

# Nanochemistry



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## *What is the Meaning of the Word “Nano”?*

The word “Nano” comes from the Greek word “Nanos,” which means “very small” or “dwarf.” In science, "Nano" is used as a prefix in the International System of Units (SI) to represent one billionth of a unit. This means that Nano corresponds to  $10^{-9}$  m. For example, a nanometer (nm) is one billionth of a meter, and a Nanosecond is one billionth of a second. The word "Nano" itself does not describe a material or a technology; it only describes the scale or size.

**The Nanoscale** is extremely small and lies between the atomic scale and the microscopic scale. To understand how it is small, the diameter of a human hair is about 80,000 to 100,000 nm, while the average size of an atom is about 1 - 2 Å (0.1 – 0.2 nm) in radius and therefore we may have (3 – 5 atoms) in one nm.

The word “Nano” is commonly used with length units, such as Nanometer, because size plays a major role in determining material behavior. However, it can also be used with time, mass, and other physical quantities, such as Nanosecond or Nanogram.

- ❖ **1 m =  $10^9$  nm**
- ❖ **1 cm =  $10^7$  nm**
- ❖ **1 mm =  $10^6$  nm**
- ❖ **1  $\mu$ m =  $10^3$  nm**
- ❖ **1 Å = 0.1 nm**
- ❖ **1 pm = 0.001 nm**

There are some important terms that should be known when studying nano.

- 1- **Nanochemistry:** Confinement of chemical reactions to the nanometer length scale to produce chemical products that with nanometer dimensions (1to100nm) or preparation and organization of nanoparticles.

- 2- **Nano:** is a very small scale that marks the boundary where matter begins to show new and unusual behavior. It helps scientists describe sizes that are too small to see but large enough to influence how materials act.
- 3- **Nanomaterials:** are materials that have at least one dimension within the nanoscale range(1-100) nm. They are characterized by extremely large surface areas, high chemical activity, novel optical, electrical, and magnetic properties, as well as high mechanical strength.
- 4- **Bulk materials:** are particles that have their size above 100 nm in all dimensions. Most of the times, we use this term in order to name a substance that is granular or lumpy and exists in free-flowing form.
- 5- **Nanoscience:** is the study of materials when their size is extremely small, usually between 1 and 100 nm. At this scale, materials show new properties that are different from larger sizes, such as color, electrical conductivity, chemical activity, and strength. Nanoscience aims to understand these changes and use them to design better materials and technologies, like stronger materials, more reactive materials, or materials that can absorb light or energy more efficiently. It focuses on studying matter at the level of atoms and molecules and combines physics, chemistry, materials science, and engineering to achieve these goals.
- 6- **Nanotechnology:** is the science and engineering of creating and controlling materials, devices, and systems at the nanoscale, usually between (1 - 100) nm. At this scale, materials behave differently than in their larger form, showing unique properties such as higher chemical reactivity, improved electrical conductivity, increased strength, and special optical behavior.  
  
Nanotechnology involves designing and manipulating matter at the level of atoms and molecules to achieve specific functions. It is used to develop a wide range of applications, including precise medical devices that can target cells, stronger and lighter materials for construction and transportation, highly sensitive sensors, more efficient energy storage devices, and advanced electronic components.

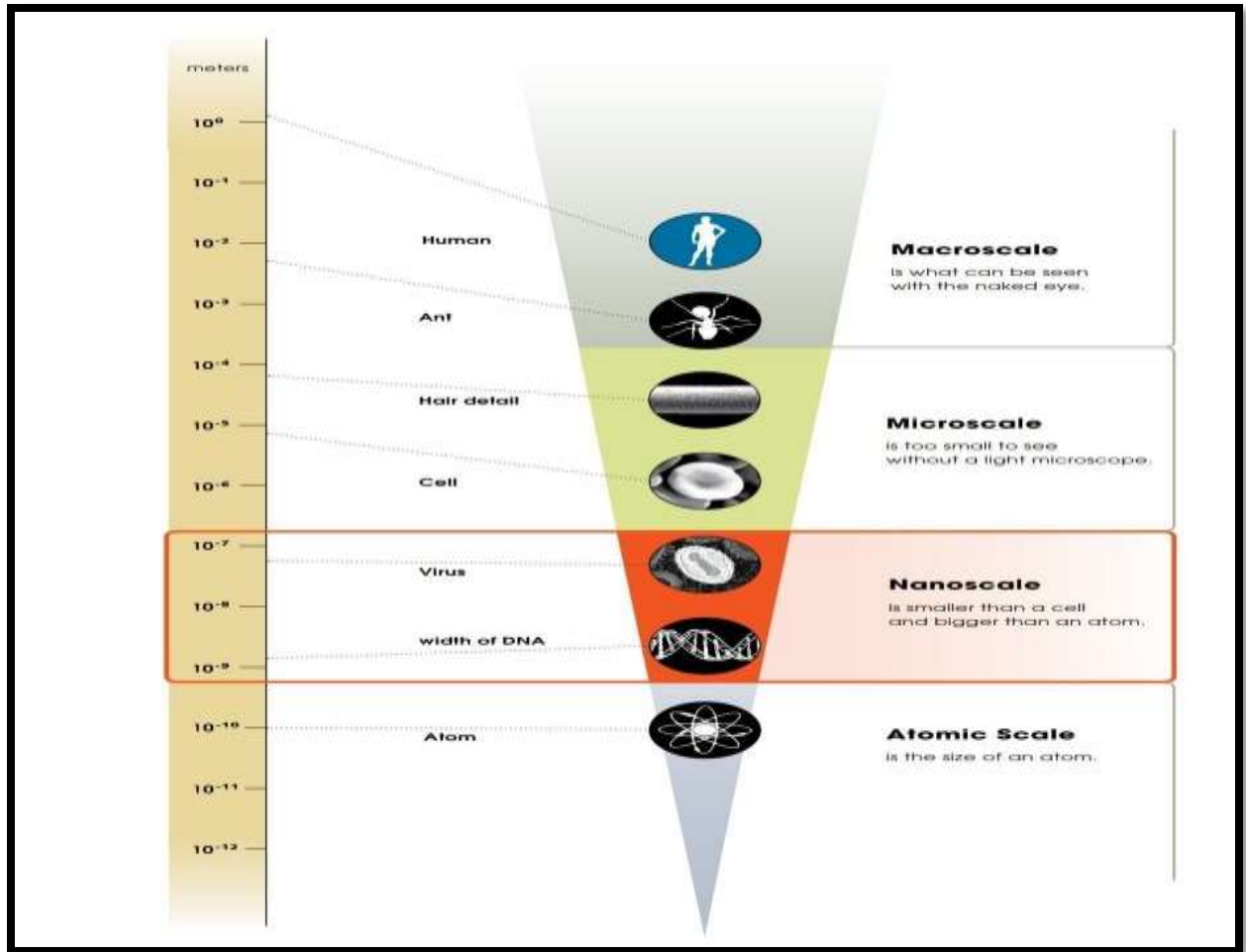


Figure.1: shows the size of the organisms.

### *Why is Nano important?*

The importance of the word "Nano" is not only related to small size but also to the fact that materials behave differently at this scale.

When the size of a material reaches the nanoscale, its physical and chemical properties may change, even though its chemical composition remains the same. This occurs as a result of the increased significance of quantum and surface effects at such small dimensions (surface-to-volume ratio). So, the importance can be summarized below:

- 1- Materials behave differently at very small sizes.
- 2- New properties appear at the Nano scale.

- 3- Nano materials have very large surface areas.
- 4- Surface atoms strongly affect material behavior.
- 5- Quantum effects occur at Nano dimensions.
- 6- Optical properties can change at the Nano scale.
- 7- Electrical properties can change at the Nano scale.
- 8- Chemical reactivity increases at Nano sizes.
- 9- Size alone can control material properties.
- 10- Nano enables the design of advanced materials.

### ***History and Development of Nanotechnology***

Interest in the concept of Nano began before modern technologies appeared, but its roots can be traced back over a century. The first person to discuss the idea of controlling matter at the atomic level was Richard Feynman in 1959, during his famous lecture “**There’s Plenty of Room at the Bottom**”. In this lecture, Feynman suggested that materials could be controlled at the atomic and molecular level, and he proposed the possibility of building extremely small devices, reaching the size of molecules and atoms. This lecture is considered the intellectual beginning of nanoscience, even though the term “Nano” was not yet used.

In fact, some nanoscale phenomena existed long before modern humans knew the concept. For example, in colored glass and decorated pottery, tiny gold or metal particles at the nanoscale caused colors to change depending on particle size and light interaction like *Lycurgus Cup* (Lycurgus Glass) Roman glass whose color changes from green to red depending on the direction of the light due to the presence of gold and silver nanoparticles inside it.

Ancient humans used these effects practically, without understanding the scientific reasons behind them, while modern scientists later explained and applied these phenomena systematically.



**Figure.2: shows Lycurgus Glass.**

In the 1960s and 1970s, scientists began to understand that materials show different physical and chemical properties when reduced to the nanoscale. However, the ability to see and manipulate matter at the nanoscale only became possible with the development of electron microscopes, especially the Transmission Electron Microscope (TEM) and Scanning Tunneling Microscope (STM) in the 1970s and 1980s. These instruments allowed scientists to observe atoms and molecules and control their arrangement precisely.

The term “Nanotechnology” was first officially used by Norio Taniguchi in 1974, when he described processes that allow precise control of matter at the nanoscale (1–100 nm). Later, in the 1980s and 1990s, nanoscience became an active research field, especially after the invention of the Scanning Tunneling Microscope (STM), which allowed moving atoms one by one, opening the door for practical applications.

## ***How Nanomaterials Differ from Bulk Materials***

When a material becomes extremely small at the nanoscale, the surface area increases significantly compared to its volume. For example, a cube with a side length of 1 m has a surface area of 6 m<sup>2</sup>. If we divide it into smaller cubes with a side length of 0.5 m, the total surface area becomes 12 m<sup>2</sup>. If we divide it again into cubes of 0.25 m, the total surface area becomes 24 m<sup>2</sup>, while the total volume remains the same. This large increase in surface area makes the surface atoms more active, which changes the material's properties, such as melting point, chemical reactivity, and electrical conductivity. Therefore, nanomaterials exhibit different properties compared to the same material in larger bulk form, like a significant decrease in the melting point of gold when particle size reaches 1 nm.

In recent decades, nanotechnology has become an official part of science and engineering. It is now recognized globally as an independent scientific and technological field, with specialized research centers worldwide developing nanomaterials, nanoelectronics, nanomedical devices, and industrial applications.

## How Nanomaterials Differ from Bulk Materials

When a material becomes extremely small at the nanoscale, the “**surface area** increases significantly compared to its volume”.

For example, a cube with a side length of 1 meter has a surface area of **6 m<sup>2</sup>**.



1 m Cube

→ Surface Area: **6 m<sup>2</sup>**

→ If we divide it into smaller cubes of 0.5 meters, the total surface area becomes **12 m<sup>2</sup>**.



0.5 m Cubes

→ Surface Area: **12 m<sup>2</sup>**

→ Dividing again into 0.25 meter cubes, the surface area becomes **24 m<sup>2</sup>**.



0.25 m Cubes

→ Surface Area: **24 m<sup>2</sup>**

This large increase in surface area makes the surface atoms more active, changing the material's properties:



**Melting Point** ↓



**Reactivity** ↑



**Conductivity** ↑

Therefore, nanomaterials exhibit *different properties* compared to the same material in larger bulk form, like a significant decrease in the melting point of gold when particle size reaches 1 nanometer.

Figure.3: Increase of Surface Area at the Nanoscale.

The surface area and volume depending on the shape can be calculated according to the following:

**Important mathematical laws:**

❖ **Cubic Volume** = length × width × height

**Surface area** = length × width × number of sides

❖ **Ball Volume** =  $\frac{4}{3} \pi (\text{radius})^3$

**Surface area** =  $4\pi \times (\text{radius})^2$

❖ **Cylinder Volume** =  $\pi \times \text{height} \times (\text{radius})^2$

**Surface Area** =  $2\pi (\text{radius})^2 + 2\pi \times \text{radius} \times \text{height}$

## Simple Mathematical Problems on Surface Area and Volume

### Problem 1: Cube

A cube-shaped object has a side length of 4 cm. Calculate the total volume and the total surface area of the cube. Explain what each result means.

Solution:

**Volume** =  $a^3 = 4^3 = 64 \text{ cm}^3$ . This value represents the amount of space occupied by the cube.

**Surface Area** =  $6a^2 = 6 \times 4^2 = 6 \times 16 = 96 \text{ cm}^2$ . This represents the total outer surface exposed to the surroundings.

### Problem 2: Sphere

A solid spherical ball has a radius of 3 cm. Find its volume and surface area, and explain the physical meaning of both values.

Solution:

**Volume** =  $(4/3)\pi r^3 = (4/3)\pi \times 3^3 = 36\pi \approx 113.1 \text{ cm}^3$ . This is the amount of material inside the sphere.

**Surface Area** =  $4\pi r^2 = 4\pi \times 3^2 = 36\pi \approx 113.1 \text{ cm}^2$ . This is the outer surface where interactions occur.

### Problem 3: Cylinder

**A cylindrical container has a radius of 2.5 cm and a height of 10 cm. Calculate the volume of the container and its total surface area, including the top and bottom.**

Solution:

**Volume** =  $\pi r^2 h = \pi \times 2.5^2 \times 10 = 62.5\pi \approx 196.35 \text{ cm}^3$ . This is the maximum amount of liquid the container can hold.

**Surface Area** =  $2\pi r^2 + 2\pi r h = 2\pi \times 2.5^2 + 2\pi \times 2.5 \times 10 = 62.5\pi \approx 196.35 \text{ cm}^2$ . This is the total area of the container exposed to air and liquid.

### *Quantum Size Effect*

The quantum size effect occurs when the size of a material is reduced to the nanoscale, typically below 10 nm. At this very small size, the dimensions of the particle become comparable to the wavelength of electrons, and classical physics is no longer sufficient to describe their behavior. Instead, quantum mechanics dominates.

In bulk materials, electrons can move freely and have almost continuous energy levels. However, when the particle size decreases to the nanoscale, electrons become confined within a very small space. This confinement causes the energy levels to become discrete rather than continuous, a phenomenon known as quantum confinement.

As a result of the quantum size effect, several physical properties of nanomaterials change significantly. The band gap increases as the particle size decreases, which directly affects the optical properties of the material. This leads to changes in light absorption and emission, causing

visible color changes. Electrical and electronic properties are also altered because electron movement is restricted.

A well-known example of the quantum size effect is observed in gold nanoparticles. Bulk gold has a yellow color, but when gold particles are reduced to nanometer sizes, they can appear red, purple, or blue. This color change occurs without any change in chemical composition and is mainly due to the quantum size effect influencing electron behavior.



**In summary**, the quantum size effect explains why nanomaterials exhibit properties that are very different from those of the same material in bulk form. When particle size decreases to the nanoscale, electron confinement leads to new optical, electrical, and physical behaviors that are unique to nanomaterials.

**Figure.4: Gold nanoparticles color change with the size.**

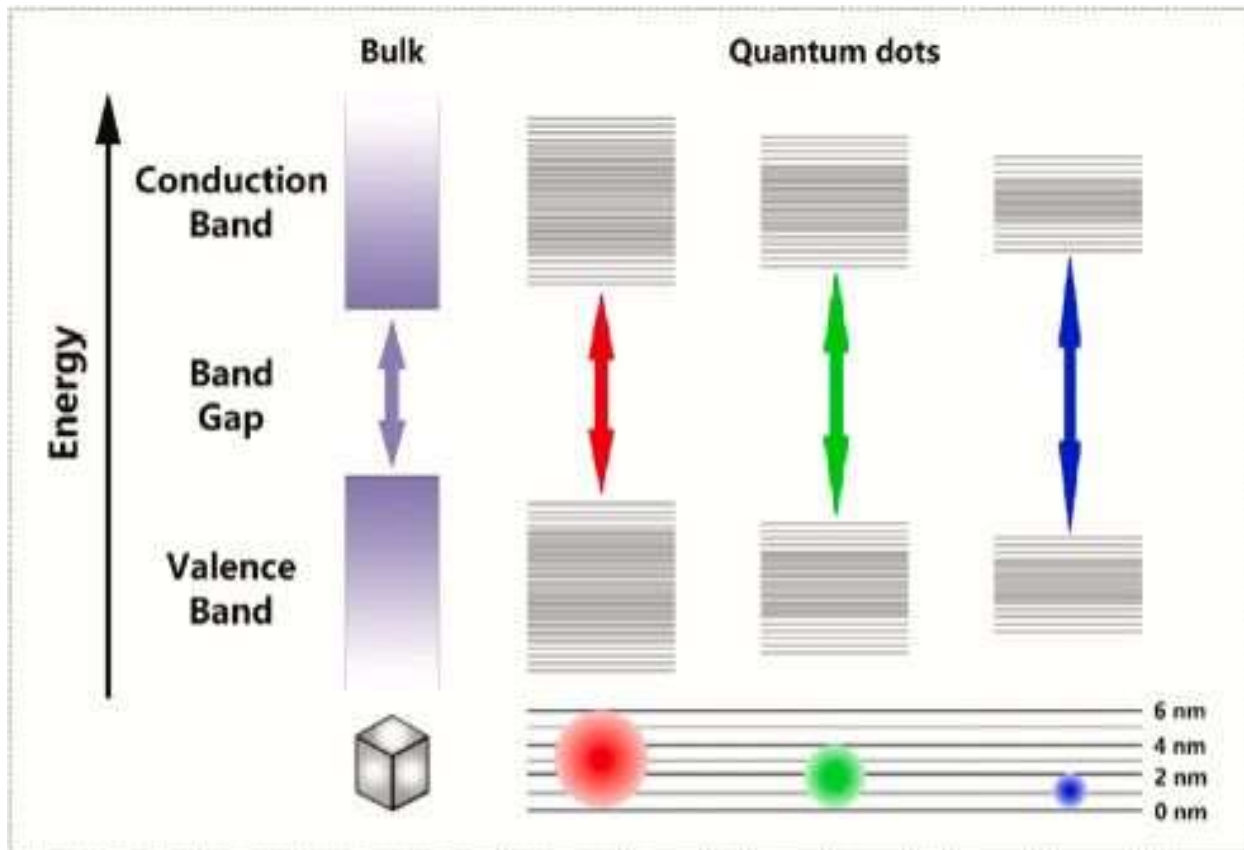


Figure.5: the quantum size effect.

## *Nanostructure Classification*

1- Nanostructure Classification Based on Dimensions

2- Nanostructure Classification Based on Shapes

3- Nanostructure Classification Based on Elemental composition

### *1- Nanostructure Classification Based on Dimensions*

#### ❖ **Zero-dimensional (0D) nanostructures:**

All three dimensions of the material are within the nanoscale (1–100 nm). Electrons are confined in all directions.

**Examples** include [nanoparticles, quantum dots, and nanoclusters].

#### ❖ **One-dimensional (1D) nanostructures:**

Two dimensions are in the nanoscale, while one dimension is larger. Electron motion is mainly along one direction.

**Examples** include [nanowires, nanotubes, and nanorods].

❖ **Two-dimensional (2D) nanostructures:**

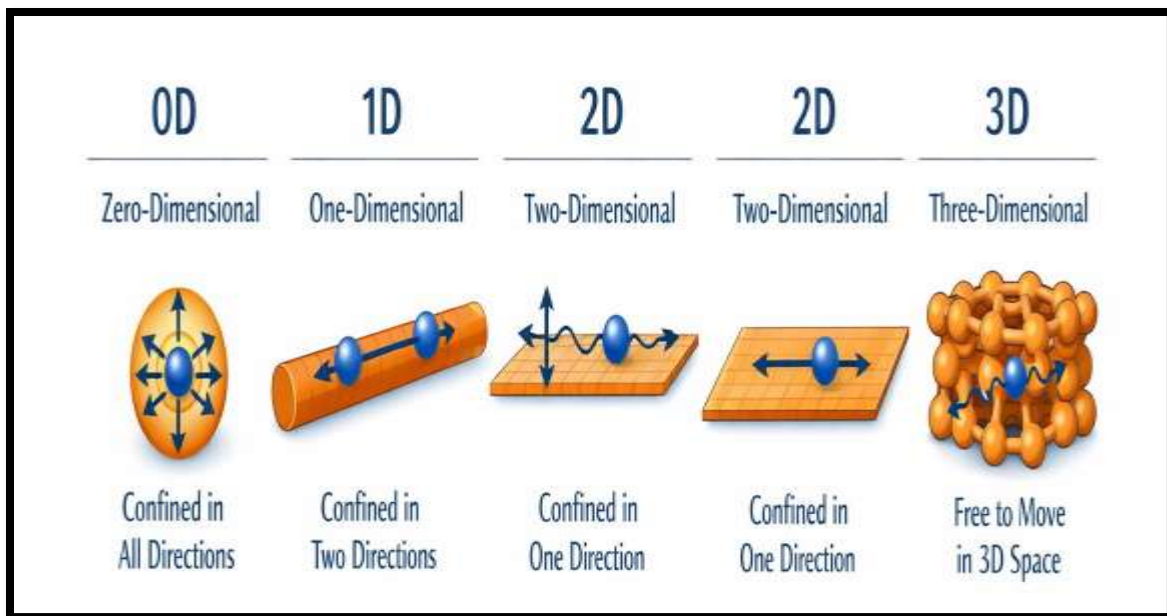
One dimension is in the nanoscale, while the other two are larger. Electrons are confined in one direction.

**Examples** include [thin films, nanosheets, graphene, and nanolayers].

❖ **Three-dimensional (3D) nanostructures:**

The material has nanostructured features, but none of the dimensions are strictly confined to the nanoscale. These materials are often composed of nanoscale building blocks.

**Examples** include [nanocomposites, nanoporous materials, and bulk materials with nanostructured grains].



**Figure.6: Nanostructures: 0D, 1D, 2D, 3D and Electron Movement.**

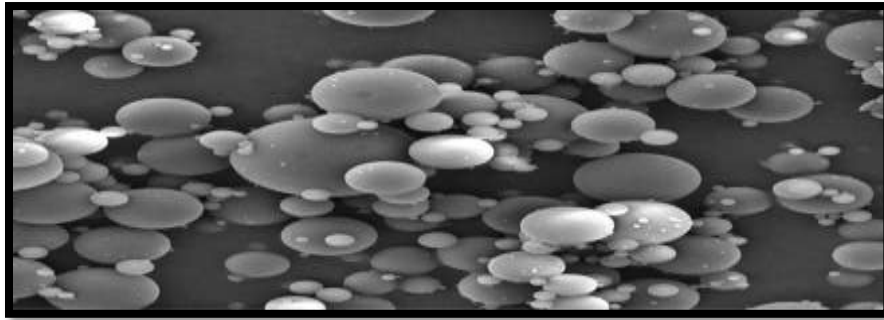
## *2- Nanostructure Classification Based on Shapes*

### *1. Nanoparticles*

**Definition:** Tiny particles with all dimensions in the nanoscale (0–100 nm) (0D).

**Properties:** High surface area, enhanced reactivity, unique optical/magnetic properties.

**Applications:** Sunscreens ( $\text{TiO}_2$ ,  $\text{ZnO}$ ), cosmetics, pollution particles, drug delivery.



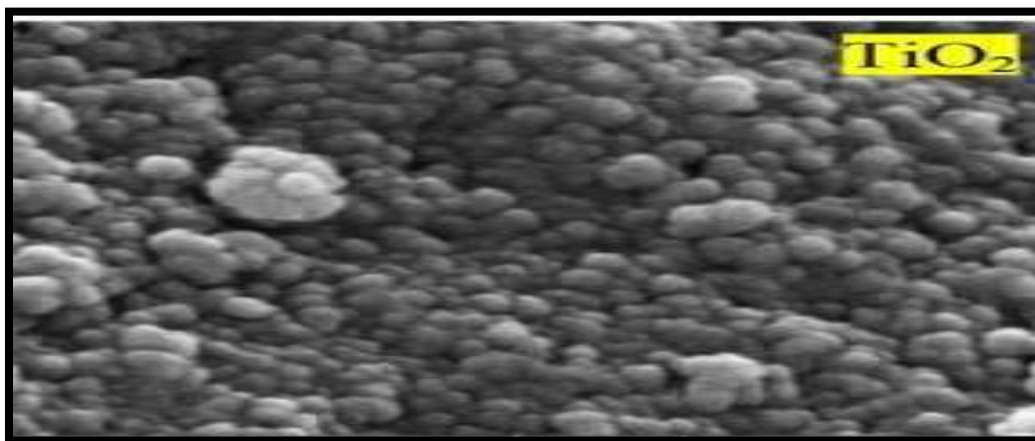
**Figure.7: Nanoparticles.**

### *2. Quantum Dots (QDS)*

**Definition:** Semiconductor nanoparticles that confine electrons in all three dimensions (0D).

**Properties:** Size-dependent optical properties, discrete energy levels, strong fluorescence.

**Applications:** Bio-imaging, LEDs, solar cells.



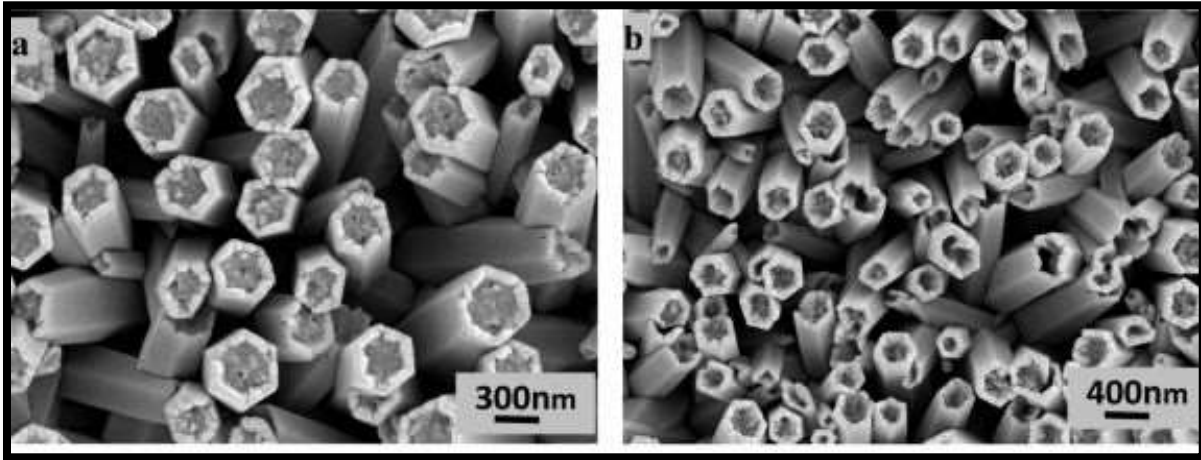
**Figure.8: Quantum dots of  $\text{TiO}_2$ .**

### ***3. Nanotubes***

**Definition:** Hollow cylindrical nanostructures (1D).

**Properties:** High mechanical strength, electrical/thermal conductivity, large surface area.

**Applications:** Electronics, batteries, reinforced materials.



**Figure.9: Nanotubes.**

### ***4. Nanowires***

**Definition:** Long, thin, wire-like nanostructures (1D).

**Properties:** Quantum confinement along diameter, high conductivity, mechanical flexibility.

**Applications:** Nanoelectronics, photodetectors, flexible circuits.

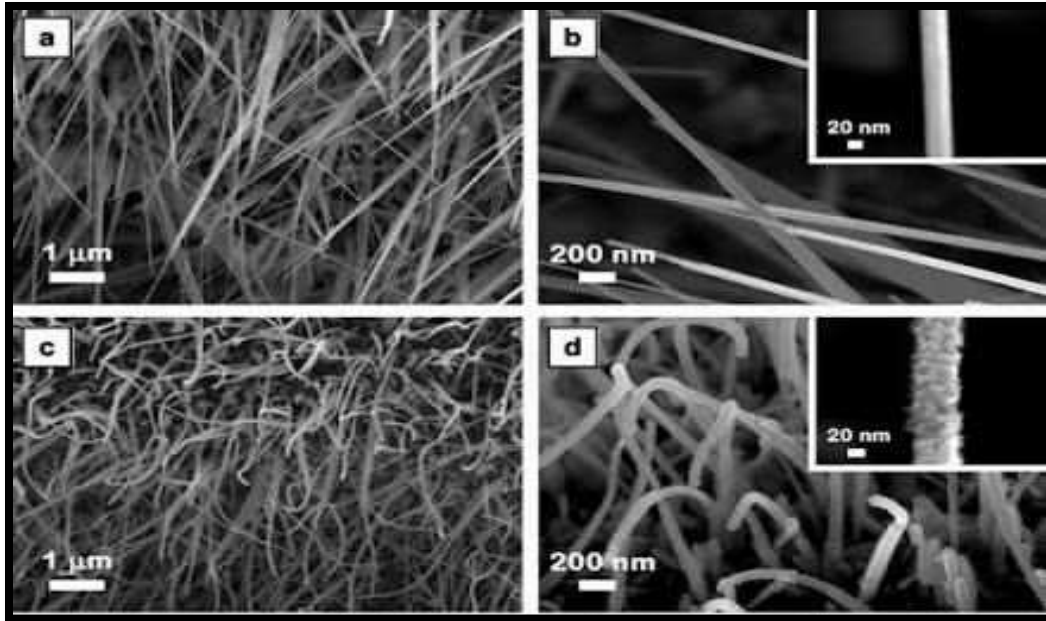


Figure.10: Nanowires.

### 5. Nanorods

**Definition:** Rod-shaped nanoparticles with high aspect ratio (1D).

**Properties:** Anisotropic optical properties, strong light absorption.

**Applications:** Biomedical imaging, photo-thermal therapy.

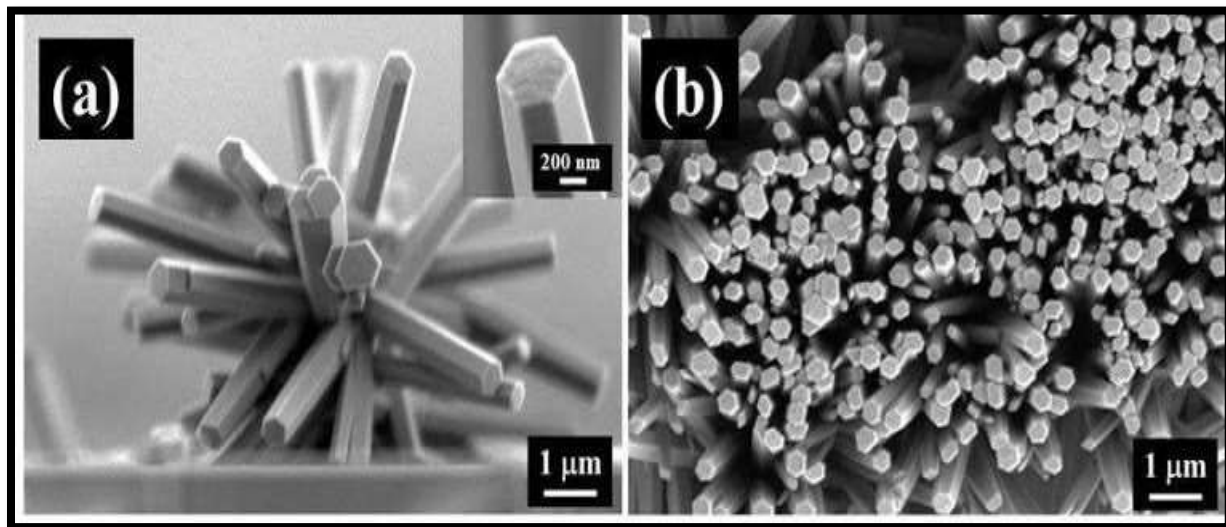


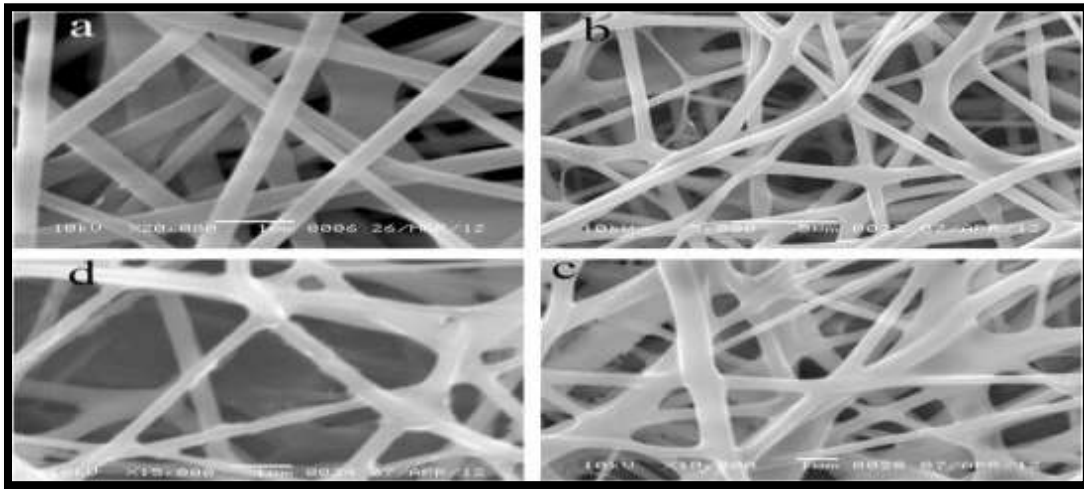
Figure.11: Nanorods.

## 6. Nanofibers

**Definition:** Fibrous nanostructures with extremely small diameters and long lengths (1D).

**Properties:** High surface-to-volume ratio, porosity, flexibility.

**Applications:** Air filters, tissue scaffolds, fabrics.



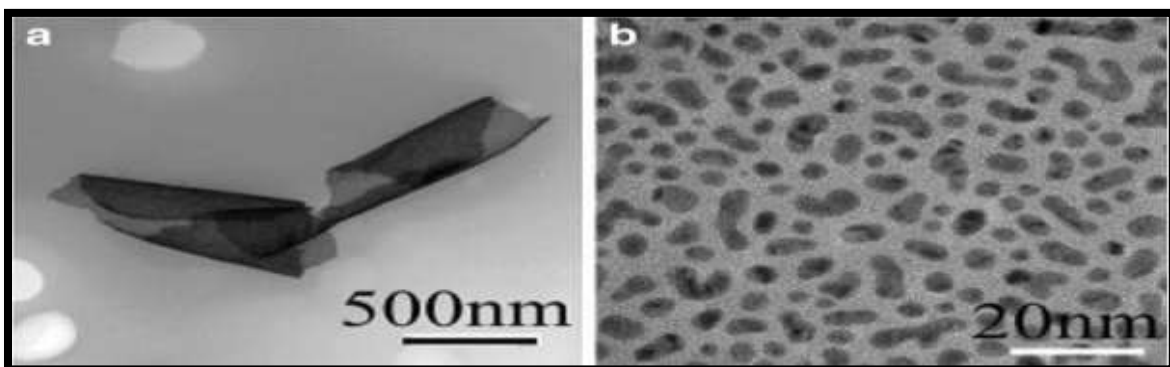
**Figure.12: Nanofibers.**

## 7. Nanofilms

**Definition:** Thin layers of material with nanoscale thickness (2D).

**Properties:** Large surface area, tunable optical/electronic properties.

**Applications:** Coatings (anti-scratch, anti-reflection), electronics, solar cells.



**Figure.13: Nanofilms.**

## ***8. Nanocomposites***

**Definition:** Materials made of nanoscale building blocks embedded in a matrix (3D).

**Properties:** Enhanced mechanical, thermal, electrical, and barrier properties.

**Applications:** Aerospace materials, sports equipment, packaging.

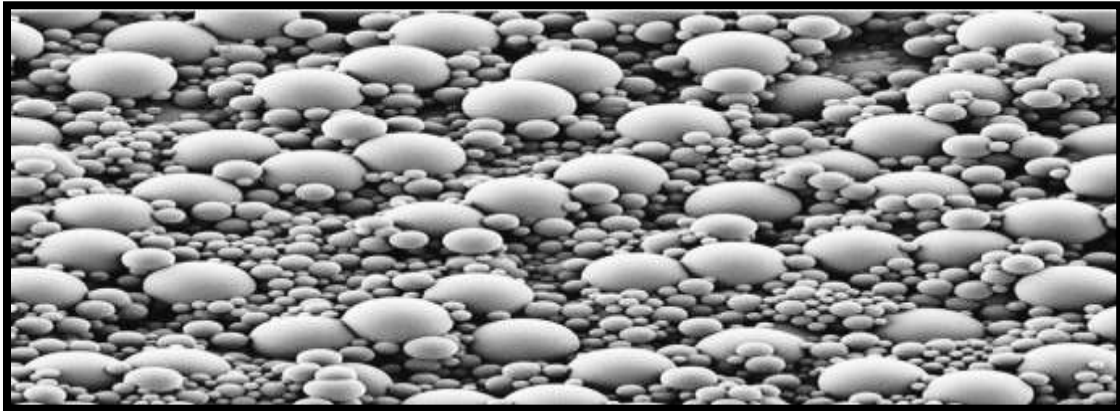


Figure.14: Nanocomposite.

### ***3- Nanostructure Classification Based on Elemental composition***

#### **1.Inorganic NPs**

They are small particle systems composed of inorganic materials and come in several types.

##### **a. Metallic Nanostructures**

**Definition:** Nanomaterials made of pure metals or alloys.

**Examples:** Gold (Au), Silver (Ag), Platinum (Pt), Copper (Cu) nanoparticles.

##### **b. Metal Oxide Nanostructures**

**Definition:** Nanomaterials composed of metal oxides.

**Examples:** Titanium dioxide (TiO<sub>2</sub>), Zinc oxide (ZnO), Iron oxide (Fe<sub>2</sub>O<sub>3</sub>).

### **c. Semiconductor Nanostructures**

**Definition:** Nanomaterials made of semiconducting elements.

**Examples:** Silicon (Si) nanoparticles, Cadmium selenide (CdSe) quantum dots.

### **2. Carbon-Based Nanostructures (Diamond / Organic)**

**Definition:** Nanomaterials made primarily of carbon.

**Examples:** Carbon nanotubes (CNTs), Graphene sheets, Fullerenes (C<sub>60</sub>), Diamond nanoparticles

### **3. Polymeric Nanostructures (Organic / Inorganic)**

**Definition:** Nanomaterials made from natural or synthetic polymers.

**Examples:** Poly (lactic-co-glycolic acid) (PLGA), Chitosan nanoparticles, dendrimers.

### **4. Hybrid Nanostructures (Combination / Organic-Inorganic)**

**Definition:** Nanomaterials combining two or more types of materials.

**Examples:** Metal–organic frameworks (MOFs), Core-shell nanoparticles.

## ***Fabrication of Nanomaterials***

The fabrication of nanomaterials involves creating materials with at least one dimension in the nanoscale (1–100 nm). Their properties (optical, electrical, mechanical, and chemical) depend strongly on size, shape, and structure. There are two main approaches to building nanomaterials:

### ***1. Top-Down Approach***

**Definition:** Breaking down bulk materials into nanoscale structures.

**Nature and Size:** Produced nanomaterials are usually crystalline or polycrystalline, often rough with defects. The size is typically (10–100 nm), but smaller sizes (<10 nm) are difficult due to equipment limits and structural defects.

**Advantages:** high purity, Large-scale production possible, good for creating precise patterns.

**Limitations:** difficult to reach very small sizes, may need surfactants to stabilize materials, and expensive.

## 2. Bottom-Up Approach

**Definition:** Building nanomaterials atom by atom or molecule by molecule.

**Nature and Size:** Nanomaterials are generally highly uniform, often single-crystal, and can form quantum dots, nanotubes, nanowires, or nanorods. Sizes can be tuned between 1–50 nm by controlling reaction conditions.

**Advantages:** precise control of size and shape, fewer defects, can form complex 3D nanostructures, less purity.

**Limitations:** Slower process, requires controlled conditions, surfactants often very essential.

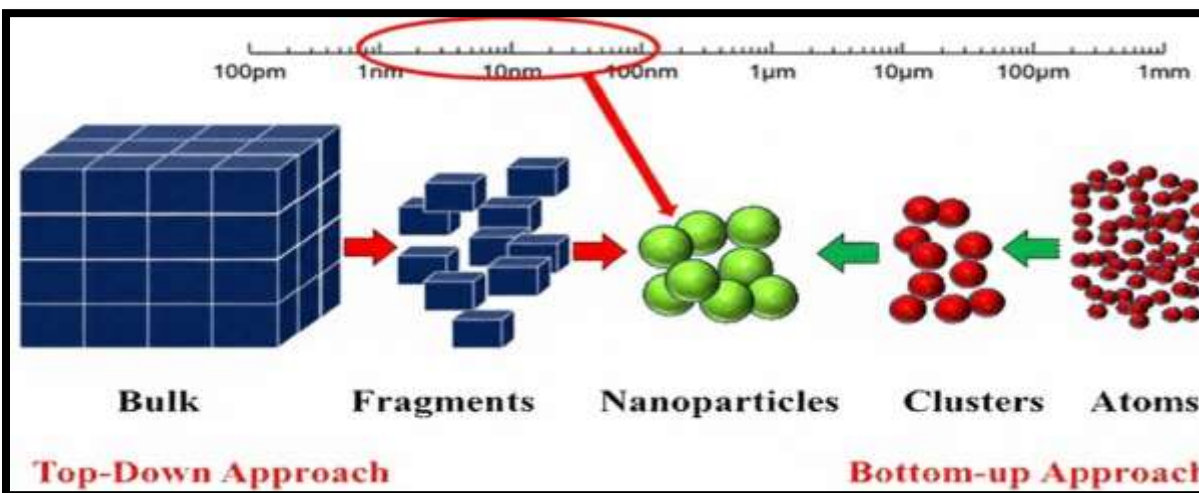


Figure.15: Top-Down and Bottom – Up synthesis methods.

### *Key Considerations in Nanomaterial Fabrication:*

1. **Size Control:** Small changes can drastically change properties.
2. **Shape Control:** Spheres, rods, tubes, or sheets influence performance.
3. **Surface Functionalization:** Adding chemical groups can enhance reactivity or compatibility.
4. **Purity and Defects:** Impurities or defects alter electrical, optical, or mechanical behavior.

## ***Applications of Fabricated Nanomaterials:***

1. Electronics and semiconductors
2. Drug delivery systems
3. Photocatalysts and solar cells
4. Sensors and imaging
5. Energy storage (batteries and supercapacitors)
6. Removal of industrial textile and pesticide waste from irrigation water and soil.

## ***Synthesis of Nanomaterials Methods***

Methods for synthesizing nanostructures are classified into two main categories:

### **1. According to the Nature of the Synthesis Method**

- ❖ Physical methods
- ❖ Chemical methods
- ❖ Biological methods

### **2. According to the Phase of the Medium**

- ❖ Vapor phase
- ❖ Liquid phase
- ❖ Solid phase

## **Vapor phase**

These are a group of methods in which a substance is converted into vapor (gas) and then condensed or deposited to form nanoparticles or nanofilms of very small size. They are among the most important preparation methods because they provide high purity and excellent control over size and shape. Most vapor-phase methods are physical, exception being CVD, which is based on chemical reactions. This method is divided into the following:

## 1- Inert Gas Condensation (IGC)

The method is based on evaporating a solid material (usually a metal) inside a vacuum chamber filled with an inert gas such as argon or helium. As the vaporized atoms cool down through collisions with the inert gas atoms, they condense to form nanoscale clusters.

### Advantages

- ❖ **High Purity:** Produces extremely pure nanoparticles without chemical residues.
- ❖ **Size Control:** Excellent control over the particle size (2–50 nm).

### Disadvantages

- ❖ **High Cost:** Requires expensive vacuum systems and high energy.
- ❖ **Low Yield:** Limited production capacity (slow process).

### Types of Materials Produced

- ❖ **Metallic Nanoparticles:** (like: Gold, Silver, Copper, Iron).
- ❖ **Metal Oxides:** Produced if oxygen is introduced into the chamber during the process.

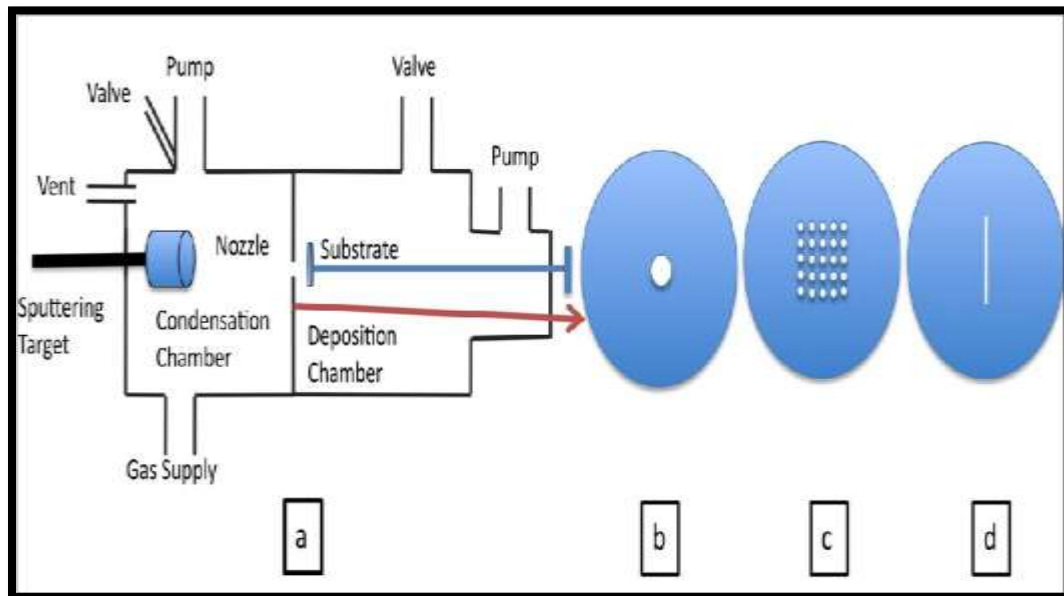


Figure.16: schematic of Inert Gas Condensation (IGC).

## 2- Arc Discharge Method

This method is based on generating a high-temperature electric arc between two electrodes (usually graphite) in an inert gas atmosphere. The intense heat causes evaporation of the electrode material, and upon cooling, the vapor condenses to form nanostructured materials.

### Advantages

- ❖ **High Quality:** Produces structurally excellent and high-quality CNTs.
- ❖ **Versatility:** Can produce SWNTs, MWNTs, and various other carbon nanostructures.

### Disadvantages

- ❖ **Product Mixture:** Produces a mix of nanotubes and unwanted carbon soot.
- ❖ **Purification Needed:** Requires extra steps to separate nanotubes from other carbon forms.

### Types of Materials Produced

- ❖ **Carbon Nanotubes (CNTs):** Both Single-Walled (SWNTs) and Multi-Walled (MWNTs).
- ❖ **Fullerenes & Nanowires:** Also produces nanocapsules, nanorods, and nanofibers.

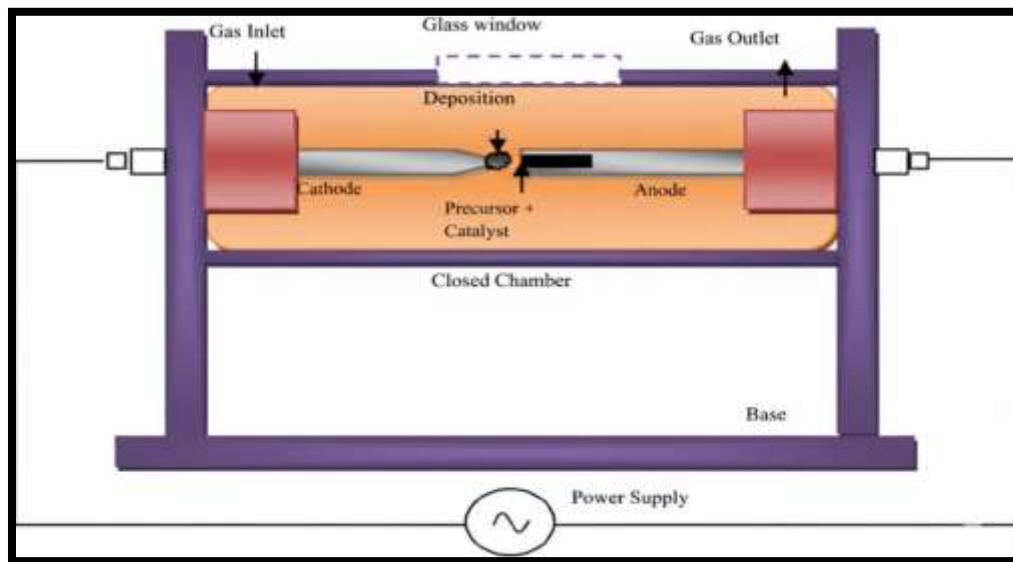


Figure.17: Arc Discharge device.

### 3- Sputtering Method

Sputtering is based on bombarding a target material with high-energy ions generated from a plasma of an inert gas, typically argon. The momentum transfer from the ions causes ejection of atoms from the target surface, which then travel and deposit onto a substrate, forming a nanostructured thin film.

#### Advantages

- ❖ **Exact Copy:** The produced film has the same composition as the source material (target).
- ❖ **Versatile:** It works for almost all materials (metals, oxides, and semiconductors).
- ❖ **Easy Control:** You can easily change the material properties by adjusting the process.

#### Disadvantages

- ❖ **Slow:** The deposition rate is slower than other methods like thermal evaporation.
- ❖ **High Cost:** The "target" materials used in the process are often expensive.
- ❖ **Heat Issues:** Most energy turns into heat, so the system needs a cooling mechanism.
- ❖ **Gas Control:** In some types (Reactive Sputtering), you must be very careful with gas levels.

#### Types of Materials Produced

- ❖ **Pure Elements:** Like Gold, Silver, and Copper.

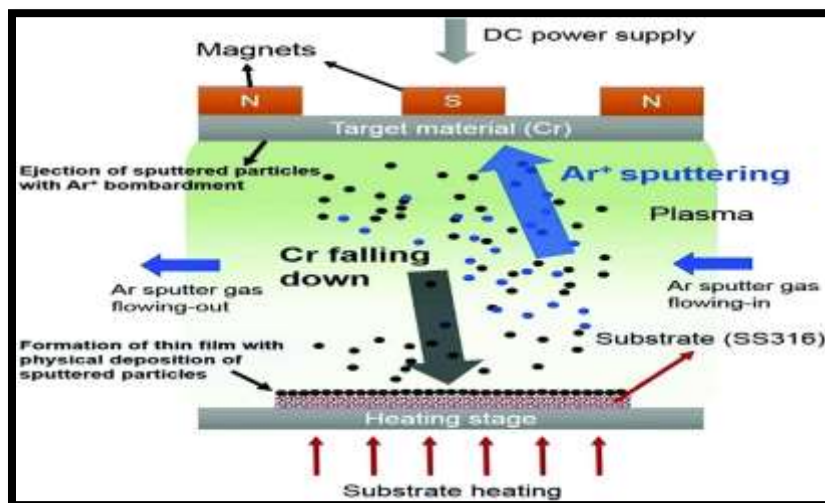


Figure.18: Sputtering method.

## 4- Chemical Vapor Deposition (CVD)

CVD is based on the chemical reaction or thermal decomposition of volatile gases on or near a heated substrate. These reactions produce a solid material that deposits on the substrate in the form of a nanostructured film or nanomaterial, while gaseous by-products are removed from the chamber.

### Advantages

- ❖ **High Quality:** Produces materials with excellent crystal quality and high purity.
- ❖ **Great Control:** It is the best method for controlling the thickness and structure of 2D materials.
- ❖ **Large Scale:** Can produce large amounts of materials (massive production).
- ❖ **Low Defects:** The materials produced have very few mistakes or flaws.

### Disadvantages

- ❖ **Extreme Heat:** Requires very high temperatures, which can be hard to maintain.
- ❖ **High Cost:** The equipment and process are expensive.

### Types of Materials Produced

- ❖ **2D Materials:** Most famous for making Graphene.
- ❖ **Metal Oxides:** Such as Zinc Oxide (ZnO) and Iron Oxide.
- ❖ **Thin Films:** Used in electronics and solar cells.

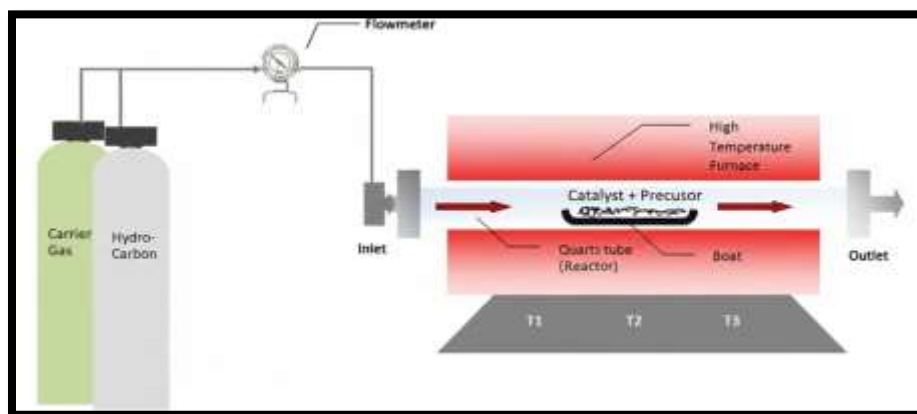


Figure.19: CVD device.

## 5- Laser Ablation in Liquid (LAL)

The method is based on focusing a high-energy pulsed laser beam onto the surface of a solid target immersed in a liquid (such as water, ethanol, or other solvents). The intense laser–matter interaction causes ablation of the target material, generating a plasma plume. Rapid cooling and confinement by the surrounding liquid lead to nucleation and formation of nanoparticles.

### Advantages

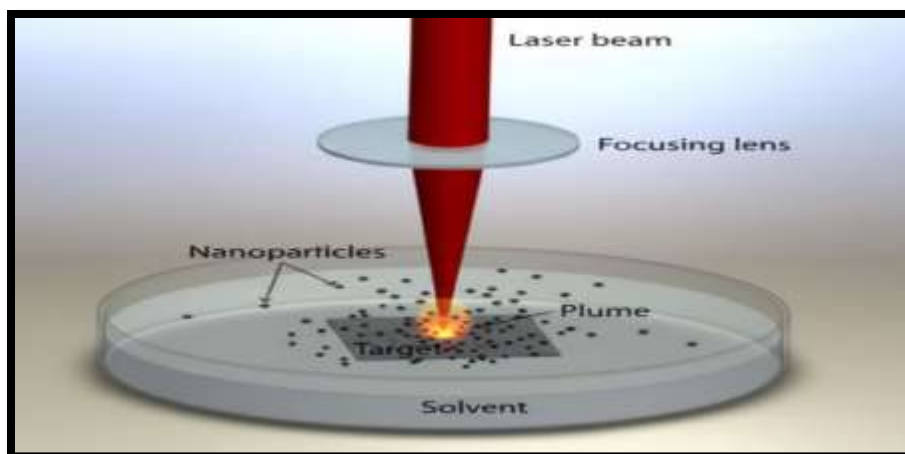
- ❖ **Green & Simple:** A clean technique that usually uses water or organic liquids.
- ❖ **Pure Surfaces:** No need to add extra chemicals (surfactants) to keep particles stable.
- ❖ **Bio-Friendly:** The nanoparticles have a natural charge that makes them perfect for medical use.
- ❖ **Ambient Conditions:** Works under normal room temperature and pressure.

### Disadvantages

- ❖ **Complex Process:** The interaction between the laser and the material is very complicated.
- ❖ **Low Production:** It is hard to produce large amounts of material compared to chemical methods.
- ❖ **High Laser Cost:** Requires expensive laser equipment and precise setup.

### Types of Materials Produced

- ❖ **Colloidal Solutions:** Stable mixtures of metal or oxide nanoparticles in liquids.



**Figure.20: Laser Ablation in Liquid (LAL).**

## Liquid Phase Methods

These are methods in which nanoparticles are prepared within a liquid solution through chemical or physicochemical reactions. These methods are widely used for preparing nanoparticles in laboratories because they are simple and inexpensive compared to Vapor methods. This method is divided into the following:

### 1- Microemulsion method

A microemulsion is a thermodynamically stable, transparent mixture of two immiscible liquids (usually oil and water) stabilized by surfactants (and sometimes co-surfactants). In this system, nanometer-sized droplets act as *nanoreactors* where chemical reactions occur, leading to the formation of nanoparticles.

#### Advantages

- ❖ **Easy to Make:** Forms automatically at room temperature (no high pressure needed).
- ❖ **Stable:** It is thermodynamically stable, meaning it lasts a long time.
- ❖ **Small & Uniform:** Produces very tiny, crystalline nanoparticles with a large surface area.

#### Disadvantages

- ❖ **Chemical Use:** Requires a lot of surfactants, which can be irritating or hard to remove.
- ❖ **Sensitive:** Stability changes if the temperature or pH changes.

## Type of Materials Produced

- ❖ **Metals:** (e.g., Gold, Platinum).
- ❖ **Semiconductors:** (e.g., Cadmium Sulfide).
- ❖ **Oxides:** (e.g., Iron Oxide, Silica).

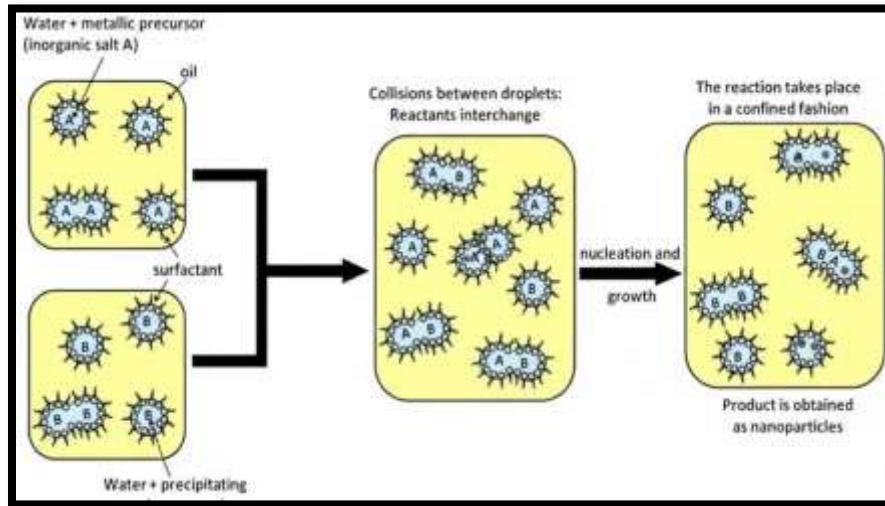


Figure.21: Microemulsion method.

## 2- Hydrothermal Method

The hydrothermal method is based on carrying out chemical reactions in aqueous solutions at high temperature and high pressure inside a sealed vessel called an autoclave. Under these conditions, the solubility and reactivity of materials increase, promoting nucleation and crystal growth of nanomaterials.

### Advantages

- ❖ **Solubility:** Can dissolve materials that don't dissolve easily under normal conditions.
- ❖ **Perfect Crystals:** Produces nanoparticles with high crystallinity and specific shapes.
- ❖ **Control:** You can easily adjust the size and shape by changing the temperature or time.

### Disadvantages

- ❖ **Expensive Equipment:** Requires strong and costly autoclaves to handle high pressure.
- ❖ **Safety:** There is a risk of explosion due to the high pressure inside the vessel.
- ❖ **The "Black Box":** You cannot see the reaction while it is happening because the vessel is sealed.

## Type of Materials Produced

- ❖ **Metal Oxides:** (e.g., Zinc Oxide, Iron Oxide).
- ❖ **Metal Sulfides:** (e.g., Zinc Sulfide).



**Figure.22: Hydrothermal method (Autoclave).**

## 3- Sol-Gel Method

The method involves the transition of a system from a liquid “sol” (colloidal solution) to a solid “gel” through hydrolysis and condensation reactions of metal alkoxides or salts. The gel is then dried and calcined to form nanostructured materials

### Advantages

- ❖ **High Purity:** The final products are very clean and pure.
- ❖ **Low Temperature:** Can be done without needing very high heat.
- ❖ **Easy Doping:** You can easily add small amounts of other materials to the mix.

### Disadvantages

- ❖ **Slow:** The reaction takes a long time to finish.
- ❖ **Chemical Hazards:** Uses organic solvents that can be harmful to health.

## Type of Materials Produced

- ❖ **Metal Oxides:** Such as Silica, Titanium Oxide and Zinc Oxide).
- ❖ **Ceramics:** Specifically high-quality powders used in medicine and dentistry.

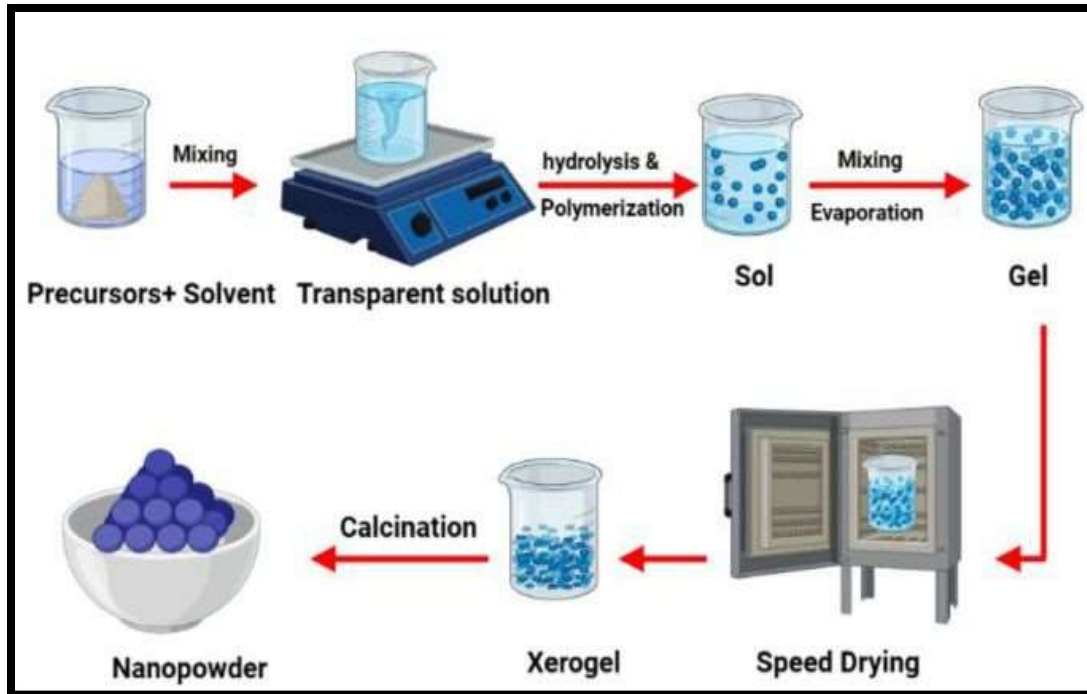


Figure.23: Sol-gel method.

#### 4- Sonochemical Method (Ultrasonic)

The method relies on ultrasound waves to generate acoustic cavitation in a liquid:

- Cavitation forms tiny bubbles that collapse violently, producing extremely high local temperatures and pressures for very short times.
- These extreme conditions can accelerate chemical reactions or break down larger particles into nanoparticles.

##### Advantages

- ❖ **Ambient Temperature:** Works at room temperature, making it safe for organic materials.
- ❖ **Fast & Simple:** High reaction rates mean it takes very little time to produce nanoparticles.
- ❖ **No Clumping:** Reduces surface tension, which prevents particles from sticking together (non-agglomerate).
- ❖ **Variety of Shapes:** Can create unique shapes like nanorings, nanobelts, and clusters.

## Disadvantages

- ❖ **Low Crystallinity:** The produced materials are often non-crystalline (amorphous).

## Type of Materials Produced

- ❖ **Metal Nanoparticles:** Such as Iron (Fe).
- ❖ **Metal Oxides:** Various types of oxides.



Figure.24: Ultrasonic device.

## 5- Co-precipitation Method

The method is based on the simultaneous precipitation of multiple ions from a homogeneous solution. When the salts react with a precipitating agent (e.g., base or reducing agent), they form insoluble compounds that can be collected, washed, and converted into nanomaterials through calcination if needed.

### Advantages

- ❖ **Simple & Fast:** The preparation process is easy and quick.
- ❖ **Eco-Friendly:** It uses water and does not require organic solvents.
- ❖ **Control:** It is easy to control the particle size.

### Disadvantages

- ❖ **Impurity Risk:** Trace impurities from the liquid can end up in the final product.
- ❖ **Consistency Issues:** It can be hard to get the exact same results every time (batch-to-batch problems).

- ❖ **Limited Use:** It does not work for uncharged materials or reactants that precipitate at very different speeds.
- ❖ **Time Consuming:** Some parts of the process (like washing or drying) can take a lot of time.

### Type of Materials Produced

- ❖ **Metals:** Formed from aqueous solutions.
- ❖ **Metal Oxides:** Common for various oxide nanoparticles.

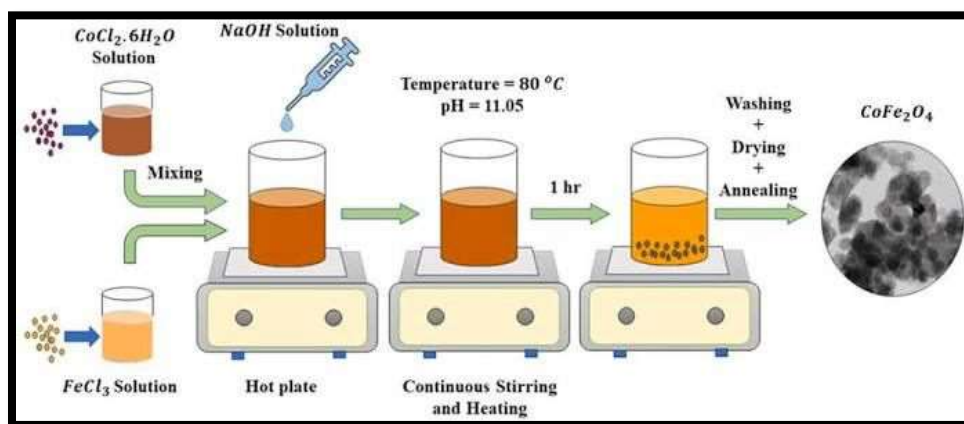


Figure.25: Co-precipitation method.

## 6- Photolysis Method (UV-Irradiation)

The method is based on exposing a salt solution to UV light, which provides energy to break chemical bonds (photolysis) in the salt molecules. This leads to the formation of atoms or ions that nucleate and grow into nanoparticles. No strong chemical reducing agents are required, making the method relatively clean and environmentally friendly.

### Advantages

- ❖ **Small Particles:** Produces much smaller nanoparticles compared to other methods.
- ❖ **Uniform Size:** The particles are "homogeneous" (they all look the same) and have a narrow size distribution.
- ❖ **High Yield:** Produces a large amount of nanoparticles efficiently.
- ❖ **Low Cost:** It is an inexpensive technique to set up and run.
- ❖ **High Purity:** Uses light to reduce metal salts into seeds, leading to high-quality growth.

## Disadvantages

- ❖ **High Heat:** Strong UV lamps (like 125 Watt) get very hot and can damage the experiment.
- ❖ **Cooling Needed:** Requires constant cooling (like an ice bath) to keep the temperature stable.

## Type of Materials Produced

- ❖ **Metal Nanostructures:** Synthesized from metal salts.
- ❖ **Metal Oxides:** Created from metal salts using light energy.

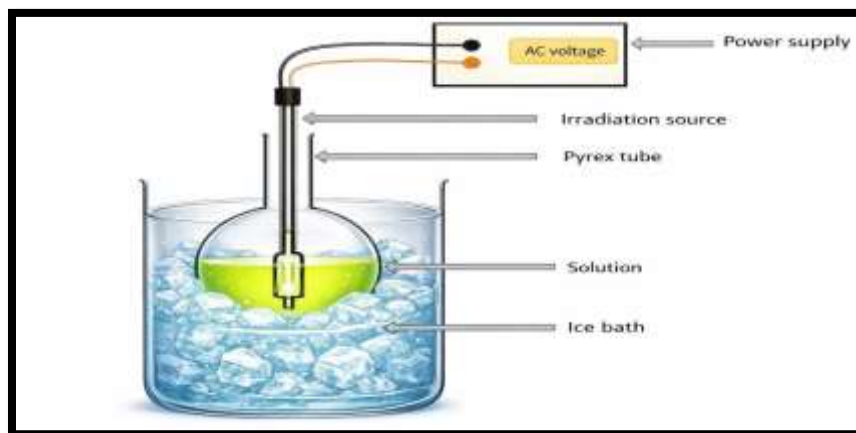


Figure.26: UV-Irradiation.

## 7- Microwave Assisted Method

Microwave radiation interacts directly with polar molecules or ions in the reaction mixture, generating rapid and uniform heating. This speeds up nucleation and crystal growth, leading to the formation of nanoparticles with controlled size and morphology.

### Advantages

- ❖ **Very Fast:** It is a quick technique that speeds up the reaction rate significantly.
- ❖ **Uniform Heating:** Provides heat from the inside out, making the temperature very even.
- ❖ **High Yield:** Produces a large amount of product with high quality.

### Disadvantages

- ❖ **Expensive:** Professional microwave reactors used for chemistry are costly.

- ❖ **Scaling Problems:** It is hard to use for very large amounts because microwaves cannot penetrate deeply into thick liquids.

### Type of Materials Produced

- ❖ **Nanomaterials:** Excellent for materials where size is sensitive to even slight temperature changes.

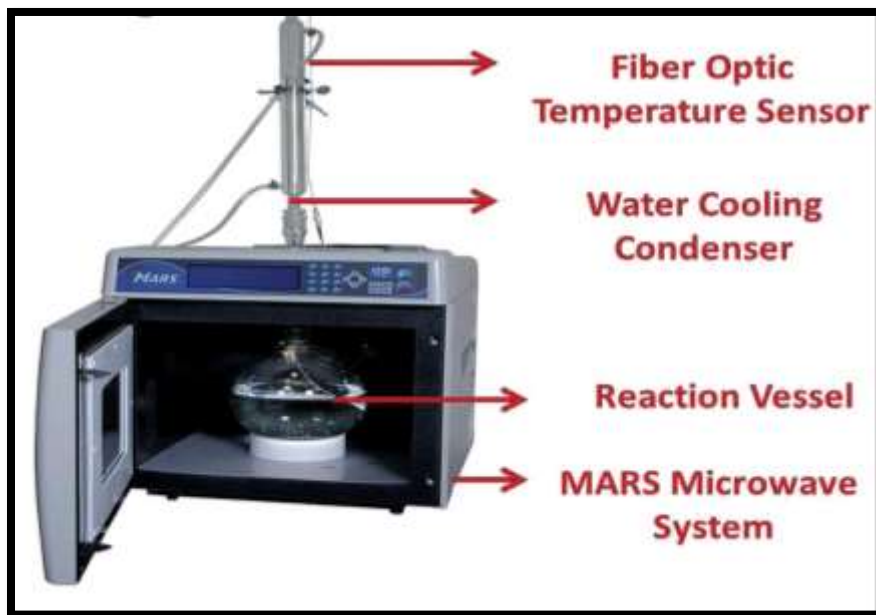


Figure.27: Microwave-assistant method.

## 8- Chemical reduction method

The method is based on the reduction of metal ions in a solution by a chemical reducing agent. The reduced metal atoms nucleate and grow to form nanoparticles. Stabilizers or capping agents are often added to prevent aggregation and control particle size.

### Advantages

- ❖ **No Heat:** Works at room temperature.
- ❖ **Control:** Easy to get the size you want.
- ❖ **Simple:** Doesn't need complex machines.

### Disadvantages

- ❖ **Toxic:** Some chemicals are harmful.
- ❖ **Not Pure:** Extra chemicals stay on the particles.

### Type of Materials Produced

- ❖ Gold and Silver nanoparticles.

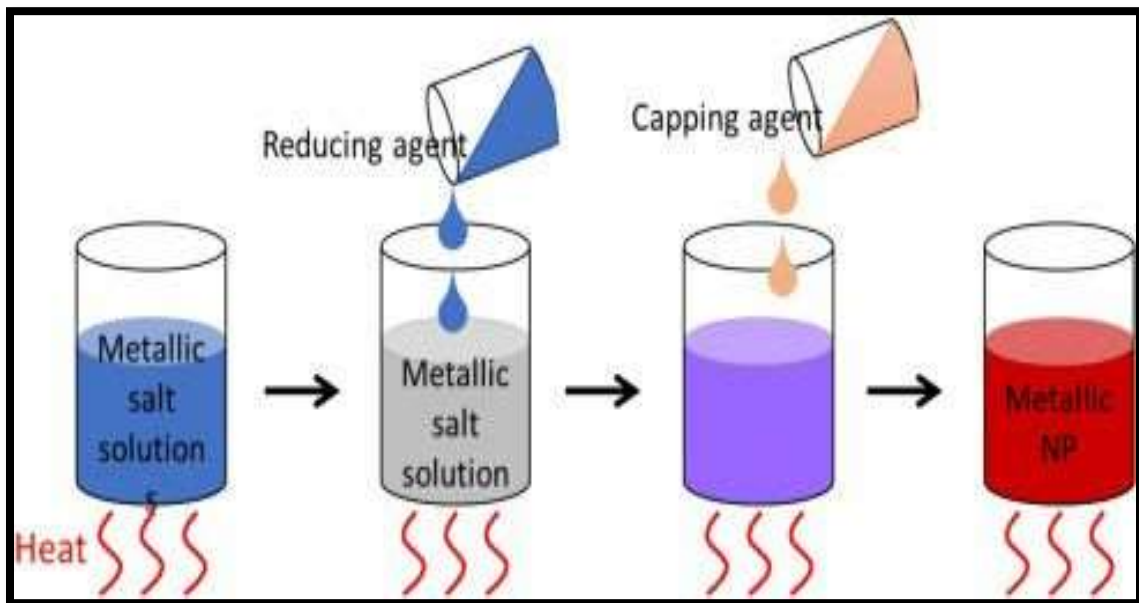


Figure.28: Chemical reducing method.

## 9- Electrochemical Method

The method is based on electrochemical reactions at electrodes, where metal ions in solution are reduced (cathode) or oxidized (anode) to form nanoparticles. The nanoparticles can either deposit on the electrode surface or be released into the solution for collection.

### Advantages

- ❖ **Green:** Friendly to the environment (no pollution).
- ❖ **Cheap:** Cost-effective and simple.
- ❖ **Size Control:** Easy to control size by changing the Current.
- ❖ **Clean:** Electrons are the main "reactant."

## Disadvantages

- ❖ **Complex Factors:** Many things to fix like pH, current, and concentration.
- ❖ **Surface Fouling:** Material can stick to the electrodes and block the process.

## Type of Materials Produced

- ❖ Metal Oxides.
- ❖ Graphene and Carbon Nanotubes.
- ❖ Nanorods.

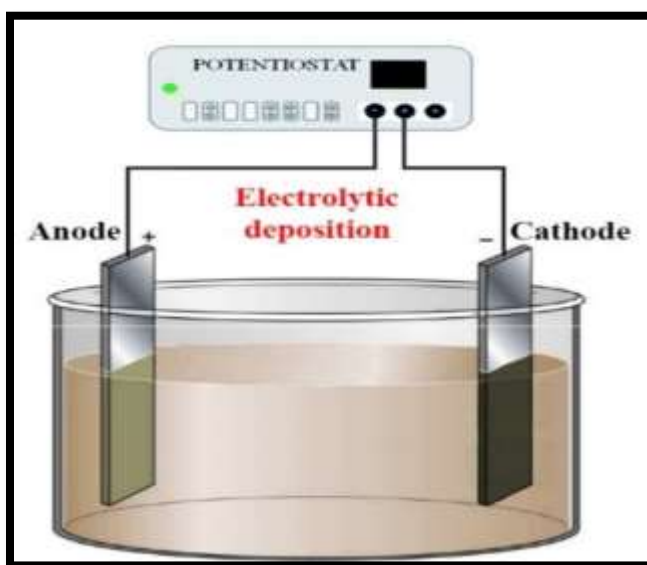


Figure.29: Electrolysis method.

## 10- Green Synthesis Method

Biological molecules (e.g., proteins, enzymes, polysaccharides, polyphenols) in natural extracts act as reducing agents, converting metal ions into metal nanoparticles. They also act as capping agents, stabilizing the nanoparticles and preventing aggregation.

### Advantages

- ❖ **Eco-Friendly:** Safe for the environment and sustainable.
- ❖ **Non-Toxic:** Uses natural materials (plants, bacteria, fungi) instead of harmful chemicals.
- ❖ **Cheap:** Low cost because it uses renewable resources and plant waste.
- ❖ **Safe:** Works at normal temperature and pressure.

## Disadvantages

- ❖ **Slow:** Biological reactions can take more time.
- ❖ **Stability:** Some particles (like Silver) might need extra "stabilizers" to stay active.

## Type of Materials Produced

- ❖ Metal.
- ❖ Metal oxide.

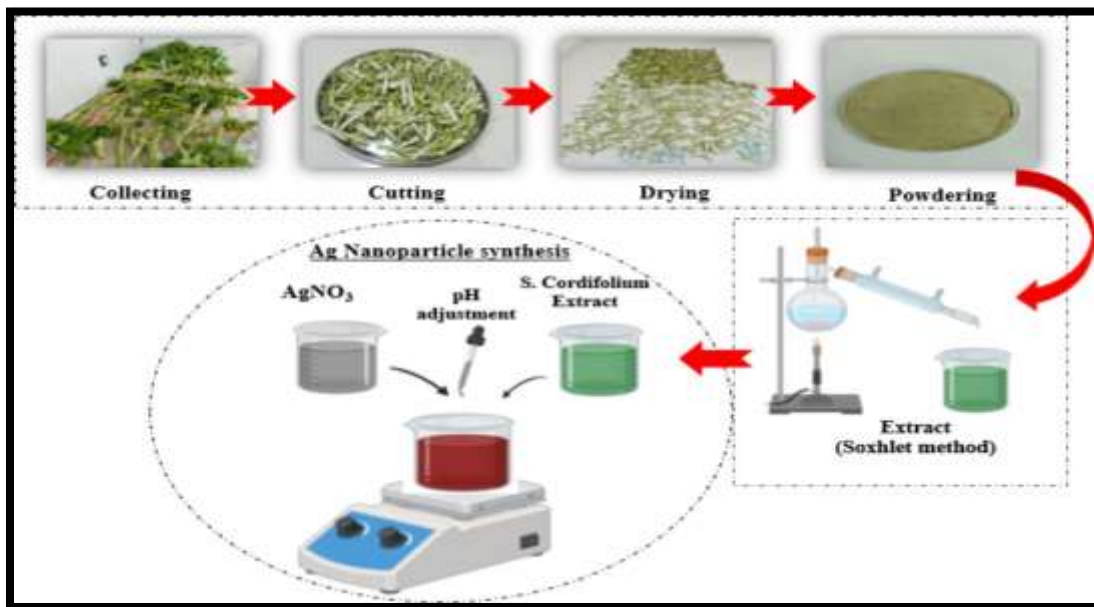


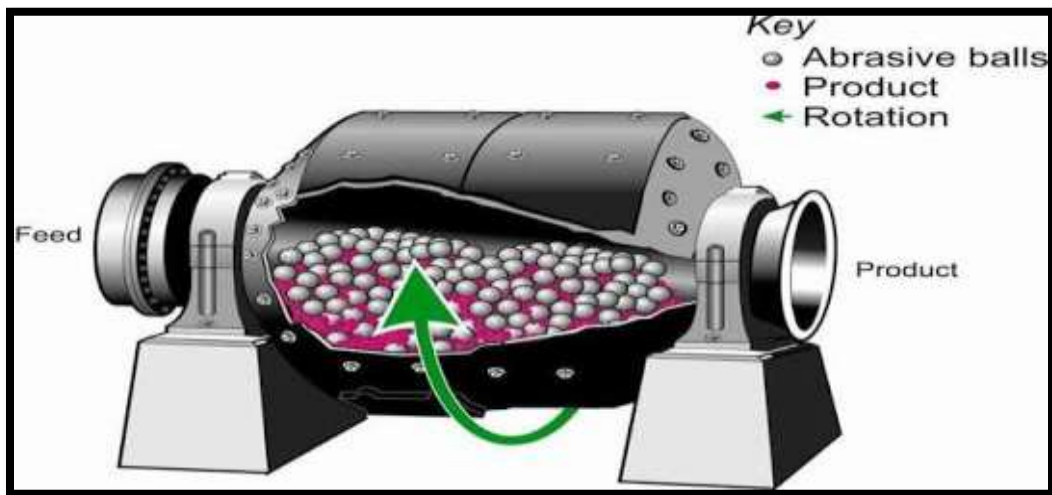
Figure.30: Green synthesis method.

## Solid Phase

### 1- High-Energy Ball Milling method (HEBM)

HEBM is a solid-phase method used to create nanoparticles by grinding materials into smaller sizes.

- ❖ **Origin:** Developed by John Benjamin in 1970 for creating strengthened alloys.
- ❖ **Mechanism:** It works by transferring kinetic energy from moving balls to the material. This energy breaks chemical bonds and creates new surfaces (smaller particles).
- ❖ **Surfactants:** While it can be done alone, adding surfactants is preferred because it helps achieve precise control over the size and shape (morphology) of the nanoparticles.



**Figure.31: Ball Milling synthesis method.**

Nanomaterials prepared by the above methods are characterized using several techniques including:

**1- Atomic Force Microscopy (AFM)**

**2- Scanning Electron Microscope (SEM)**

- What are the differences between SEM and AFM?

	<b>SEM</b>	<b>AFM</b>
<b>Dimensions</b>	2D	3D
<b>Measurements</b>	Chemical composition	Physical properties
<b>Environment</b>	vacuum	Vacuum, air, liquid

### 3- Transmission Electron Microscopy (TEM)

- What are the differences between SEM and TEM?

Feature	SEM	TEM
What it shows	Surface details	Internal structure
How it works	Electron beam scans the surface	Electron beam passes <i>through</i> the sample
Image type	3D-like appearance	2D projection
Resolution	~1–10 nm	~0.1–0.2 nm (much higher)
Sample prep	Relatively simple	Very complex
Common use	Morphology, texture, surface topography	Crystal structure, organelles, defects
acceleration voltages	30 kV	60–300 kV
Magnification	1-2 million times	More than 50 million

### 4- X-ray Diffraction (XRD)

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material. XRD analysis by way of the study of the crystal structure is used to identify the crystalline phases present in a material and thereby reveal chemical composition information.

(Scherrer Equation) :

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D= Average crystalline size (nm),  $\beta$  = line broadening in radians, the full width at half maximum (FWHM),  $\theta$  = Bragg angle,  $\lambda$  = x-ray wavelength=1.5406 angstrom, K= Scherrer constant = 0.9.

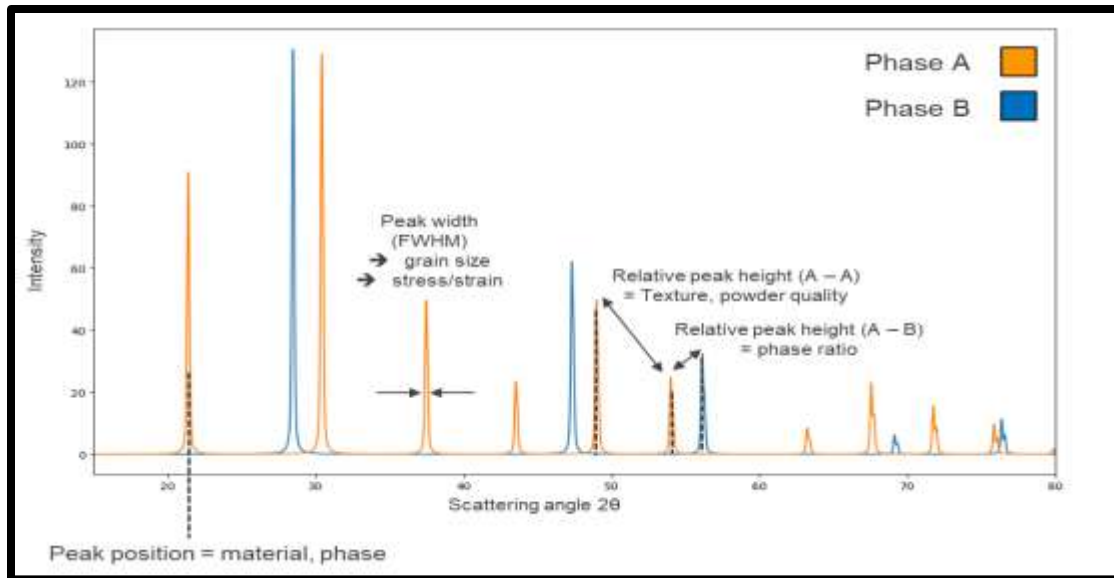


Figure.31: X-ray Diffraction (XRD)

## Safety and toxicity of nanomaterials

### A- Green Nanotechnology (Eco-Friendly Benefits)

1- **Resource Efficiency:** Nanomaterials make products lighter and stronger to save energy.

**Example:** Using Carbon Nanotubes (CNTs) in airplanes makes them lighter, which burns less fuel and reduces CO<sub>2</sub> emissions.

2- **Water Purification:** Nanoparticles can remove very small pollutants that regular filters miss.

**Example:** Nano-iron is used to pull heavy metals like lead and arsenic out of contaminated groundwater.

3- **Renewable Energy Storage:** They help batteries last longer and charge faster.

**Example:** Silicon Nanowires in lithium batteries can store 10 times more energy, making electric cars more practical.

4- **Clean Energy Production:** They improve how much electricity we get from the sun.

**Example:** Quantum Dots help solar panels absorb more sunlight colors, producing more power from the same area.

5- **Sustainable Agriculture:** Reducing the use of harmful chemicals.

**Example:** Nano-fertilizers release nutrients slowly only when the plant needs them, preventing chemicals from leaking into the soil.

## **B- Risks Associated with Poor uses of nanomaterials (Toxicity and Safety)**

**1- Bioaccumulation:** Because they are tiny, they stay in nature and enter the food chain.

**Example:** Nano-plastics are eaten by fish and eventually reach humans, which can cause health issues.

**2- Environmental Toxicity:** They can kill "good" bacteria that the planet needs.

**Example:** Nano-silver from washing machines can leak into rivers and kill the bacteria that naturally clean the water.

**3- Fire and Explosion Hazards:** Their high surface area makes them very reactive and flammable.

**Example:** Nano-aluminum powder can catch fire or explode instantly if it touches a small spark in the air.

**4- Biological Penetration:** They can enter the lungs and blood easily because of their size.

**Example:** Breathing in Carbon Nanofibers without a mask can cause lung scarring (fibrosis) similar to asbestos.

**5- Recycling Challenges:** It is very hard to separate nanomaterials from normal trash.

**Example:** Old batteries containing Cobalt Nanoparticles can leak "invisible" toxins into the ground that are almost impossible to clean up later.

## Practical Examples and Case Studies

- ❖ **Gold nanoparticles** are used in cancer treatment and diagnosis, where they help deliver drugs directly to tumor cells and enhance imaging techniques.
- ❖ **Silver nanoparticles** are widely applied in medical dressings and coatings because of their strong antibacterial properties.
- ❖ **Titanium dioxide (TiO<sub>2</sub>) nanoparticles** are used in sunscreens to block ultraviolet (UV) radiation while remaining transparent on the skin.
- ❖ **Carbon nanotubes** are used in lightweight and high-strength materials for aerospace and automotive applications.
- ❖ **Quantum dots** are applied in bioimaging and medical diagnostics due to their size-dependent fluorescence properties.
- ❖ **Graphene nanosheets** are used in supercapacitors and batteries to improve energy storage capacity and electrical conductivity.
- ❖ **Nanofilms and nanocoatings** are used to protect surfaces from corrosion, wear, and environmental damage.
- ❖ **Iron oxide nanoparticles** are used in magnetic resonance imaging (MRI) as contrast agents and in targeted drug delivery.
- ❖ **Case study:** The use of nanostructured catalysts in chemical reactions has significantly increased reaction efficiency and reduced energy consumption.
- ❖ **Case study:** Nanotechnology-based water filtration systems using nanomaterials have improved the removal of heavy metals and harmful contaminants.