Physics of Nanoparticles

Introduction

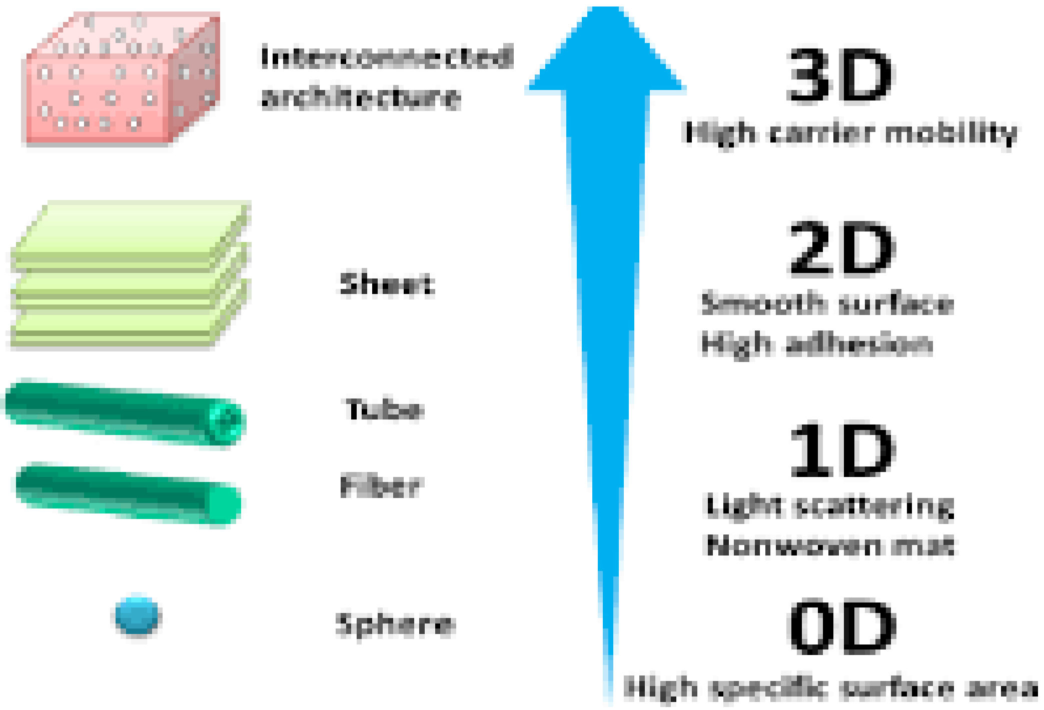
- Nanomaterials : physical size (at least one dimension) in range ; 1 to 100 nm

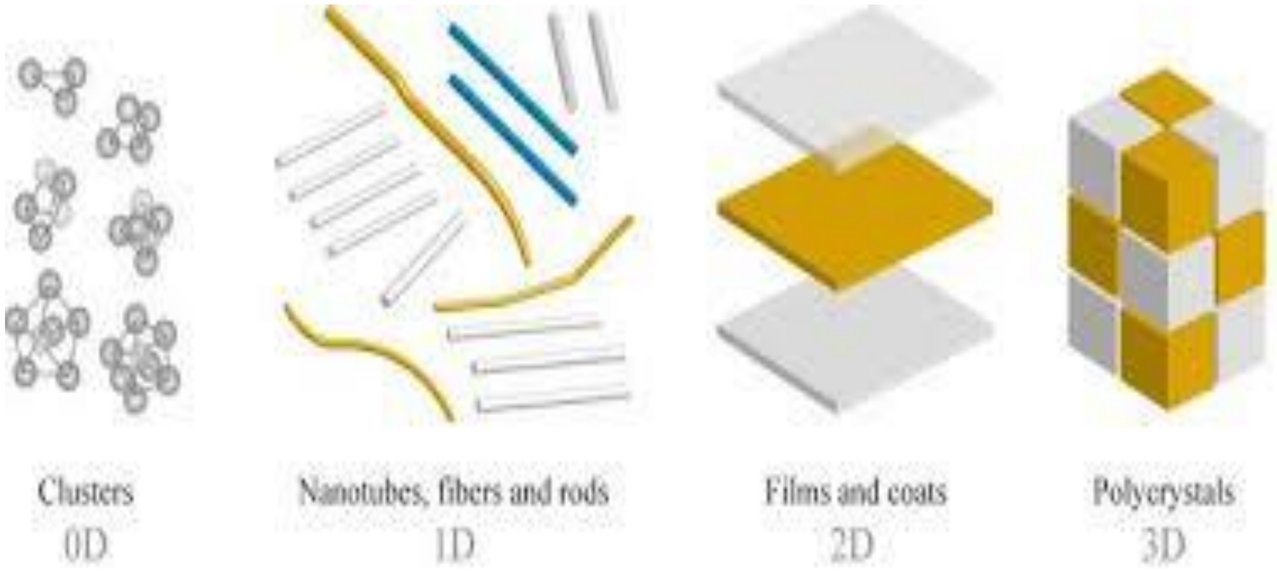
- Physical and Chemical properties: explained by QM

- 3D: Bulk solid

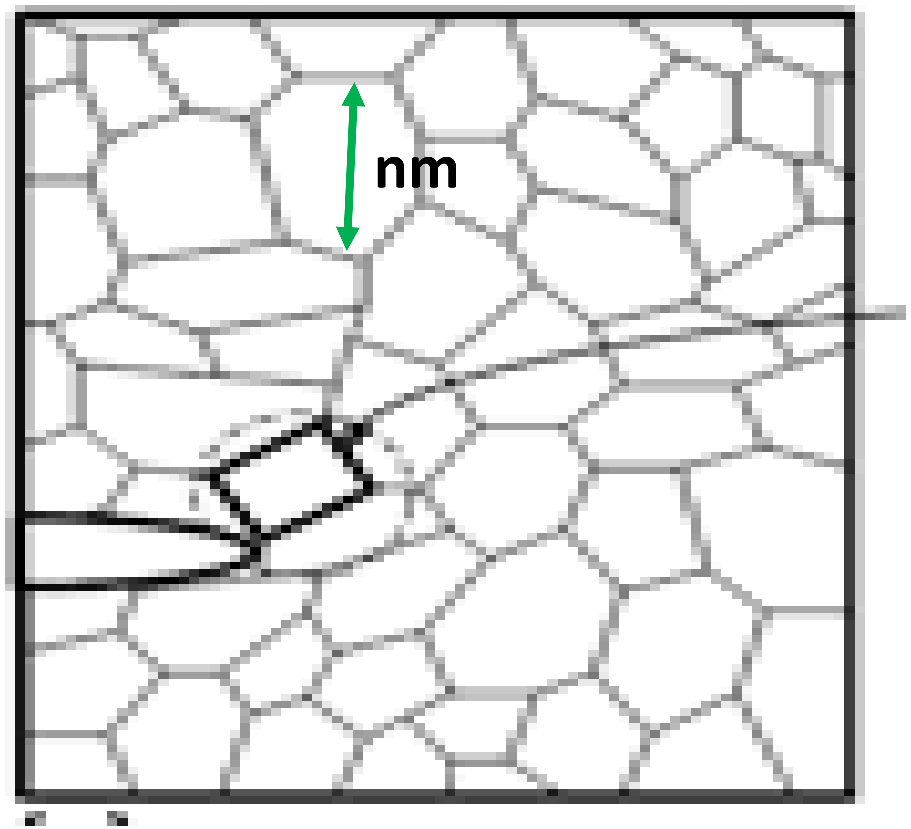
- 1D: one dimension is reduced to nanorange
- 2D: two dimensions are reduced to nanorange
- 0D: three dimensions are in nanorange (**Quantum dots**)

- Bulk material: 1 gm – 10^{23} atoms
- Nanomaterial: 1 to 100 nm size – 1000 to 10^{6} atoms





Below critical size; properties not only become size dependent but shape dependent



Nanocrystalline Solid

Michael Faraday's gold colloids

These liquids are some of the first examples of metallic gold colloids, made by Michael Faraday over 150 years ago.

Date: 1856

Place made: Basement laboratory at the Ri

Properties of Nanomaterials

1. Optical:

Metallic nanoparticles: explained by Mie theory (Maxwell's electromagnetic theory)

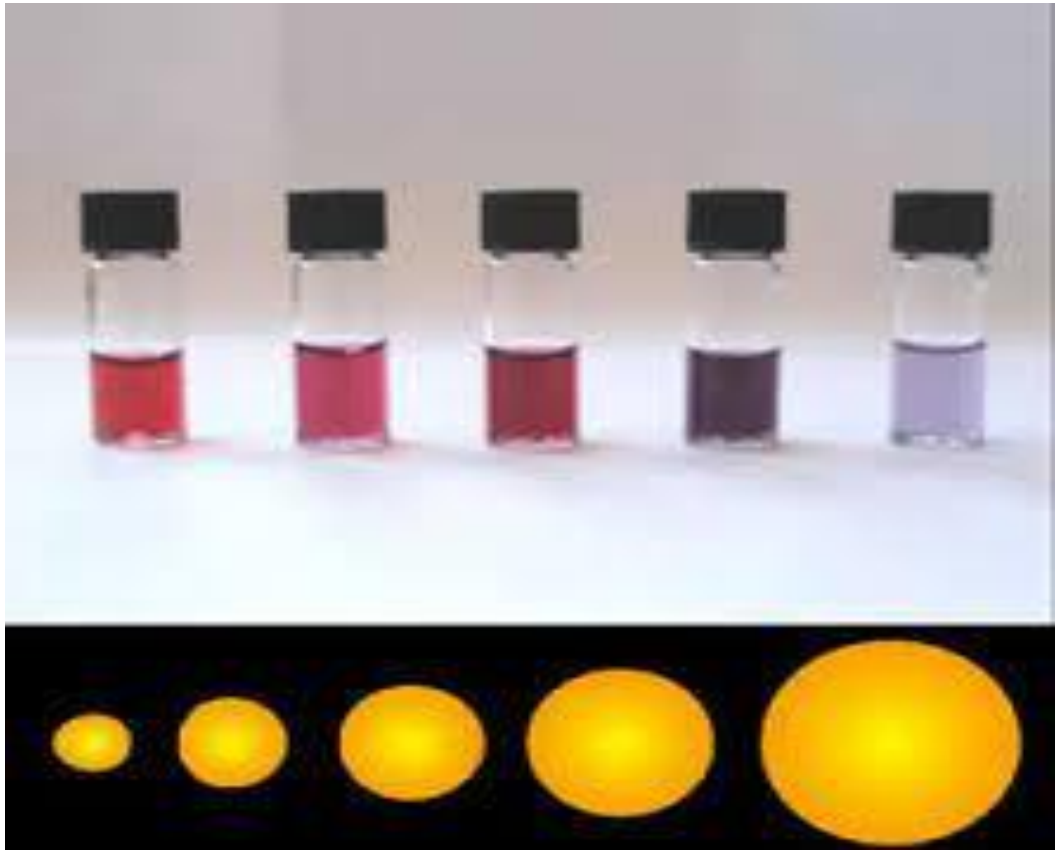
Colour of NPs is different due to discrete energy levels
Au : yellow (bulk) and red (nanosize)

Semiconductor nanoparticles: explained by quantum mechanics

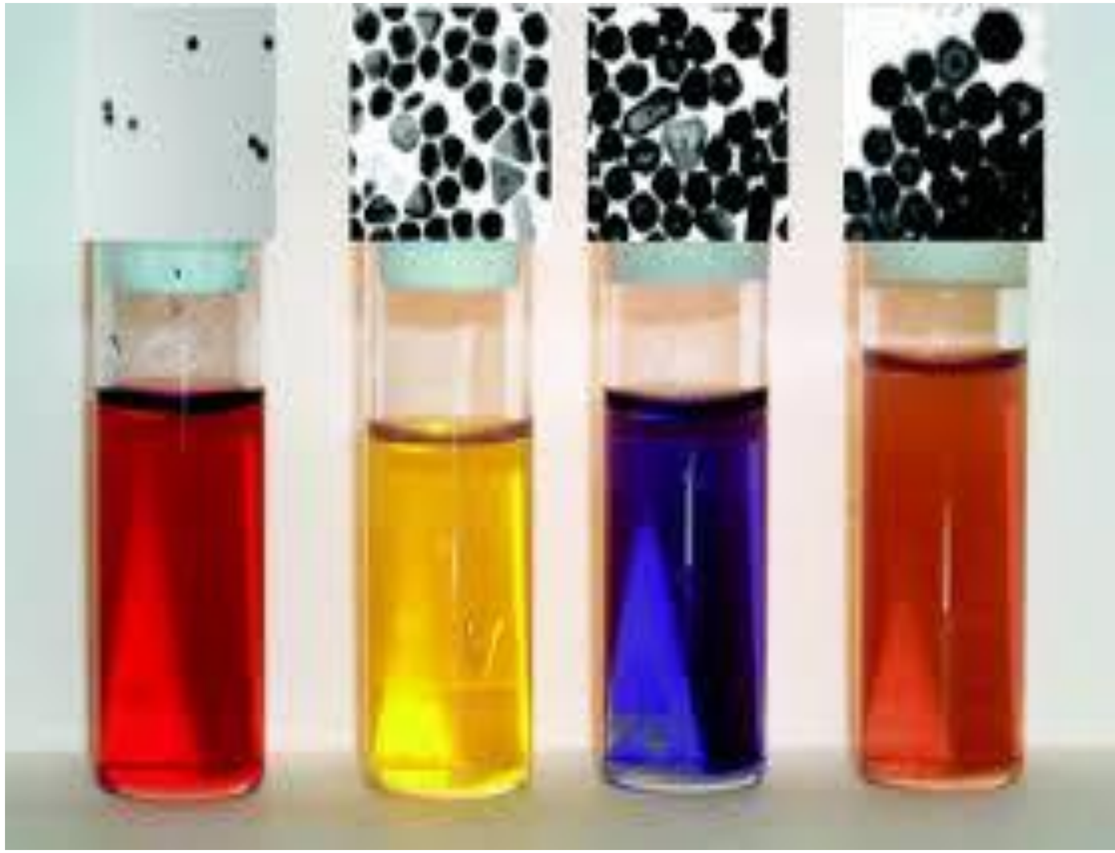
$E = n^2h^2 /8mL^2$

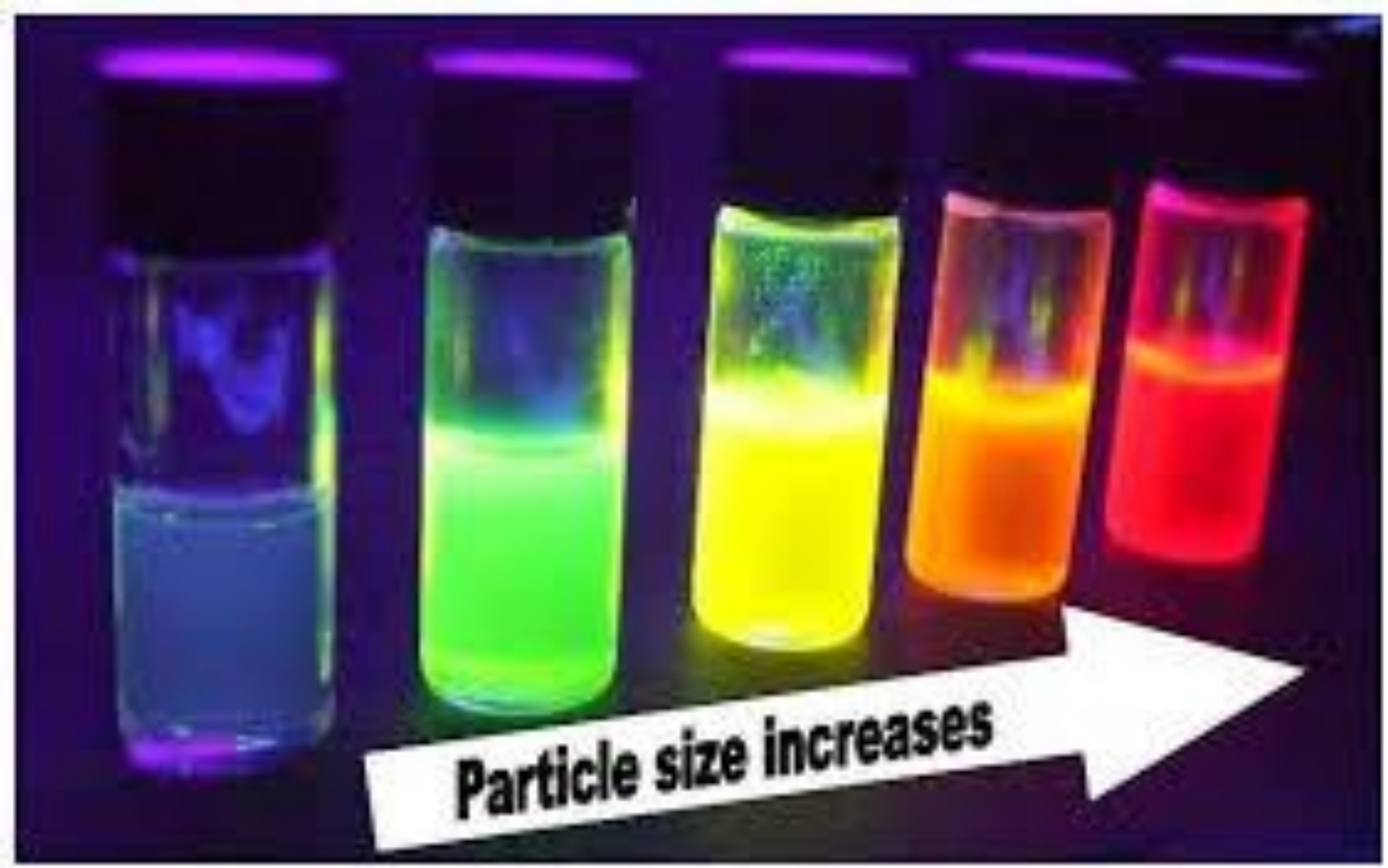
Energy band gap increases with reduction in size

Au Nanoparticles



Au-Ag Nanoparticles




Particle size increases

2. Electrical:

- Higher electrical resistivity than bulk due to nanosize grain boundaries
- Single electron tunnelling and coulomb blockade (confinement of electron)

3. Magnetic:

- Bulk: Magnetism is due to orbital and spin motion of electrons (magnetic moment). Orientation of Magnetic domains is important (Para or Ferromagnetic)
- Ferromagnetic (bulk): different domains have different orientations (hysteresis loss)
- Superparamagnetic (nano): single domain (no hysteresis loss)

4. Structural :

- Different crystal structure than bulk material due to different surface to volume ratio
- Different lattice parameters and also bond length

5. Mechanical:

- Hardness, elasticity, ductility: depend upon composition and bond between atoms (metallic, covalent, ionic etc.)
- Presence of imperfection and impurity (like C, O, N, P, S), defects, grain boundaries etc.
- Nanoparticle: pure and free from imperfection or single crystal but some defects are present
- NPs are stronger than bulk
- Elastic modulus of Mg NPs for grain size ≈ 12 nm is $3900 N/mm^2$ and polycrystalline for grain size > 1μm ($4100 N/mm^2$)
- Hardness increases on decreasing grain size (nanometer)
- Hardness increases with increase of grain size (micrometer)
- CNTs are strongest material

Synthesis Methods

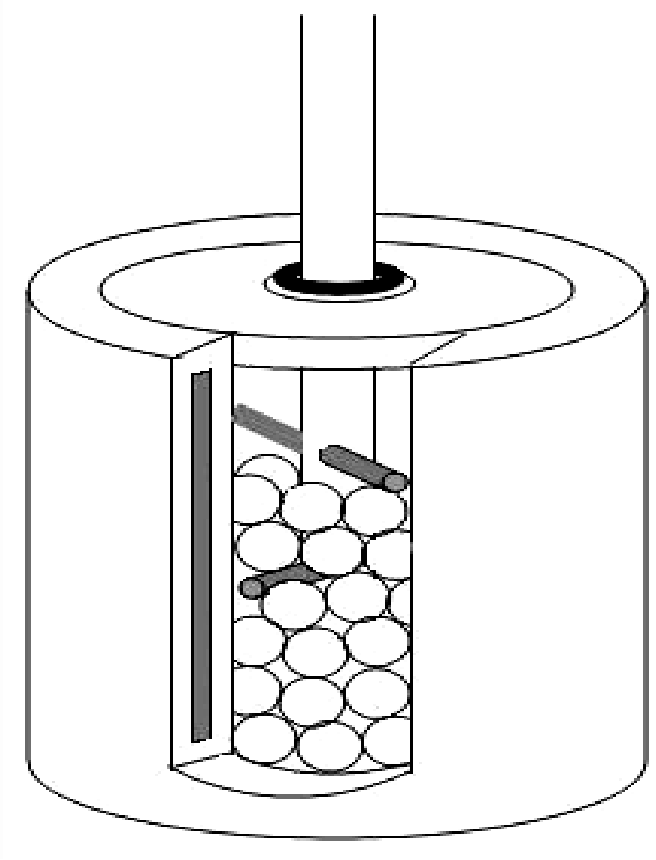
- **Physical**
  - **Mechanical**
    - High enrgy ball milling, melt mixing
  - **Vapour deposition**
    - Physical vapour deposition, Laser ablation, Sputter deposition, electric arc deposition, ion implantation
- **Chemical**
  - Colloids, sol-gel, L-B films, Inverse micelles
- **Biological**
  - Using biomembranes, DNA, enzymes and micro organisms
- **Hybrid**
  - Electrochemical, Chemical vapor deposition, Particle arresting in glass or zeolites or polymers, Micro emulsion-zeolite

Physical Methods

- Mechanical method (Planetary ball milling)
- Laser pyrolysis
- Chemical vapour deposition

Planetary ball milling

- Simple and nanoparticles will be in powder form
- Planetary ball mill : tungsten carbide balls are put in containers with powder of material (50 micron)
- 2:1 mass ratio of balls to material; cylinder is less than half filled (get more efficiency)
- Container rotation: high speed (hundreds of rpm) around its own axis and also center axis like planets
- Powder forced towards wall and pressed against wall due to centrifugal force
- Small size particles due to large size balls but defects are more (also due to air)
- Temperature: 100 to 1100 ^{0}C due to collision
- NPs size: few nm to 100 nm by controlling speed and time of rotation

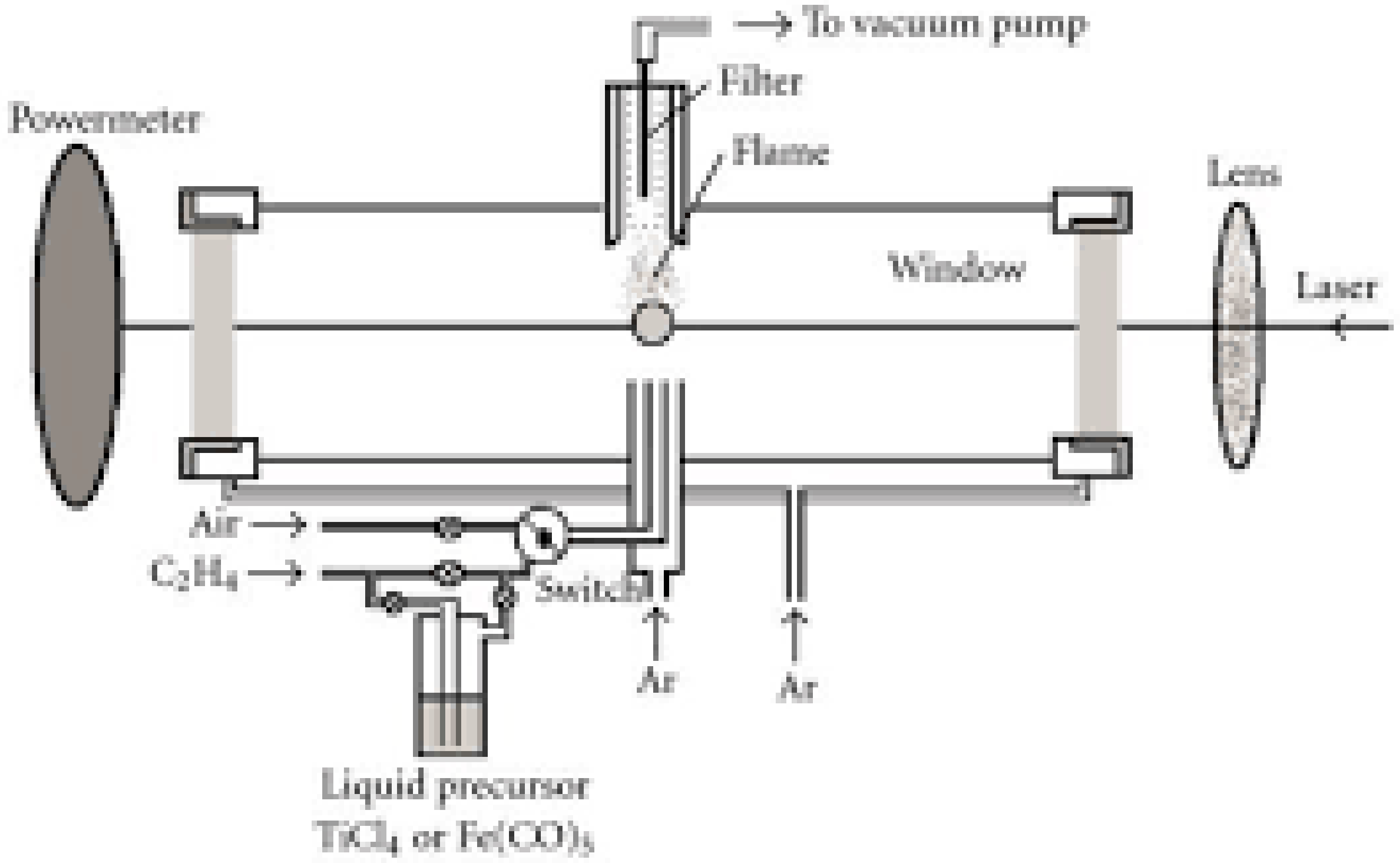


Schematic diagram (sectional) of a ball mill vessel.

Laser Pyrolysis (decomposition at high temperature)

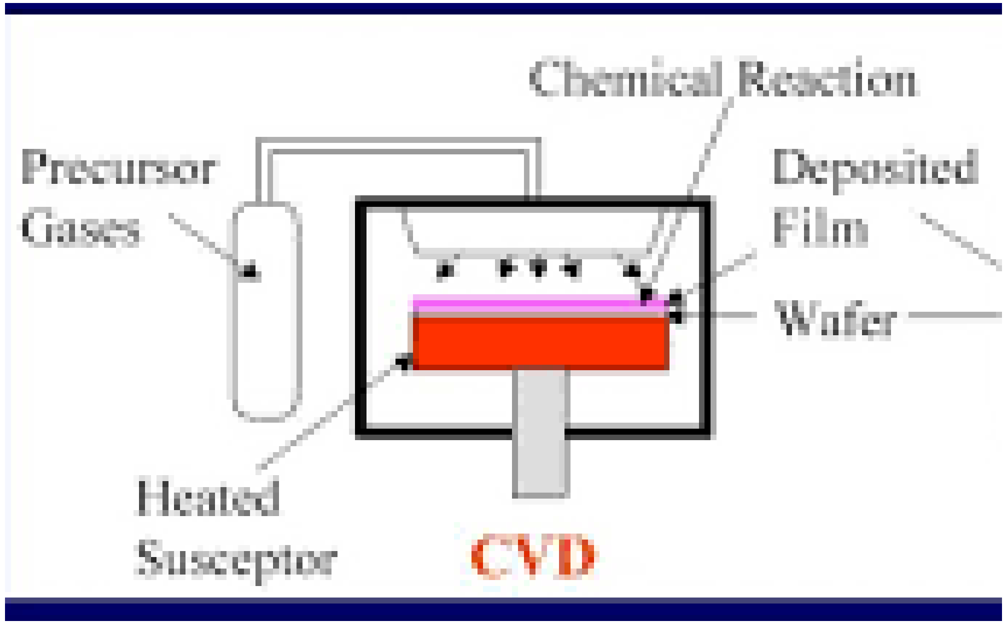
- Decomposition of reactant gases using high power laser beam (CO_2 laser)
- Inert gases (He, Ar) are used
- Decomposed atoms interact with each other: grow in size to get nanomaterial and deposited on silicon substrate
- For example: reactant gases like C_2H_2, C_2H_4, $Fe(CO)_5$ are used
- Nanoparticle size and its distribution: gas pressure and substrate temperature
- NPs in the form of Thin film, CNTs, Al_2O_3, Si_3N_4 etc.

Laser Pyrolysis



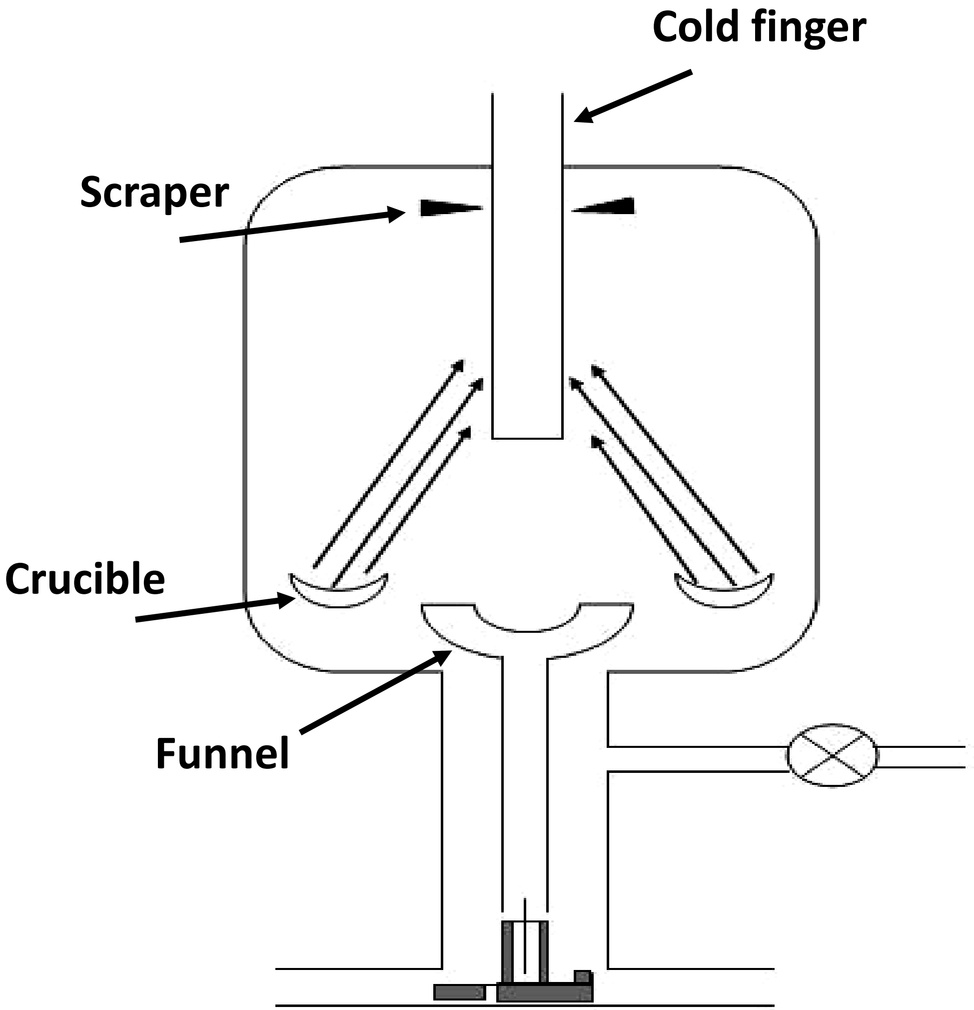
Chemical Vapour Deposition

- Evaporation and deposition of material on hot substrate
- Metal or alloy in the form of vapour are pumped in chamber using gases
- Transported towards hot substrate (300 to 1200 ^{0}C)
- Deposited due to chemical reaction between vapour and substrate
- NPs in the form of thin film on substrate
- Simple and cheap compared to other techniques



Physical Vapour Deposition

- Principle: evaporation of materials
- Inert gas or reactive gas is used for collision of material vapour
- Cold finger: for NPs condensation
- Scraper : for collecting NPs
- High vacuum chamber



Chemical Method

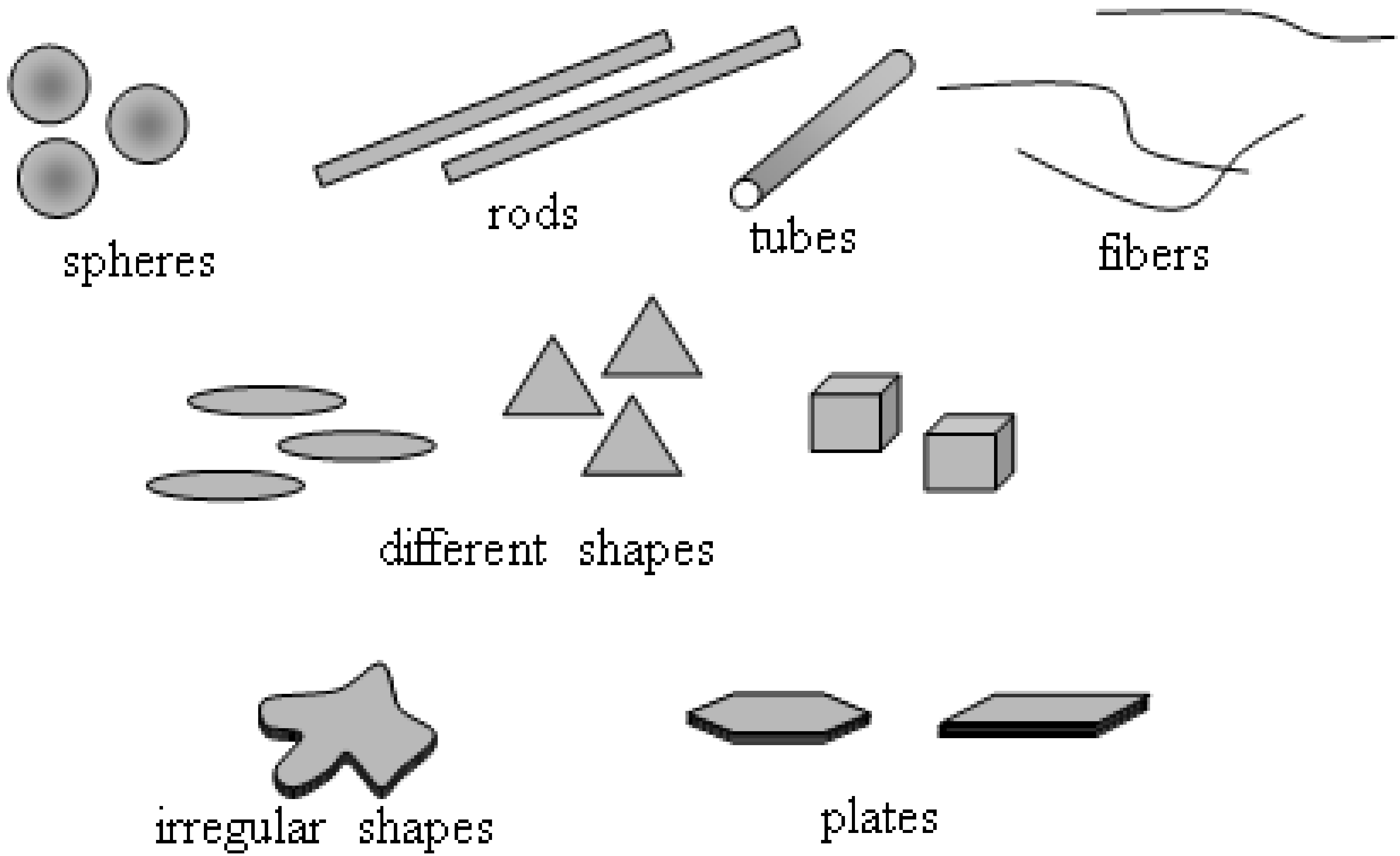
- Simple techniques
- Inexpensive, less instrumentation compared to many physical method
- Low temperature (< 350 °C) synthesis
- Doping of foreign atoms (ions) possible during synthesis
- Large quantities of the material can be obtained
- Variety of sizes and shapes are possible
- Materials are obtained in the form of liquid but can be converted into dry powder or thin films quite easily

- Colloids are formed : chemical method

- Colloids: mixture of two or more same or different phase and material (solid-liquid, liquid-liquid)

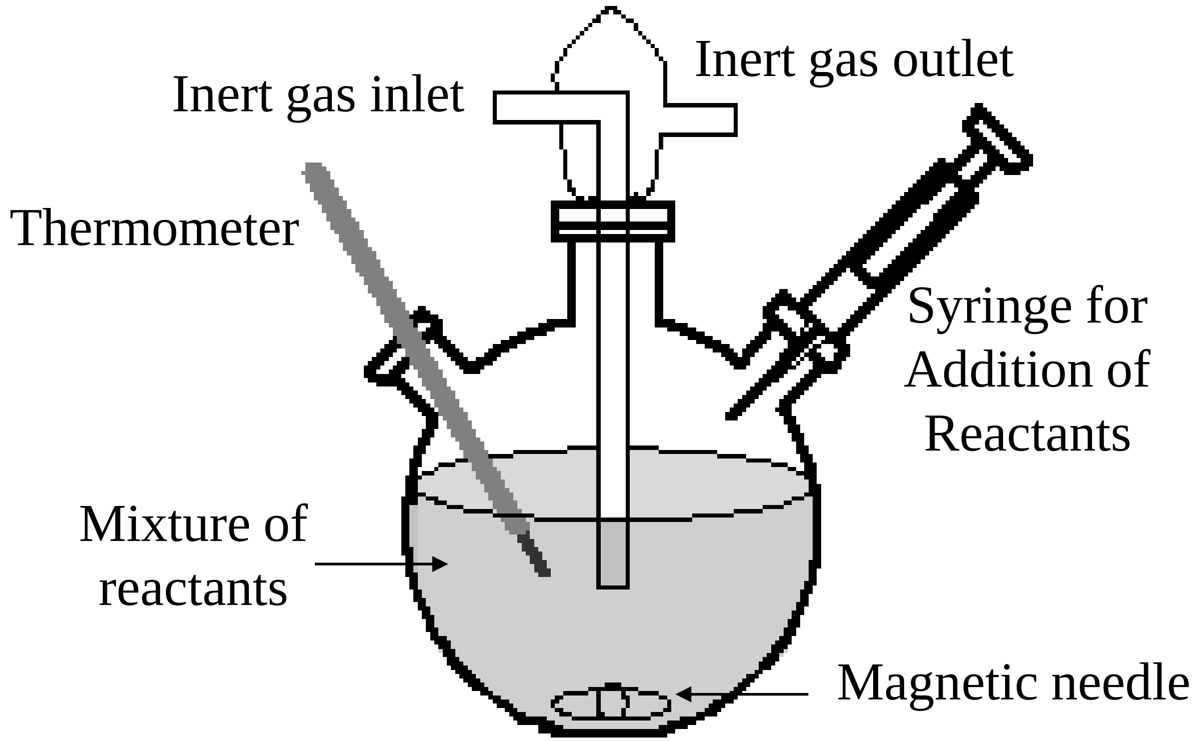
- Size and shape of colloids: 1-100 nm and sphere, rod, tubes, wires, or plates etc

- NPs are suspended in host matrix



spheres
rods
tubes
fibers
different shapes
irregular shapes
plates

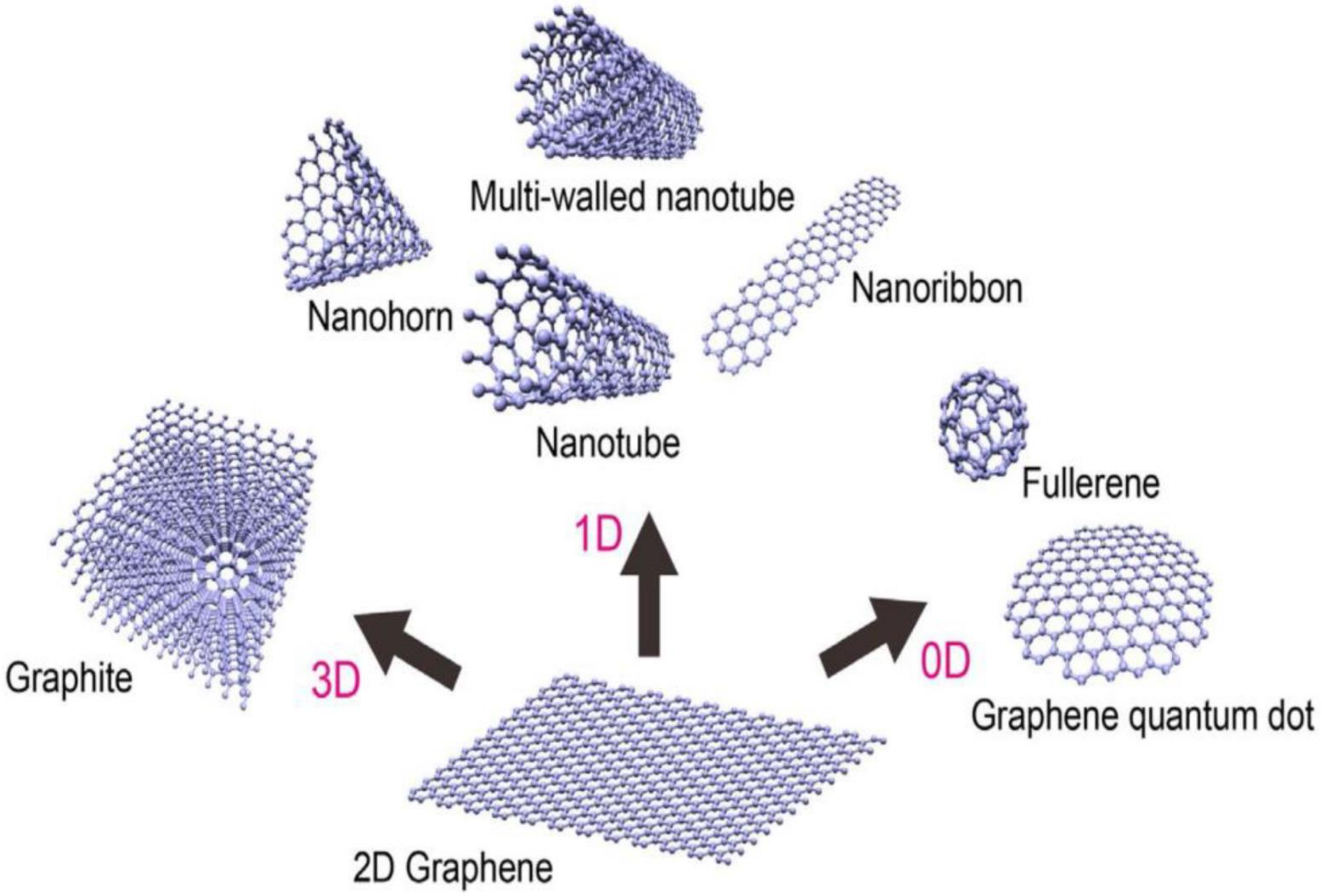
Chemical reactor to synthesize nanoparticles



Carbon based Nanostructures

- Graphene
- Carbon Nanotubes
- Fullerene

Graphene Nanostructures



What is Graphene ?

Graphene is a single layer (monolayer) sheet of carbon atoms that are bonded together in a repeating pattern of hexagons.

This sheet is only one atom thick. Monolayers of graphene stacked on top of each other form graphite.

Since a typical carbon atom has a diameter of about 0.33 nanometers, there are about 3 million layers of graphene in a 1 mm thick sheet of graphite.

Harder than diamond yet more elastic than rubber; tougher than steel yet lighter than aluminum – graphene is the strongest known material.

Properties of Graphene

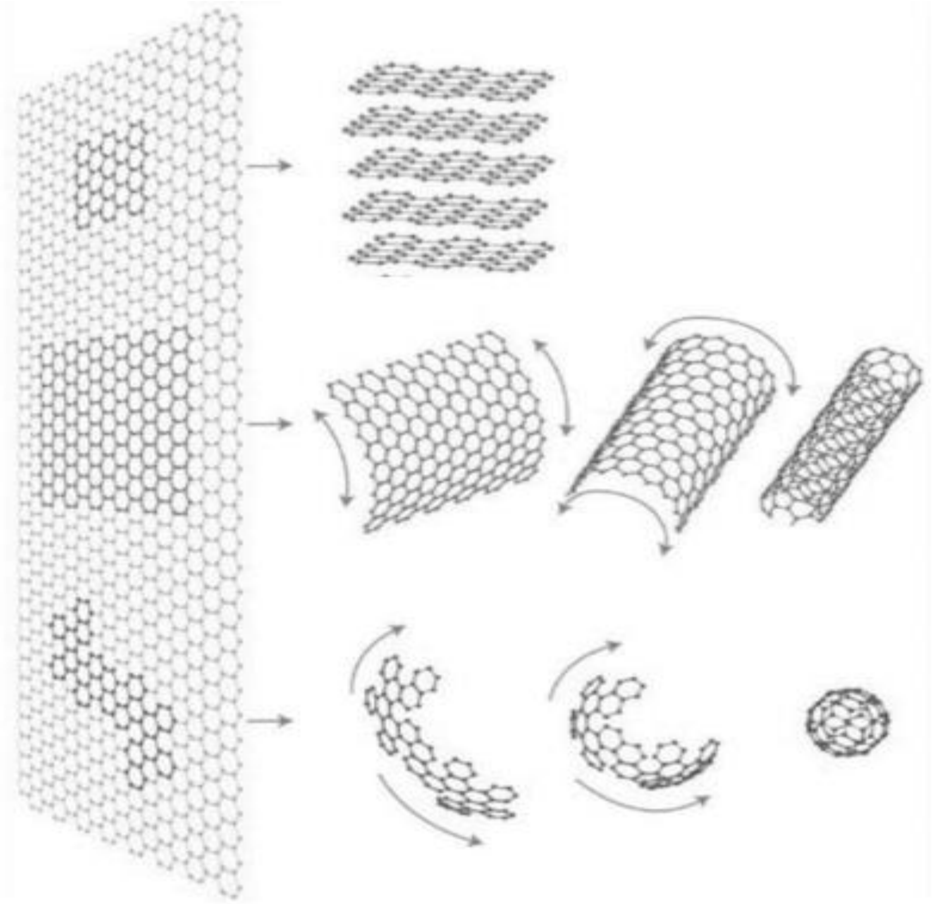
- High thermal conductivity.
- High electrical conductivity.
- High elasticity and flexibility.
- High hardness.
- High resistance.
- Able to generate electricity by exposure to sunlight.
- Transparent material.

Graphene uses and applications

- ❖Energy storage and solar cells
- ❖ biological and chemical sensor
- ❖Graphene membranes
- ❖Biomedical
- ❖Graphene ink
- ❖Transistors and memory
- ❖Flexible, stretchable and foldable electronics
- ❖Photodetectors
- ❖Many more

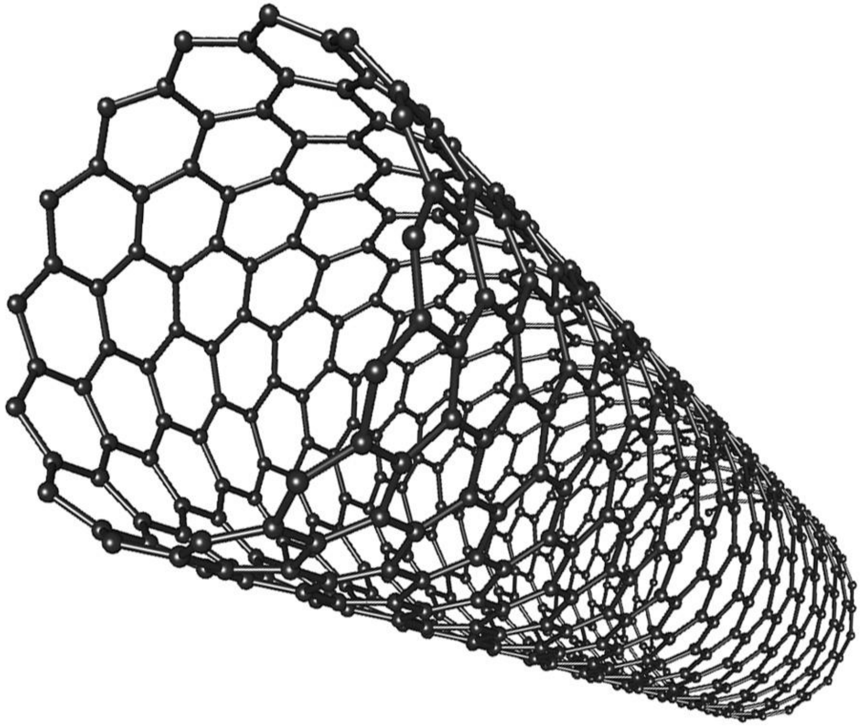
To know more about graphene

https://www.nanowerk.com/what_is_graphene.php#:~:text=Graphene%20has%20emerged%20as%20one,electricity%3B%20it%20is%20optically%20transparent%2C

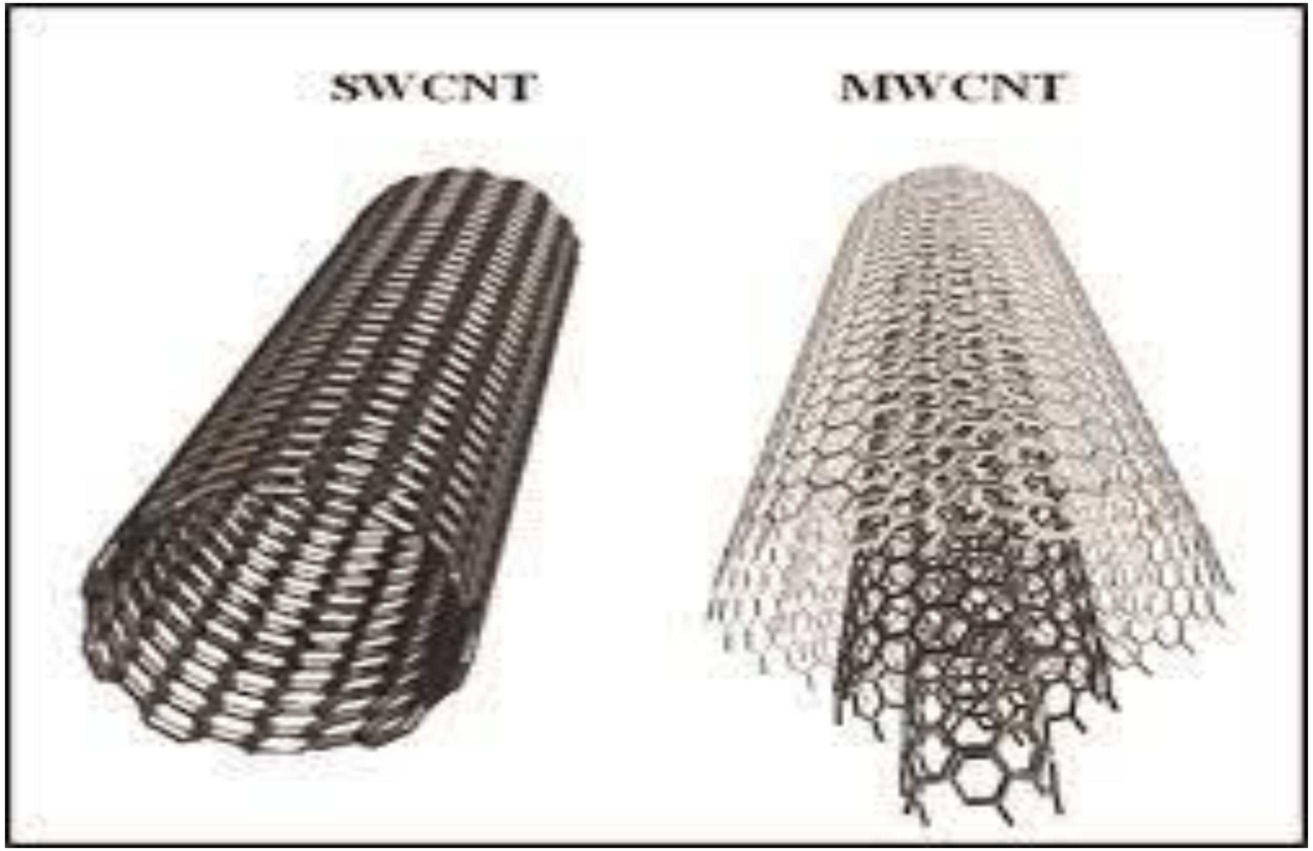


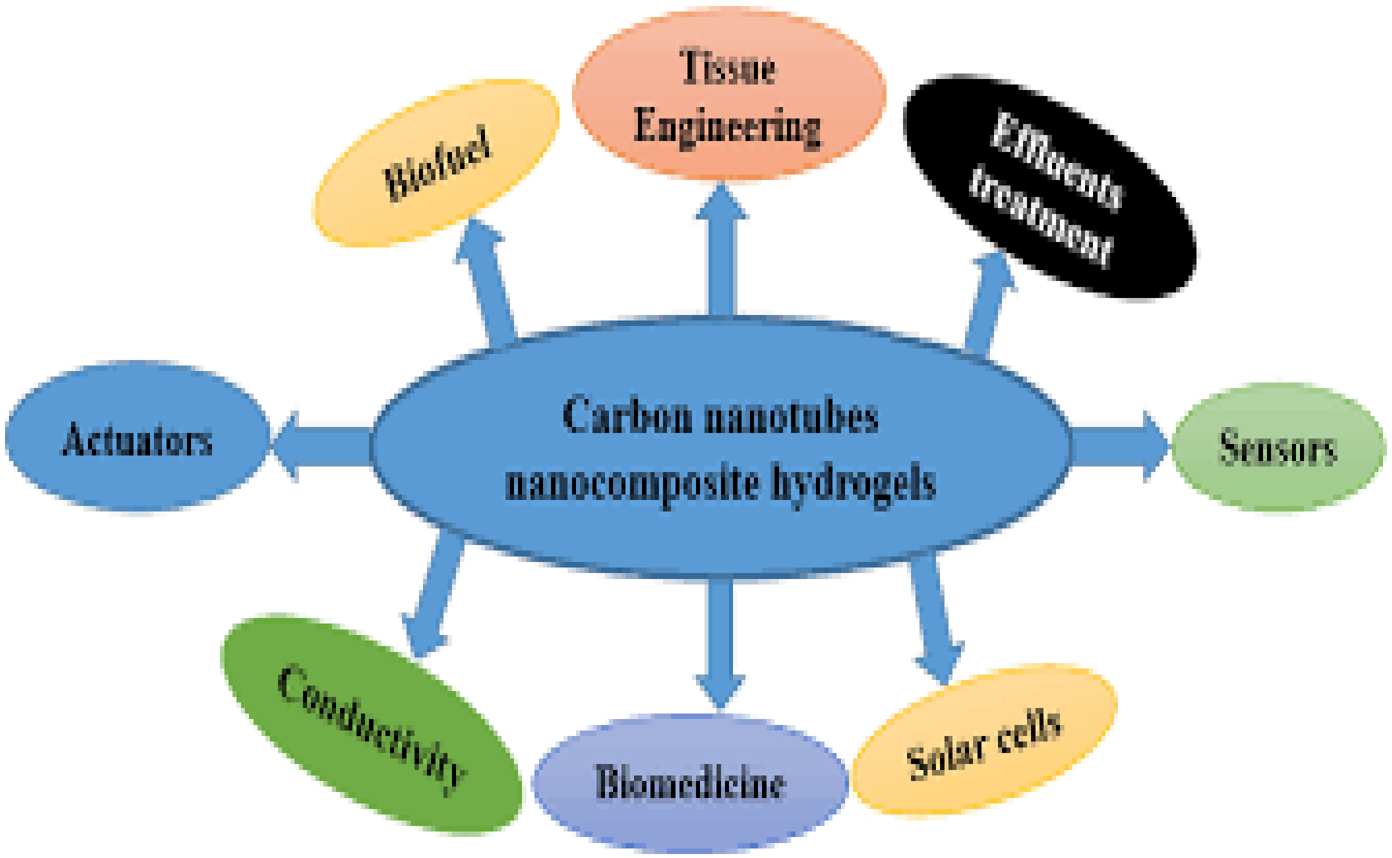
Graphene sheets are building blocks for other graphitic materials: Bonded on top of each other make graphite; rolled up make a **carbon nanotube**; cut and folded into a spherical shape make a **fullerene**.

Carbon Nanotubes

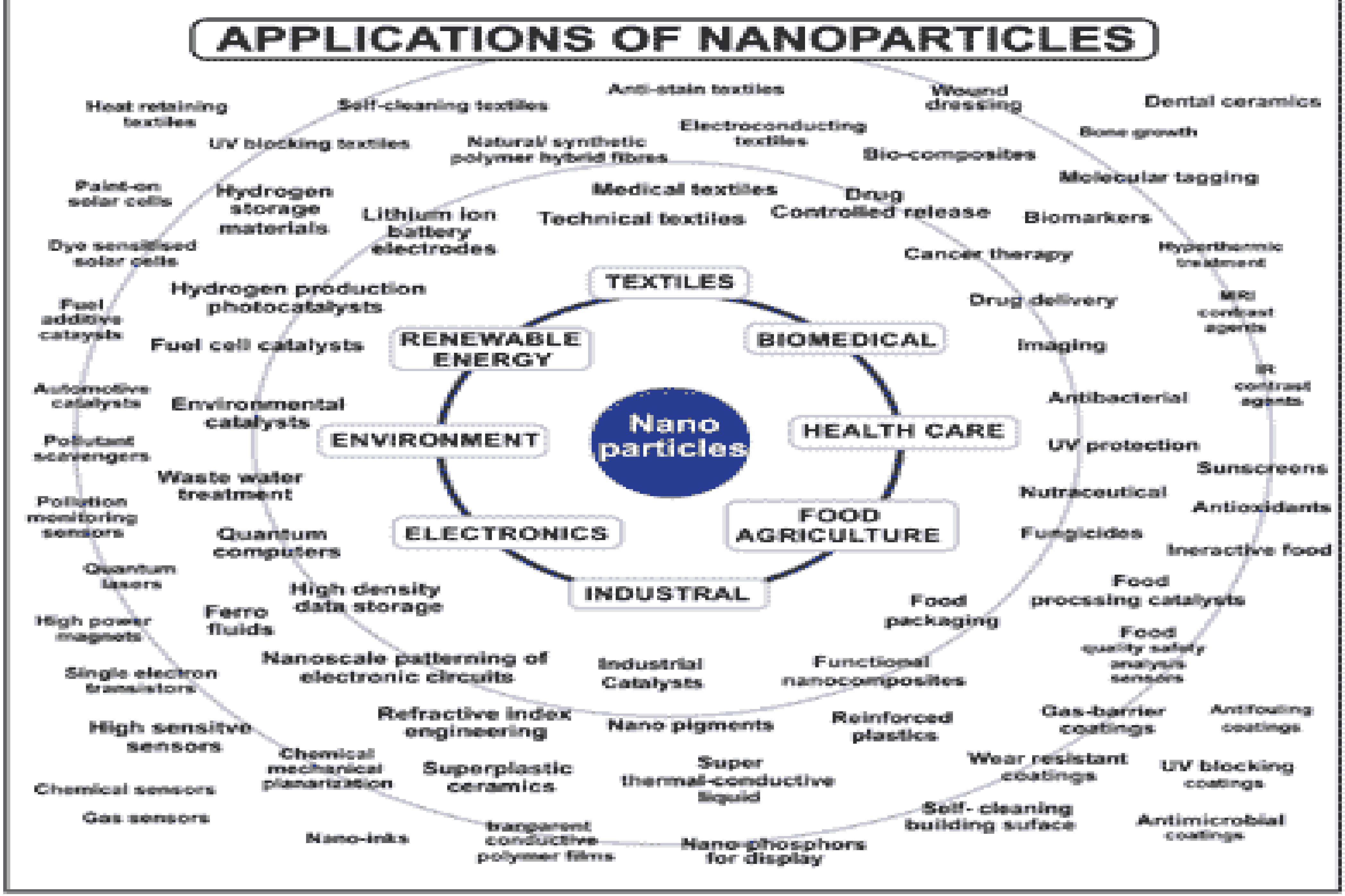


Types of CNT





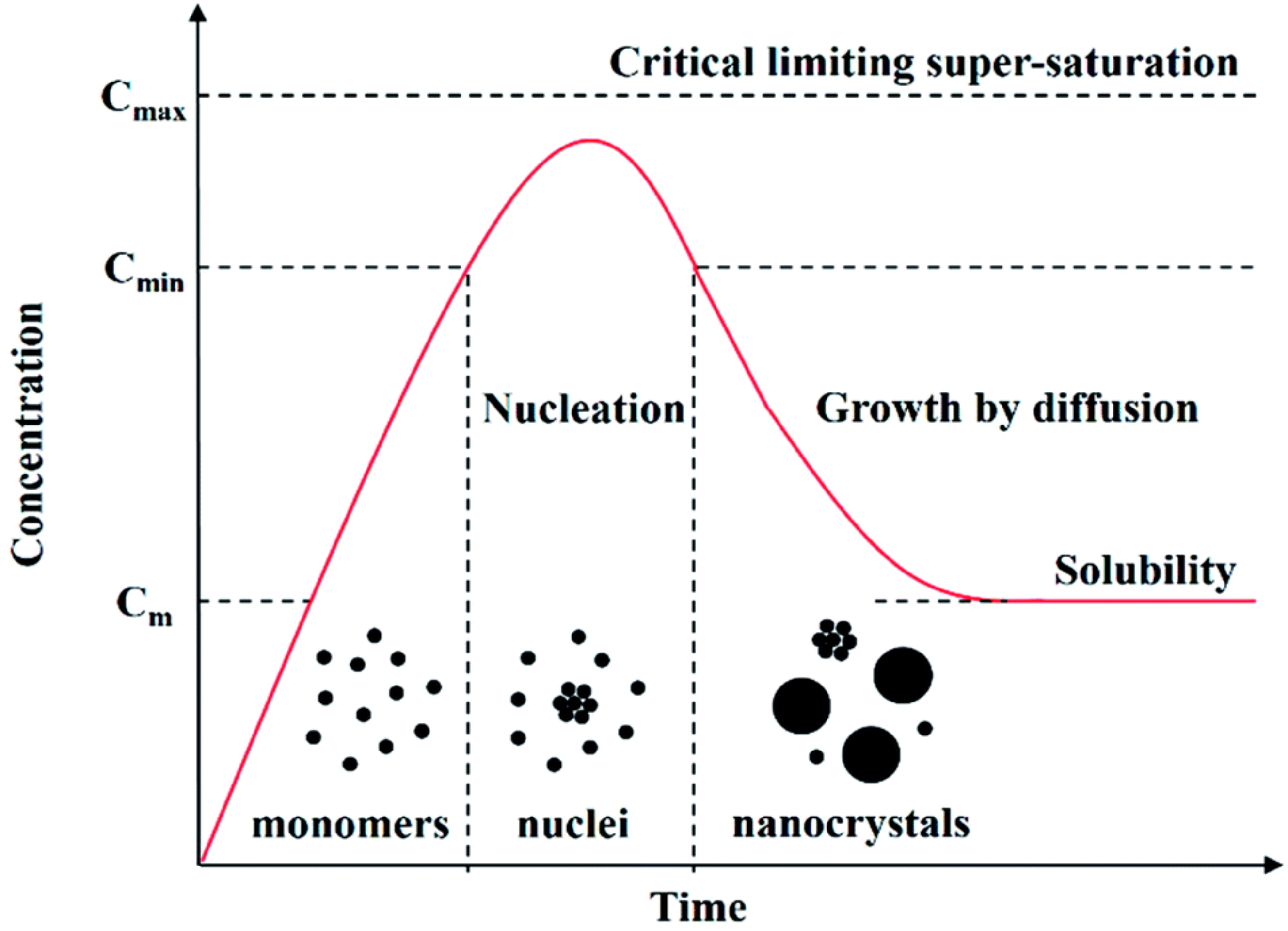
Biofuel
Tissue Engineering
Effluents treatment
Actuators
Carbon nanotubes nanocomposite hydrogels
Sensors
Conductivity
Biomedicine
Solar cells

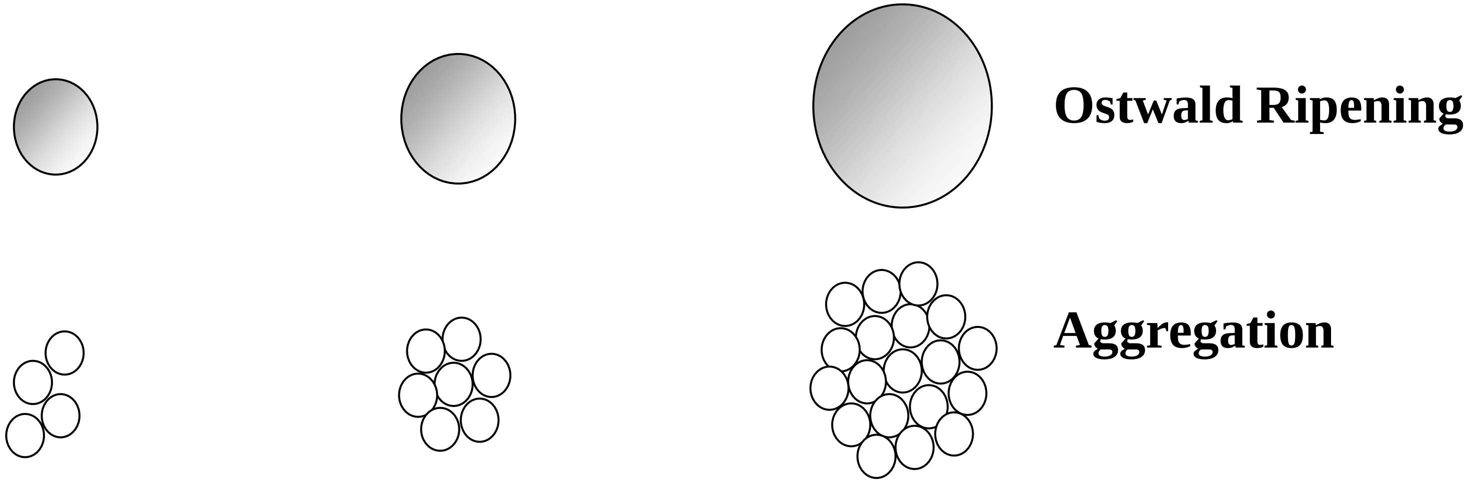

APPLICATIONS OF NANOPARTICLES
Nano particles
TEXTILES
BIOMEDICAL
HEALTH CARE
FOOD AGRICULTURE
INDUSTRIAL
ELECTRONICS
ENVIRONMENT
RENEWABLE ENERGY
Heat retaining textiles
Self-cleaning textiles
Anti-stain textiles
Wound dressing
Dental ceramics
UV blocking textiles
Natural/ synthetic polymer hybrid fibres
Electroconducting textiles
Bone growth
Bio-composites
Molecular tagging
Paint-on solar cells
Hydrogen storage materials
Lithium ion battery electrodes
Medical textiles
Technical textiles
Drug Controlled release
Biomarkers
Dye sensitised solar cells
Cancer therapy
Hyperthermic treatment
Hydrogen production photocatalysts
Drug delivery
MRI contrast agents
Fuel additive catalysts
Fuel cell catalysts
Imaging
IR contrast agents
Automotive catalysts
Environmental catalysts
Antibacterial
Pollutant scavengers
UV protection
Sunscreens
Waste water treatment
Nutraceutical
Antioxidants
Pollution monitoring sensors
Quantum computers
Fungicides
Ineractive food
Quantum lasers
High density data storage
Food processing catalysts
Food packaging
High power magnets
Ferro fluids
Food quality safety analysis sensors
Single electron transistors
Nanoscale patterning of electronic circuits
Industrial Catalysts
Functional nanocomposites
High sensitive sensors
Refractive index engineering
Nano pigments
Reinforced plastics
Gas-barrier coatings
Antifouling coatings
Chemical mechanical planarization
Superplastic ceramics
Super thermal-conductive liquid
Wear resistant coatings
UV blocking coatings
Chemical sensors
Gas sensors
Nano-inks
transparent conductive polymer films
Nano-phosphors for display
Self- cleaning building suface
Antimicrobial coatings

Growth of Nanoparticles

- Nucleation and growth of NPs: LaMer diagram
- Regions I: for saturation
- Region II: nucleation
- Region III: growth

LaMer Diagram

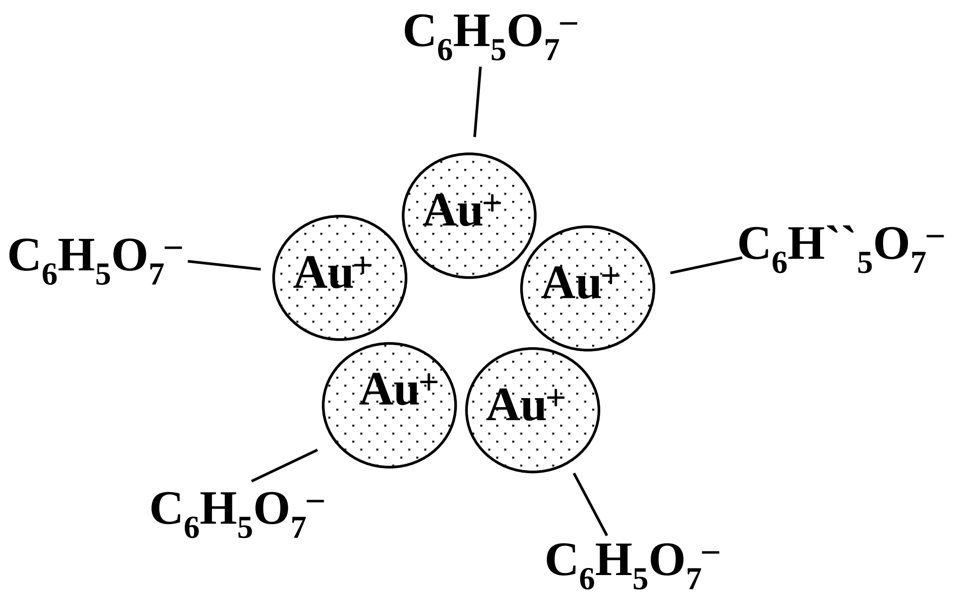



Ostwald Ripening
Aggregation

Synthesis of Metal Nanoparticles by Colloidal Route

- Gold NPs: reduction of gold chloride acid with tri sodium citrate
- Different colors (red, pink or purple): depending on size
- Capping agent or stabilized : columbic repulsion

$$HAuCl_4 + Na_3C_6H_5O_7 \longrightarrow Au^+ + C_6H_5O_7^- + HCl + 3\ NaCl$$


$C_6H_5O_7^-$
$C_6H_5O_7^-$
$C_6H``_5O_7^-$
Au^+
Au^+
Au^+
Au^+
Au^+
$C_6H_5O_7^-$
$C_6H_5O_7^-$