**Nanochemistry** is a branch of chemistry that focuses on the **synthesis, properties, and applications of materials at the nanoscale**—typically between **1 and 100 nanometers**. It combines principles from **chemistry**, **nanoscience**, and **materials science** to design and manipulate matter with atomic- or molecular-level precision.

**Nanomaterials** are materials that have at least one dimension in the **nanometer scale**—typically **between 1 and 100 nanometers (nm)**. To put that in perspective, a nanometer is **one-billionth of a meter** (1 nm = $10^{-9}$ m), which is about 100,000 times smaller than the width of a human hair.

### Key Features of Nanomaterials:

1. **Extremely small size** (1–100 nm)
2. **High surface area-to-volume ratio**
3. **Unique physical, chemical, and biological properties** compared to bulk materials
4. **Size-dependent properties** (e.g., quantum size effects)

### Types of Nanomaterials:

- **Natural**: volcanic ash, clay, and some biological structures
- **Engineered/Synthetic**: quantum dots, carbon nanotubes, Fullerenes, nanowires, Au-nanoparticles, etc.

## Classifications of Nanomaterials:

### A. Based on Dimensionality

Nanomaterials can also be classified based on their **dimensions**, referring to how many dimensions are within the nanometer scale (typically 1–100 nm). This classification highlights the **dimensionality** of the nanostructure and how it affects their physical properties.

### 1. Zero-Dimensional (0D) Nanomaterials

- **All three dimensions** are in the nanoscale.
- No length, width, or height is outside the nanometer range.
- **Examples:**
    - **Au and Ag-Nanoparticles**
    - **Quantum dots**
    - **Fullerenes**

### 2. One-Dimensional (1D) Nanomaterials

- **Two dimensions** are in the nanoscale; **one dimension (length)** is larger.
- Have a long structure like wires or rods.
- **Examples:**
    - **Nanorods**

    - **Nanowires**
    - **Carbon nanotubes**
    - **Nanofibres**

**3. Two-Dimensional (2D) Nanomaterials**

- **One dimension (thickness)** is in the nanoscale; other two (length and width) are larger.
- Sheet-like structure.
- **Examples:**
    - **Graphene**
    - **Nanosheets**
    - **MXenes**

**4. Three-Dimensional (3D) Nanomaterials**

- **All dimensions** are beyond the nanoscale, but composed of nanoscale building blocks.
- Networked or bulk nanostructures.
- **Examples:**
    - **Nanocomposites**
    - **Dendrimers**
    - **Nanostructured foams**

**B. Based on Aspect Ratio:**

Nanomaterials can be classified based on their **aspect ratio**, which is the ratio of their length to their diameter (or thickness). This classification helps to distinguish nanomaterials by their shape and dimensionality:

**1. Isotropic Nanomaterials (Low Aspect Ratio)**

- **Aspect Ratio ≈ 1**
- Nearly equal dimensions in all directions.
- **Examples:**
    - **Nanoparticles** (spherical, cubic, or equiaxed particles)
    - **Quantum dots**
    - **Nanospheres**

*****Quantum Dots:** Semiconductor nanoparticles like CdSe or PbS.

Their **color depends on size** due to the quantum size effect

**2. One-Dimensional Nanomaterials (High Aspect Ratio)**

- **Aspect Ratio >> 1**
- Length is much greater than the other two dimensions.
- **Examples:**
  - **Nanorods**
  - **Nanowires**
  - **Nanotubes** (e.g., carbon nanotubes)
- These materials exhibit unique mechanical, electrical, and optical properties due to their elongated shapes.

**3. Two-Dimensional Nanomaterials (Intermediate Aspect Ratio)**

- **High lateral dimensions**, but **very thin thickness** (aspect ratio in one direction is very small).
- **Examples:**
  - **Nanosheets**
  - **Graphene**

## Applications of Nanomaterials:

- **Medicine**: drug delivery, cancer treatment
- **Electronics**: nanoscale transistors, memory chips
- **Energy**: solar cells, batteries
- **Environment**: water purification, pollution control
- **Cosmetics**: sunscreens, anti-aging product
- **Heat Transfer**

## Quantum Size Effect:

The **quantum size effect** refers to the change in the physical and electronic properties of materials when their size is reduced to the **nanoscale**, particularly below about **10 nm**. At this scale, the behavior of electrons becomes **quantized** due to confinement in very small spaces.

□ **Example:**

- .
  - **Smaller dots → larger band gap → blue shift**
  - **Larger dots → smaller band gap → red shift**

## Surface Area to Volume Ratio:

The **surface area-to-volume ratio (SA:V)** is calculated by dividing the **surface area (SA)** of an object by its **volume (V)**.

This ratio is especially important for nanomaterials because **as size decreases, SA/V ratio increases significantly**, leading to enhanced reactivity and unique properties.

**SA to Volume ration for Common Shapes:**

### *1. Sphere*

- Surface Area: $SA=4\pi r^2$
- Volume: $V=4/3\ \pi r^3$
- SA:V Ratio: $4\pi r^2/4/3\ \pi r^3=3/r$

As radius **decreases**, SA/V ratio **increases** dramatically.

### *2. Cube*

- Surface Area: $SA=6a^2$
- Volume: $V=a^3$
- SA:V Ratio: $6a^2/a^3=6/a$

**Why It Matters for Nanomaterials?**

- High SA/V ratio → More surface atoms → Higher reactivity
- This is critical in **catalysis, drug delivery, sensors, and energy storage**

## Synthesis of Nanomaterials:

The **synthetic routes of nanomaterials** are generally categorized into two main approaches:

**1. Top-Down Approach**

This method starts from **bulk materials** and breaks them down into nanosized structures using physical or mechanical means.

□ **Common Top-Down Techniques:**

| Method | Description | Examples |
|---|---|---|
| **Mechanical Milling** | Grinding bulk material into nanoscale powder | Ball milling |

| Method | Description | Examples |
|---|---|---|
| **Lithography** | Etching nanoscale patterns on surfaces | Electron-beam, photolithography |
| **Laser Ablation** | Using laser pulses to vaporize material into nanoparticles | Nanoparticle generation in gas |
| **Etching** | Chemically or physically removing layers from surfaces | Reactive ion etching |

**Limitations of Top-down Approach:**

1. Time consuming process
2. Difficult to get uniform sized and shaped nanomaterials
3. Introduces defects in the Nanomaterials

### 2. Bottom-Up Approach

This method **builds nanomaterials atom-by-atom or molecule-by-molecule**, often through chemical or biological reactions.

□ **Common Bottom-Up Techniques:**

| Method | Description | Examples |
|---|---|---|
| **Sol-Gel Process** | Metal alkoxides or salts hydrolyzed to form gels | Silica nanoparticles, coatings |
| **Chemical Vapor Deposition (CVD)** | Gaseous reactants form a solid film or particles on a substrate | Carbon nanotubes, graphene |
| **Hydrothermal/Solvothermal Synthesis** | Crystallization in sealed vessels under high temp/pressure | ZnO nanorods, $TiO_2$ nanoparticles |
| **Co-precipitation** | Ions are precipitated to form nanoparticles in solution | Magnetic iron oxide nanoparticles |
| **Micelle/Template Methods** | Self-assembled structures guide nanoparticle formation | Mesoporous silica, quantum dots |
| **Biological Methods** | Use of bacteria, fungi, or plant | "Green" synthesis of |

| Method | Description | Examples |
|---|---|---|
| | extracts | silver/gold NPs |

**Advantages of Bottom-up approach:**

1. **Cost-effective**: Reduces the need for expensive chemicals and equipment.
2. **Energy-efficient**: Often occurs at room temperature and pressure, saving energy.
3. **Scalable and simple**: Can be performed easily without complex setups.
4. **Waste reduction**: Generates minimal hazardous waste compared to traditional methods.
5. **Fast process**
6. **Uniform size particles are obtained**
7. **Defect free particles are obtained**

## Size-Dependent Optical Properties of Gold Nanoparticles (Au-NPs)

Gold nanoparticles (Au-NPs) exhibit **unique optical properties** that **change with particle size**, shape, and the surrounding environment. This behavior arises primarily due to a phenomenon called **Surface Plasmon Resonance (SPR)**.

### What is Surface Plasmon Resonance (SPR)?

- **SPR** is the collective oscillation of conduction electrons on the nanoparticle surface when exposed to light at a specific wavelength.
- This resonance causes **strong light absorption and scattering**, giving AuNPs vibrant colors.

### Size-Dependent SPR Behavior

| Size (diameter) | SPR Peak (UV-Vis) | Observed Color |
|---|---|---|
| < 2 nm | Weak/absent | Pale yellow |
| ~10–30 nm | ~520 nm | Ruby red |
| 30–80 nm | 520–550 nm | Purple to blue |
| > 100 nm | >550 nm, red-shifted | Grayish-blue |

- As **size increases**, the **SPR peak shifts to longer wavelengths (red-shift)** and **broadens**, indicating changes in both **absorption** and **scattering** behavior.

**Raw Materials** required for the Green synthesis of Nanomaterials using plant extract:

1. Precursor

2. Reducing Agent

3. Capping Agent

4. Solvent

**What is a Precursor?**

In chemistry and nanotechnology, a **precursor** is a **starting material** or **reactant** that undergoes chemical transformation to form a **desired product**, such as **nanoparticles**.

**Example:**

- **Gold nanoparticles (AuNPs)** synthesis
  → **Precursor**: **Chloroauric acid ($HAuCl_4$)**
  → **Product**: Metallic gold nanoparticles ($Au^0$)

**Types of Precursors (Examples by Element):**

| Element | Common Precursor | Used In |
|---|---|---|
| Gold (Au) | Chloroauric acid ($HAuCl_4$) | Gold nanoparticles |
| Silver (Ag) | Silver nitrate ($AgNO_3$) | Silver nanoparticles |
| Zinc (Zn) | Zinc Nitrate, $Zn(NO_3)_2$ | ZnO nanoparticles |

# Green Synthesis of Nanomaterials:

**Green synthesis** refers to the eco-friendly and sustainable method of producing **nanoparticles**, using **biological materials** like plant extracts, bacteria, fungi, or enzymes. It's aiming to minimize environmental impact and avoid the use of toxic chemicals.

**Advantages of Green Synthesis:**

8. **Eco-friendly**: Uses natural, renewable resources and avoids harmful chemicals.

9. **Non-toxic and biocompatible**: Safer for medical, pharmaceutical, and environmental applications.
10. **Cost-effective**: Reduces the need for expensive chemicals and equipment.
11. **Energy-efficient**: Often occurs at room temperature and pressure, saving energy.
12. **Scalable and simple**: Can be performed easily without complex setups.
13. **Waste reduction**: Generates minimal hazardous waste compared to traditional methods.
14. **Fast process**
15. **Uniform size particles are obtained**
16. **Defect free particles are obtained**

## Factors affecting the green synthesis of NMs:

Several **factors affect the yield, size, shape, stability, and functional properties** of the resulting nanomaterials.

Key factors include:

**1. Source of Reducing and Capping Agents**

- **Type of biological material** (plant extract, bacteria, fungi, algae) determines the availability of phytochemicals (e.g., flavonoids, phenols) that reduce and stabilize nanoparticles.
- **Concentration** of extract affects the rate and extent of reduction.

**2. pH of the Reaction Medium**

- Influences nanoparticle size, morphology, and stability.
- Alkaline pH generally favors smaller and more uniform nanoparticles.

**3. Temperature**

- Higher temperatures typically increase the reaction rate and influence the nucleation and growth of nanoparticles.
- Extremely high temperatures might denature biological molecules, reducing effectiveness.

**4. Reaction Time**

- Longer reaction times often result in more complete reduction and larger particle sizes due to agglomeration.

**5. Metal Salt Precursor**

- **Type of metal ion** (e.g., $Ag^{+}$, $Au^{3+}$, $Fe^{2+}$) and its **concentration** are crucial.

- Excess metal ions can lead to uncontrolled growth and agglomeration.

**6. Agitation/ Stirring Speed**

- Affects mixing efficiency, mass transfer, and uniformity of the reaction.
- Uniform stirring ensures better size distribution.

**7. Light Exposure**

- Some green syntheses are photo-mediated.
- Light can affect the rate of reduction and shape of nanoparticles (especially in silver and gold nanoparticle synthesis).

**8. Solvent**

- Water is commonly used in green synthesis, but its purity (e.g., deionized vs tap) can influence outcomes.
- Other green solvents (like ethanol) may also affect solubility and interaction with biomolecules.

**9. Incubation Conditions**

- Aerobic vs anaerobic conditions can influence microbial-mediated synthesis.
- Incubation duration and medium composition are especially important in microbial methods.

10. **Viscosity of the medium**

# Applications of Nanomaterials

Nanomaterials, characterized by their nanoscale dimensions (1-100 nanometers), possess unique physical, chemical, and mechanical properties that have enabled a wide range of applications across various fields. Below are some prominent applications:

**1. Medicine and Healthcare**

- **Drug Delivery:** Nanoparticles such as liposomes and dendrimers are used to target drugs to specific cells, reducing side effects and improving efficacy.
- **Imaging:** Quantum dots and gold nanoparticles are employed in medical imaging, such as MRI and CT scans, for better resolution and contrast.
- **Therapeutics:** Nanomaterials are used in photothermal therapy and targeted cancer treatments.
- **Biosensors:** Nanoscale sensors detect specific biomolecules, enabling early disease diagnosis.

**2. Energy**

- **Solar Cells:** Nanostructured materials like quantum dots and nanowires enhance light absorption and efficiency in photovoltaic cells.
- **Batteries and Supercapacitors:** Nanomaterials like carbon nanotubes and graphene are used to improve energy storage capacity and charging rates.
- **Hydrogen Storage:** Metal-organic frameworks (MOFs) and other nanostructured materials aid in efficient hydrogen storage.

### 3. Environmental Applications

- **Water Purification:** Nanomaterials such as titanium dioxide and silver nanoparticles are used for filtration, disinfection, and photocatalysis.
- **Pollution Control:** Nanocatalysts degrade pollutants and convert them into harmless products.
- **Sensing Contaminants:** Nanosensors detect pollutants and toxic chemicals at low concentrations.

### 4. Electronics and Computing

- **Semiconductors:** Nanowires and nanotubes are used to develop smaller and faster transistors.
- **Displays:** Quantum dots improve the color and energy efficiency of LED and OLED displays.
- **Data Storage:** Nanomaterials are used in high-density storage devices like SSDs and HDDs.

### 5. Construction and Materials Science

- **Strengthened Materials:** Nanoparticles such as carbon nanotubes and silica nanoparticles improve the strength, durability, and lightweight nature of construction materials.
- **Self-Cleaning Surfaces:** Nano-coatings impart self-cleaning and anti-corrosive properties to surfaces.
- **Thermal Insulation:** Nanostructures provide efficient thermal barrier coatings.

### 6. Automotive and Aerospace

- **Lightweight Components:** Carbon-based nanomaterials reduce the weight of vehicles, improving fuel efficiency.
- **Tire Wear Indicators:** Nanomaterials enhance the durability and performance of tires.
- **Sensors:** Nanosensors are employed for real-time monitoring of mechanical stress and temperature.

### 7. Consumer Goods

- **Cosmetics:** Nanoparticles like titanium dioxide and zinc oxide are used in sunscreens for better UV protection.

- **Textiles:** Nano-coatings provide water resistance, stain resistance, and antimicrobial properties to fabrics.
- **Food Packaging:** Nanocomposites enhance the strength, transparency, and shelf-life of packaging materials.

**8. Defense and Security**

- **Armor:** Nanomaterials improve the strength and flexibility of body armor and bulletproof vests.
- **Detection:** Nanosensors are used for detecting explosives and hazardous materials.
- **Stealth Technology:** Nanostructured coatings reduce radar and thermal detection.

**9. Agriculture**

- **Nano-fertilizers:** Nanoparticles deliver nutrients more efficiently to plants.
- **Pesticides:** Nanoscale formulations increase the effectiveness of pesticides while reducing environmental impact.
- **Soil Monitoring:** Nanosensors detect soil conditions like moisture and nutrient levels.

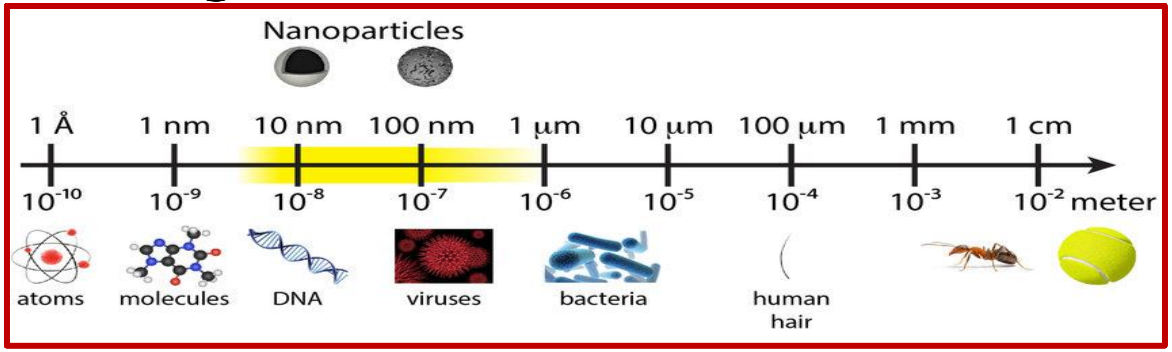
**10. Biotechnology**

- **Gene Delivery:** Nanoparticles transport genes into specific cells for genetic engineering.
- **Protein Engineering:** Nanostructures aid in the study and manipulation of proteins

Dr. Manoranjan Behera

# Nanoparticles

- *Nanoparticles* are isolated solid-phase objects having at least one dimension in the range of 1-100 nm. **Nanomaterials (NMs)** are materials created using nanoparticles. NMs are materials in which the dimension of individual particles are in the range of 1-100 nm.




**The International Organization for Standardization (ISO) has described NMs as a "material with any external nanoscale dimension or having internal nanoscale surface structure"**

# Why we study Nanoparticles?

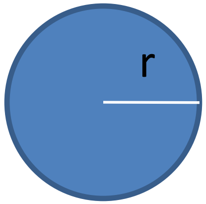
**Three major physical properties of Nanoparticles**

(A) Nanoscale materials have far larger surface area-to-volume ratio than bulk materials. As surface area per volume increases, materials can become more reactive.

Surface area = $4\pi r^2$

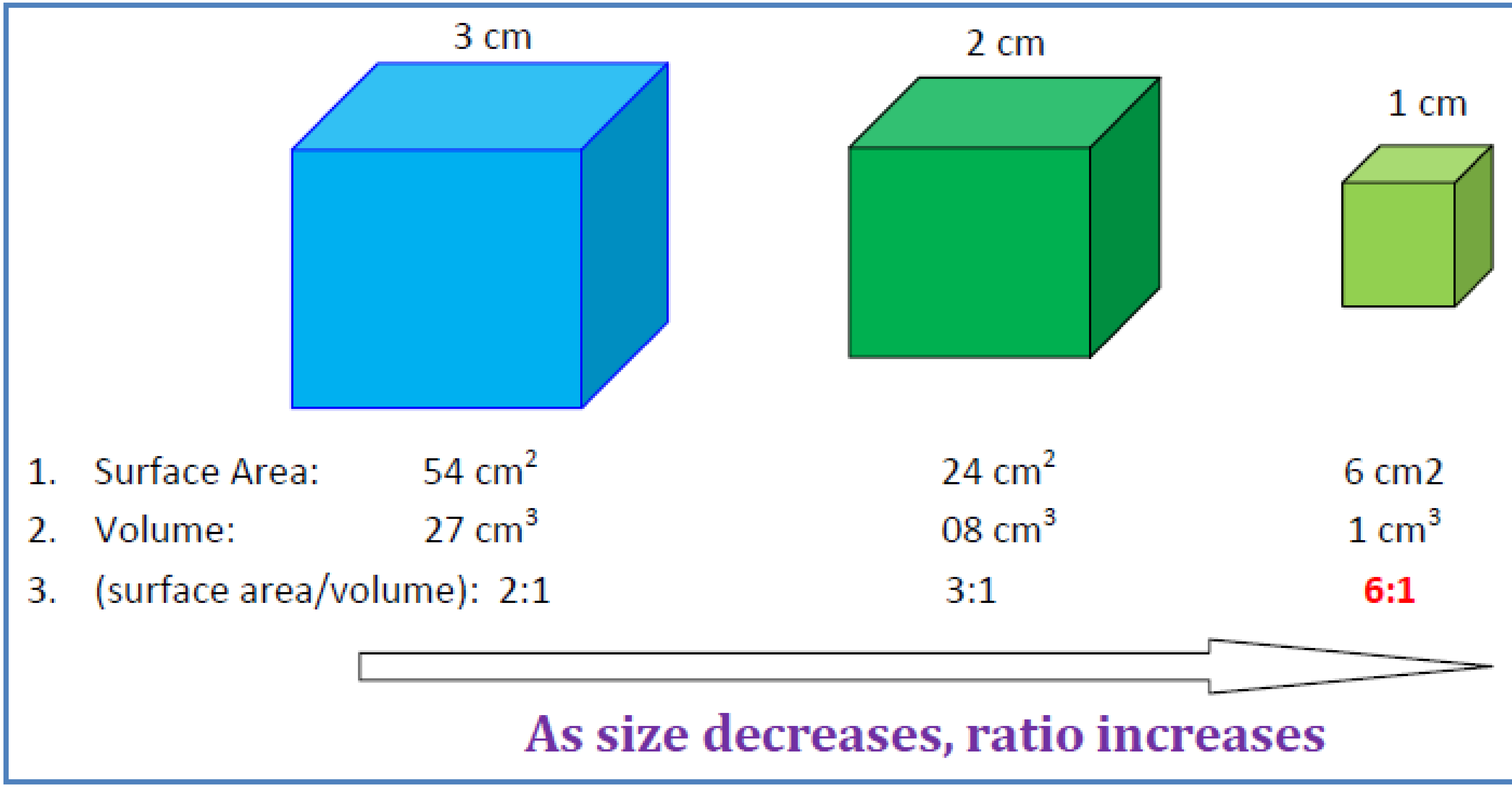
Volume = $4/3\pi r^3$

**Spherical Nanoparticle**




Surface area to volume ratio (SVR) = $3/r$

=> **As size decreases, surface area to volume ratio increases**

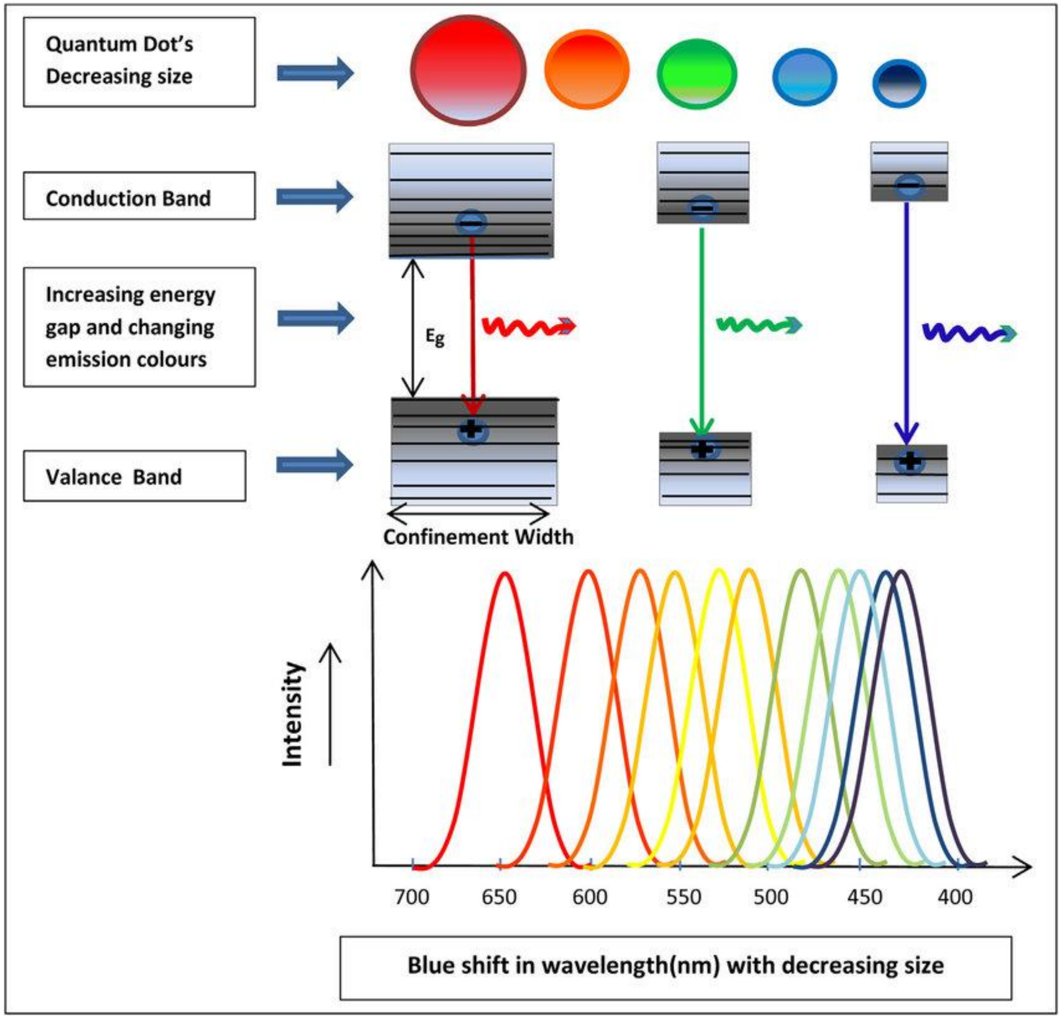



Surface area = 6 $a^2$

Volume = $a^3$

Where, a = edge length of cube

# (B) Exhibit Quantum effect




**Band gap (Eg) increases as we go from bulk to nano**

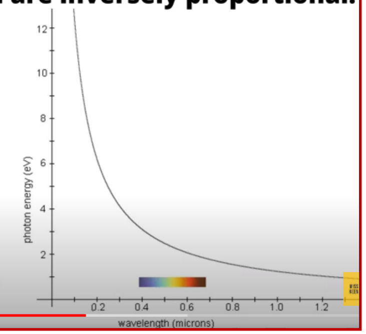
$E_g = n^2h^2/8ma^2$

**As 'a' decreases, i.e., size decreases, Eg increases and wavelength decreases**

**Energy and wavelength are inversely proportional.**

$E = hc/\lambda$

E = radiation energy
h = Planck's constant
c = speed of light
λ = wavelength of radiation




# (C) They are highly mobile in the free state

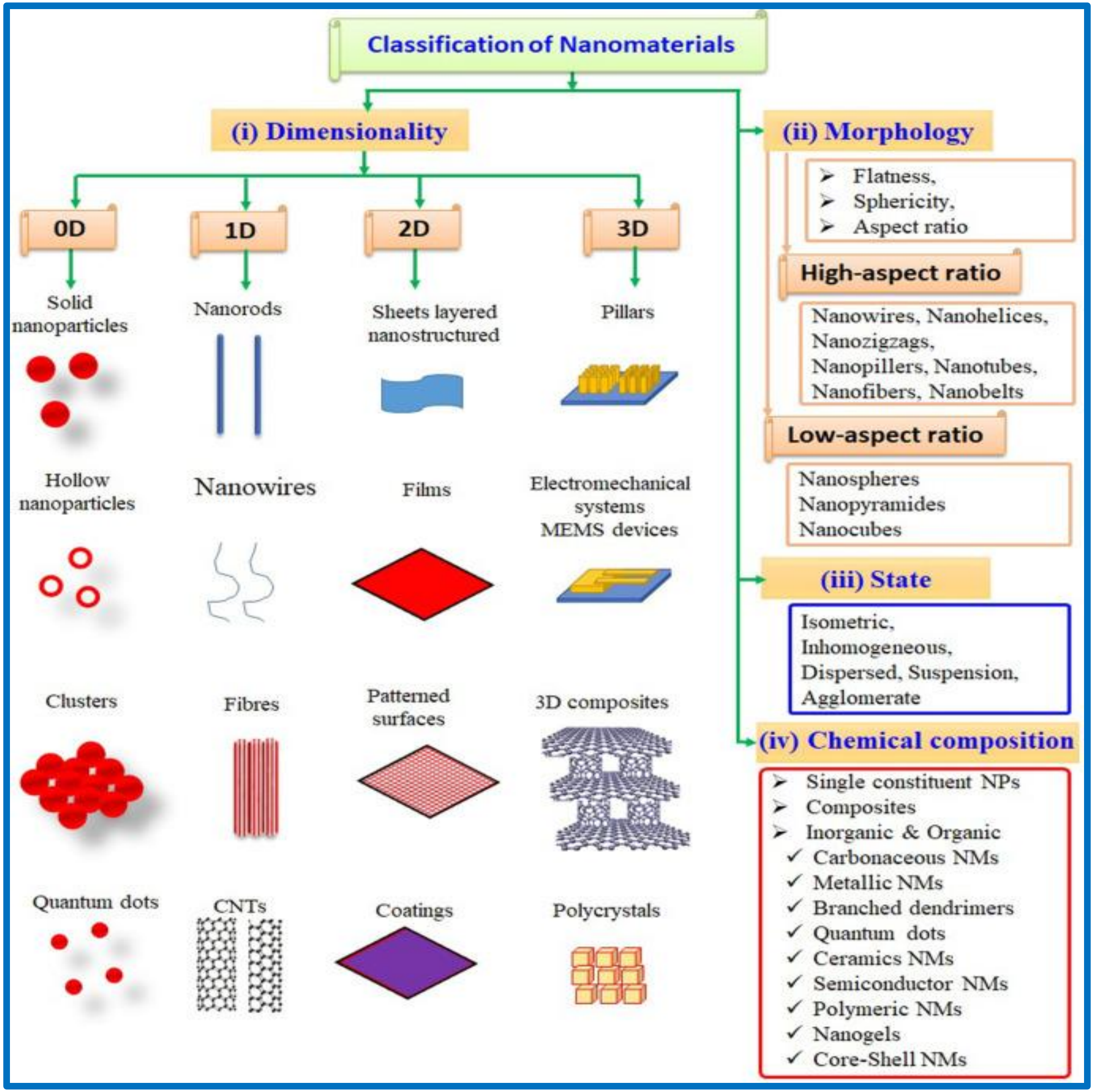
# Size Dependent Properties

- Properties of Nanomaterials are significantly different from those of bulk materials (size: mm to cm range).

- **A. Thermal Properties**
- **B. Optical Properties**
- **C. Magnetic Properties**
- **D. Electrical Properties**
- **E. Surface Properties**
- **F. Mechanical Properties**
- **G. Catalytic Properties**
- **H. Medicinal Properties**

- Nano titanium dioxide to coat the plastic chairs we have in the garden, make the surface self-cleaning.
- Copper, as an example, is known as a soft, malleable metal – but copper nanoparticles smaller than 50 nm diameter are known as ultra-hard materials.
- Bulk Au and Pt are non-magnetic but exhibit magnetic nature at nanoscale.

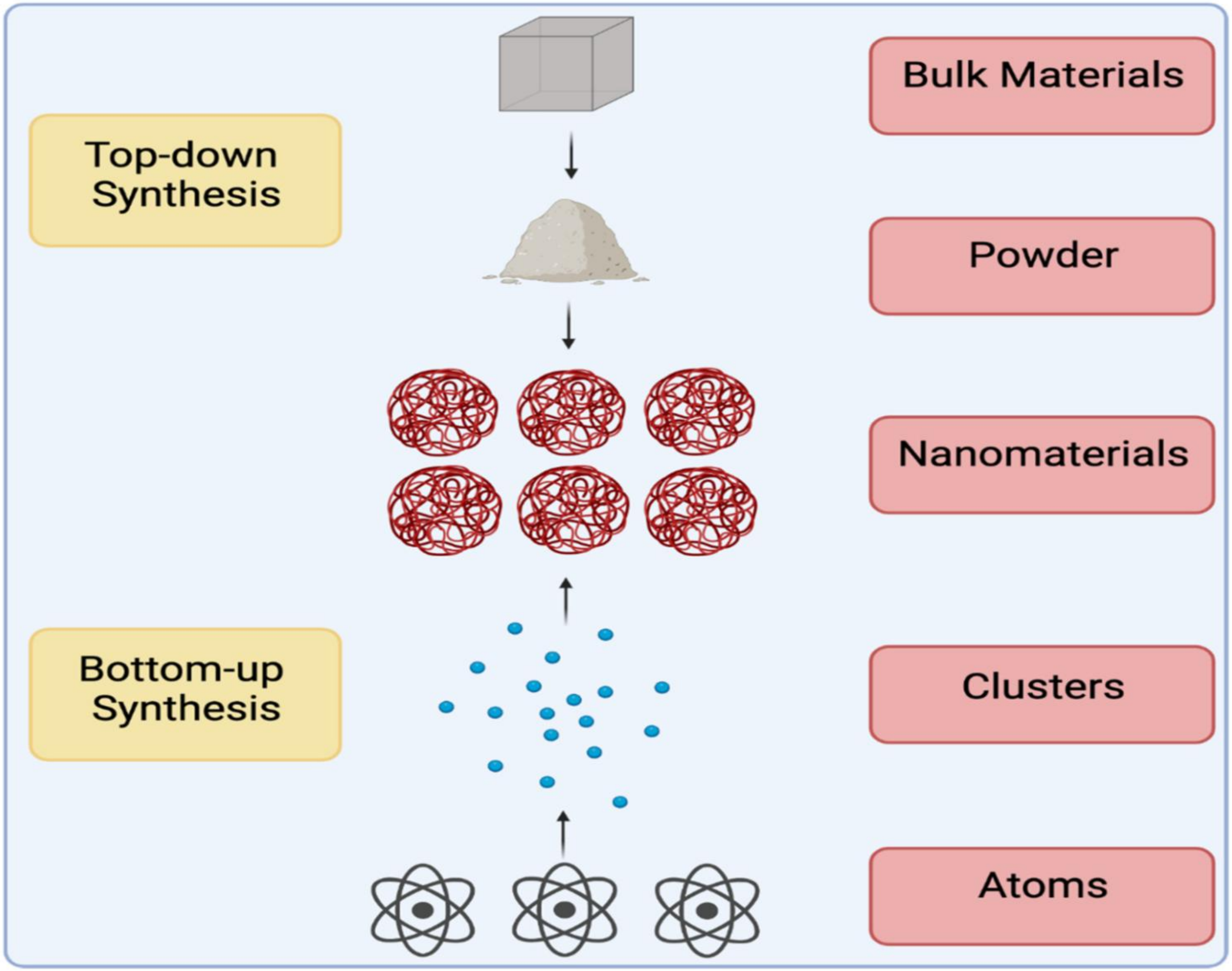
# Classifications of Nanomaterials



# Synthesis of Nanoparticles

## A. Top-Down Approach

## B. Bottom-Up Approach



# Limitations of Top-down approach

- Broad size distribution (10-1000 nm)
- Varied particle shape or geometry
- Parameter controlling job is a tough task
- Impurities get introduced
- Stress, defects get introduced
- Expensive technique

# Why to use Green Synthesis?

- Reduce toxic chemical concentration
- Eco-friendly approach
- Economically Viable
- Easier to tailor size, shape and distribution of particles by changing pH, Temperature, etc.
- Defect free particles are obtained

# Raw Materials for Synthesis of Nanoparticles

- **Three Important Requirements:**

➢ **Precursor Salt:** $HAuCl_4$ for Gold, $AgNO_3$ for Silver, $Zn(NO_3)_2$ for ZnO, $CuSO_4$ for $Cu_2O$, etc.

➢ **Reducing Agent:** Phyto-chemicals and Enzymes

➢ **Stabilizing/Capping Agent:** Phyto-chemicals like saponin, Quercetin, polyphenols.

# Factors affecting particle size/shape

- Type of capping agent
- Nature of Reducing agent
- Concentration of precursor salt
- Concentration of reducing agent
- pH of the medium
- Reaction time
- Reaction Temperature
- Stirring rate

Manoranjan