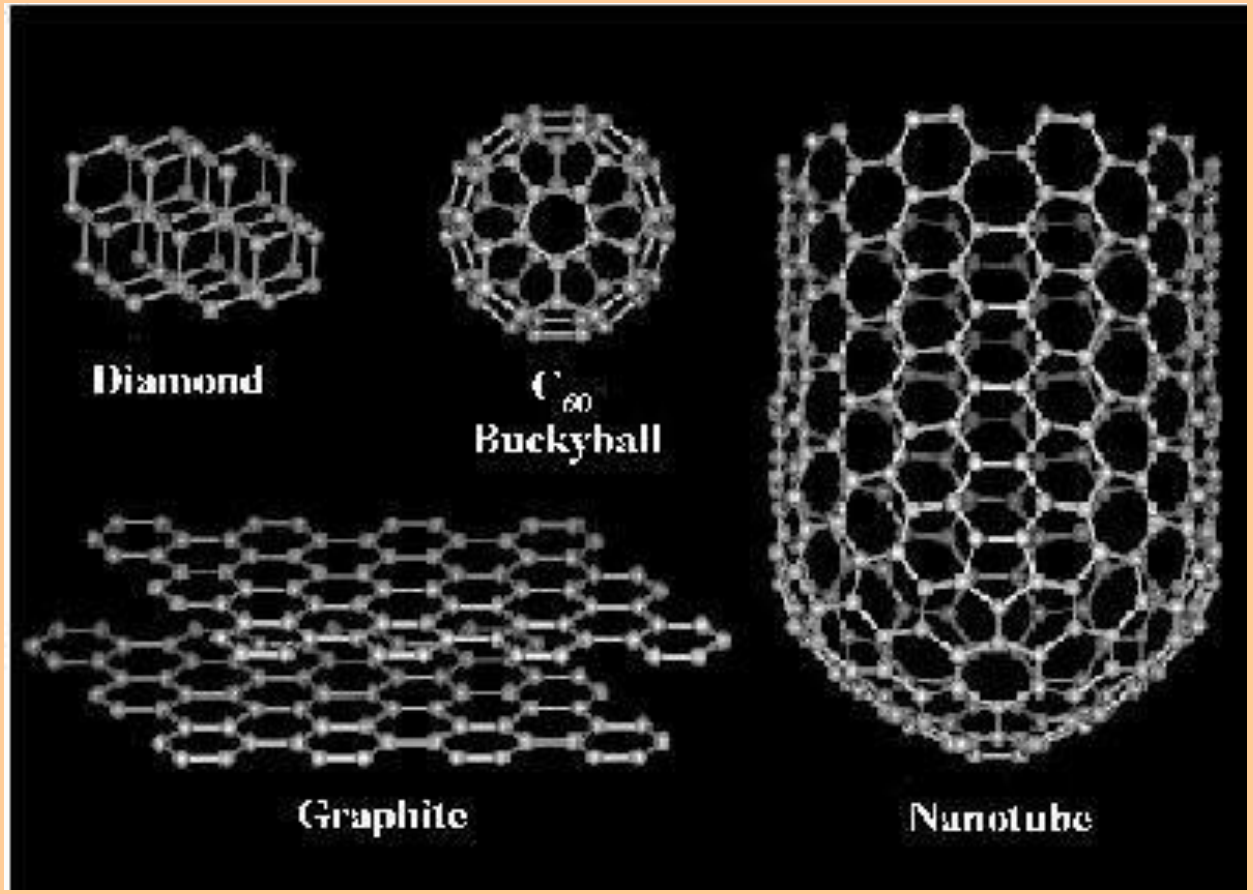
Carbon nanotube (CNT)

- The carbon atoms are arranged in a hexagonal pattern, bonded together with extremely strong covalent bonds
- The strength of the sp^2 carbon-carbon bonds gives carbon nanotubes amazing mechanical properties
- Length from several hundred nm to μm, diameter of 0.4-2 nm (SWANT) and 2 - 100nm (MWNT)

Carbon nanotube (CNT)

- High aspect ration with diameters in nanometers, length in microns
- Super strength combined with low weight
- Stability
- Flexibility
- High electrical conductivity
- High thermal conductivity
- Single wall NT can be metallic or semi-conducting
- Large surface area and a host of intriguing electronic properties.

Forms of Carbon

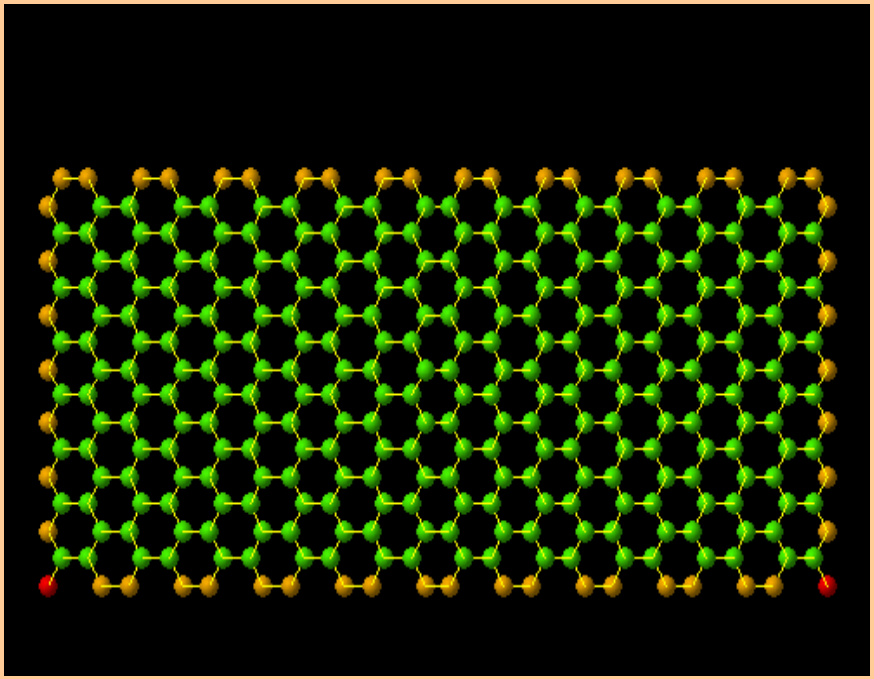


What Are Carbon Nanotubes?

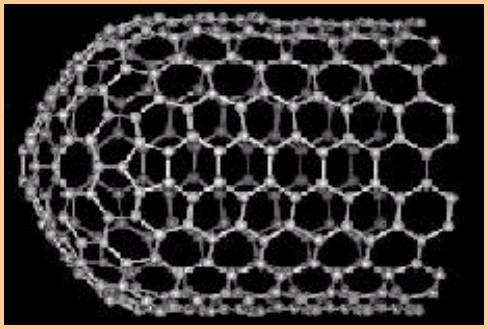
- Carbon nanotubes (CNT) are basically graphene sheets rolled up in a certain direction.
- Graphene is a one-atom-thick planar sheet of carbon atoms that is densely packed in a honeycomb crystal lattice.
- “Chiral vector” or “chirality” describes how a graphene sheet is rolled up to form CNT.
- Nanotubes are metallic, semiconducting, or insulating,depending on their preparation (depending on its chirality)

What Are Carbon Nanotubes?

- CNT can be described as a sheet of graphite (graphene) rolled into a cylinder
- Constructed from hexagonal rings of carbon
- Can have one layer or multiple layers



- Can have caps at the ends making them look like pills
- Tube ends can be opened by nitric acid and then filled with various metal oxides.
- Caps - half buckyballs on one or both ends



Types of carbon nanotubes

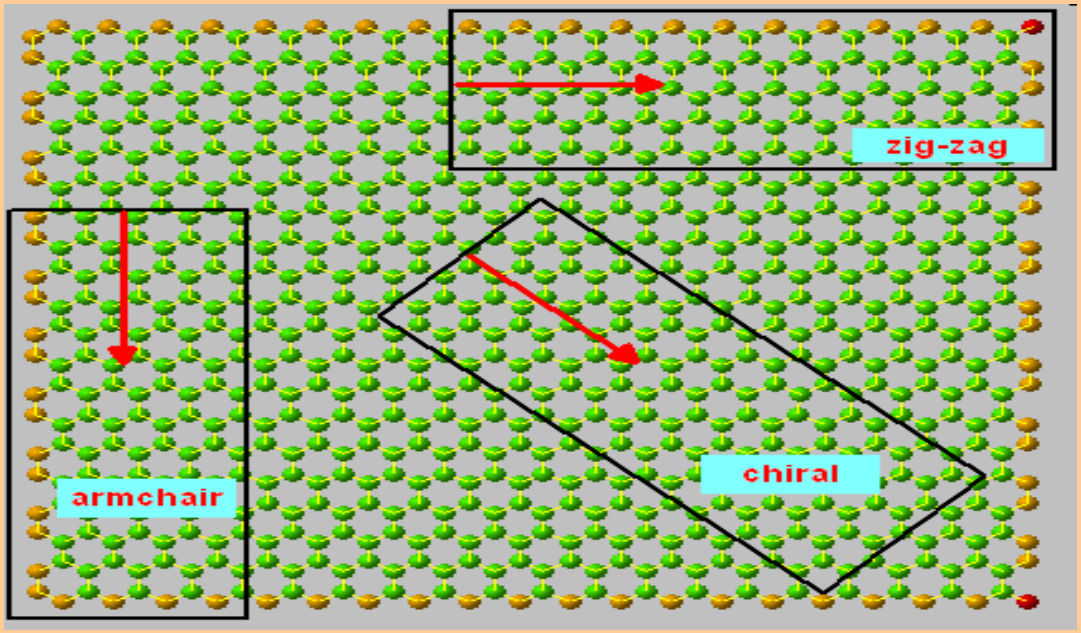
Single walled CNT Differ based on symmetry in to

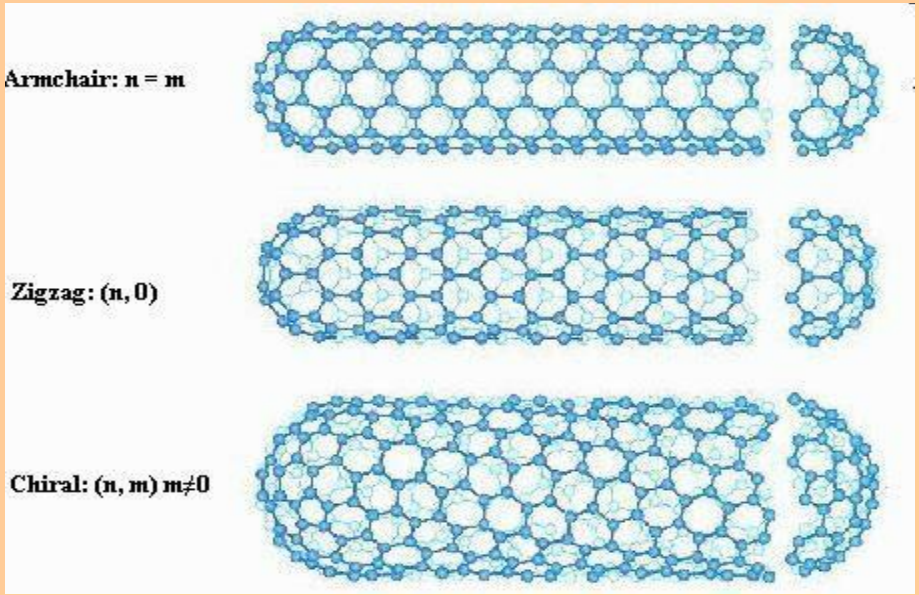
1. ***Armchair***
2. ***Zig-zag and***
3. ***Chiral (helical)***

- The carbon nanotubes can be thought of as graphene planes 'rolled up' in a cylinder

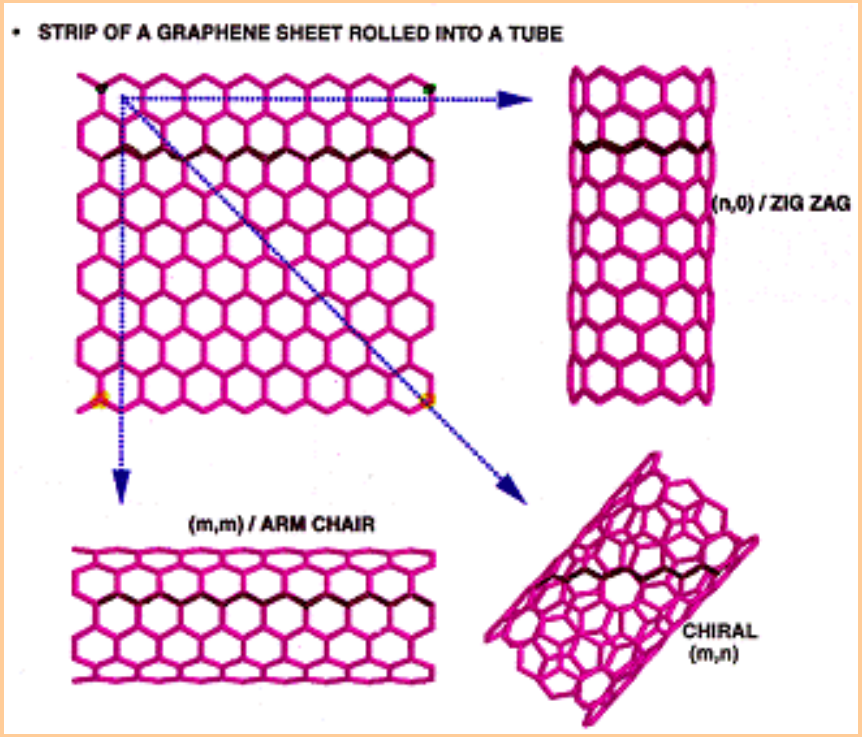
- Depending on how the graphene plane is 'cut' and rolled up, three types of carbon nanotubes are obtained.

Types of carbon nanotubes

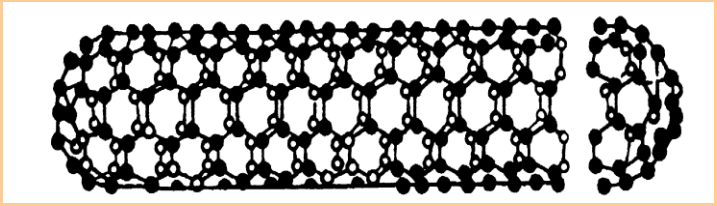




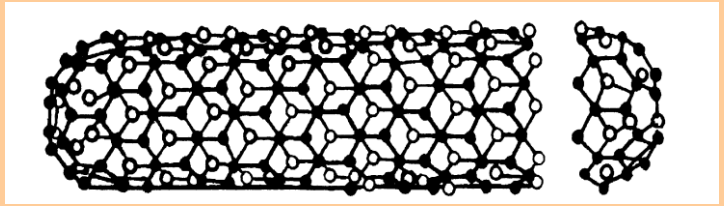
Types of carbon nanotubes



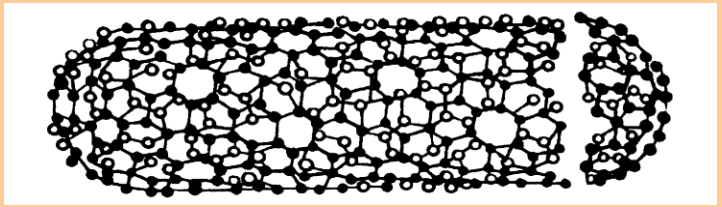
Armchair **metallic characteristics**



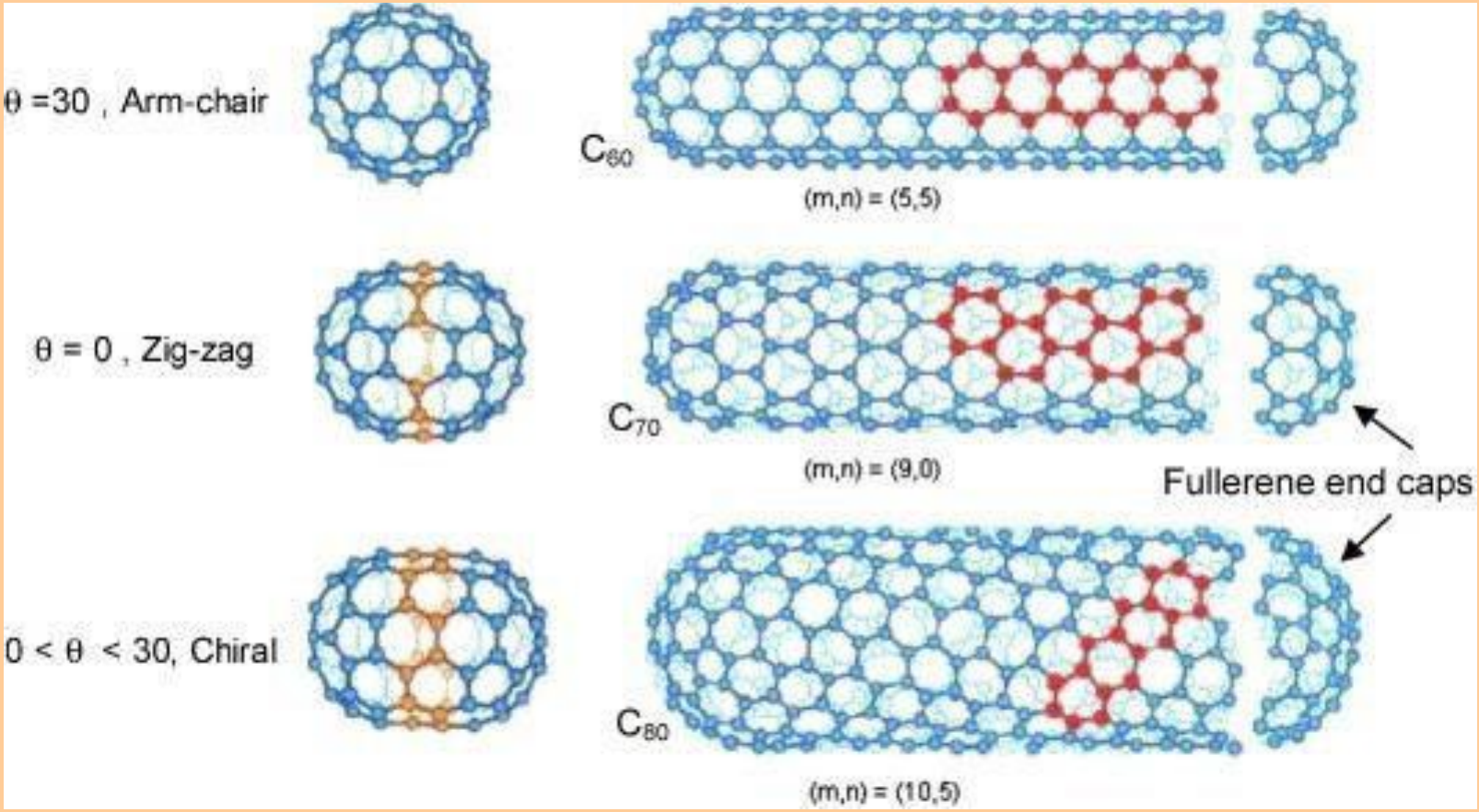
Zigzag **semiconductors**



Chiral **semiconductors**

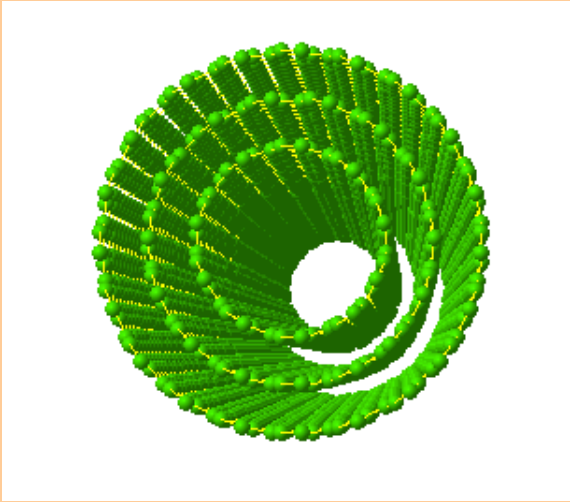


Types of carbon nanotubes

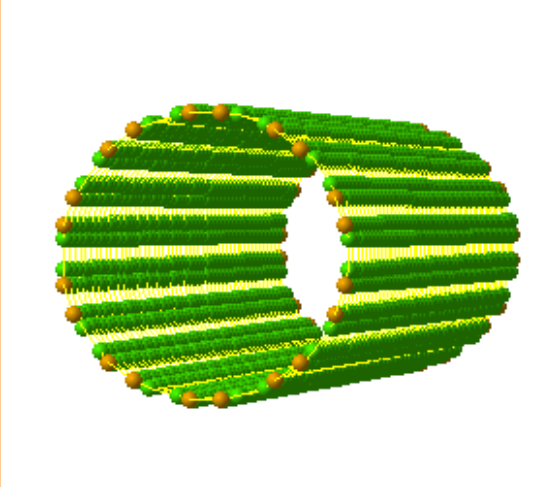


Nanotube Classification

- MWNT
  - Consist of 2 or more layers of carbon
  - Diameter – 5-80 nm



- SWNT
  - Consist of just one layer of carbon
  - Diameter – 1-2 nm



Comparison between SWNT and MWNT

S.No	SWNT	MWNT
1	Single layer of graphene.	Multiple layer of graphene
2	Catalyst is required for synthesis.	Can be produced without catalyst.
3	Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition.	Bulk synthesis is easy.
4	Purity is poor.	Purity is high.
5	A chance of defect is more during functionalization.	A chance of defect is less
6	Less accumulation in body.	More accumulation in body.
7	Characterization and evaluation is easy.	It has very complex structure.
8	It can be easily twisted and are more pliable.	It can not be easily twisted.

Properties of Carbon nanotubes

- **Carbon Nanotubes possess many unique and remarkable properties (chemical, physical, and mechanical) which make them desirable for many applications.**

Properties of Carbon nanotubes

1. Strength and Elasticity

- CNTs are very strong
- Their tensile strength - a measure of the amount of force which a specimen can withstand before tearing- is approximately 100 times greater than that of steel at only one sixth of the weight
- Strength of CNTs results from the covalent sp^2 bonds formed between the individual carbon atoms.
- This bond is stronger than the sp^3 bond in diamonds.

Properties of Carbon nanotubes

- CNTs are held together by Van der Waals forces forming a rope-like structure
- Another reason why they are so strong is because they are just one large molecule.
- Unlike other materials, carbon nanotubes do not have weak-spot, such as grain boundaries as seen with steel.
- CNTs also have a high elastic modulus, a measure of the material's tendency to deform elastically when a force is applied to it.

Properties of Carbon nanotubes

2. Electrical properties

- The electrical properties of nanotubes are very different
- They can be excellent conductors (with conductivity 1000 times of copper) or semiconductors depending on their structure.
- Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon
- The nanotube's chirality, along with its diameter, determines its electrical properties.
- The armchair structure has metallic characteristics.
- Both zigzag and chiral structures produce band gaps, making these nanotubes semiconductors

Properties of Carbon nanotubes

3. Thermal properties

- Thermal conductivity as high as diamond
- The thermal properties of carbon nanotubes are quite unique too because these nanotubes are mostly expected to have good conduction.
- Ballistic conduction (electrons are not scattered on the wire of length) is actually a property that is shown by the nanotubes as they go about their thermal conduction.

Applications

- The most immediate application for nanotubes is in making strong, lightweight materials
- Carbon nanotubes have been added to strengthen materials for sports equipment, vehicles, rockets, and building materials
- Aircraft built with stronger and lighter materials will have longer life spans and will fly at higher temperatures, faster and more efficiently
- Build a car that is lighter than its human driver, yet strong enough to survive a collision with a tank
- stronger and lighter tennis rackets, golf equipments
- For building materials, CNTs have potential applications in concrete, bridges - Used to increase the tensile strength of concrete

Thank you

Unique Properties of Nanomaterials – Physical, Chemical and Optical Properties

Compiled by

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- **Nanomaterials are (**Nano = 10^{-9}m) one billionth in size and with dimensions and tolerances in the range of 100 nm to 0.1 nm. At the nanometer scale, the various physical and chemical properties of materials become size-dependent.

(1) Physical properties – Mechanical hardness, Fracture strength, Density etc

(2) Chemical properties – Thermal Melting temperature, Lattice constant

(3) Optical properties – absorption and scattering of light

(4) Electrical properties – tunneling current

(5) Magnetic properties – Superparamagnetic effect

The basic properties of NM results of the physics and chemistry of solids depend on the microstructure,

microstructure in term classified into ,

(a) **chemical composition**- the arrangement of the atoms (the atomic structure)

(b) the **size of a solid** in one, two or three dimensions.

Why it is so important?

Because, If one changes or several of these parameters, the properties of a solid vary.

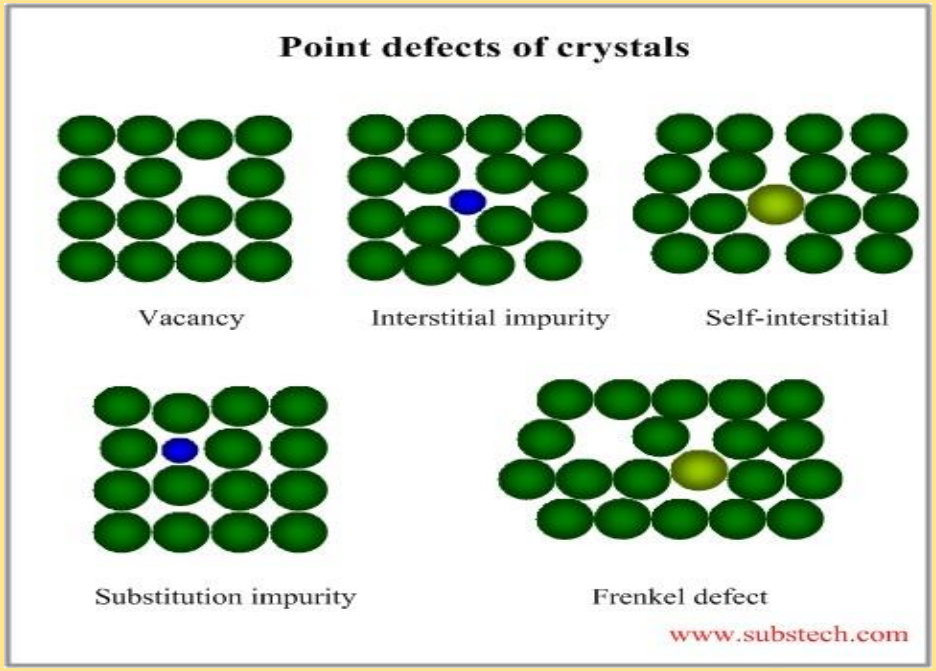
Parameters influencing structure are:

- atomic defects, dislocations and strains
- grain boundaries and interfaces
- porosity, connectivity and percolation
- short range order

Defects are usually absent in either metallic or ceramic clusters of nanoparticles because dislocations are basically unstable or mobile.

When these clusters are assembled under uniaxial pressure into a pellet, a fully consolidated nanophase material looks very much like a normal, dense polycrystalline aggregate, but at a far smaller scale

- A **grain** is a single crystal within a bulk/thin films form
- **Plasticity** is defined as the property of material remain deformed after the force is removed.
- **Creep** is the tendency of a solid material to move slowly or deform permanently under the influence of mechanical stresses.
- Crystals contain internal interfacial defects, know as **grain boundaries**, where the lattice orientation changes.



Hall-Pelch effects

- The Hall-Petch relation (law) gives a quantitative description of an **increase in the yield stress of a polycrystalline material as its grain size decreases**.

- This relationship is based on dislocation mechanisms of plastic deformation: grain boundaries hinder the movement of dislocations.

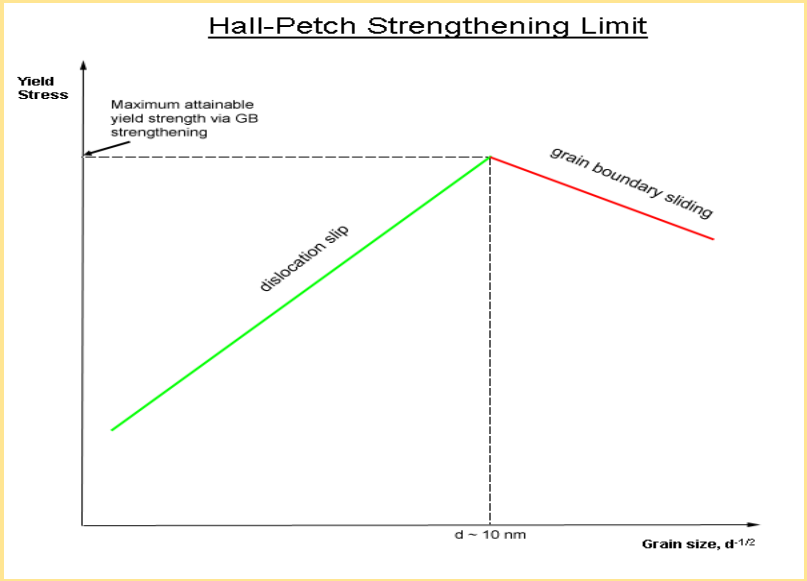
- The variation in strength can be described by a power-law relationship

$$\sigma_y = \sigma_0 + k_d/d^{1/2}$$

Where σ_y - yield stress,

- K_d - Strengthening coefficient,
- d - the average grain diameter
- σ_o - materials constant for the starting

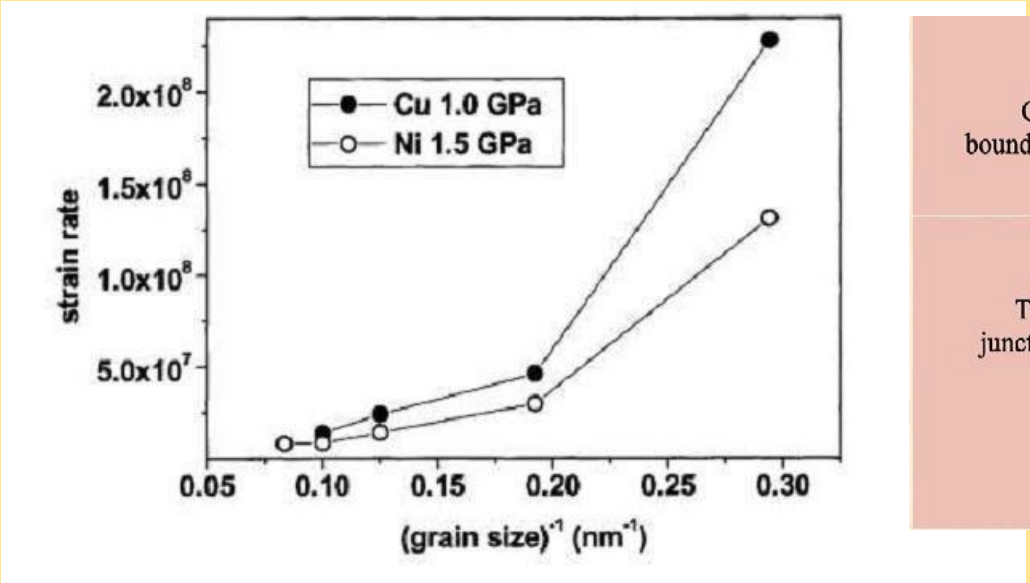
stress for dislocation movement (or the resistance of the lattice to dislocation motion)

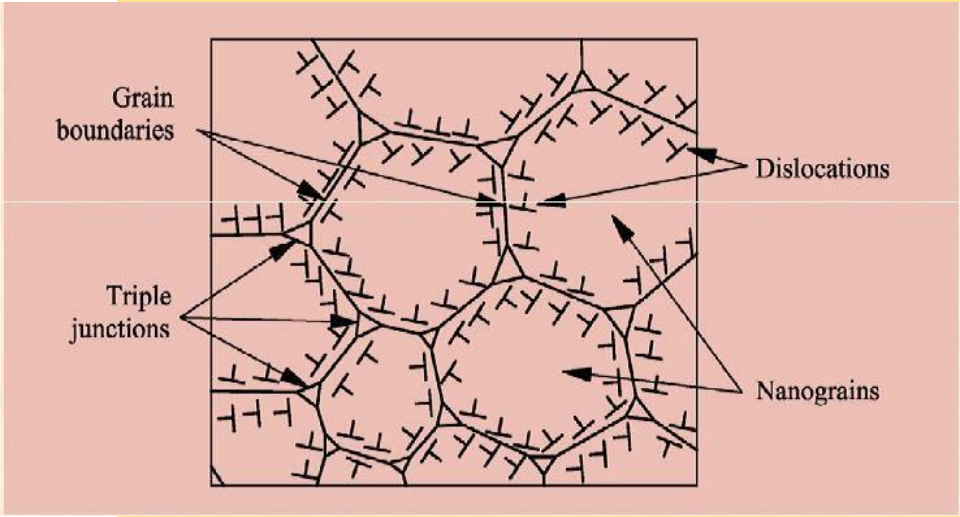


Hall-Petch strengthening limit

- Hall-Petch Strengthening is limited by the size of dislocations.
- **Once the grain size reaches about 10 nm, grain boundaries start to slide.**

- At the smallest grain sizes all deformation is accommodated in the grain boundaries and grain boundary sliding, a process based on mechanical and thermally activated single atomic jumps, dominates the contribution to deformation.
- At large grain sizes, a combination of sliding and intra-grain dislocation activity is observed.
- Hence, at the smallest grain sizes all the deformation is accommodated in the grain boundaries.
- At larger grain sizes lattice dislocation activity is observed
- At smaller grains sizes a gradual reduction of the modulus is observed
- **Dislocation** is a line defect within a crystal which arise during crystal growth or as a results of mechanical deformation of a crystal





- **Diffusion creep**

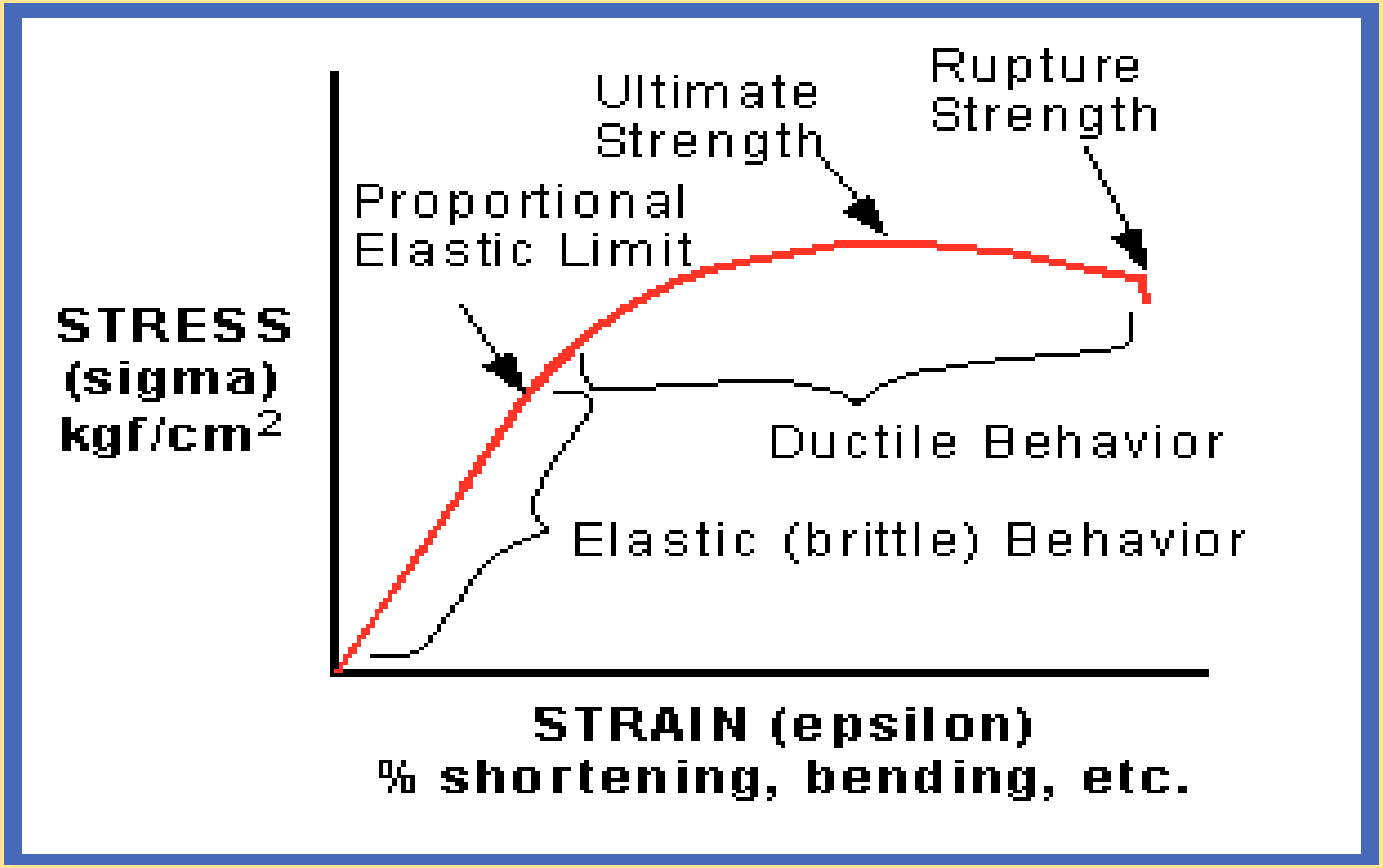
- Diffusion creep is caused by the migration of crystalline defects through the lattice of a crystal such that when a crystal is subjected to a greater degree of compression in one direction relative to another, defects migrate to the crystal faces along the direction of compression, causing a net mass transfer that shortens the crystal in the direction of maximum compression.

- Diffusion creep results in plastic deformation rather than brittle failure of the material.

- Diffusion creep is more sensitive to temperature than other deformation mechanisms. It usually takes place at high homologous temperatures (i.e. within about a tenth of its absolute melting temperature).

- The migration of defects is in part due to vacancies, whose migration is equal to a net mass transport in the opposite direction.

- Stress - force per unit area causing the deformation
- „Strain - measure of the a amount of deformation
- „The elastic modulus is the constant of proportionality between stress and strain



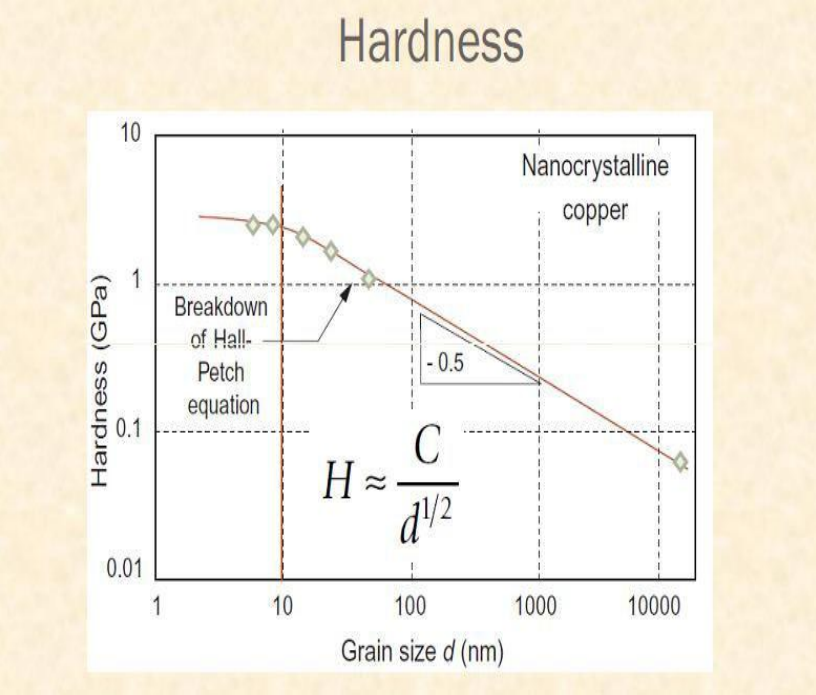
Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a compressive force is applied

Fracture toughness is a property which describes the ability of a material containing a crack to resist fracture, and is one of the most important properties of any material for many design applications.

The Hall-Petch model treats grain boundaries as barriers to dislocation motion, and thus dislocations pile up against the boundary.

Upon reaching a critical stress, the dislocations will cross over to the next grain and induce yielding.

Hall Petch Model says the smaller the grain size the stronger the material.

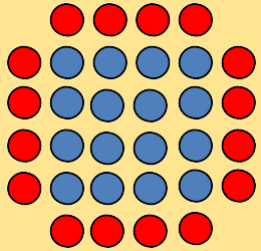


Yield strength: $\sigma_{TS} = \sigma_0 + \frac{K_{TS}}{\sqrt{d}}$

Hardness: $H = H_0 + \frac{K_H}{\sqrt{d}}$

where σ_{TS} is the yield stress, σ_o and H_0 are materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion), K is the strengthening coefficient (a constant specific to each material), and *d* is the average grain diameter.

Chemical Properties of Nanomaterials



(Fig. 3.5)

Reason for the material size < 100 nm having a lower melting point (the difference can be as large as 1000 deg C) and reduced lattice constant is the dramatic changes in surface energy to volume energy ratio.
What is easier to get off? Surface atom or Volume atom (Fig. 3.5)

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 Energy

The extra energy possessed by the surface atoms is described as surface energy, surface free energy or surface tension.

Surface energy, by definition, is the energy required to create a unit area of "new" surface.

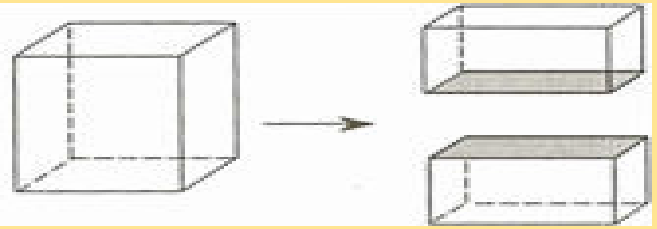
Concepts of thermodynamics are used to calculate the surface energy of a material.

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

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

ΔG = ΔH – T ΔS ; H is the eŶthalpy, T is the tewperature aŶd S is the eŶtropy (disorder).

If one keep cutting to increase the overall surface free energy and Gibbs Free Energy by increasing the number of free bonds (H internal energy)



Surface energy is expressed for most materials a first order estimate is given by:

$$\gamma = 1/2 n_b \varepsilon$$

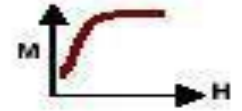
ε: bondstrength in the bulk (close enough assumption)

n_b: number of broken bonds per unit area on the new surface

Magnetic Properties of Nanomaterials

Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetism disappears and transfers to superparamagnetism (Fig. 3.7) in the nanometer scale due to the huge surface energy.

Types of Magnetism (H is applied field and M is magnetization)

Magnetism	Susceptibility	Critical temperature	Atomic behavior	Magnetic behavior
Diamagnetism	Small & negative	None		
Paramagnetism	Small & positive	None		
Ferromagnetism	Large & positive	Curie		
Anti-ferromagnetism	Small & positive	Neel		
Ferrimagnetism	Large & positive	Curie		
Super-paramgnetism	Large & positive	Curie		

Paramagnet, Ferromagnet & Superparamagnets

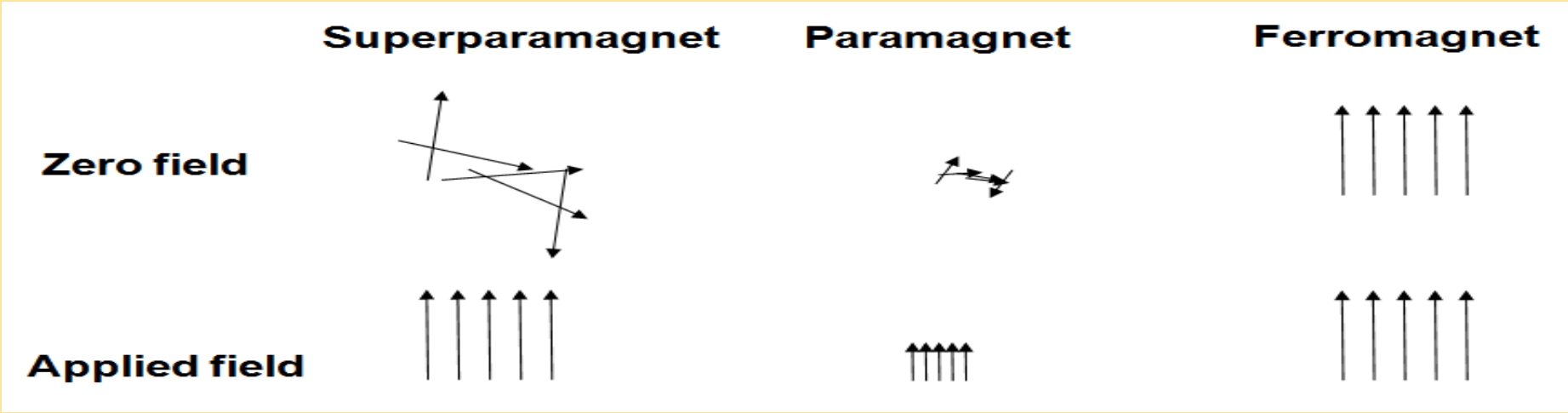
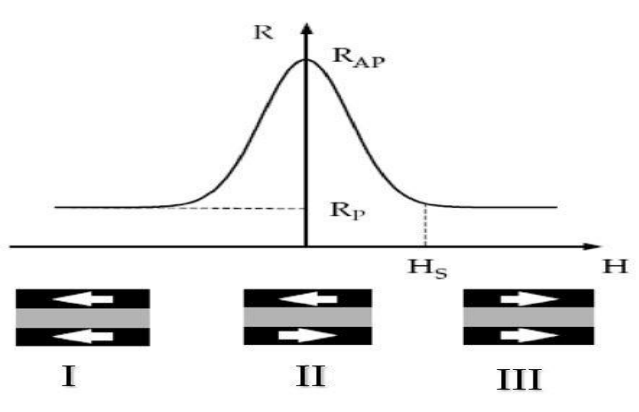


Fig. 3.7

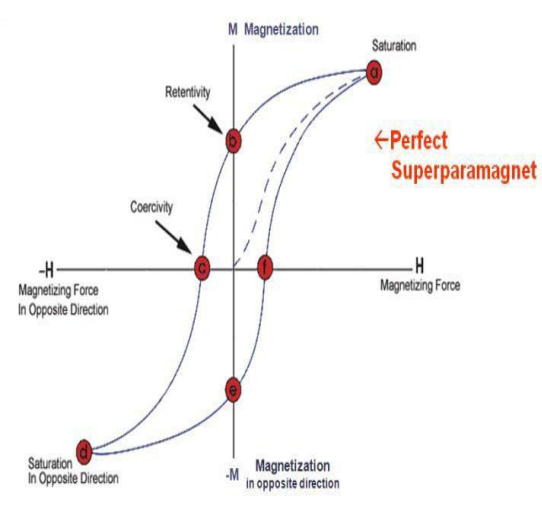
	Superparamagnet	Paramagnet	Ferromagnet
at Zero Magnetic Field	Domain moments that would couple as in Ferromagnet do not do so because of small size—boundary effect.	Domain moments align randomly—no net moment.	Domain moments coupled (below Curie temp.) to produce strong, permanent moment.
at Magnetic Field Applied	Domains "find" each other and now it generates a moment comparable to Ferromagnet.	Net moment appears; the applied magnetic field helps the domains "find" each other to become coupled.	Even higher magnetic moment.

Application of Super-paramagnetic Nanoparticles

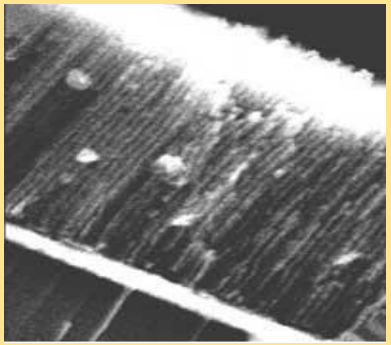
Giant Magneto



Hysteresis Plot



Magnetic nanowires



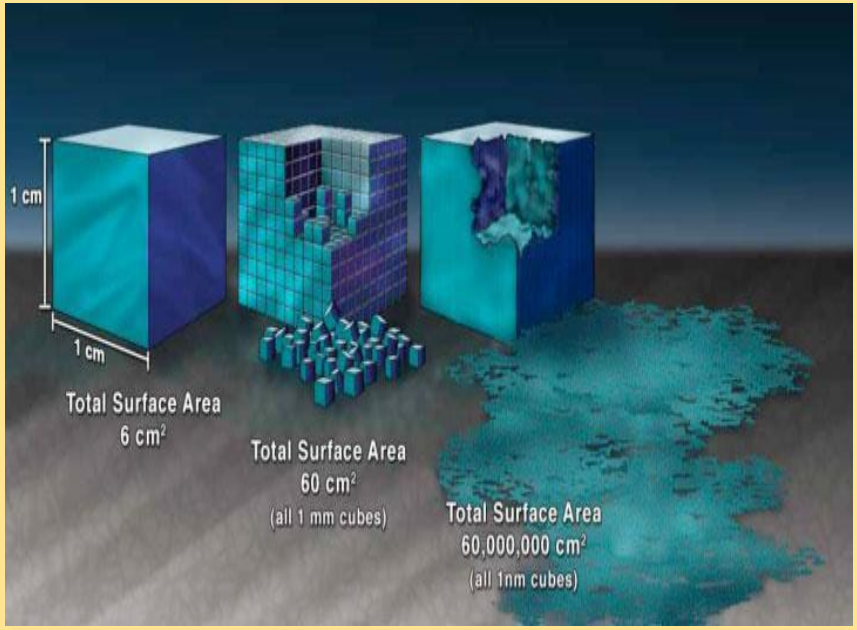
Ex: Cobalt nanowires on Si substrate

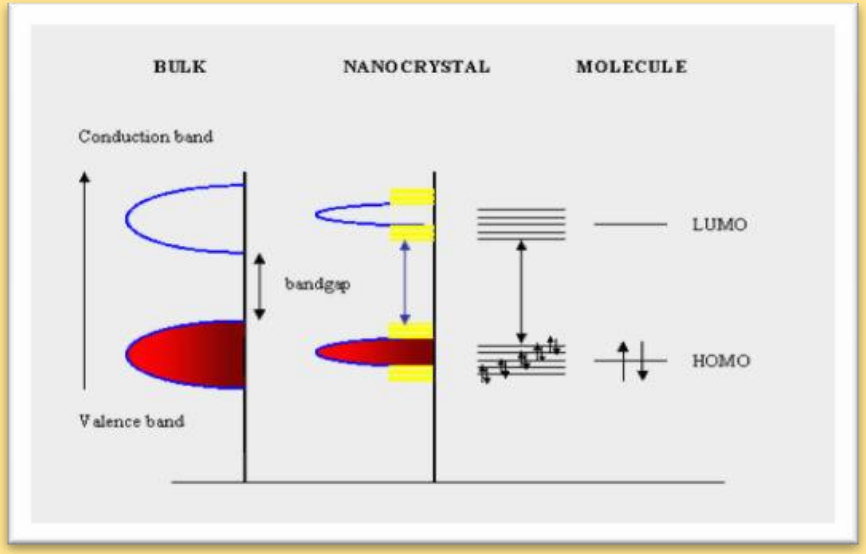
Nano particles can have very high magnetic susceptibility with permanent magnetic dipole. Small clusters consisting of a single ferromagnetic domain follow the applied field freely (super-paramagnetism). The magnetic susceptibility of superparamagnetic particles is orders of magnitude larger than bulk paramagnetic materials. Giant magnetoresistance occurs when the magnetic layers above and below the conductor are magnetized in opposite direction.

Magnetic hard drives are based on a nanostructured device, called giant magnetoresistance sensor (Albert Fert, Peter Grünbers Nobel Prize in Physics 2007). The magnetization on the surface of the disk can be read out as fluctuations in the resistance of the conducting layer.

ELECTRICAL PROPERTIES OF NANOMATERIALS

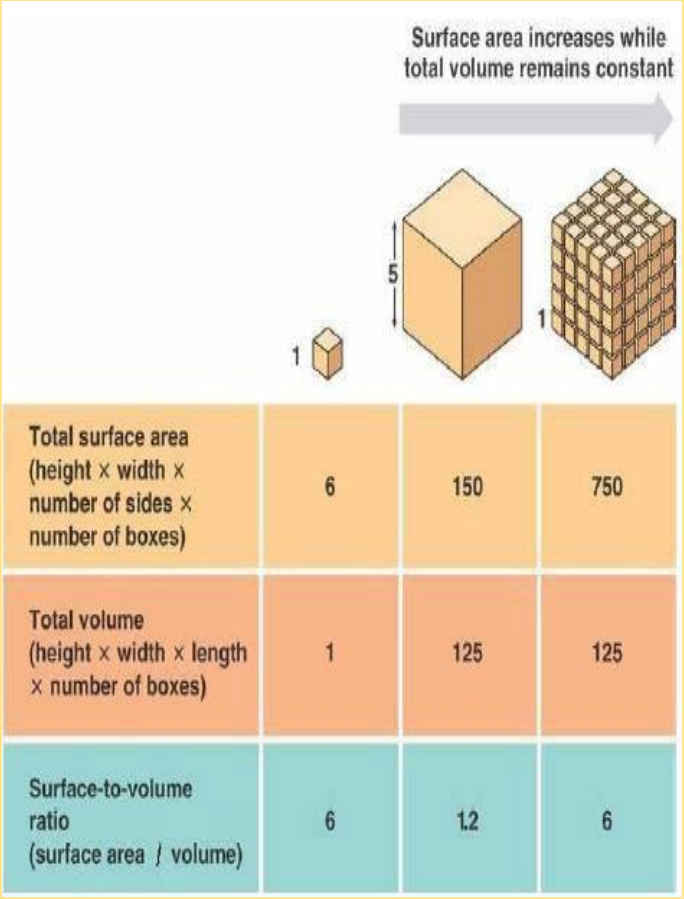
- Nanocrystalline particles represent a state of matter in the transition region between bulk solid and single molecule.
- As a consequence, their physical and chemical properties gradually change from solid state to molecular behaviour with decreasing particle size.
- The reasons for this behaviour can be summarised as two basic phenomena:
  - Increase in surface-to-volume ratio
  - *Size quantization effect*





(i) Increase in surface-to-volume ratio

- Owing to their small dimensions, the surface-to-volume ratio increases
- Number of surface atoms may be higher than those located in the crystalline lattice core
- When no other molecules are adsorbed onto the nanocrystallites, the surface atoms are highly unsaturated and their electronic contribution to the behaviour of the particles is totally different from that of the inner atoms.
- These effects may be even more marked when the surface atoms are ligated.
- This leads to different mechanical and electronic transport properties, which account for the catalytic properties of the nanocrystalline particles



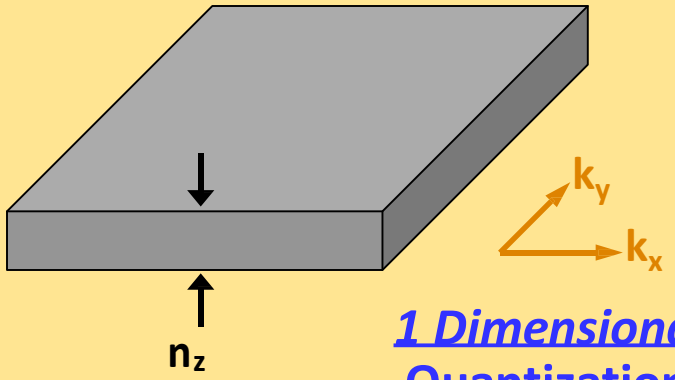
Total surface area (height × width × number of sides × number of boxes)	6	150	750
Total volume (height × width × length × number of boxes)	1	125	125
Surface-to-volume ratio (surface area / volume)	6	1.2	6

Size Quantization and Quantum Confinement in Nanostructures: Overview

Electrons *Confined in 1 Direction*:

Quantum Walls (thin films)**:**

⇒ **Electrons** can easily move in ***2 Dimensions*!**

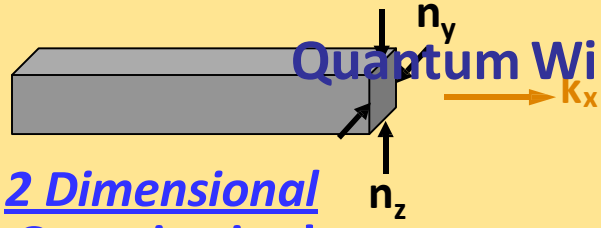


1 Dimensional **Quantization!**

Electrons *Confined in 2 Directions*:

⇒ **Electrons** can easily move in ***1 Dimension*!**

Quantum Wires:

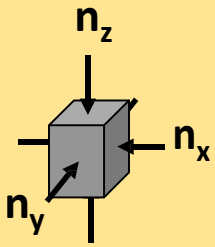


2 Dimensional **Quantization!**

Electrons *Confined in 3 Directions*:

⇒ **Electrons** can easily move in ***0 Dimensions*!**

Quantum Dots:



3 Dimensional **Quantization!**

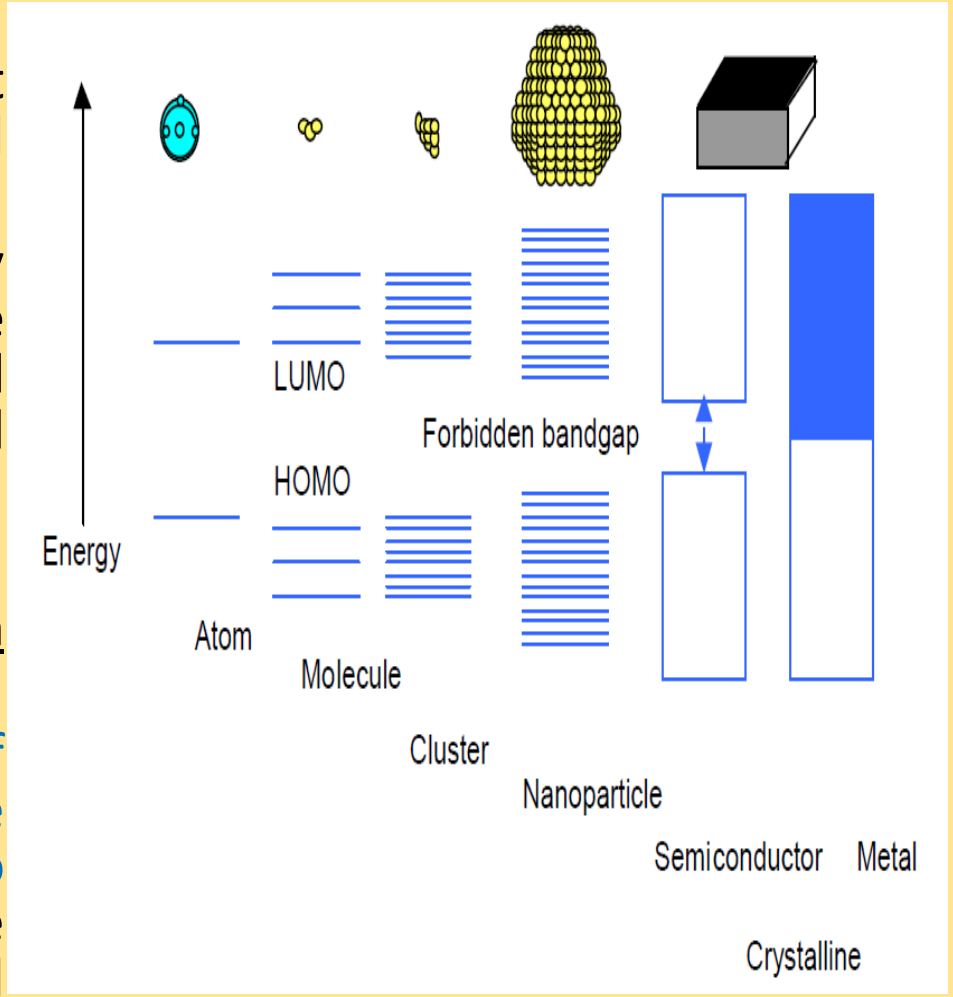
Each further confinement direction changes a continuous k component to a discrete component characterized by a quantum number n.

(ii) Size quantization effect

- Totally an electronic effect that occurs in metal and semiconductor nanoparticles.
- The band structure gradually evolves with increasing particle size, i. e., molecular orbital convert into delocalised band states.

- ***Size quantization effect*** **in metals:**

  The quasi-continuous density of states in the valence and the conduction bands splits into discrete electronic levels, the spacing between these levels and the band gap increasing with decreasing particle size



Size Quantization Effect in Semiconductors:

- The band gap increases when the particle size is decreased and the energy bands gradually convert into discrete molecular electronic levels.
- If the particle size is less than the De Broglie wavelength ($\lambda = h/p$ or h/mv) of the electrons, the charge carriers may be treated quantum mechanically as "particles in a box", where the size of the box is given by the dimensions of the crystallites.
- In semiconductors, the quantization effect is observed for clusters ranging from 1 nm to almost 10 nm.
- Metal particles consisting of 50 to 100 atoms with a diameter between 1 and 2 nm start to loose their metallic behavior and tend to become semiconductors.
- Particles that shows *size quantization effect* are sometimes called *Q-particles* or *quantum dots*.
- *Magic numbers:* In semiconductor nanoparticles such as CdS, the growth of the initially formed smallest particles with an agglomeration number *k* occurs by combination of the particles.
- Thus, particles so formed would have the agglomeration number of 2*k*, 3*k* and so on.
- Metals have a cubic or hexagonal close-packed structure consisting of one central atom, which is surrounded in the first shell by 12 atoms, in the second shell by 42 atoms, or in principle by $10n^2+2$ atoms in the *n*th shell.
- Eg.: Most famous ligand stabilized metal clusters is a gold particle with 55 atoms (Au55) first reported by G. Schmid in 1981.

Quantum Confinement and Conductance

The conductance

$$G = I / V,$$

is the ratio of the total current **I** to the voltage drop **V** across the sample of length **L** in the direction of current flow.

- The quantum confinement of a carrier in a strip of width **w** leads to the discretization of energy levels given by

$$\epsilon_n = n^2h^2/(8m^*w^2).$$

where ϵ_n is the energy of discrete energy levels; n is the principle quantum numer; h is the Plancks constant, m^* is the mass of electron and w is the nanostrip dimension.