NANOMATERIALS

Geetha Nazareth
Associate Professor
St Aloysius University
Mangaluru

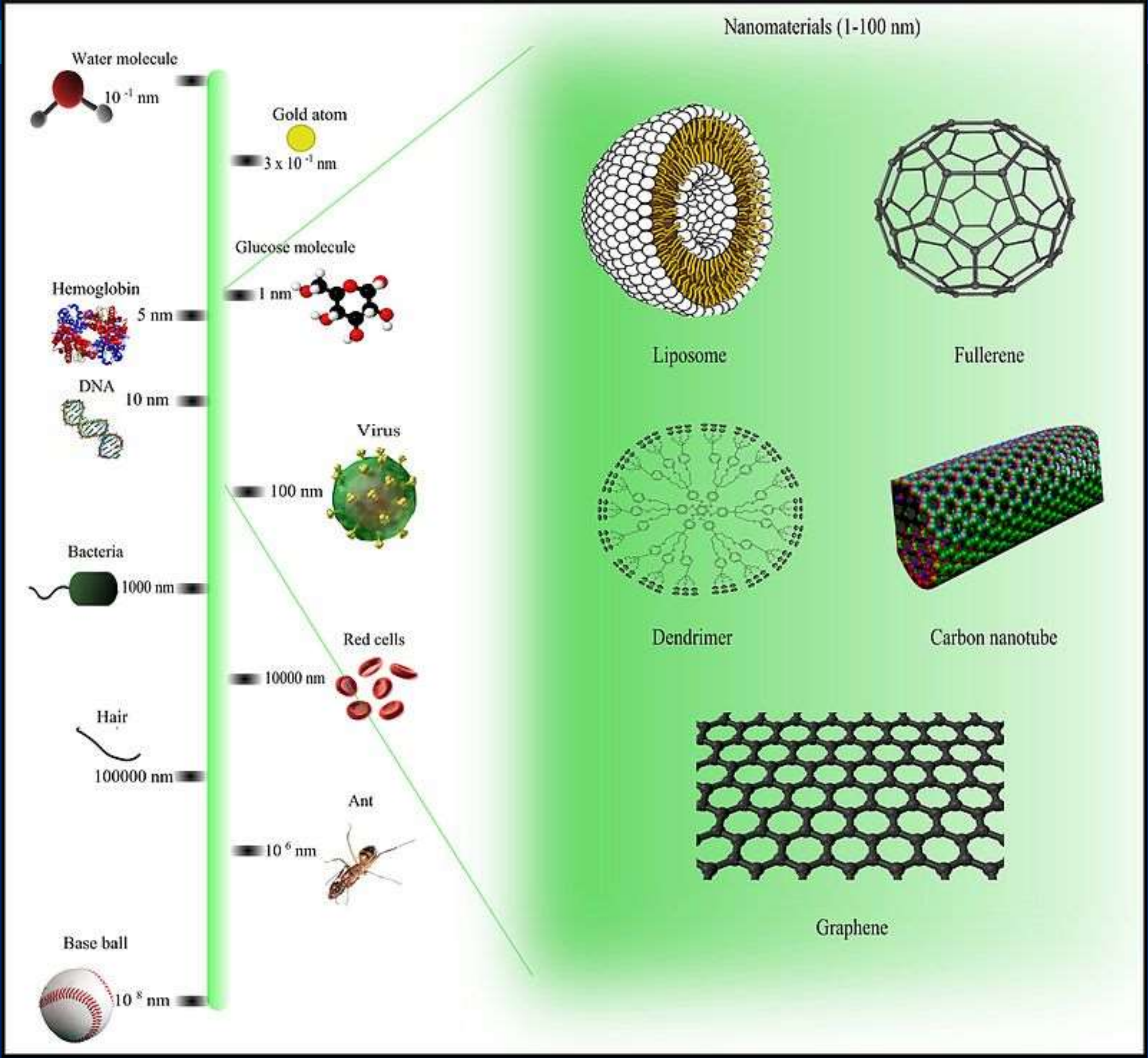
WHAT ARE NANOMATERIALS?

Nanoscience & nanotechnology concerns objects that are very small.

How small?

1 → 100 nanometres

(1 nm = 10^{-9} m)



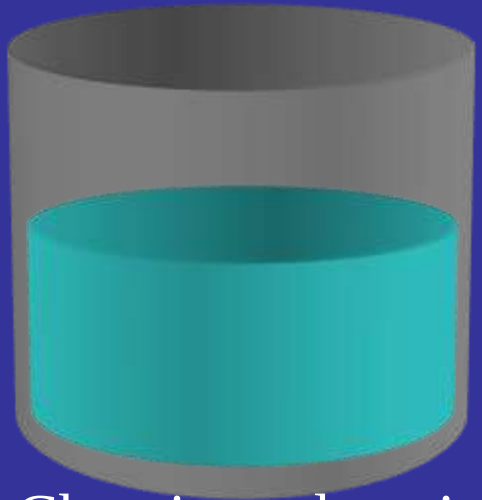
Nanomaterials (1-100 nm)
Water molecule
10^{-1} nm
Gold atom
3×10^{-1} nm
Glucose molecule
1 nm
Hemoglobin
5 nm
DNA
10 nm
Virus
100 nm
Bacteria
1000 nm
Red cells
10000 nm
Hair
100000 nm
Ant
10^{6} nm
Base ball
10^{8} nm
Liposome
Fullerene
Dendrimer
Carbon nanotube
Graphene

NANOCHEMISTRY

Branch of nanosciene which deals with

- Synthesis
- Properties &
- Applications

of nanoparticles



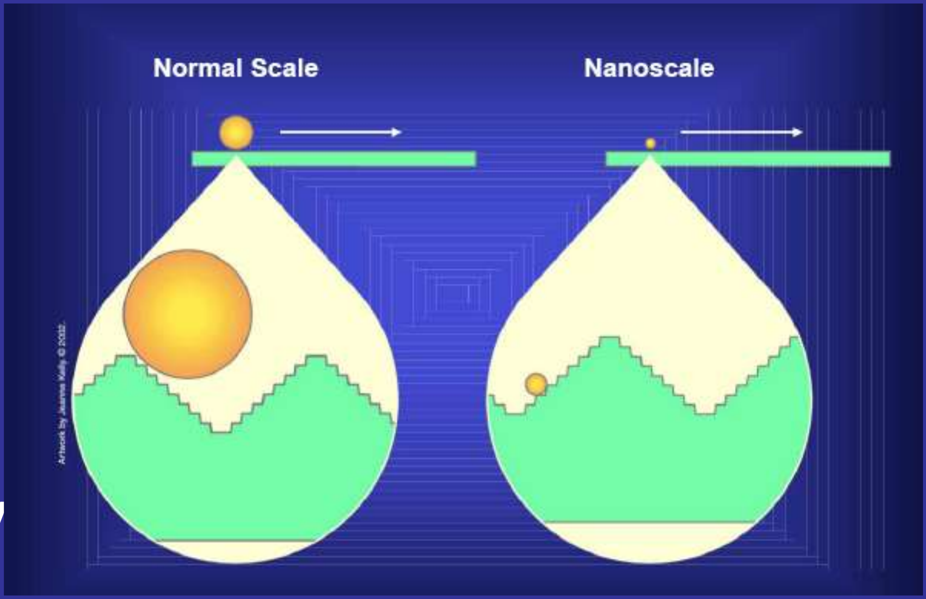
Chemistry done in beakers

Synthetic chemistry employed to make nanoscale building blocks of desired shape, size, composition and surface structure.

Why Nano??????

Nanomaterials have superior properties than a bulk substances

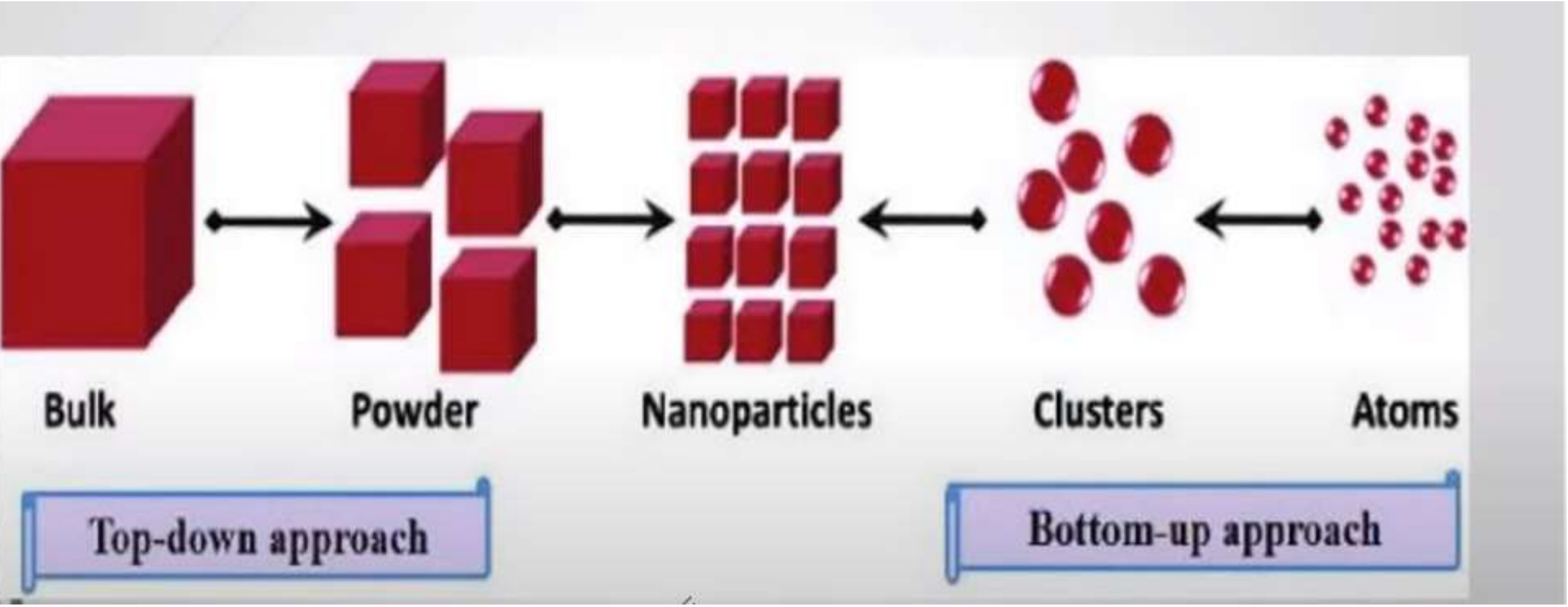
- mechanical strength
- Thermal stability
- Catalytic activity
- Electrical conductivity
- Magnetic properties
- Optical properties



SYNTHETIC APPROACHES

- Top-down - Breaking down matter into more basic building blocks

- Bottom-up – Building complex systems by combining simple atomic level components


Bulk
Powder
Nanoparticles
Clusters
Atoms
Top-down approach
Bottom-up approach

Common synthetic methods

- Mechanical Milling
- Sol-gel method
- Electrodeposition
- Coprecipitation
- Hydrothermal synthesis
- Vapour deposition

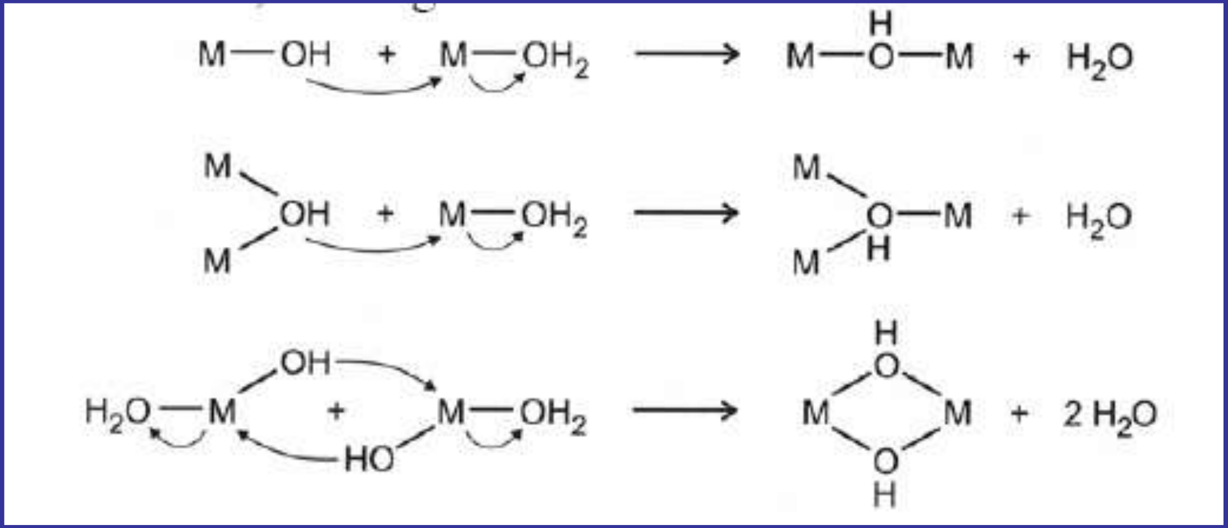
MECHANICAL MILLING (Top down approach)

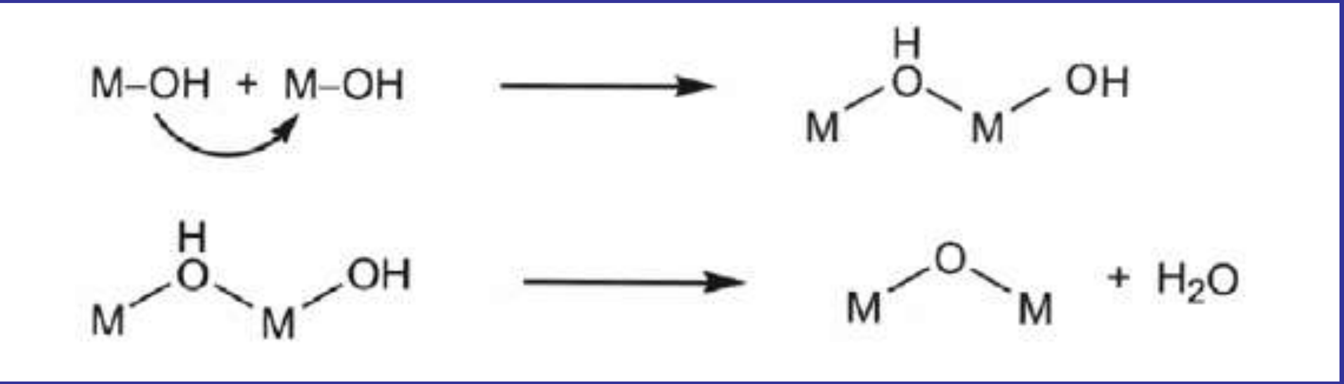
- ❑ Grinding of metal precursors using a volatile solvent (Alcohol, acetone)
- ❑ Mechanical grinding requires grinding the metal precursors with tungsten-carbide (WC) spheres.
- ❑ If required, the product has to be sintered.
- ❑The objective of milling is to reduce the particle size and blending of particles in new phases.
- ❑The energy transfer is governed by many parameters such as the type of mill, the powder supplied to drive the milling chamber, milling speed, size and size distribution of the balls, dry or wet milling, temperature of milling and the duration of milling.

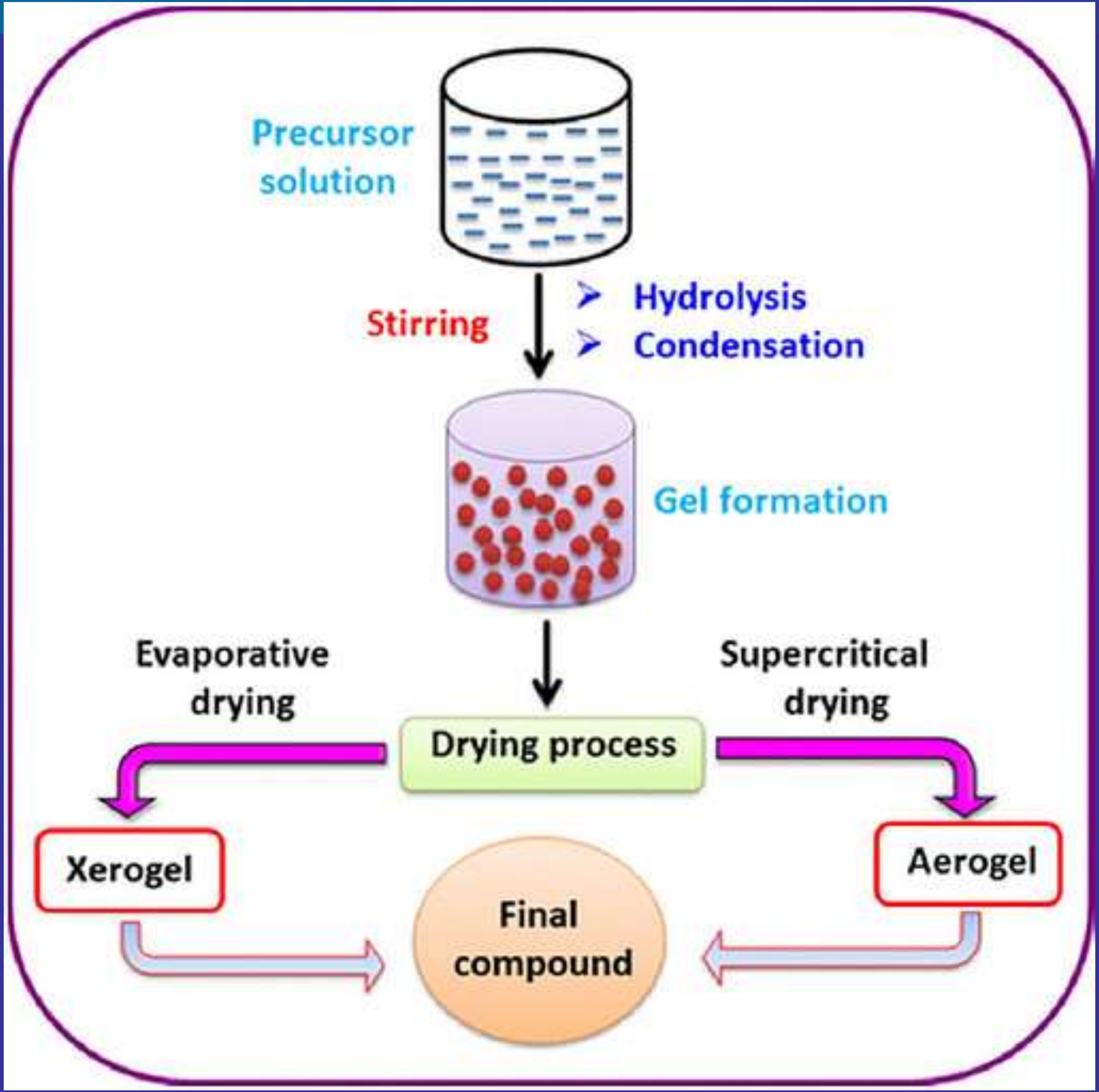
SOL-GEL METHOD

- In sol gel process initially a stable colloidal solution called sol is formed.
- The sol is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron.
- It can be obtained by hydrolysis and partial condensation of precursors such as an inorganic salt or a metal alkoxide.

Hydrolysis and Condensation






Precursor solution
Stirring
Hydrolysis
Condensation
Gel formation
Evaporative drying
Supercritical drying
Drying process
Xerogel
Aerogel
Final compound

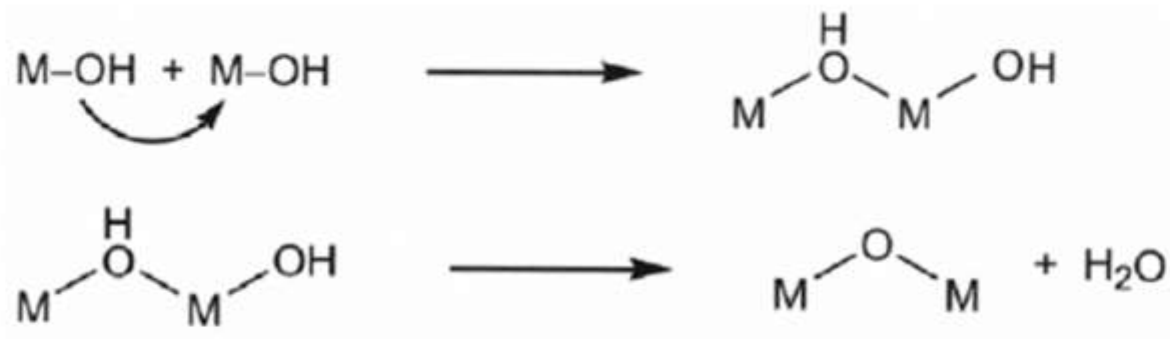
The stages of the Sol-Gel process

1. Hydrolysis of precursor (sol formation):

The precursor is an aqueous solution of the metal alkoxide: M-OR, where R is the alkyl group.

Eg: C_2H_5ONa

The metal alkoxide reacts with the surrounding water and forms the colloidal suspension (sol) of the metal hydroxide, M-OH according to the hydrolysis reaction



2.I

It results in a formation of the Gel - a rigid 3-D network of polymeric molecules surrounded with the solvent.

Reactions involved are

Hydrolysis

$$MOR + H_2O \xrightarrow[\text{TEOS}]{Si(oeT)_4} M\text{-}OH + R\text{-}OH$$

(metal alkoxide) (Tetra ethylortho silicate)

Poly condensation

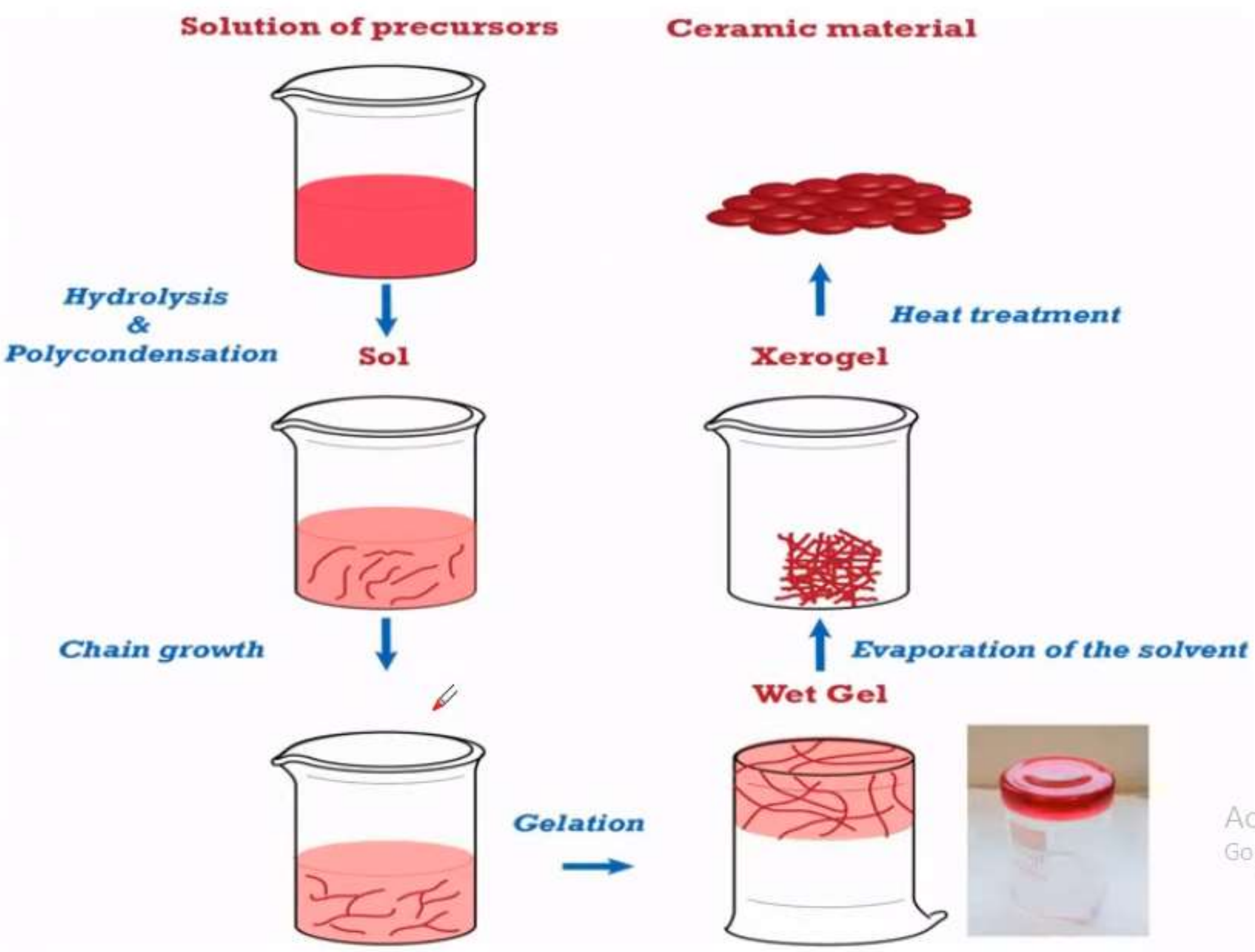
$$MOH + MOR \text{------------>} M_2O + R\text{-}OH$$

$$M\text{-}OH + M\text{-}OH \text{----------------->} M_2O + H_2O$$

3.Aging

During the aging stage the ploycondensation reactions continue completing the formation of the gel.

The gel structure is reinforced with additional cross-links, which cause contraction of the gel matrix and expulsion of the solution from the shrinking pores.


Solution of precursors
Ceramic material
Hydrolysis
&
Polycondensation
Sol
Heat treatment
Xerogel
Chain growth
Evaporation of the solvent
Wet Gel
Gelation

4.Drying

The water and other liquids entrapped within the pores of the gel structure are removed during this stage.Drying is performed at a temperature of about 400ºF (~200ºC).After drying, the gel converts into a high density micro-porous structure called **Xerogel.**

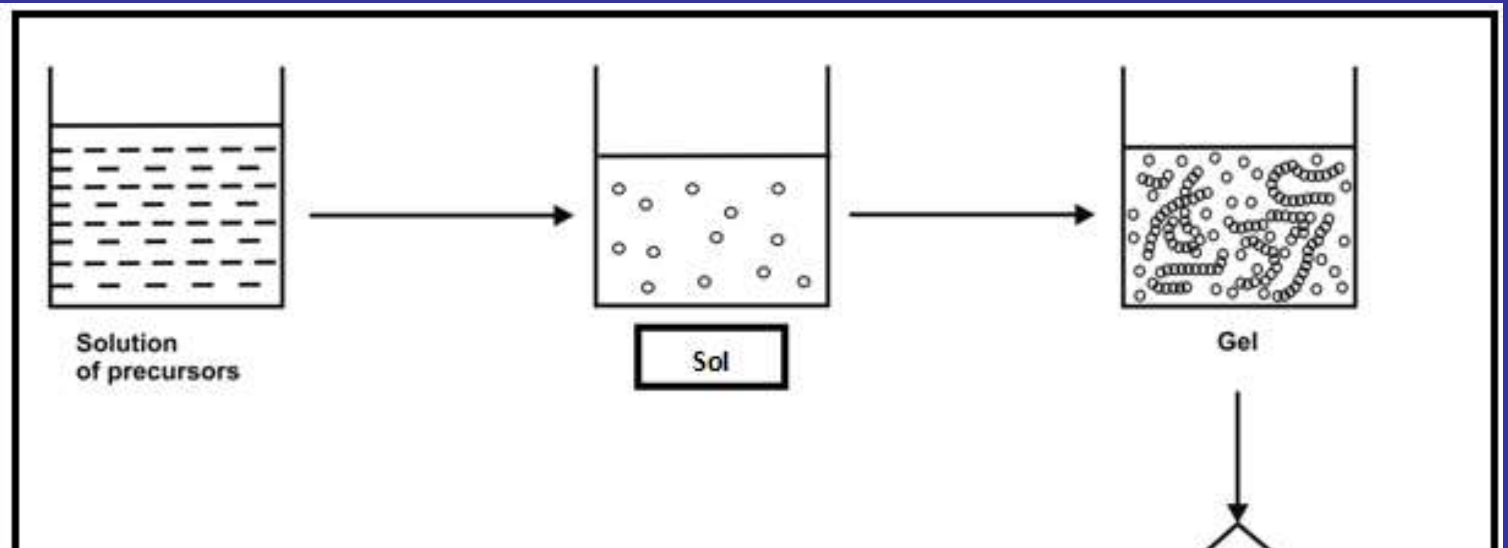
Drying at super-critical conditions(removal of liquid in a precise and controlled way) preventing collapsing of the gel network results in a formation of a macro-porous low density structure called **Aerogel.**

5.Calcination

Calcination is performed at increased temperatures varying within the range 750-1470ºF (400-800ºC).It prevents rehydration of the gel. Calcined gel contains nanosized metal oxide particles.

The Process

$Fe(NO_3)_3$+$HOCH_2CH_2OH$ $\longrightarrow$ Sol Gel $\longrightarrow$ Xerogel $\longrightarrow$ annealed under vacuum $\longrightarrow$ Fe_3O_4



VAPOUR DEPOSITION

1. Synthesis of nanostructures on a substrate material by **converting a solid or liquid precursor into vapor**, then **condensing it into nanoparticles** on a substrate or in a medium.

2. Chemical Vapour Deposition

CVD

- The basic definition of CVD process is "in which thermal decomposition of a hydrocarbon vapor is achieved in the presence of a metal catalyst'. it is also known as thermal CVD or catalytic CVD.

- Watch video on CVD(Nano particles: Synthesis and applications
- https://youtu.be/7z8TQ5Qnd2A?t=51
-

1. Thermal Chemical Vapour Deposition (Thermal CVD)

Principle:

In Thermal CVD, the chemical reaction of gaseous precursors is initiated **purely by heat.** The substrate is heated (usually between **300°C–1200°C**) so that the reactant gases decompose or react to form a solid film on its surface.

Example:

- **Deposition of Silicon (Si):**

$$\mathrm{SiH_4}\ (g) \rightarrow \mathrm{Si}\ (s) + 2\mathrm{H_2}\ (g)$$

  Here, **silane gas (SiH_4)** decomposes at high temperature to deposit a thin film of **silicon** on the substrate.
  This method is widely used in **semiconductor industries** for manufacturing **microchips** and **solar cells.**

Advantages:

- Produces high-quality and uniform films.
- Simple and effective for many materials.

2. Low-Pressure Chemical Vapour Deposition (LPCVD)

Principle:

In **LPCVD**, the process is carried out under **reduced pressure (low pressure)** to improve the uniformity and quality of the film.

Lower pressure reduces unwanted gas-phase reactions and enhances step coverage on complex shapes.

Example:

- **Deposition of Silicon Dioxide (SiO_2):**

  $$\mathrm{SiH_4 + O_2 \rightarrow SiO_2 + 2H_2}$$

  Silane reacts with oxygen at low pressure to form a **SiO_2 film**, commonly used as an **insulating and protective layer** in microelectronics.

Advantages:

- Produces **uniform, high-purity films.**
- Suitable for **large-scale semiconductor manufacturing.**

Hydrothermal method

- Hydrothermal synthesis is a method used to produce nanomaterials through chemical reactions that occur in a high-temperature and high-pressure aqueous (water-based) environment. The term "hydrothermal" refers to the use of water as a solvent, and "synthesis" indicates the creation of new materials through chemical reactions.

- The process typically involves placing precursor materials (chemicals that will react to form the desired nanomaterial) in a sealed container along with water and then subjecting the mixture to elevated temperatures and pressures. The reaction conditions are carefully controlled to induce the formation of nanoscale structures with specific properties.
- This approach has been employed in the synthesis of various nanomaterials, such as metal oxides, semiconductor nanoparticles, and carbon-based nanomaterials.
- https://youtu.be/N_OhrKP3iFo

0.02M $FeCl_3.6H_2O$
Add NaOH drop by drop
to adjust pH at 12 and 14
0.1M NaOH
160° C, 8h
80 mL
FeO(OH) ppt
Annealing 400° C, 2h
Fe_2O_3 at pH 12
Fe_2O_3 at pH 14

ZnO nanoparticles

1. **Prepare precursor solutions (room temperature).**

   a. Dissolve **~2.98 g $Zn(NO_3)_2 \cdot 6H_2O$** in **~50 mL DI water** in a beaker; stir until clear.

   b. In a separate beaker dissolve **~0.80 g NaOH** in **~40–45 mL DI water** (cool if solution warms). If you use a concentrated NaOH stock solution instead, calculate the required volume to reach 0.2 M final.

   c. (Optional) Dissolve the chosen surfactant (e.g., **PVP 0.1 wt%**) in the Zn solution; this helps control particle growth.

2. **Mixing & pH adjustment.**

   Slowly add the NaOH solution to the Zn solution while stirring. Add dropwise over several minutes to avoid local supersaturation/rapid precipitation. Monitor pH — the mixture will become basic (target **pH ≈ 10–11**). A white suspension (precipitate) of zinc hydroxide/oxide precursor should appear.

3. **Transfer to autoclave.**

   Pour the mixed suspension into the Teflon liner of the autoclave. Leave appropriate headspace per autoclave manufacturer instructions (do not overfill).

4. **Hydrothermal treatment.**

   Seal the autoclave and heat it in an oven or furnace to **150°C** and maintain for **12 hours**. Typical ranges: **120–180°C** and **6–24 hours** depending on desired crystallinity/particle size. Heating generates autogenous pressure; follow autoclave safety sp

5. **Cool-down.**

   After reaction time, allow the autoclave to **cool naturally** to room temperature (do not open while hot/pressurized). Once cooled, carefully open and collect the white precipitate.

6. **Washing & separation.**

   a. Centrifuge the suspension (e.g., 6000 rpm, 5–10 min) or filter through vacuum filtration.

   b. Wash the precipitate **3×** with DI water to remove nitrates and Na^+ (check supernatant conductivity or test for nitrate if necessary).

   c. Do one wash with ethanol (optional) to help drying and removal of organics/surfactant.

7. **Drying.**

   Dry the washed powder in an oven at **60–80°C** for **6–12 hours** (or until constant weight).

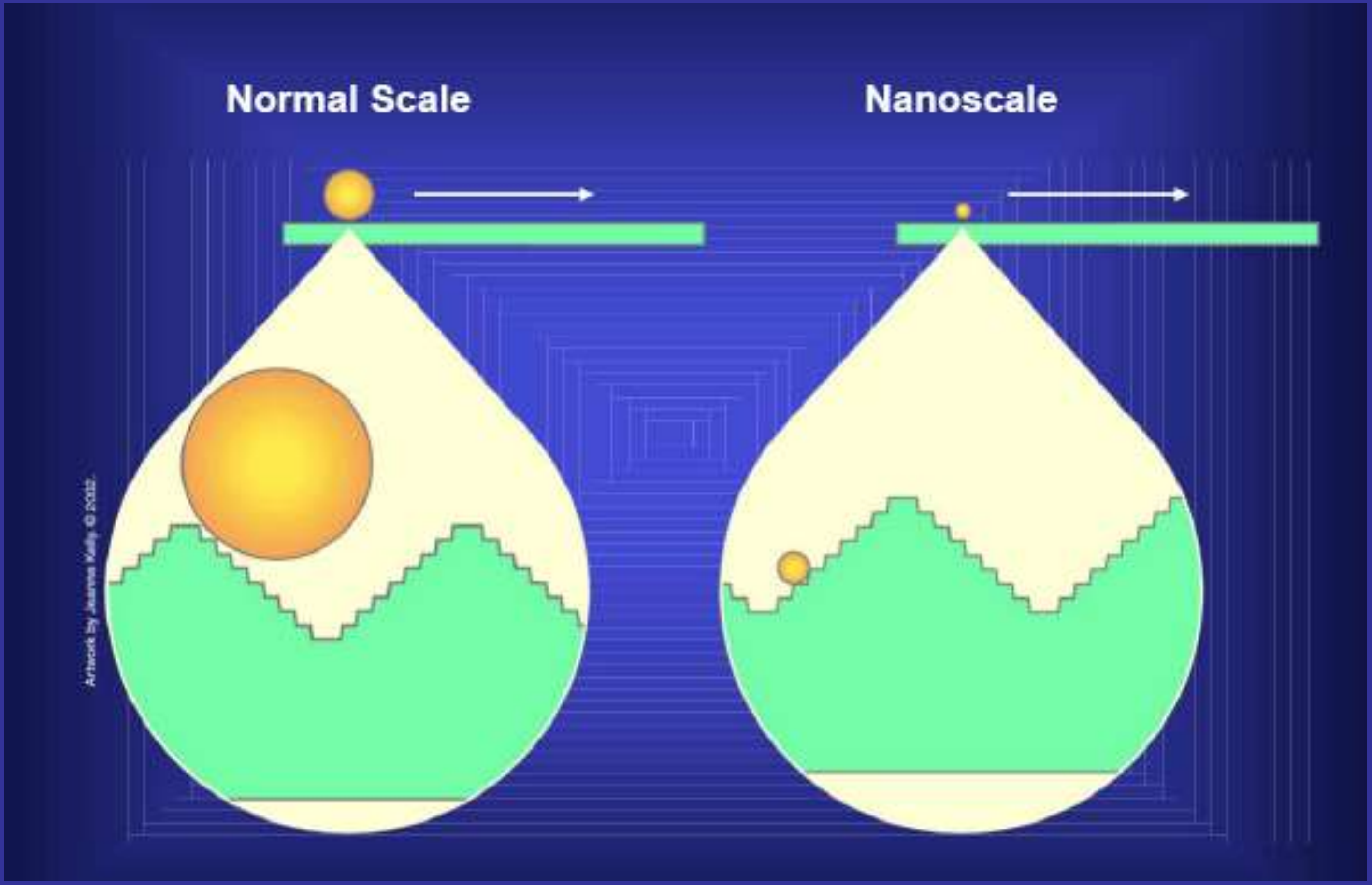
8. **Optional calcination (to improve crystallinity / remove organics).**

   Calcine the dried powder in a muffle furnace at **300–500°C** for **1–3 hours** (ramp 5°C/min). Typical: **400°C, 2 h**. Calcination increases crystallinity and can slightly increase particle size.

PROPERTIES OF NANOMATERIALS

- Mechanical
- Optical
- Electrical

MECHANICAL PROPERTIES

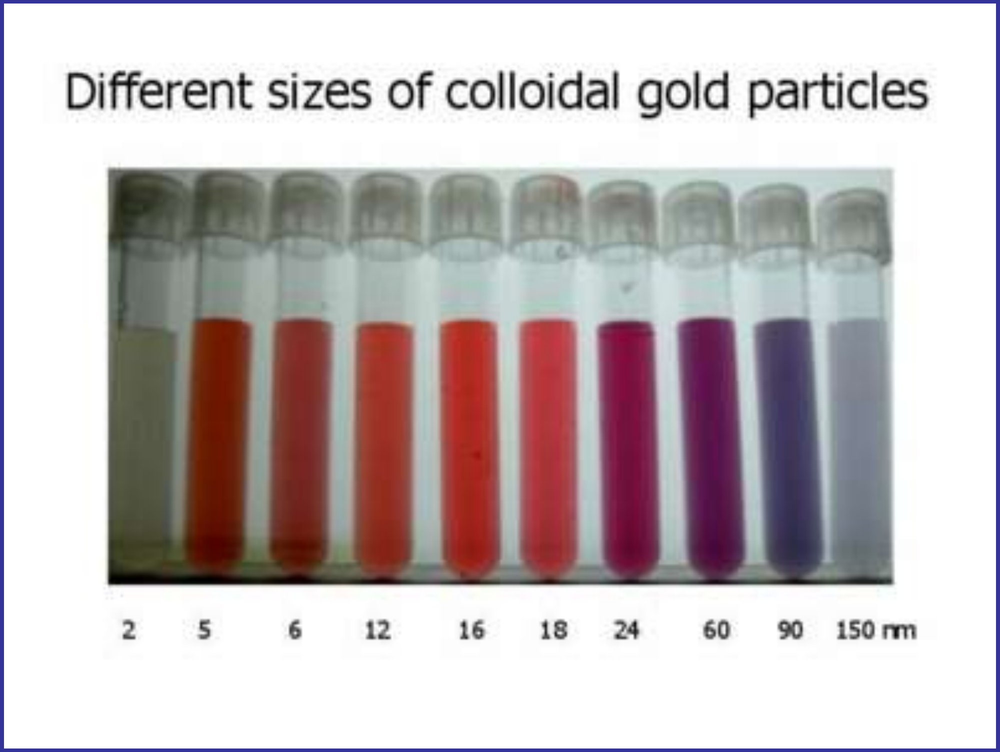


- Mechanical strength of a “body” is the stress required to separate it into “two parts”, with the separation taking place simultaneously across the cross-section.

- Ability of a material to ‘resist’ cracking and once the cracks start appearing, its ability to ‘resist’ further crack propagation.

- Do nanomaterials resist cracking more than bulk?
- YES and NO
- YES if the nanomaterial is perfectly fabricated
- NO if the nanomaterial is not sintered well.
- Surface flaws, inclusions, voids having a very large diameter of 100 nm can lead to ‘fracture-inducing’ flaws leading to micro-cracks.

OPTICAL PROPERTIES



What is the origin of colour? Surface plasmon

OPTICAL PROPERTIES

Metal **nanoparticles** are widely used to construct structures that possess unique electronic, photonic and catalytic **properties** such as local surface plasmon resonance (SPR).

Surface plasmon resonance of metallic **nanoparticles** is one of the reasons of their unique **optical properties**.

Surface Plasmon Resonance

- Surface plasmon resonance (SPR) in nanoparticles is a fascinating phenomenon related to how light interacts with small particles, typically made of metals like gold or silver.

ELECTRONIC PROPERTIES

- Materials which are insulators or semi conductors in their bulk form show good conductivity in their nano form.

- Reason : Surface effects and quantum confinement effects (size-dependent changes in the electronic band structure).

- Nanoparticles have unique electronic properties compared to bulk materials because of their small size and the way their electrons behave.

Quantum Effects Dominate

When nanoparticles become very small (a few nanometers), the electrons in them behave differently due to a phenomenon called **quantum confinement**. This happens because there’s less space for electrons to move around, which changes their energy levels.

- In bulk materials, electrons can have a continuous range of energies.
- In nanoparticles, these energy levels are discrete (like steps instead of a ramp).

Nanocarbon: Types, Preparation, Properties, and Applications

Learning Objectives

- Nanocarbon allotropes
- Synthesis methods
- Properties
- Applications

Introduction to Nanocarbon

Definition: Carbon materials with nanoscale dimensions (1–100 nm)

Examples: Fullerenes, CNTs, Graphene, Nanodiamonds

Importance: Lightweight, strong, conductive, versatile

Carbon Allotropes Overview

Traditional: Graphite, Diamond

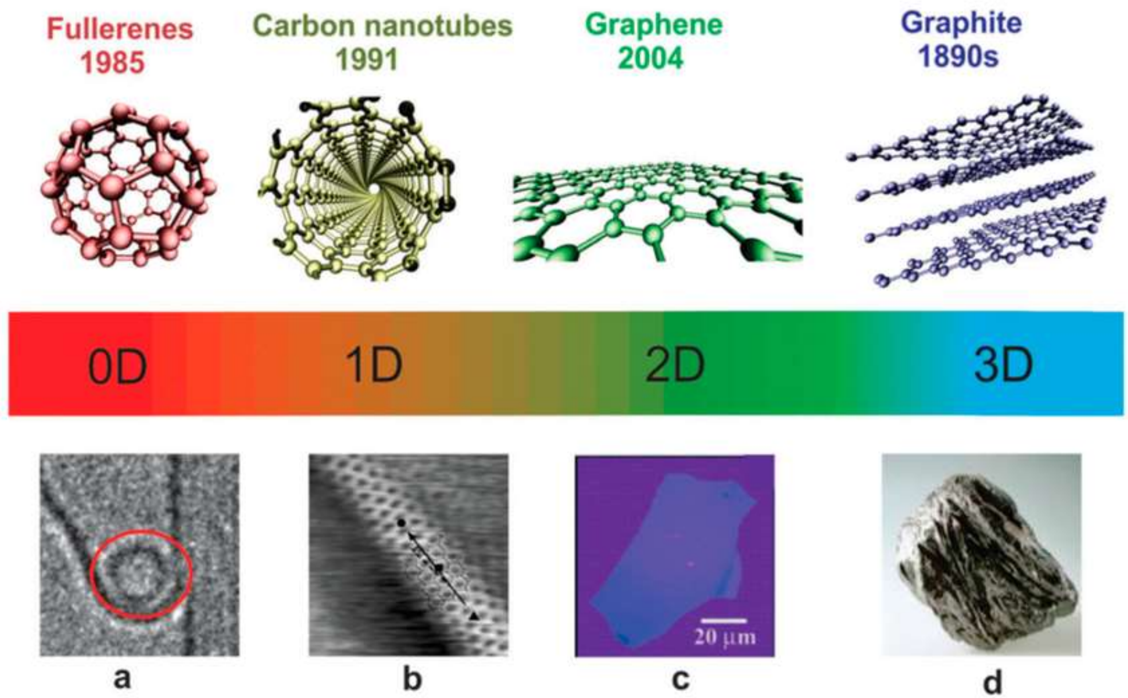
Nanoforms

0D – Fullerenes

1D – CNTs

2D – Graphene

3D – Nanodiamonds

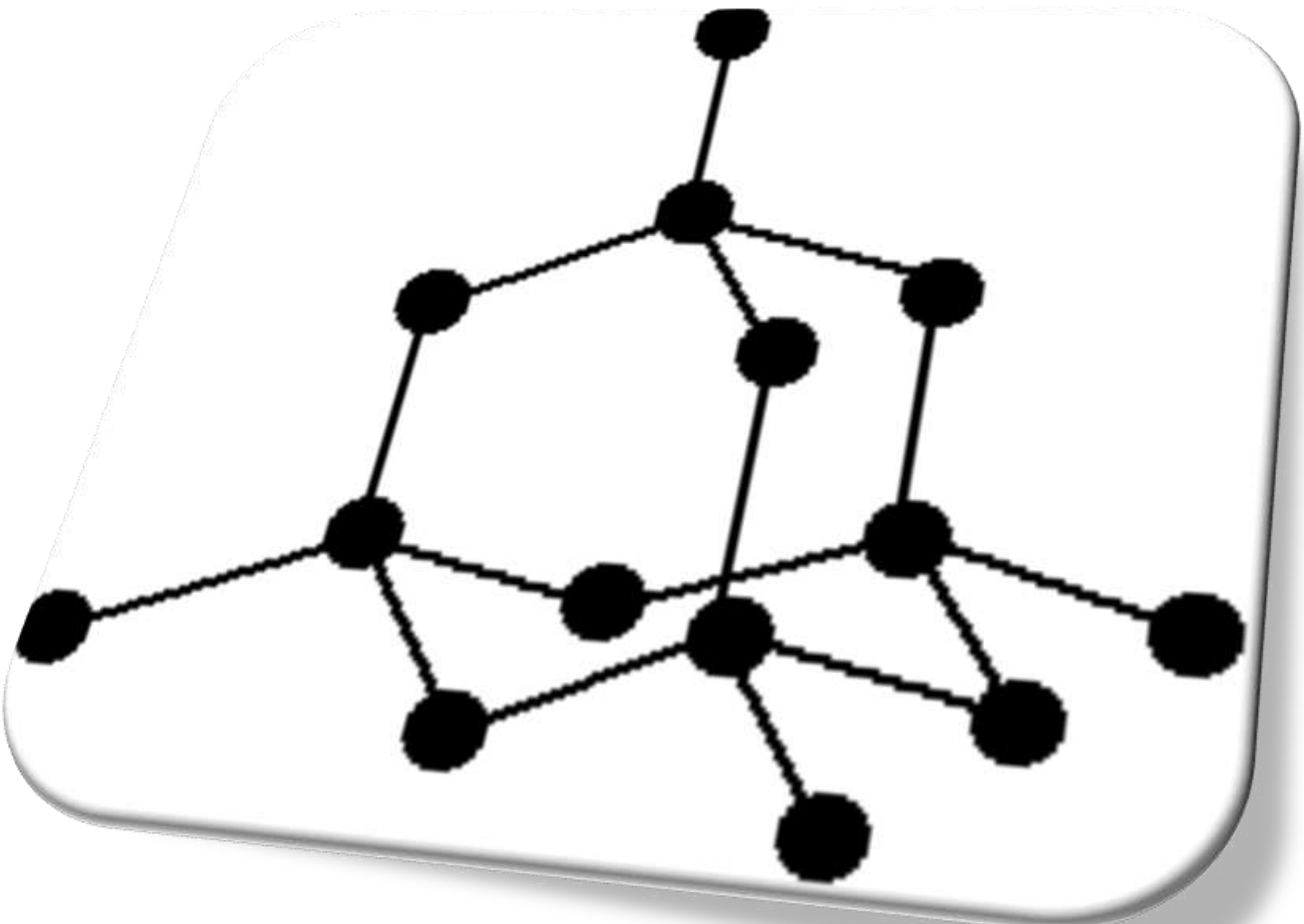


POLYMORPHISM IN CARBON

- 2 MAIN FORMS
- DIAMOND AND GRAPHITE

Structure of DIAMOND

- Electronic configuration of carbon in the ground state
- Electronic configuration of carbon in the excited state
- In diamond, each carbon atom then undergoes sp^3 hybridisation.
- Each hybrid orbital contains one unpaired electron.
- Every carbon atom covalently combines with four more neighbouring carbon atoms resulting in tetrahedral arrangement.
- In the resulting structure each carbon is at the centre of a regular tetrahedron and four more carbon atoms are placed at the corners of the tetrahedron leading to the formation of giant strong and compact crystalline lattice.



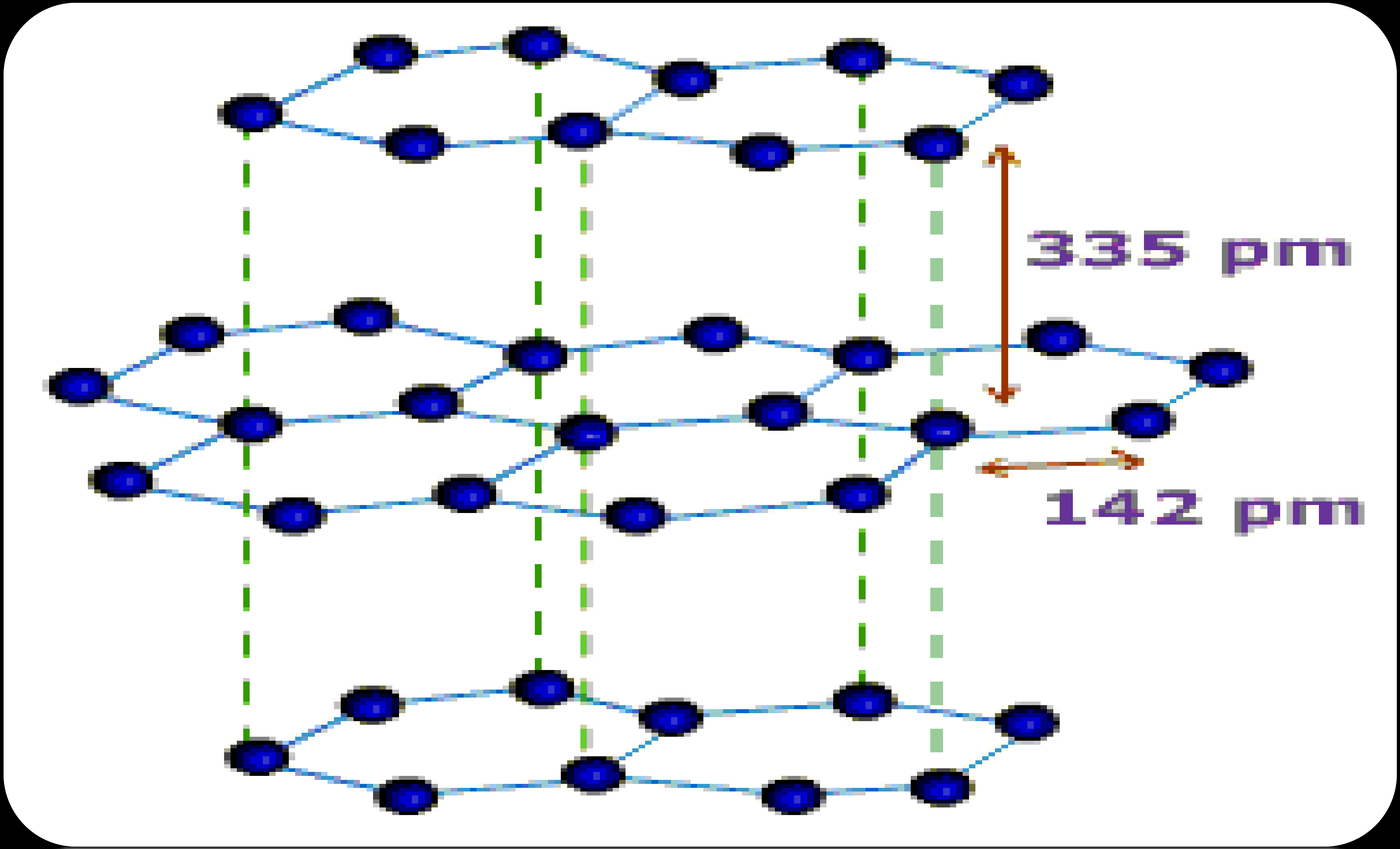
Structure of DIAMOND

Properties of diamond

- **High specific gravity (density)**
  - closely packed rigid crystalline structure with high specific gravity
- **Hardness and melting point :**
  - hard and has high melting point
  - To break diamond a large number of strong covalent bonds are to be broken - requires a large amount of energy.
- **Electrical conductivity and thermal conductivity**
  - All the electrons are localized and used up in bond formation.
  - So no free electrons are available to carry current and hence diamond is an insulator
  - cannot conduct heat.

Structure of GRAPHITE

- Electronic configuration of carbon in the ground state is
- The configuration of carbon in the excited state is
- In graphite each carbon atom undergoes sp^2 hybridisation.
- The three hybrid orbitals containing one unpaired electron each lie on a plane.
- Each carbon atom then covalently combines with three more carbon atoms using hybrid orbitals.
- This gives a plane of carbon atoms containing regular hexagons.
- Graphite contains a number of such planes arranged parallel to one another.
-


335 pm
142 pm

Structure of GRAPHITE

- The planes are bound to one another by weak Van der Waal's forces of attraction
- Each carbon atom contains a unhybridised 2p orbital containing one unpaired electron which lies perpendicular to the plane of hybrid orbitals.
- They form p bonds with the adjacent carbon atoms.
- The electrons hence get delocalized and become free to move about in the entire plane containing the hexagons.

Properties of GRAPHITE

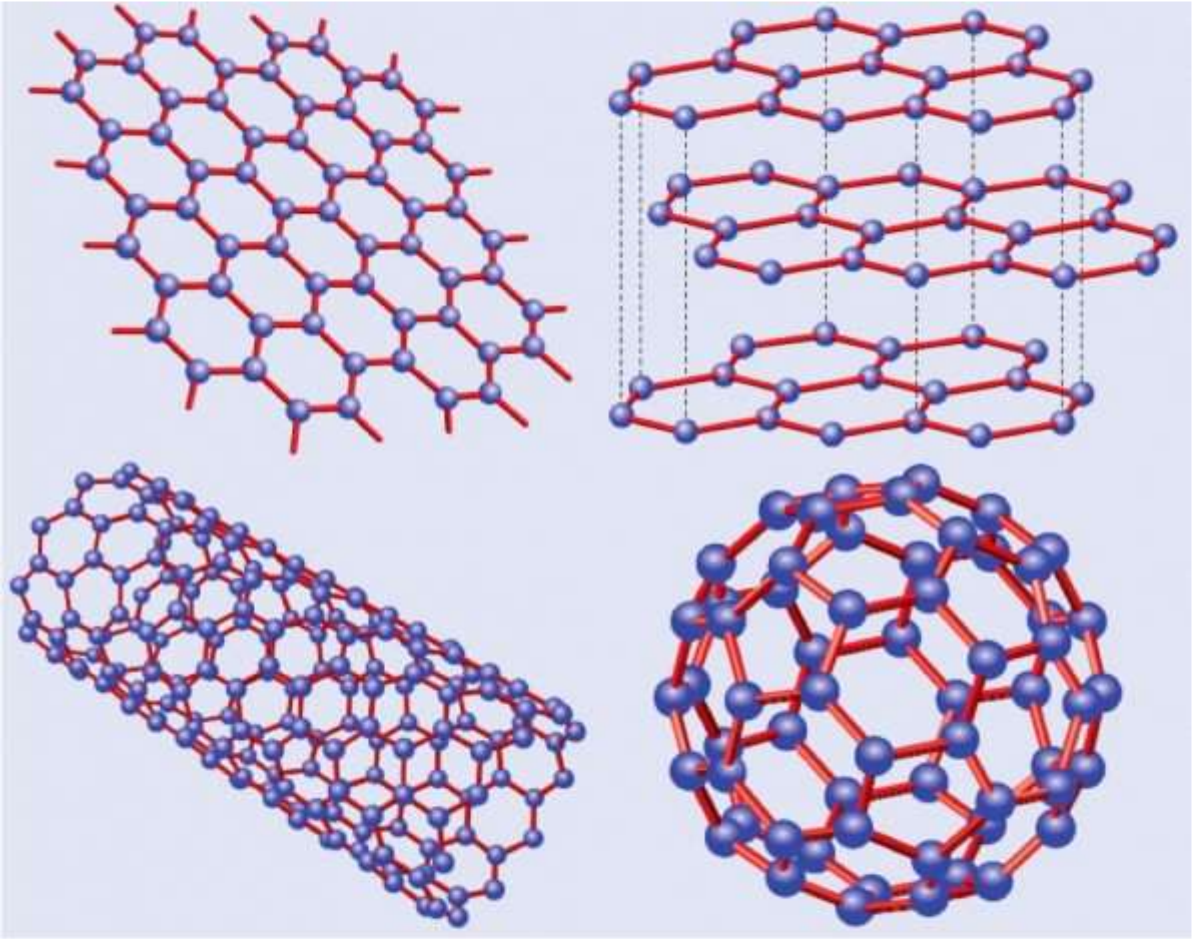
- **Density**
  - Density of graphite is much less compared to that of diamond. Further the density varies from sample to sample
  - Graphite has a layered structure.
  - Large gaps are found between these layers.
  - So graphite does not have a closed packed structure.
  - the interplanar distance is not a constant.
  - Hence density of graphite varies.
- **Hardness**
  - Graphite has a layered structure.
  - Only weak Van der Waal's forces of attraction exist between the planes.
  - the planes easily slide one over the other
  - graphite is soft, greasy to touch and acts as a lubricant.
  - Since the layers can slide, they move on to paper and leave a mark when graphite pencil is used to write on paper.

Properties of GRAPHITE

- **Melting point**
  - Melting point of graphite is high.
  - Graphite lattice consists of several such planes.
  - In every plane each carbon atom is linked to three more carbon atoms by strong covalent bonds,
  - To break this crystal lattice during melting, a large number of covalent bonds in each plane and the vanderwaals interaction between the plane are to be broken.
  - This requires a large amount of energy.
  - Hence melting point of graphite is high.
- **Electrical and thermal conductivity**
  - Graphite is a good conductors of heat and electricity.
  - The p electrons get delocalized over the entire plane - makes graphite a good conductor of electricity

Comparison

Allotrope	Hybridization	Dimensionality	Bond Type	Structure Type
Diamond	sp^3	3D	σ-bonds only	Tetrahedral network
Graphite / Graphene	sp^2	2D (Graphene) / Layered 3D (Graphite)	σ + delocalized π-bonds	Hexagonal layers
CNTs	sp^2	1D (rolled sheet)	σ + delocalized π-bonds	Cylindrical graphene
Fullerenes	sp^2 (with curvature)	0D	σ + π (curved)	Spherical cage



Carbon Nanotubes (CNTs)

- Discovered by Iijima (1991)
- SWCNTs & MWCNTs
- Rolled graphene sheets
- Strong, conductive

Other Nanocarbons

- CQDs, Nanohorns, Nanofibers, Carbon Aerogels

Chemical Vapor Deposition (CVD)

- Hydrocarbon gases decomposed on metal catalyst
- Produces CNTs, graphene
- Scalable and controllable

Pyrolysis & Hydrothermal Methods

- Pyrolysis: organic precursors
- Hydrothermal: aqueous reactions
- Used for CQDs, nanodiamonds

Ball Milling / Sol-Gel

- Mechanical exfoliation
- Used for graphene flakes, amorphous nanoparticles

Mechanical Properties

- Graphene & CNTs: very strong (Young's modulus ~1 TPa)
- Nanodiamonds: extreme hardness

Thermal Properties

- High conductivity (Graphene ~5000 W/m·K)
- Excellent heat dissipation

Optical Properties

- CQDs: fluorescence
- Graphene: broadband absorption

Chemical & Surface Properties

- Reactive surfaces, functionalization improves solubility

Applications in Electronics

- Graphene transistors
- CNT sensors
- Transparent conductors

Energy Storage Applications

- CNT/graphene in Li-ion batteries, supercapacitors, fuel cells

Composites & Structural Uses

- CNT-reinforced polymers/ceramics
- Lightweight materials for aerospace

Biomedical Applications

- Drug delivery (Fullerenes/CNTs)
- Imaging (CQDs)
- Antibacterial coatings

Environmental Applications

- Adsorption of pollutants
- Water purification membranes
- Gas sensors

Challenges & Limitations

- Cost, scalability
- Purity & toxicity
- Functionalization needs

Future Prospects

- Quantum electronics
- Wearable devices
- Green synthesis methods

Applications of Nano Materials

1. Nanotechnology Applications in Medicine

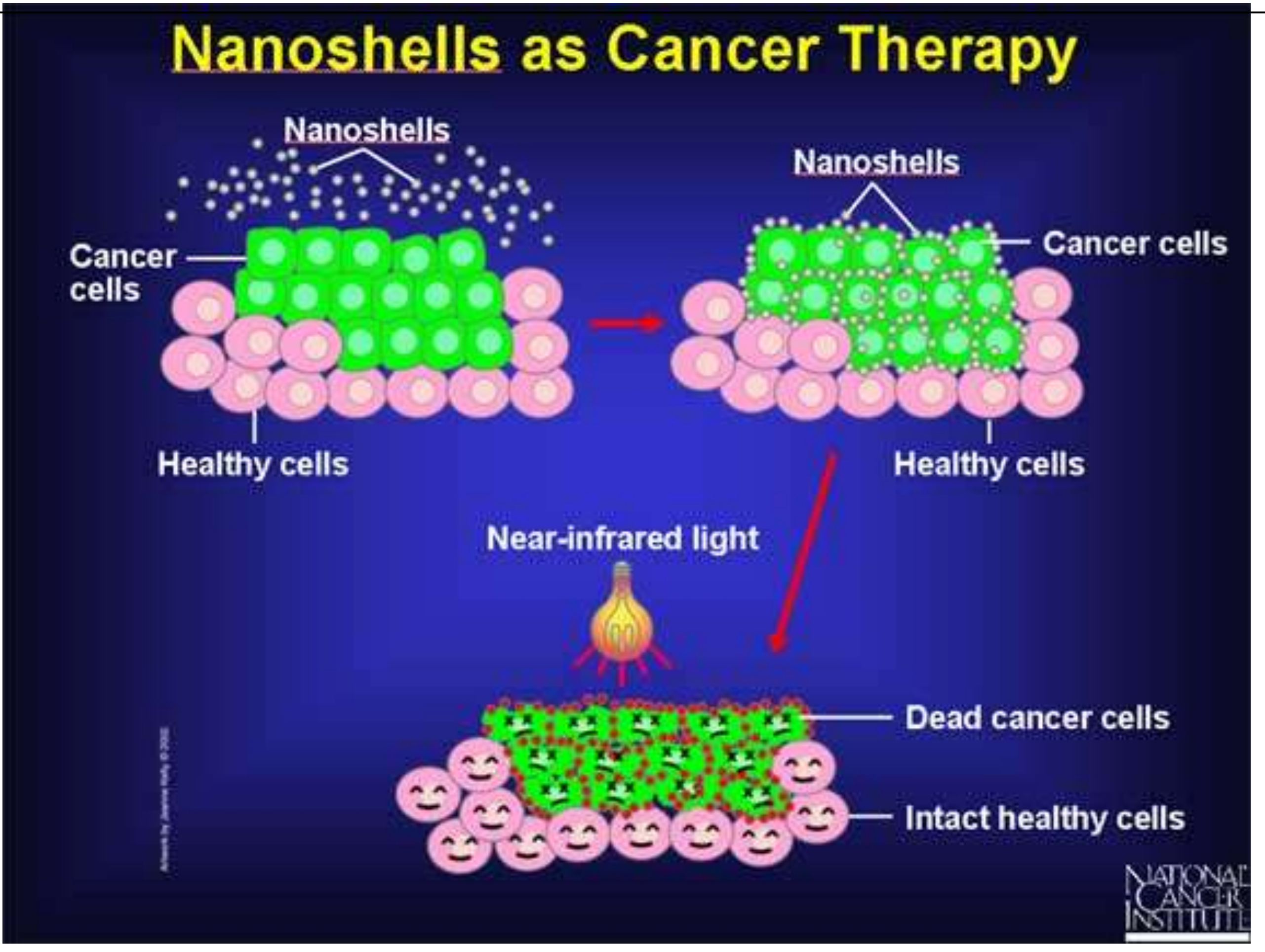
- Because of their small size, nanoscale devices can readily interact with biomolecules on both the surface of cells and inside of cells.
- By gaining access to so many areas of the body, they have the potential to detect disease and the deliver treatment.

- Nanoparticles can deliver drugs directly to diseased cells in your body.
- Nanomedicine is the medical use of molecular-sized particles to deliver drugs, heat, light or other substances to specific cells in the human body.

- **Quantum dot**- that identify the location of cancer cells in the body.
- **Nano Particles** - that deliver chemotherapy drugs directly to cancer cells to minimize damage to healthy cells.
- **Nanoshells** - that concentrate the heat from infrared light to destroy cancer cells with minimal damage to surrounding healthy cells.
- **Nanotubes**- used in broken bones to provide a structure for new bone material to grow.

Nano shells as Cancer Therapy

Nano shells are injected into cancer area and they recognize cancer cells. Then by applying near-infrared light, the heat generated by the light-absorbing Nano shells has successfully killed tumor cells while leaving neighboring cells intact.

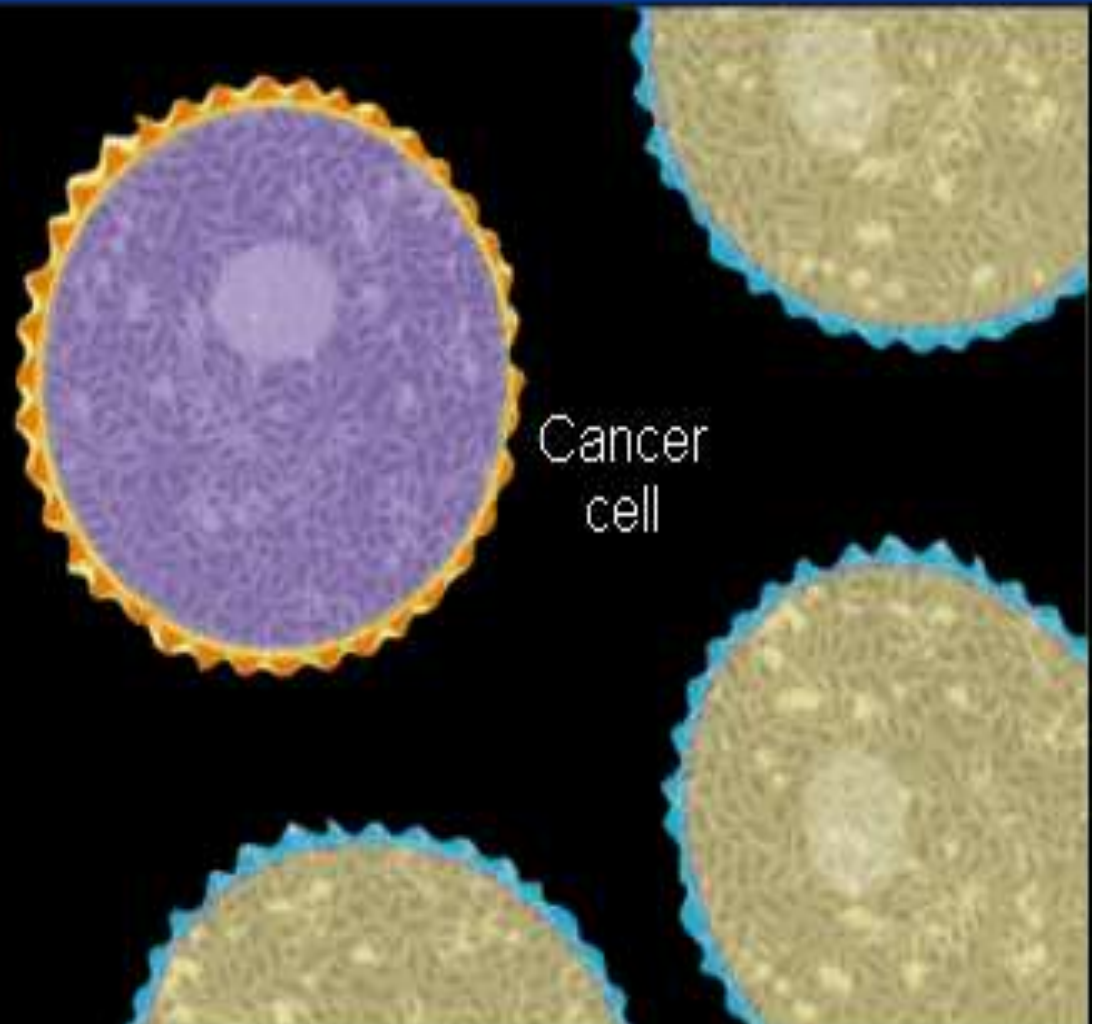


Nanoshells

Nanoshells kill tumor cells selectively

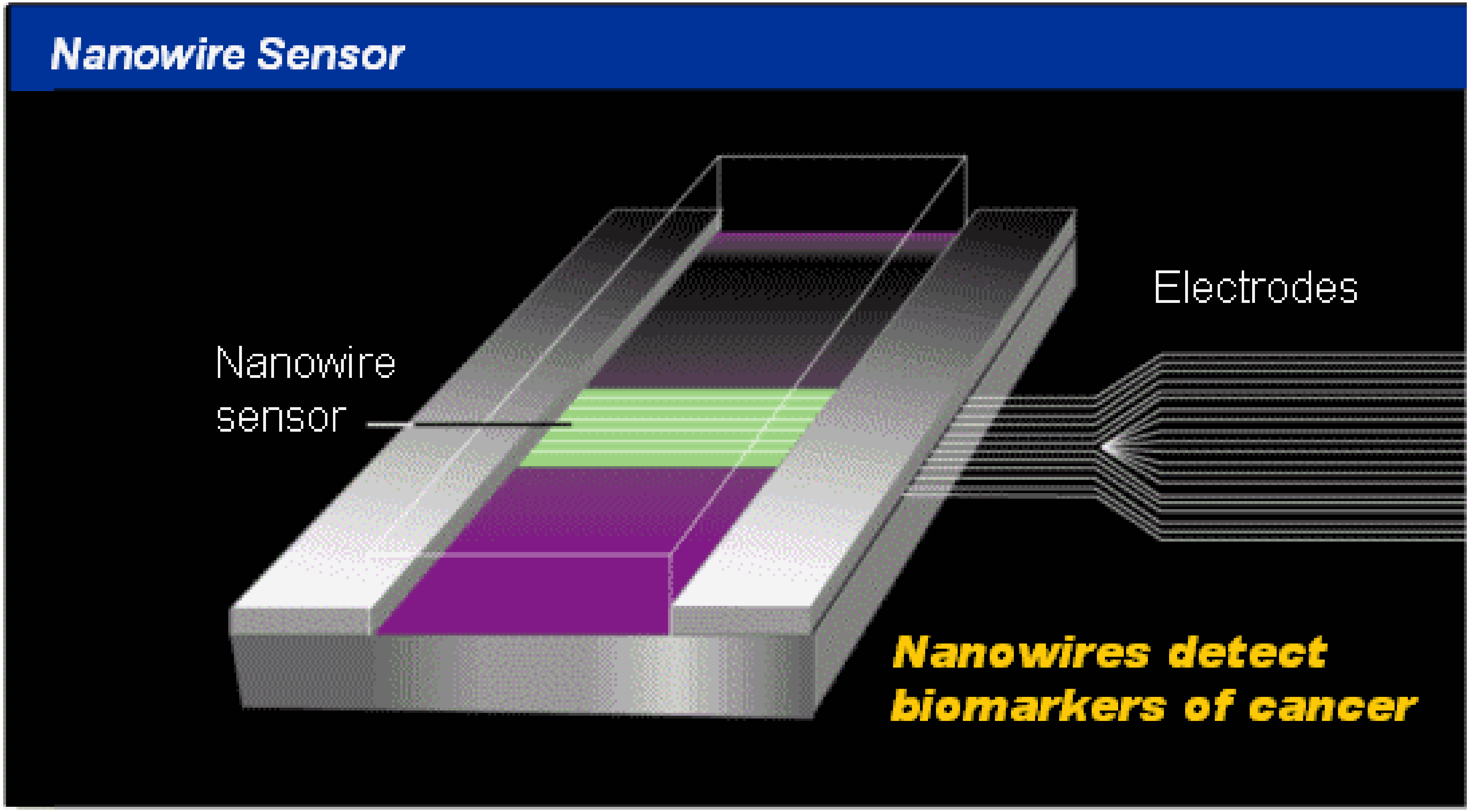
Nanoparticles

Nanoparticles used for molecular imaging of malignant lesions



Nanowires – used as medical sensor

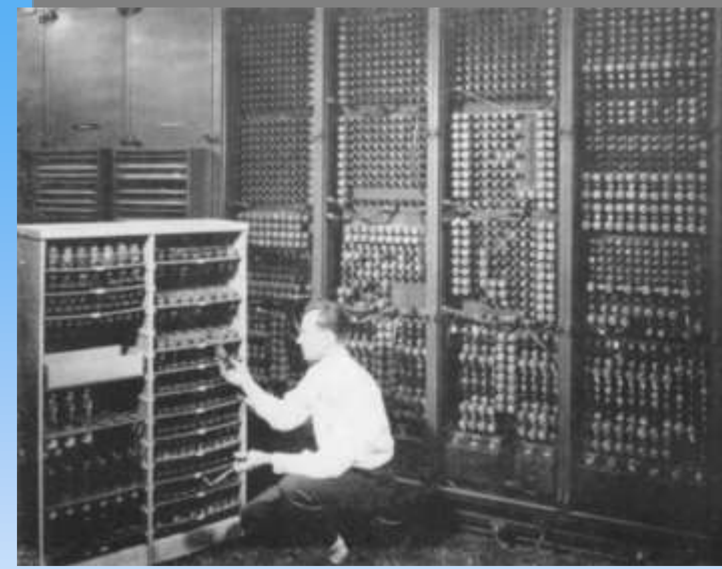
- In this diagram (next page), Nano sized sensing wires are laid down across a micro fluidic channel. As particles flow through the micro fluidic channel, the Nanowire sensors pick up the molecular identifications of these particles and can immediately relay this information through a connection of electrodes to the outside world.
- These Nanodevices are man-made constructs made with **carbon, silicon Nanowire**.
- They can detect the presence of altered genes associated with cancer and may help researchers pinpoint the exact location of those changes


Nanowire Sensor
Electrodes
Nanowire
sensor
Nanowires detect
biomarkers of cancer

2. Nano Computing Technology

<u>Past</u>

Shared computing → thousands of people sharing a mainframe computer



<u>Present</u>

Personal computing

<u>Future</u>

Ubiquitous computing → thousands of computers sharing each and everyone of us; computers embedded in walls, chairs, clothing, light switches, cars….; characterized by the connection of things in the world with computation.

3. Sunscreens and Cosmetics

- Nanosized titanium dioxide and zinc oxide are currently used in some sunscreens, as they absorb and reflect ultraviolet (UV) rays.
- Nanosized iron oxide is present in some lipsticks as a pigment.

4. Fuel Cells

The potential use of nano-engineered membranes to intensify catalytic processes could enable higher-efficiency, small-scale fuel cells.

5. Displays

- Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride are candidates for the next generation of light-emitting phosphors.
- CNTs are being investigated for low voltage field-emission displays; their strength, sharpness, conductivity and inertness make them potentially very efficient and long-lasting emitters.

6. Batteries

- With the growth in portable electronic equipment (mobile phones, navigation devices, laptop computers, remote sensors), there is great demand for lightweight, high-energy density batteries.

- Nanocrystalline materials are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than conventional ones.

- Nickel–metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require less frequent recharging and to last longer because of their large grain boundary (surface) area.

7. Catalysts

In general, nanoparticles have a high surface area, and hence provide higher catalytic activity.

8. Magnetic Nano Materials applications

- It has been shown that magnets made of nanocrystalline yttrium–samarium–cobalt grains possess unusual magnetic properties due to their extremely large grain interface area (high coercivity can be obtained because magnetization flips cannot easily propagate past the grain boundaries).

- This could lead to applications in motors, analytical instruments like magnetic resonance imaging (MRI), used widely in hospitals, and microsensors.

- Nanoscale-fabricated magnetic materials also have applications in data storage.

- Devices such as computer hard disks storage capacity is increased with Magnetic Nano materials

9. Medical Implantation

- Unfortunately, in some cases, the biomedical metal alloys may wear out within the lifetime of the patient. But Nano materials increases the life time of the implant materials.

- Nanocrystalline zirconium oxide (zirconia) is hard, wear resistant, bio-corrosion resistant and bio-compatible.

- It therefore presents an attractive alternative material for implants.

- Nanocrystalline silicon carbide is a candidate material for artificial heart valves primarily because of its low weight, high strength and inertness.

10. Water purification

- Nano-engineered membranes could potentially lead to more energy-efficient water purification processes, notably in desalination process.

THANK YOU