Nanomaterials

Presented by

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Nanomaterials: Introduction

- Nanomaterials - Scientific Definition ***Definition***

- Nano & Nanometer? (How small it is?) ***Length Scale***

- Why Nanomaterials? What is so special about them? ***Magic***

- Properties of ***Structures*** at Nanometer Scale: One example each

    Size (Gold to nanoparticles of gold)

    Optical Properties (Color of gold nanoparticles)

    Electrical Properties (Graphite to Graphene)

    Magnetic Properties (ferromagnetite)

    Thermal Conductivity (Graphite to Graphene)

    Chemical properties (TiO_2 coating on glass)

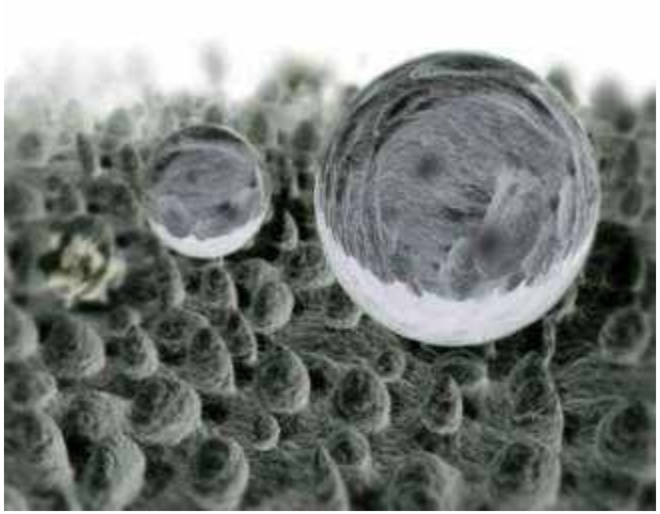
- Lessons learnt from nature

  (to develop novel products from nanomaterials)

- Nanotechnology i.e. Applications of nanomaterials

Lotus Effect: Superhydorphobicity

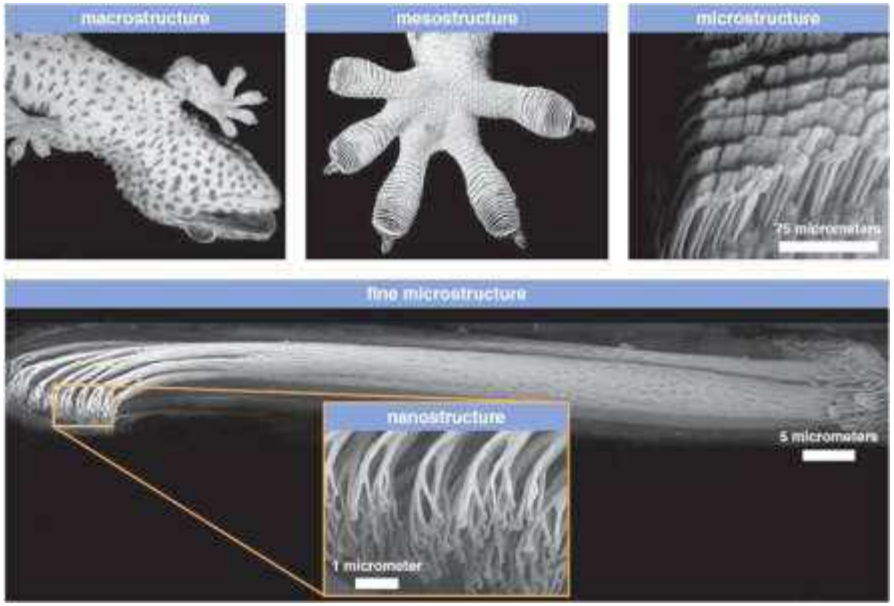
Lotus Leaf- Non wetted surface



Higher Magnification
Nanostructured surface
minimizing the contact area

BASF (Germany) artificially developed superhydrophobic nanostructured coating by mimicking Lotus effect for self- cleaning paints and spray

Source: https://nanografi.com/blog/lotus-effect-self-cleaning-and-nanotechnology/



Gecko Feet:
Natural Superglue with dual properties- High Shear adhesion & low normal adhesion using van der wall's forces

CNTs mimicking Gecko's Feet: Superglue in the form of Dry adhesive (non-chemical); Stiffness of tapes can be modified by changing the number of walls in nanotubes

Source: https://googleimages.com/

**Seashell &
its brick and
mortal structure**

- Seashell & Chalk both are made up $CaCO_3$, still Seashells has very high mechanical strength than chalk stick
- Understand & mimicing natural Technology can be used to build materials high mechanical strength for the usage in aircrafts, spacecrafts, engines etc.

Source: https://googleimages.com/

Nanomaterials: Classification

- **Classification based on Dimensions:** From Bulk materials to low Dimensional structure- occurs based on reduced dimensions.

Dimensionality refers to the number of degrees of freedom in the particle momentum rather than particle confinement direction

- **Three-dimensional (3D) structure or Bulk structure:** Particle is free (No quantization of Particle motion occurs)

  E.g. Graphite, Diamond

- **Two-dimensional (2D) structure or Quantum wells:** Particle is free to move in two directions (Quantization of Particle motion occurs only in one direction) **E.g. Graphene, Thin Films**

  Typical nanoscale dimensions(1-1000 nm thickness)

Nanomaterials: Classification

- **One-dimensional (1D) structure or Quantum wire:** Particle is free to move in only one direction (Quantization of Particle motion occurs in two directions) **E.g. Nanowires, nanorods, nanotubes, nanopillars, Carbon NanoTubes (CNT)**

  Typical nanoscale dimensions(1-100 nm thickness)

- **Zero-dimensional (0D) structure or Quantum Dots:** Quantization occurs in all 3 directions **E.g.: Quantum dots, Nanodots, Fullerenes;** Typical nanoscale dimensions(1-10nm radius)

➢ **Classification based on composition**:

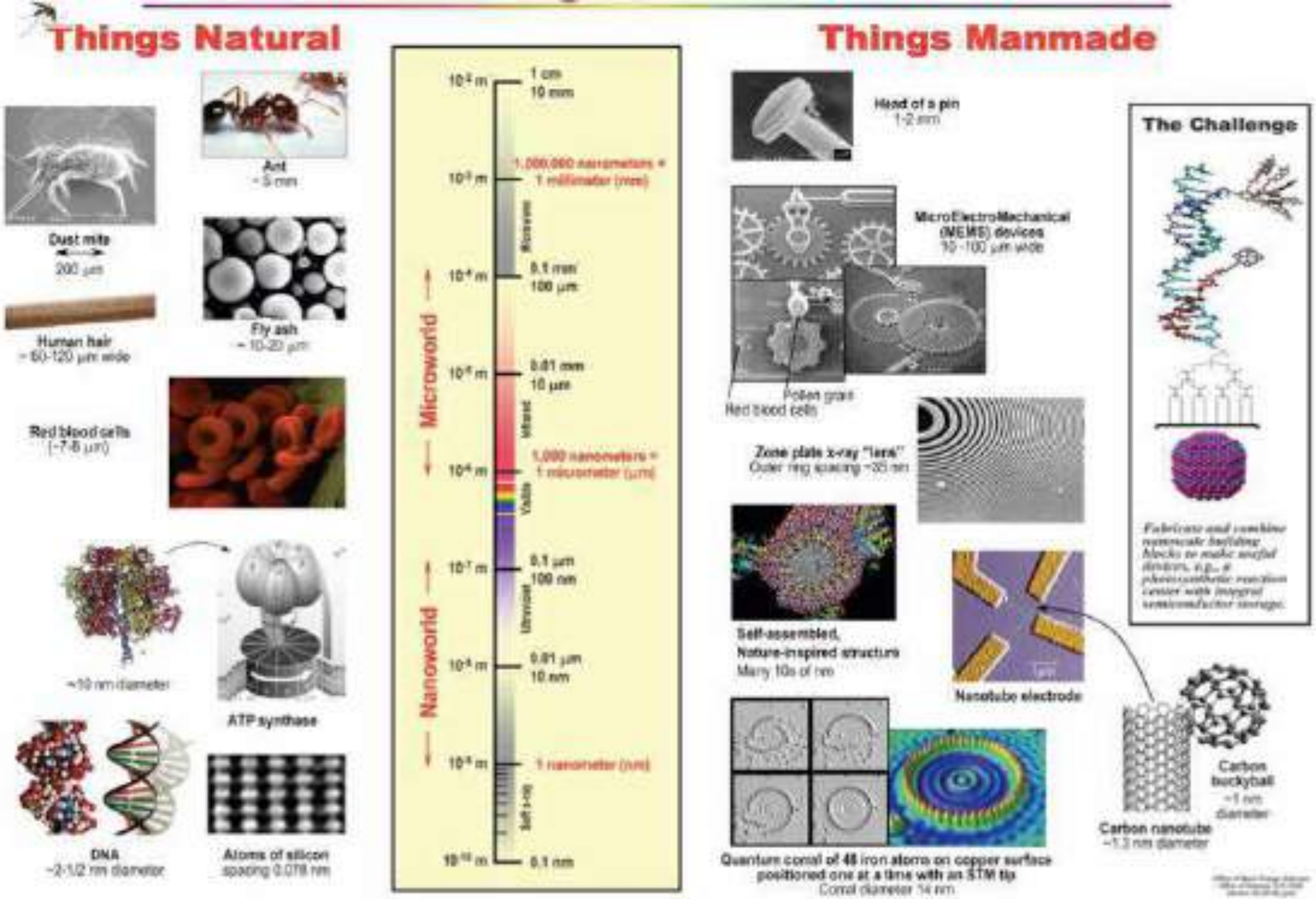
  ➢ Organic: Carbon based nanomaterials (Graphene, CNT), Nanobiomaterials, Dendrimers/Polymers

  ➢ Inorganic: Metals, Metal Oxide, Semiconductors (QD)

  ➢ Nanocomposites: Organic/Inorganic

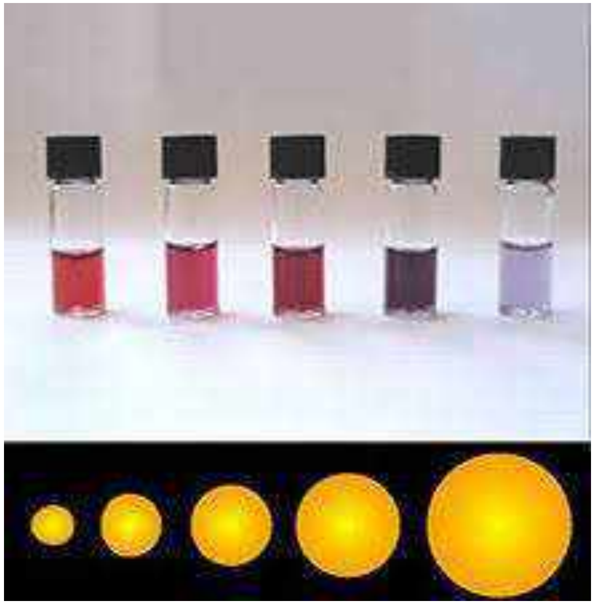
Nanomaterial Introduction : Definition

Nanomaterials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers



Source: https://googleimages.com/

Bulk Gold to Gold Nanoparticles



Nanodimensional Structures

What are nano dimensional Structures?

- When one or more of the dimensions of a solid are reduced significantly, its physicochemical characteristics notably depart from those of the bulk solid.
- With reduction in size, novel electrical, mechanical, chemical, magnetic, and optical properties can be introduced. The resulting structure is then called a low-dimensional structure (or system).
- Nanostructures constitute a bridge between molecules and bulk materials.
- Suitable control of the properties and responses of nanostructures can lead to new devices and technologies.

Nanomaterials: Classification

Classification based on:

- **Origin**
- **Composition**
- **Dimensions**

Classification based on Origin:

- Natural
- Artificial

Nanomaterials: Classification

Classification based on Composition:

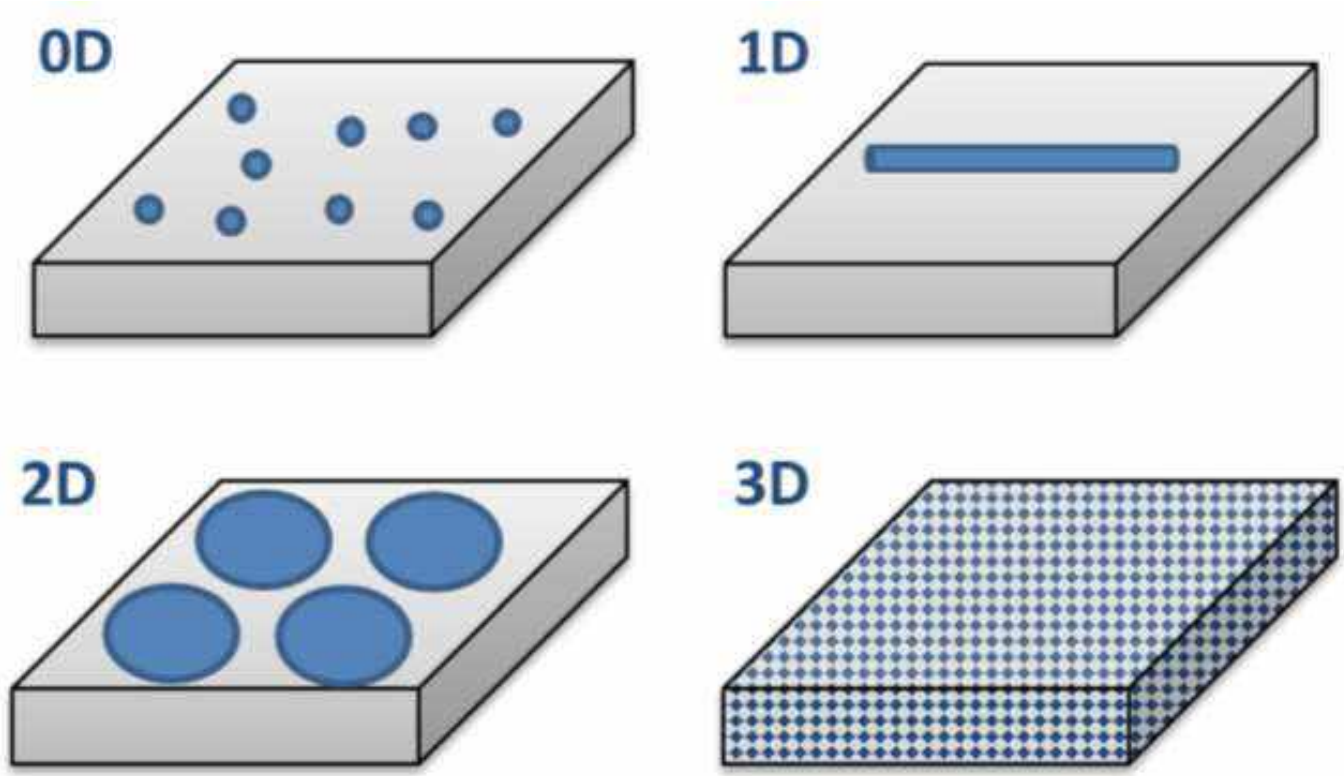
- Organic: Carbon based nanomaterials (Graphene, CNT), Nanobiomaterials, Dendrimers/Polymers
- Inorganic: Metals, Metal Oxide, Semiconductors (QD)
- Nanocomposites: Organic/Inorganic

Nanomaterials: Classification

Classification based on Dimensions:

- Three-dimensional (3D) structure or Bulk nanostructure
- Two-dimensional (2D) structure or Quantum wells
- One-dimensional (1D) structure or Quantum wires
- Zero-dimensional (0D) structure or Quantum Dots

Nanomaterials: Classification



Dimensionality refers to the number of degrees of freedom in the particle momentum rather than particle confinement direction

Nanomaterials: Classification

- **Three-dimensional (3D) structure or Bulk nanostructure:**

Particle is free (No quantization of Particle motion occurs)

These nanomaterials display internal nanoscale features but no external dimension at the nanoscale

E.g. Nanocomposites, Nanostructured materials

Natural: Bones with calcium hydroxyapatite nanocrystals dispersed in a collagen matrix

Manmade: Polymer matrix

nanocomposites

Nanomaterials: Classification

- **Two-dimensional (2D) structure or Quantum wells**

  Particle is free to move in two directions (Quantization of Particle motion occurs only in one direction)

  These nanomaterials display only one external dimension at nanoscale

E.g. Thin nanofilms, nanocoatings, nanoplates

Natural: Smectic clay

Artificial: Manufactured 2D structure like Graphene, silver, gold, bismuth selenide, bismuth telluride nanoplates

Nanomaterials: Classification

- **One-dimensional (1D) structure or Quantum wire:**

  Particle is free to move in only one direction

(Quantization of Particle motion occurs in two directions)

  Two external dimensions at the nanoscale and the third one being usually at the microscale.

E.g. Nanowires, nanorods, nanotubes, nanofibers

Very well known example:

Carbon NanoTubes (CNT)

Nanomaterials: Classification

➢ **Zero-dimensional (0D) structure or Quantum Dots:**

Quantization occurs in all 3 directions

Nanomaterials with all external dimensions at the nanoscale, i.e., between 1 and 100 nm

E.g.: Quantum dots, Nanodots,

Typical nanoscale dimensions (1-10nm radius)

- Quantum dots

  (semiconductor nanoparticles)

- Fullerene

Nanostructures	Typical nanoscale dimension
Thin films and quantum wells (two-dimensional structures)	1–1000 nm (thickness)
Quantum wires, nanowires, nanorods and nanopillars (one-dimensional structures)	1–100 nm (radius)
Nanotubes	1–100 nm (radius)
Quantum dots, nanodots (zero-dimensional structures)	1–10 nm (radius)
Porous nanomaterials, aerogels	1–50 nm (particle size, pore size)
Sculptured thin films	10–500 nm

Structure, Properties and Applications:

- Graphene
- Carbon nanotubes (CNT)
- Quantum dots (semiconductor nanoparticles)

Nanomaterials: Graphene

- **Structure**: Dimensionality, Details of Carbon atoms arrangement and bonding, Figure (sheet) required
- **Properties:** Chemical, Physical or Mechanical, Electrical property (electronics) and optical property, thermal conductivity etc.
- **Applications**: Potential uses based on different properties

Nanomaterial: Graphene

- One of the most promising nanomaterial
- **Discovery of Graphene:** In 2004 by Andre Geim and Konstantin Novoselov
- Single atom-thick layer of tightly bonded Carbon atoms, arranged in flat hexagonal honeycomb like lattice structure
- Monolayer Graphene can be viewed as an individual plane of Carbon stoms extracted from Graphite, hence building block

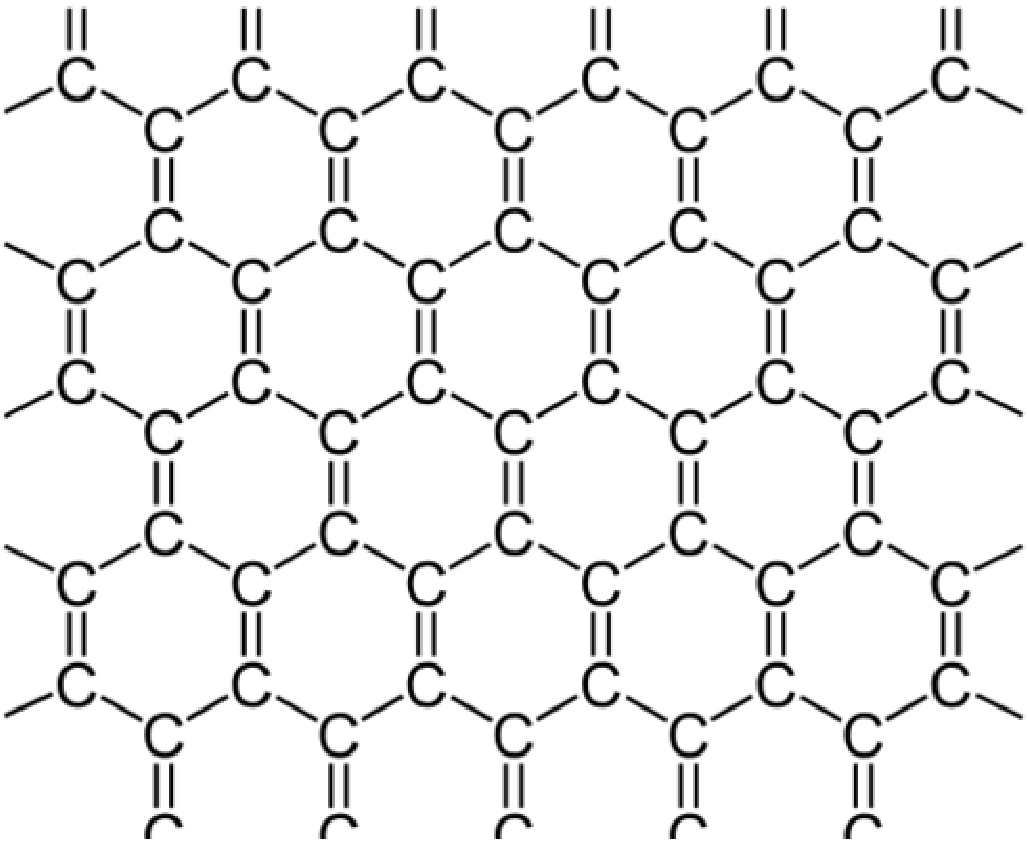
  for other Graphitic materials

WONDER Material

Structure of Graphene

- **Dimensionality:** 2D structure

  (atomic thickness: 0.345 nm)



- All Carbon atoms are sp2 hybridized

Source of Image: https://www.sculpteo.com

Key Properties of Graphene

- Physical Properties: Atomic thickness, strength, toughness, surface area, impermeability, thermal Conductivity
- Chemical Properties: Reactivity
- Electrical Properties: Electron mobility
- Optical Properties: Transparency

Physical Properties of Graphene

- One of the **thinnest** (only one carbon atom thick ~0.34 nm)
- **Flexible material**; most stretchable crystal (stretch upto 20%-25% of initial size w/o breaking it)
- **Toughest 2D material**: Harder than either steel (200 times stronger than steel) or diamond of the same dimensions
- **High tensile strength**

  (of over 1 Tpa)

Physical Properties of Graphene

- **Lightweight**; it weighs just 0.77 mg/m^2
- **Highest surface area to Volume ratio**, since single 2D sheet
- **Highly impermeable** (even He atoms cannot go through it)
- **Perfect thermal conductor:** Conducts heat in all directions - it is **an isotropic conductor**
- The measured thermal conductivity of Graphene is in the range of **3000 to 5000 W/m/K** at room temperature which is among the highest of any other known material

Chemical Properties of Graphene

- An **inert material** and **does not readily react** with other atoms (Even though all of graphene's atoms are exposed to the environment).
- However, "absorb" different atoms and molecules. This can lead to changes in the electronic properties.
- Can also be **functionalized** by various chemical groups, which can result in different materials such as graphene oxide or fluorinated graphene

(functionalized with fluorine).

Electrical Properties of Graphene

- **High electrical current density** (million times that of copper) and intrinsic mobility (100 times that of silicon)
- **Lower resistivity** than any other known material at room temperature, including silver.
- There are also some methods to turn it into a superconductor (carry electricity with 100% efficiency)
- Although graphene, **the fastest and most efficient conductor**, it cannot be readily used to make transistors as it does not have a bandgap.
- There are several methods to open a bandgap that are in existence and some that are under development

Optical Properties of Graphene

- Extremely thin, but still a visible material, as it **absorbs about 2.3% of white light** (which is quite a lot for a 2D material) i.e. **98% of visible light passes through graphene**, making it **transparent**

- Combine this with graphene's amazing electronic properties, and it turns out that graphene can theoretically be used to make very efficient solar cells

- In addition, absorbing 2.3% of visible light still makes graphene very much transparent to the human eye, which may have various uses. E.g.: Used to make transparent conductors

Potential Uses of Graphene

Water Filtration Systems: For purification of water as it allows water to pass, but not other liquids and gases

Touch Screens in Devices: Transparency and conductivity of graphene can be used in displays and touchscreens, however more expensive to produce than currently used indium tin oxide

In Electronic Devices: Touted as Siliocon's successor and has been used to make very fast transistors. However, its conductivity cannot be switched off as Silicon can.

Potential Uses of Graphene

Sensors :Graphene as sensor is ultrasensitive as every atom is exposed to it's surrounding allowing it to sense changes in the surrounding. For e.g.

- To produce Smart food Packaging that detects atmospheric changes caused by decaying food.
- To protect the crops as Farmers would be able to monitor the existence of any harmful gases and determine ideal areas for growth of certain crops depending on atmospheric conditions
- To monitor stresses and strains in constructional components
- To detect biological agents like drugs in our body
- To detect light and used in camera

It is **Multifunctional material** and allows

To create **micrometer sized** sensor

Potential Uses of Graphene

Drug delivery in Medical field:

- Several biomedical applications are being explored for graphene, including drug delivery, cancer therapy, etc. However, its toxicity profile must be investigated before clinical use

Energy Storage & Composites:

- Used in normal batteries and supercapacitors as a Substitute for graphite that can store more energy, charge faster

Graphene Products

Head You Tek Graphene Instinct Tennis Racquet (In 2013)

Uses Graphene coating on the shaft to make it stronger and better controlled racket

Huawei’s Mate 20 X smartphone uses Graphene film cooling technology for heat management purpose

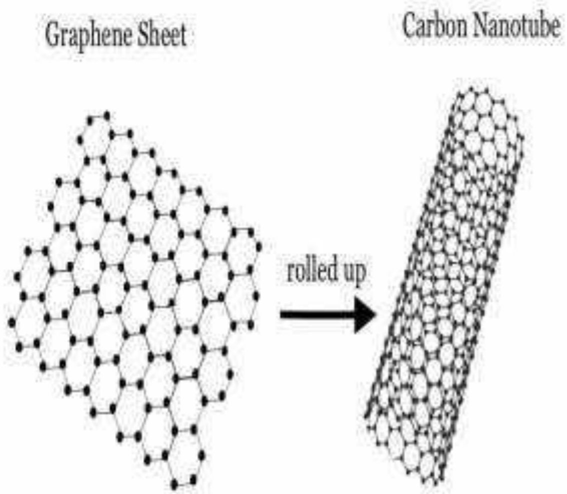
Cardea uses a graphene based biosensors and AGILE system which allows for real time detection of small molecules which offer faster sample processing, greater accuracy, portability and cost savings

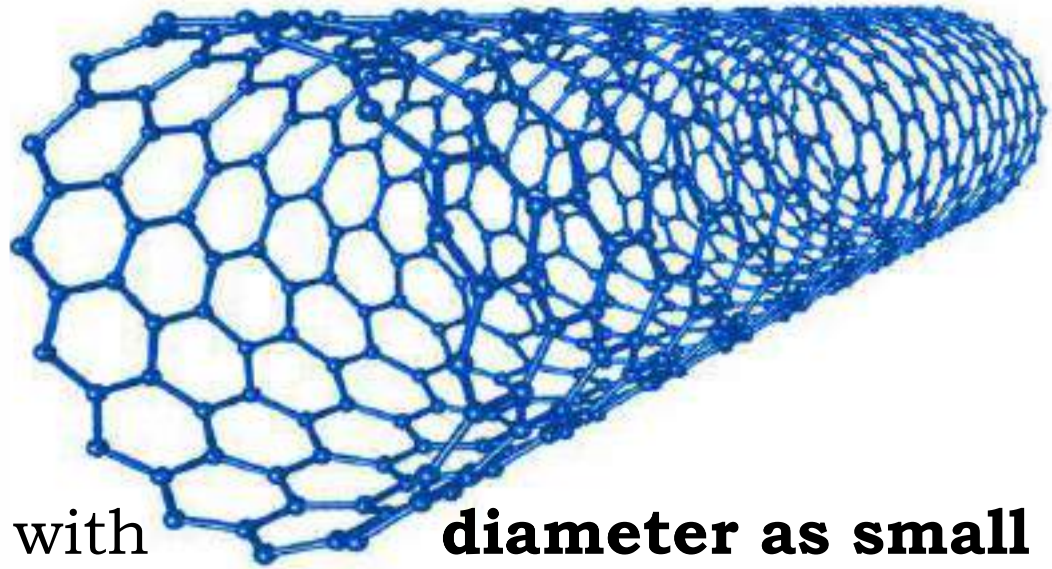
Ford used Graphene reinforced foam covers for noisy components in its 2019 F-150 and Mushtang cars

Nanomaterials: Carbon Nanotube

- **Structure**: Dimensionality, Details of Carbon atoms arrangement and bonding, Figure (sheet) required
- **Properties:** Chemical, Physical or Mechanical, Electrical property (electronics) and optical property, thermal conductivity etc.
- **Applications**: Potential uses based on different properties

Structure of Carbon Nanotube





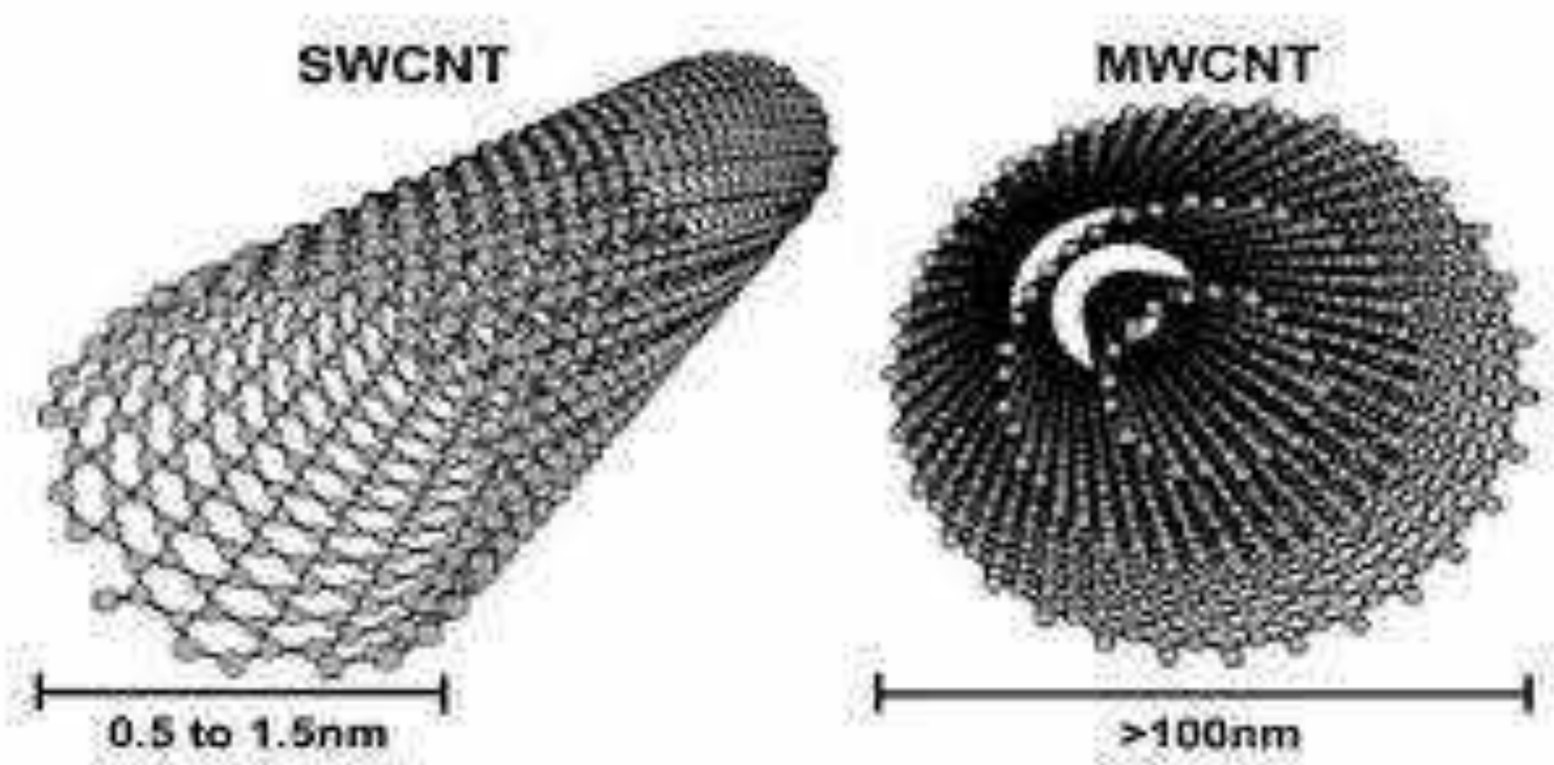
- Tubular form of carbon with **diameter as small as 0.5 to 1 nm and Length: few nm to microns.**
- **Dimensionality: 1D**

(but configurationally equivalent to

2D graphene sheet rolled into a tube)

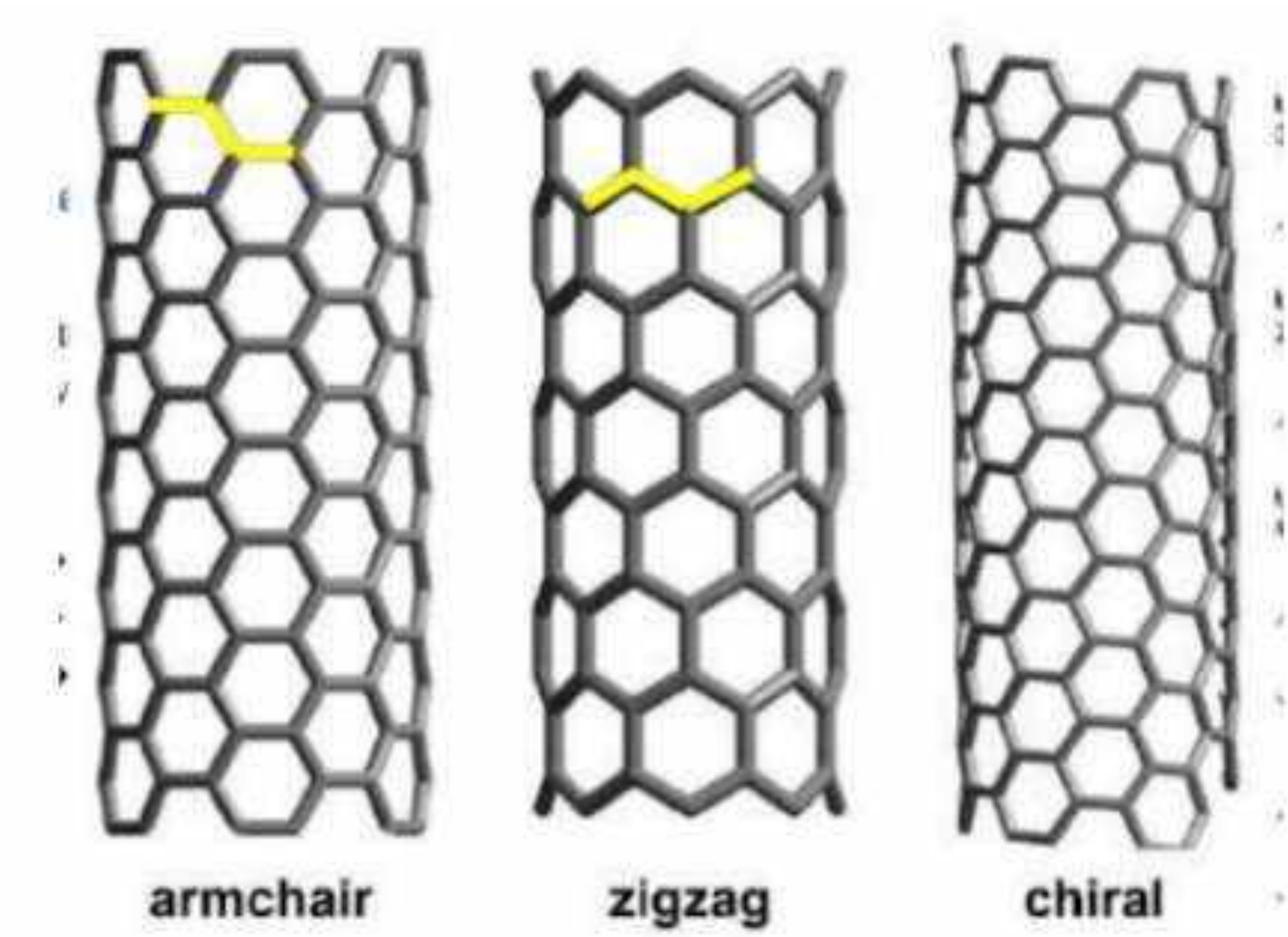
- All Carbon atoms are **sp2 hybridized**

Types: Carbon NanoTubes



- **Single Wall CNT (SWCNT):** One-atom thick single tube
- **Multi-Wall CNT (MWCNT):** Buildup of a number of concentric tubes

Based on the arrangement of Carbon atoms, Carbon Nanotubes are further classified as:



Properties: Carbon Nanotubes

- **High Electrical Conductivity**
- Very **High Tensile Strength** (Higher than steel and Kevlar)
- **Highly Flexible**- can be bent considerably without damage
- **High Thermal Conductivity**
- **Light weight**
- **Highly Absorbent**
- **High Aspect Ratio**

  (length = ~1000 x diameter)
- Low Thermal Expansion Coefficient
- Very Elastic ~18% elongation to failure

Electrical Properties of CNT

High Electrical properties:

Electrical Conductivity in nanotubes is based on the degree of chirality – i.e. the degree of twist and size of the diameter of the actual nanotube - which results in actually **extremely conductive** (making it suitable as an interconnect on an integrated circuit) **or non-conductive** (making it suitable as the basis for semi-conductors) nanotube.

- Electron transport occurs only along the axis of the tube.
- Single walled nanotubes can route electrical signals at speeds up to 10 GHz

Thermal Properties of CNT

High Thermal Conductivity:

The strength of the atomic bonds in carbon nanotubes allows them to withstand high temperatures

Very good thermal conductors.

- When compared to copper wires, which are commonly used as thermal conductors, the carbon nanotubes can transmit over 15 times the amount of W/m K
- The thermal conductivity of CNT depends on the temperature of tube and the outside environment

Synthesis of Carbon Nanotubes

Carbon nanotubes can be synthesized by:

- Arc Discharge method
- Laser Ablation
- Chemical Vapour Deposition (CVD)

➢ CVD has the highest potential for mass production of CNT It can produce bulk amounts of defect-free CNTs at relatively low temperatures.

➢ Arc Discharge method: Used to synthesize CNTs in small quantities

➢ Laser Ablation

Applications of Carbon Nanotubes

Drug delivery:

CNT-Promising Drug Delivery Carrier

- Carbon nanotubes present the opportunity to work with effective structures that have **high drug loading capacities** and **good cell penetration** qualities
- Carbon nanotubes function with a **larger inner volume** to be used as the drug container, **large aspect ratios** for numerous functionalization attachments, and the ability to be **readily taken up by the cell**

Applications of Carbon Nanotubes

Waste-water treatment:

- CNTs have a very large surface area (e.g.,~ 500 m^2 per gram of nanotube) that gives them a **high capacity to retain the pollutants**
- Can also be Used as air filtration

Solar cells:

- Due to their strong UV/Vis-NIR absorption characteristics, SWNTs are a potential candidates

` for use in solar panels.

Applications of Carbon Nanotubes

Catalysts Support:

- CNTs provides an opportunity for Catalyst supports because **large surface area** and ability to attach any chemical species to their sidewalls (**Functionalization**)

Composites and Adhesives/Coatings:

- CNT Ceramic Reinforced Composite
- Used as adhesives of different **stiffness** by varying the concentration of CNTs

Applications of Carbon Nanotubes

Electronics Field:

- **SWNT ropes** are the most conductive carbon fibers known
- SWNT can be used as High performance and thin film **Field Effect Transistors** (CNT based sensors) are widely used to detect gases such as greenhouse gases in environmental applications
- **Bucky paper thin tube** can be used as Heat Sink for chipboards

.

Applications of Carbon Nanotubes

Used in various fields:

1) Medical field
2) Filtration Units
3) Structural materials
4) Textiles (Fabric and Fibers)
5) Plastic
6) Energy Storage
7) Composites etc.

Nanomaterials: Quantum Dots

- **Introduction**: Definition, Common QD materials (group) Dimensionality,
- **General Feature**: Effect of Interaction of UV light with different sizes, Band gap tuning by size (splitting of energy levels due to size/composition)
- **Properties**: Electronic and Optical
- **Applications**: Uses in Different domains

Nanomaterials: Quantum Dots

- **Definition:** Quantum dots (QDs) are often referred to very tiny man-made semiconductor nanoparticles/nano structures whose sizes are normally not more than 10 nanometers (2-10nm), that exhibit 3-dimensional quantum confinement, which leads to many unique optical and transport properties
- QDs have ability to absorb the light and then emit a light of specific λ with the release of energy

(Broadly, Quantum confinement means restricting the motion of randomly moving electrons in very small particle to a specific discrete energy levels rather than a quasi continuum of energy bands)

Nanomaterials: Quantum Dots

- **Dimensionality:** 0-dimensional nanostructure

Degree of freedom of particle momentum is zero while motion of electron-hole pair is confined/restricted in all 3 spatial dimensions

Examples: Typically, QD composed of the elements of periodic groups II-VI, III-V and IV-VI materials like CdSe, CdS_2, InSe, PbSe, InP, GaAs, CdSe/ZnS etc.

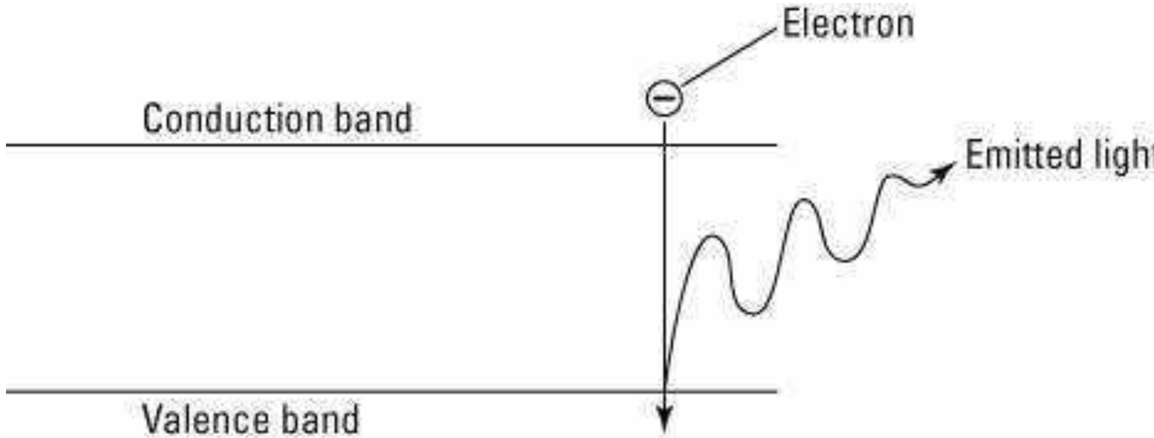
Types of Quantum Dots

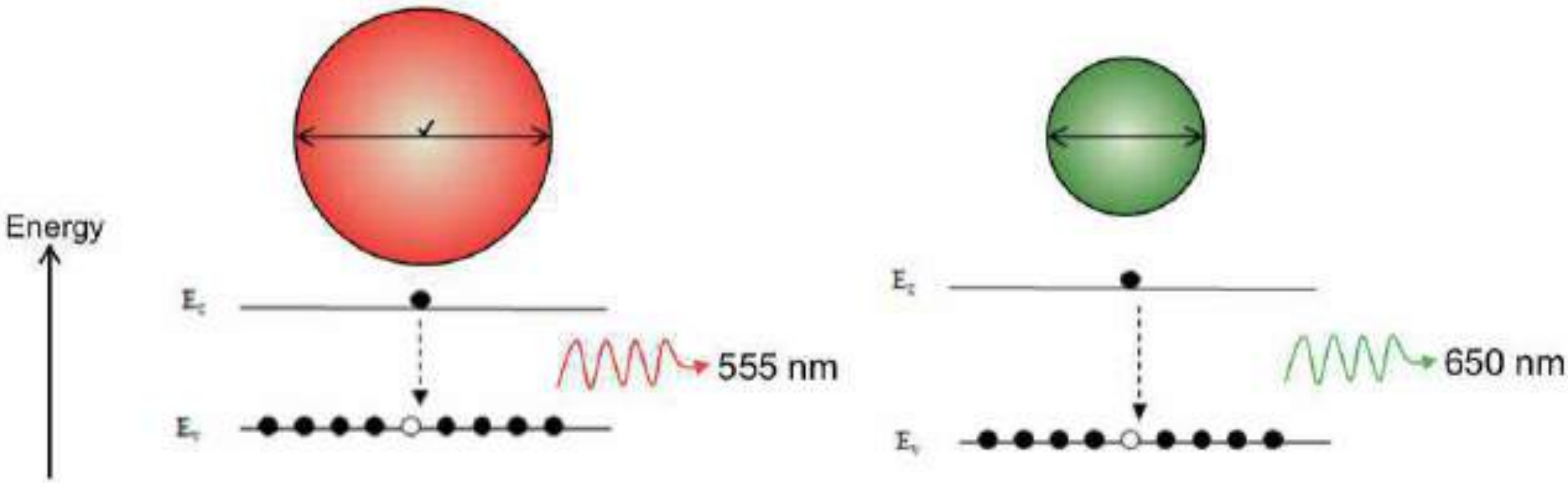
Quantum Dots can be classified based on their composition and structure:

- **Core Type QD:** Single component material with uniform composition like Chalcogenides (selenides,sulfides or telurides) of metals like Cd, Pb or Zn
- **Core Shell QD:** Particles of one material embedded in other, e.g. QD with CdSe in the core and ZnS in the shell
- **Alloyed QD:** Alloying together two semiconductor with different composition

General Feature of Quantum Dots

- When illuminated by UV light, some of the electrons receive enough energy to break free from the atoms.
- This capability allows them to move around the nanoparticle, creating a conductance band in which electrons are free to move through a material and conduct electricity. When these electrons drop back into the outer orbit around the atom (the valence band), they emit light.
- **The color of that light depends on the energy difference between the conductance band and the valence band**
- A majority of **QDs** have the **ability to emit light of specific wavelengths** if excited by light or electricity.





Absorption and emission occur at specific wavelengths, which are related to QD size.

Source: www.nanohub.org

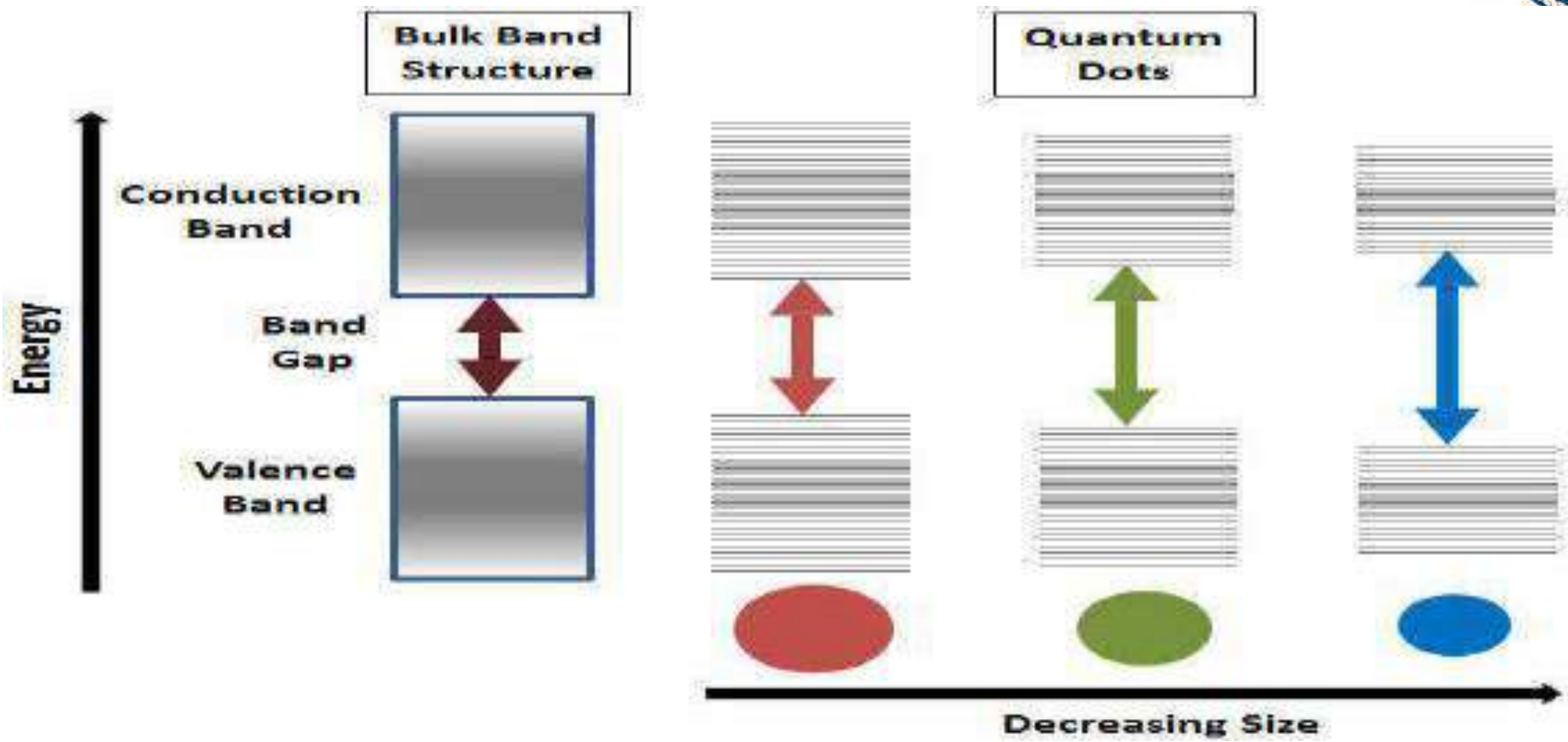
Properties of Quantum Dots

- QDs properties can be determined by their size, shape, composition and structure.
- QDs show **color glow when illuminated** by UV light of specific λ

Typically, smaller QDs (e.g., radius of 2~3 nm) emit shorter wavelengths generating colors such as violet, blue or green. While bigger QDs (e.g., radius of 5~6 nm) emit longer wavelengths generating colors like yellow, orange or red.

Quantum Size Effect: Splitting of energy levels in QD

Source: www.sigmaaldrich.com/



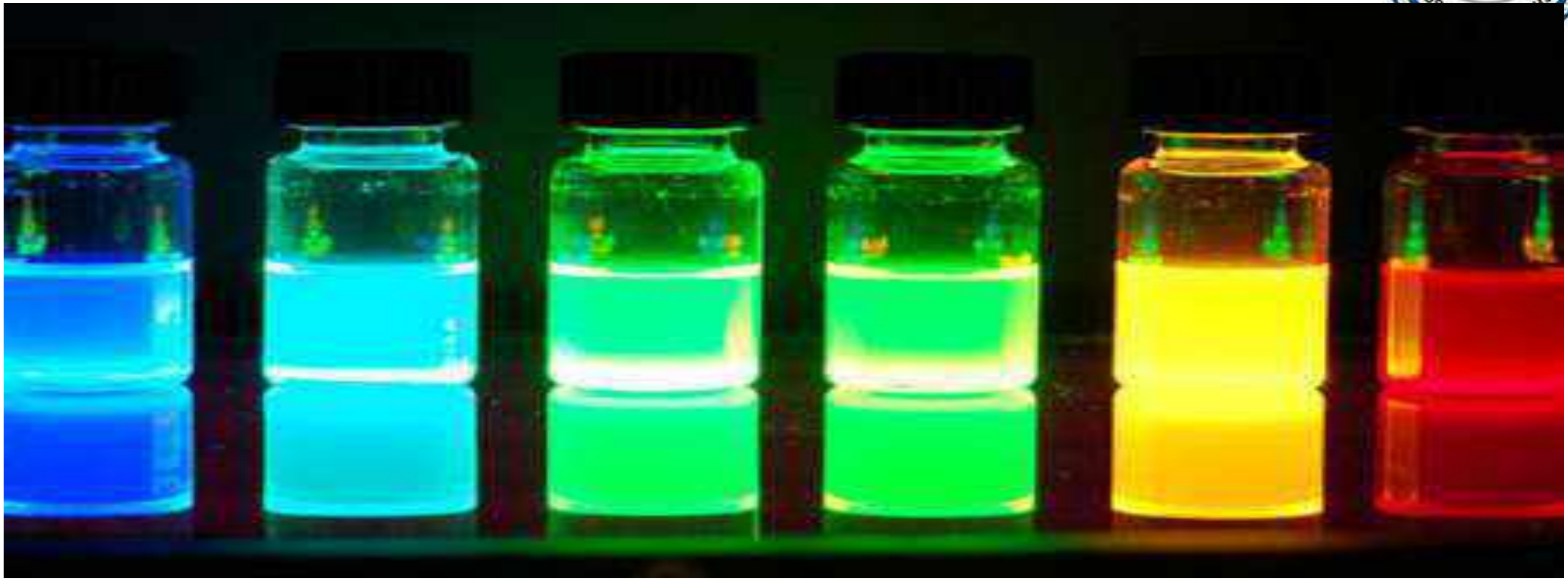
Energy levels become discrete, and energy becomes larger compared to bulk of same material

Semiconductor band gap increases with decrease in size of the nanocrystal

Properties of Quantum Dots

- Smaller QDs have a large bandgap
- Absorbance and luminescence spectrums are blue shifted with decreasing particle size
- QDs are bandgap tunable by size/composition which means optical and electrical properties can be engineered to meet specific applications

Emission of different color of light by tuning the composition



Photoluminescence of **alloyed CdS_xSe_{1-x}/ZnS** quantum dots of **6nm** diameter. The material emits different color of light by tuning the composition

Source: www.sigmaaldrich.com/

Potential Uses of Quantum Dots

QDs find variety of applications in different domains:

- BioImaging
- LEDs
- Solar Cells
- Dyes
- Miniature Lasers communication devices
- TV/Electronic devices Displays etc.

Potential Uses of Quantum Dots

BioImaging:

- QDs are coated with hydrophilic polymers and also be conjugated to obtain multifunctionality. They can be linked with biological agents such as antibodies, peptides, oligonucleotides, inhibitor molecules etc.

E.g. QDs can be used in **cancer detection**.

Detection of tumor in human body,

Multicolor Imaging of the tumor tissue by QDs in **live animals**

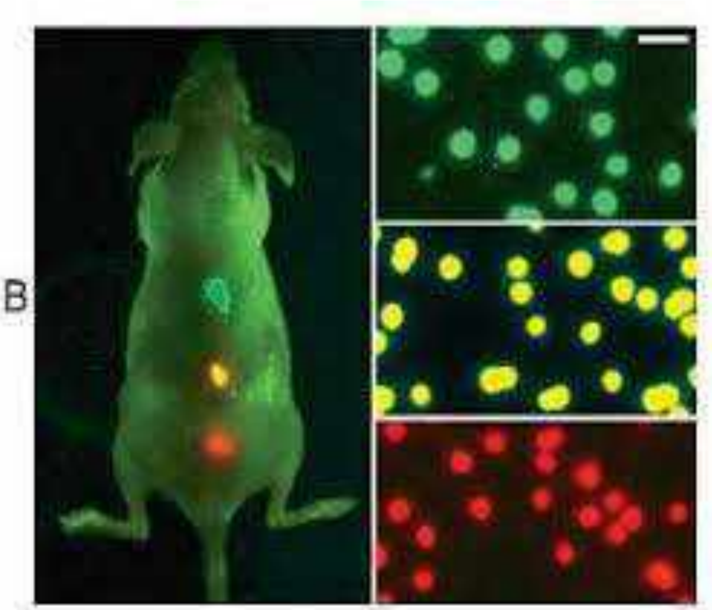
Potential Uses of Quantum Dots

BioImaging:

- In-vivo imaging poses problems with the clearance of the particles from body.

  (Toxicity and hazards effects needs to be evaluated thoroughly)
- QDs of different colors are used for imaging multiple target simultaneously.

Source: www.nanohub.org



CdSe/ZnS QDs used to image cancer cells

Gao, Xiaohu. "In vivo cancer targeting and imaging with." Nature Biotechnology 22(2004): 8

Potential Uses of Quantum Dots

- **Light Emitting Diodes:**

Quantum dot light emitting diodes (QD-LED) and 'QD-White LED' are very useful for displays in electronic devices QD-LED displays can render colors **very accurately** and use much **less power** than traditional displays.

Quantum-dot-based LEDs emission wavelength can be easily tuned by changing the size of the quantum dots

Potential Uses of Quantum Dots

Solar Cells:

- Quantum dot (QD) solar cells have the potential to **increase the maximum** conversion of efficiency of solar photon conversion up to about 66% by utilizing hot photogenerated carriers to produce higher photovoltages or higher photocurrents
- Cost effective
- Cu-InSe sulfide QD–nontoxic than QDs containing Pb/Cd

Potential Uses of Quantum Dots

Alternative to traditional Dyes:

- Quantum dots are an attractive alternative to traditional organic dyes because of their **high quantum yield** (brighter emission) **and photostability**.
- The quantum yield of some QDs is 20 times greater than traditional organic fluorophores