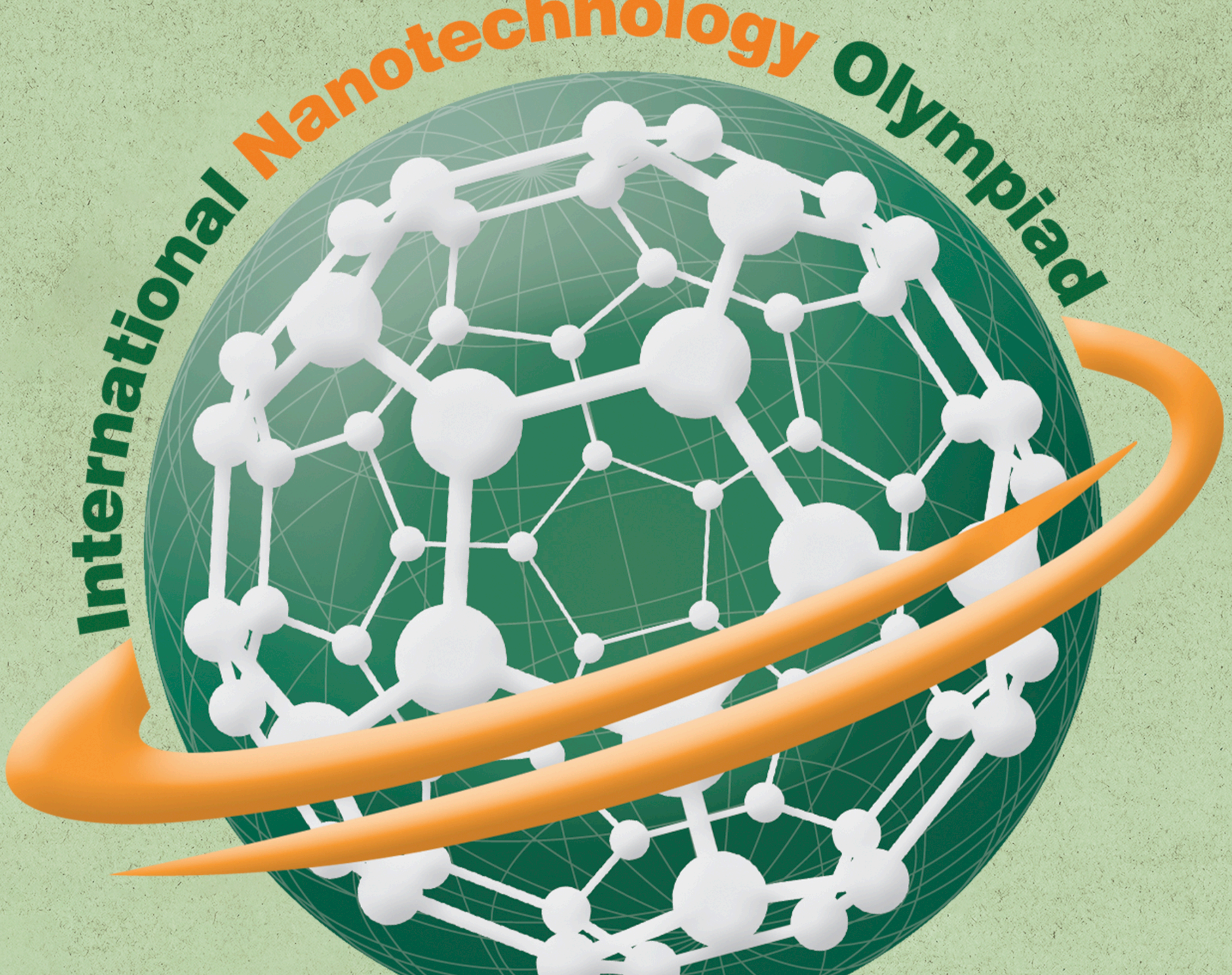
# Introduction to Nanoscience and Technology Booklet



March 2025

## Introduction to Nanoscience and Technology:

- **Introduction to Nanotechnology, Nanoscale Dimensions and Nanostructures**
- **Crystal Networks**
- **Defects in Crystals**

## Introduction to Nanotechnology, Nanometer Scale, and Nanostructures

### Introduction

The concept of nanotechnology was first introduced in 1959 by Dr. Richard Feynman a physics Nobel laureate, in a lecture at the American Physical Society. At a time when little was known about nanoscience, he raised questions about the possibility of working with materials and objects at very small scales, sparking the curiosity of all who listened . He also made suggestions about the differences between nanoscience and fundamental physics. Although his ideas seemed surprising and impossible back then, today we see many of them becoming reality. With the rapid advancement of human knowledge and technology, and the ability to manipulate matter at extremely small scales, it is predicted that all of his ideas will eventually become part of human scientific knowledge.

Nanotechnology involves the study and manipulation of materials at atomic, molecular, and macromolecular scales, which leads to significant changes in the properties of materials at the nanometer scale compared to larger scales. Generally, nanotechnology can be defined as the design, production, and application of nanostructures. Different definitions of nanotechnology reflect its wide range of scientific fields, making it an interdisciplinary science.

### Nanometer Scale

The prefix "nano" comes from the Greek word nanos, meaning "dwarf" or "very small." Today, the term "nano" is widely recognized in advanced science, and many nanowords have recently been added to dictionaries. Terms like nanometer, nanoscale, nanotechnology, nanostructure, nanotube, nanowire, and nanorobot are examples of this wide usage. "Nanometer" is a unit of measurement that refers to one-billionth of a meter, or $10^{-9}$ meters. For comparison, a nanometer is about the length of 10 hydrogen atoms lined up or five silicon atoms in a row. The diameter of a human hair is about 60,000 nanometers. (figure1)

Table 1: Some Size Prefixes

| **Common Prefixes used with SI Units** | | | |
|---|---|---|---|
| Prefix | Symbol | Meaning | Order of Magnitude |
| *giga-* | G | 1 000 000 000 | $10^9$ |
| *mega-* | M | 1 000 000 | $10^6$ |
| *kilo-* | k | 1 000 | $10^3$ |
| *hecto-* | h | 100 | $10^2$ |
| *deka-* | da | 10 | $10^1$ |
| | base unit | 1 | $10^0$ |
| *deci-* | d | 0.1 | $10^{-1}$ |
| *centi-* | c | 0.01 | $10^{-2}$ |
| *milli-* | m | 0.001 | $10^{-3}$ |
| *micro-* | µ | 0.000 001 | $10^{-6}$ |
| *nano-* | n | 0.000 000 001 | $10^{-9}$ |

The importance of the nanometer scale lies in how the properties and characteristics of materials change at these small sizes. Properties like strength, flexibility, electrical conductivity, magnetism, color, reactivity, etc., change at the nanometer scale and new characteristics emerge. This leads to the creation of new materials with unique properties that don’t exist at larger scales. Small sizes allow for more efficient use of space. Materials at the micrometer scale typically show physical properties similar to their macroscopic forms, but materials at the nanoscale exhibit very different properties.

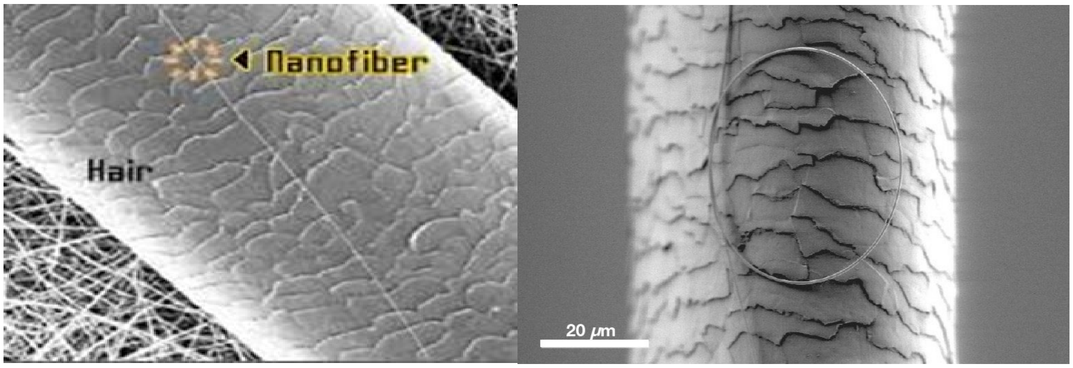


Figure 1: (a) SEM image of human hair, (b) Comparison of human hair size with nanofibers.

Many materials in nature have structures at the micro and nano scales. The natural world is full of systems with nanostructures, such as milk (a nanometer-scale colloid), proteins, cells, viruses, and more, some of which are shown in Figure 2. Many organisms use nano-sized structures in their bodies. For example, a gecko's high ability to stick to surfaces is due to the nanoscale spines on its feet.

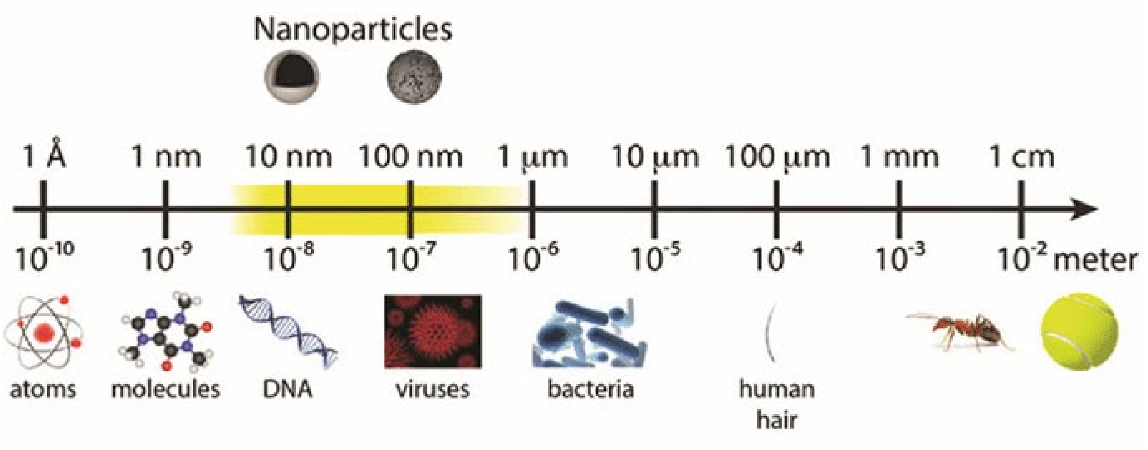


Figure 2: Comparison of biological materials at the nanoscale and microscale

## 1.3 Why Do the Properties of Materials Change at the Nanoscale?

As mentioned, materials at the nanoscale exhibit new and unique properties. The chemical and physical properties of materials, such as optical, electrical, thermal, magnetic, reactivity, and mechanical properties, undergo significant transformations when reduced to the nanoscale. But what does cause these dramatic changes in properties? Why do materials experience such transformations simply by reducing their size to the nanoscale, without any change in their composition? There are two main reasons for these changes in properties: surface effects and the transition of the physical properties from the classical physics into the realm of quantum physics.

### 1.3.1 Surface Effects

A simple example of the effect of surface area is burning of a tree log and wood shavings. A log burns slowly, while wood shavings catch fire quickly. As you know, wood shavings have a smaller size, which means they have a larger surface area in contact with the air and the oxygen present in it, allowing them to burn faster.

Nanomaterials, due to their very small size, have an extremely high surface-to-volume ratio. To better understand this concept, imagine a cube with a side length of 1 cm. Now, suppose you want to shrink this cube until each side is only 1 nanometer long. As shown in the figure below, you reduce the cube step by step, halving it each time. In the first step, you get eight smaller cubes.

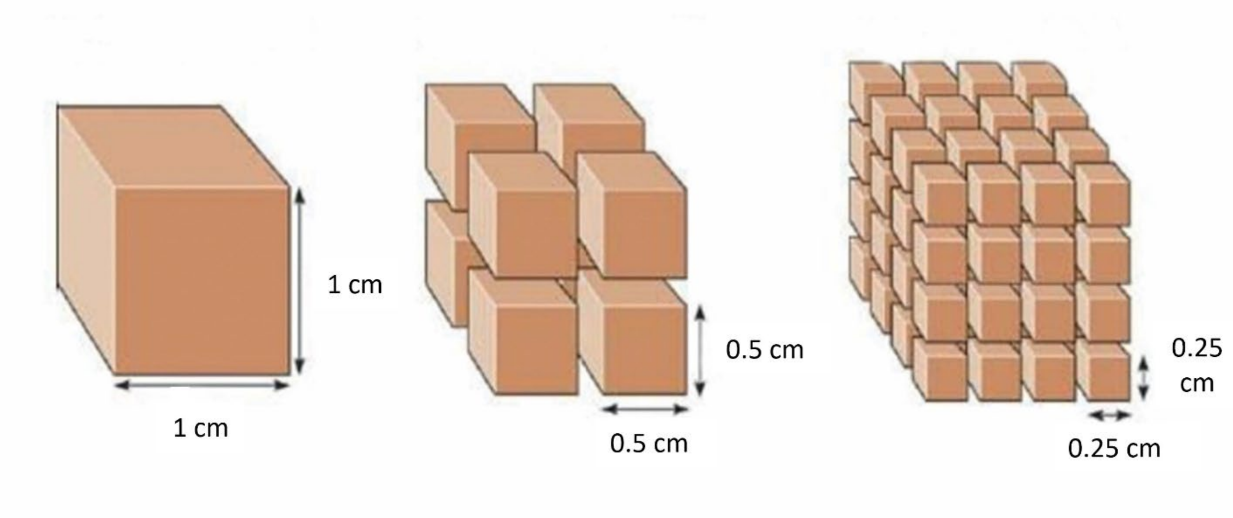


Figure 3: Each step of cutting results in eight smaller cubes.

Now, let's consider and calculate the following points: First, how many cutting steps are needed to reduce the original 1 cm cube into cubes with a side length of 1 nanometer? Second, how many times should we repeat this cutting process? Finally, what is the total surface area at each step? You can perform these calculations. The results of these questions are presented in Table 2.

Table 2: Results of the cube cutting process and external surface area at each step.

| Number of divisions | Number of pieces | Dimensions | External surface (m$^{۲}$) |
|---|---|---|---|
| 0 | 0.01 | 0.0006m | 0.0006 |
| 1 | 8 | 0.005m | 0.0012 |
| 2 | 64 | 0.0025m | 0.0024 |
| 3 | 512 | 0.00125m | 0.0048 |
| 4 | 4096 | 0.000625m | 0.0096 |
| 5 | 32768 | 0.0003125m | 0.0192 |
| 6 | 262144 | 0.00015625m | 0.0384 |
| 7 | 2097152 | 0.000078125m | 0.0768 |
| 8 | 1677721 | 39.625 µm | 0.01536 |
| 9 | 134217728 | 19.5313 µm | 0.03072 |
| 10 | 1073741824 | µm 9.76563 | 0.6144 |
| 11 | 8589934592 | 4.88281 µm | 1.2288 |
| 12 | 68719476736 | 2.44141 µm | 2.4576 |
| 13 | 11+5.49756E | 1.2207 µm | 4.9152 |
| 14 | 12+4.39805E | 0.610352µm | 9.8304 |
| 15 | 13+3.51844E | 0.305176µm | 19.6608 |
| 16 | 14+2.81475E | 0.152588µm | 39.3216 |
| 17 | 15+2.2518E | 76.2939 nm | 78.6432 |
| 18 | 16+1.80144E | 38.147 nm | 157.2864 |
| 19 | 17+1.44115E | 19.0735 nm | 314.5728 |

| | | | |
|---|---|---|---|
| 20 | 18+1.15292E | 9.53674 nm | 629.1456 |
| 21 | 18+9.22337E | 4.76837 nm | 285.2912 |
| 22 | 19+7.3787E | 2.38419 nm | 2516.5824 |
| 23 | 20+5.90296E | 1.19209 nm | 5033.1548 |

As you can see in Table 2, the original 1 cm cube initially had only 0.00006 $m^2$ of surface area (equivalent to 6 $cm^2$). For a better understanding, this surface area could only cover a small part of a tile on the floor. However, after 23 steps of cutting the cube into smaller pieces, around $10^{20}$ smaller cubes are produced, each with a side length of just 1/2 nm. The surprising result is that with this number of tiny cubes, a surface area of 5033 $m^2$ can be covered! This is almost the surface area of a soccer field! In other words, if we reduce a 1 cm cube to a huge number of very small cubes, we can cover nearly a soccer field's area!

This example clearly demonstrates how dramatically the surface-to-volume ratio increases when particles reach the nanoscale.

Also, if you take a closer look at Table 2, you will see that while there is an increase in the surface-to-volume ratio when reducing the cube size from centimeters to micrometers, the effect is not significant. However, this change becomes remarkable once the size reaches below 100 nanometers, and the effect grows stronger as the size is further reduced. For example, reducing a cube from 4.8 nm to 1.2 nm increases the surface area from 1258 $m^2$ to 5033 $m^2$. This illustrates how the transition to the nanoscale dramatically affects the surface-to-volume ratio.

As the particle size decreases from meters to micrometers, there is no significant change in the percentage of surface atoms. However, once the particle size is reduced to below 100 nanometers, the percentage of surface atoms increases significantly. The smaller the particle, the higher the percentage of surface atoms. In these very small dimensions, the number of atoms on the surface becomes greater than the number of atoms in the volume of the particle.

As a result, surface atoms can significantly influence the chemical and physical properties of the material. The next question is: what makes surface atoms different from atoms in the bulk? To answer this, consider the following diagram:

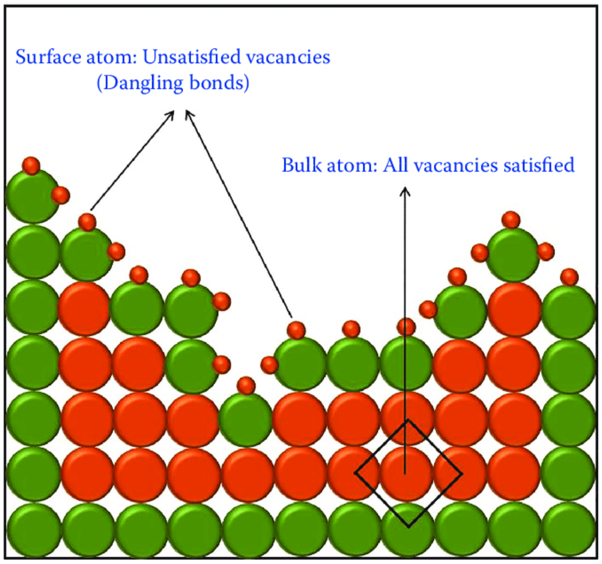


Figure 4: Comparison between surface atoms and bulk atoms.

In Figure 4, the coordination of bulk atoms (atoms that are not on the surface) and the surface atoms are schematically shown. As you can see, bulk atoms have established all possible bonds (in this example, four bonds), so they are fully saturated. However, surface atoms have some broken or incomplete bonds, which are represented by small red circles. Therefore, the difference between surface atoms and bulk atoms is that surface atoms have broken bonds or are "unsaturated." These atoms, due to their broken bonds, are more reactive and unstable compared to bulk atoms, and they tend to seek bonding to complete their saturation. This is why when the number of surface atoms in a particle increases, the particle becomes much more reactive. The increase in surface area is the cause for many changes in the properties of nanomaterials, such as increased reactivity, reduced melting point, enhanced absorbing properties, and more.

### 1.3.2 Transition to the World of Quantum Physics

The second reason for the special properties of some nanomaterials, such as their optical properties, is the transition into the realm of quantum physics and the characteristics connected to discrete energy levels that emerge at the nanoscale. This topic will be explained in the article on the optical properties of nanomaterials.

## 1.4 Classification of Nanostructures Based on Dimensions

### 1.4.1 What are Nanomaterials?

Earlier, you learned about nanoscience and nanotechnology. A question that may come to mind is: What materials are considered nanomaterials?, every material has three dimensions. If at least one of these dimensions is in the nanoscale range (between 1 and 100 nanometers), the material is considered a nanomaterial. The dimension that is not in the nanoscale is called a "free dimension" because it can be any size.

### 1.4.2 Classification of Nanostructures Based on Free Dimensions

Nanostructures are classified based on the number of free dimensions into four categories: zero-dimensional nanomaterials, one-dimensional nanomaterials, two-dimensional nanomaterials, and three-dimensional nanomaterials. Figure 5 shows different types of nanostructures.

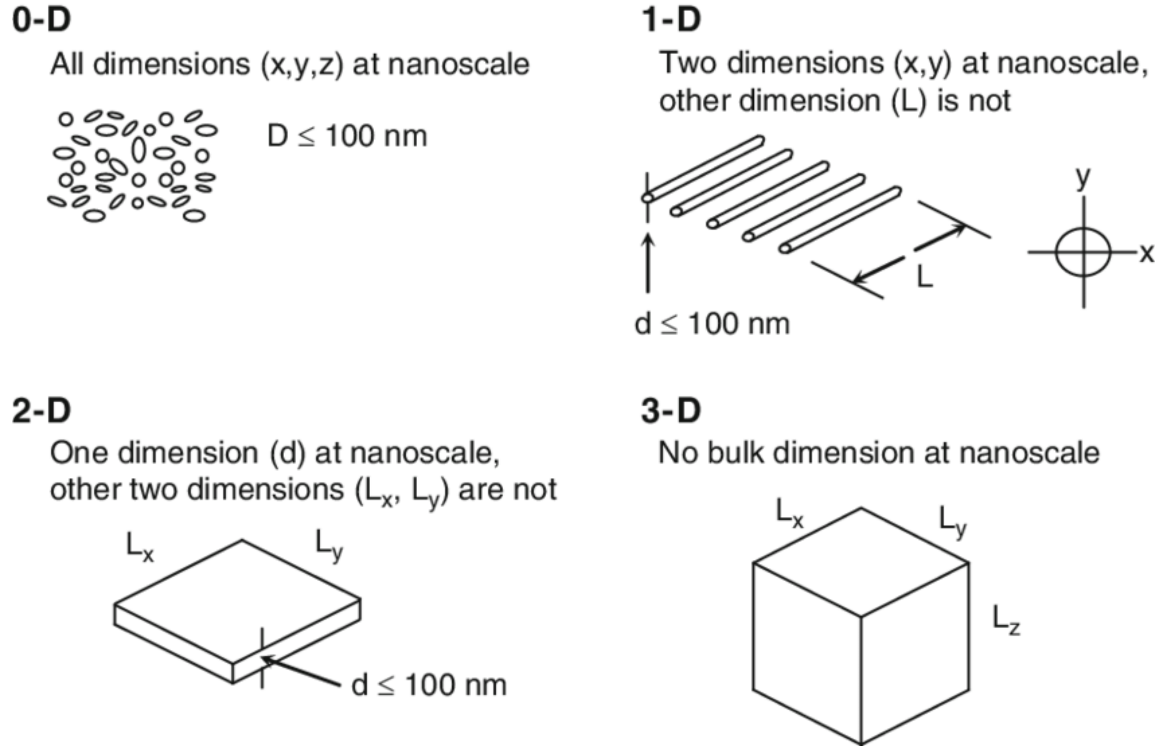


Figure 5: Types of nanostructures based on the number of free dimensions.

#### 1.4.2.1 Zero-Dimensional Nanomaterials (0D)

These materials have nanometer size in all three dimensions, with no free dimensions. According to some classifications, these nanostructures are also called nanoparticles. The properties of nanoparticles are influenced by their size and material. Figure 6 shows examples of nanoparticles as zero-dimensional nanostructures. Nanoparticles can be spherical, oval, cubic, cylindrical, etc., and they may consist of a single material or a combination of different materials. They are used in various industries such as automotive (for scratch-resistant coatings, anti-fogging glass, durable tires, etc.), medicine (for creating new drugs and diagnosing diseases), water purification, electronics, and military applications.

Among the zero-dimensional nanomaterials are metal nanoparticles, which exhibit unique optical, electrical, and magnetic properties due to their very high surface-to-volume ratio and intrinsic properties. The optical properties of these nanoparticles determine the color of the nanoparticles. By using the relationship between the color of metal nanoparticles and their size, their sensor properties can be used in various applications. These metal nanoparticles, such as nano platinum, are also known as very strong nano catalysts. Other applications of metal nanoparticles include superparamagnetic properties, color additives to glass, antibacterial properties, and very strong electrical and thermal conductors.

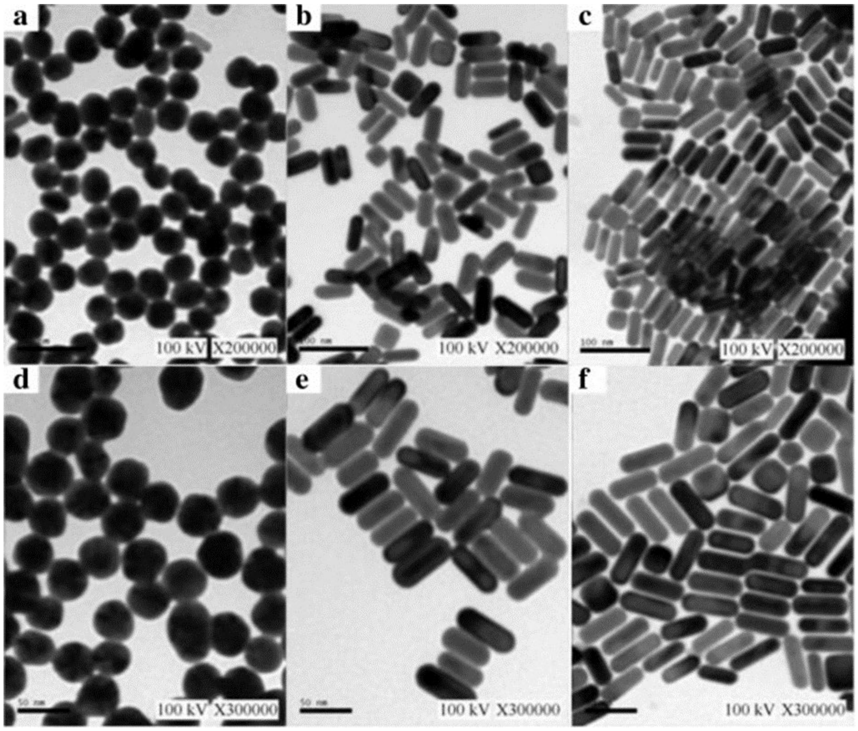


Figure 6: Images of nanoparticles with different shapes as zero-dimensional nanostructures.

### 1.4.2.2 One-Dimensional Nanomaterials (1D)

One-dimensional nanomaterials have two dimensions in the nanoscale and one free dimension. Nanowires, nanorods, nanotubes, and nanofibers are examples of one-dimensional nanomaterials. Figures 7 and 8 show examples of one-dimensional nanostructures. The properties of one-dimensional nanostructures are influenced by the material and the length-to-diameter ratio (L/d). The most important property of one-dimensional metallic nanostructures is their electrical conductivity along the axis of the wire. Nanowires are used in various applications, such as making very small, high-speed computers, tiny lasers, disease diagnostics, and magnetic memory. Nanofibers are nanometer-sized threads with diameters smaller than one micron and lengths several microns long. These one-dimensional nanomaterials exhibit special physical and chemical properties due to their high length-to-diameter ratio and surface area, leading to diverse applications in various industries.

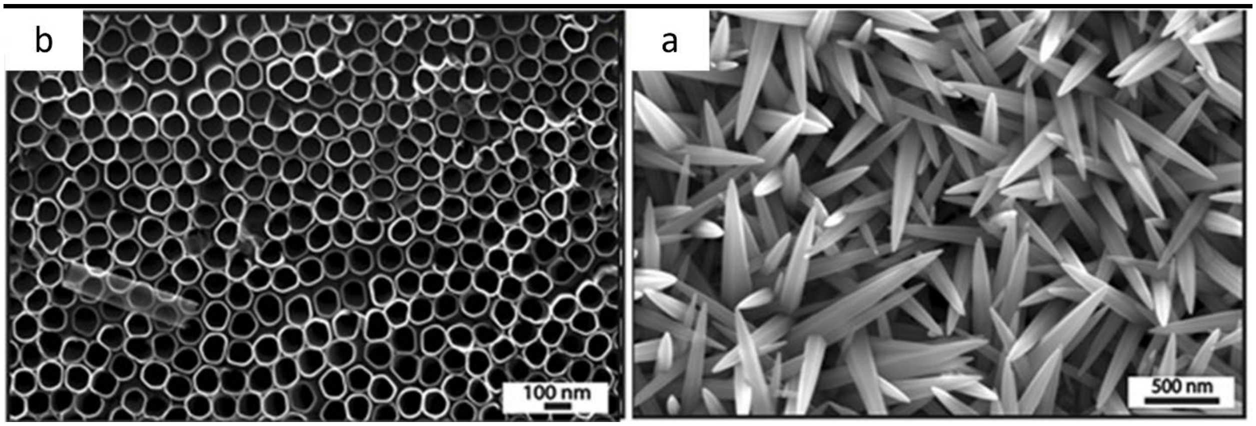


Figure 7: Images of one-dimensional nanostructures: (a) Titanium oxide nanotubes, (b) Zinc oxide nanorods.

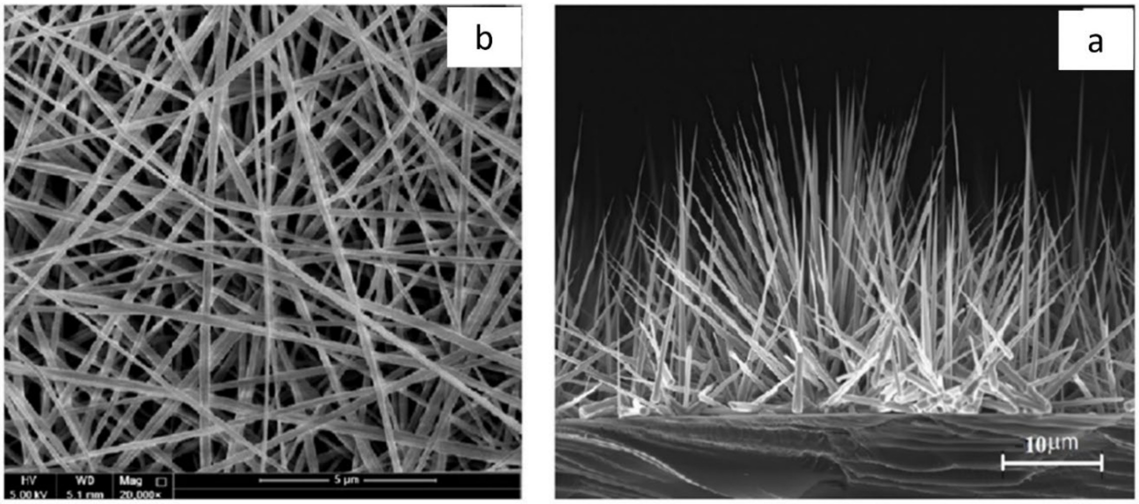


Figure 8: Images of one-dimensional nanostructures: (a) Zinc oxide nanowires, (b) PVP nanofibers.

### 1.4.2.3 Two-Dimensional Nanomaterials (2D)

These materials have two free dimensions and one dimension in the nanoscale. Two-dimensional nanomaterials primarily include thin layers or surface coatings. Figure 9 shows examples of two-dimensional nanostructures. The properties of thin coatings are influenced by their material and thickness. For example, food packaging films are coatings. If their thickness is in the nanoscale, they are called nanocoating. Nanocoating are layers with thicknesses ranging from 1 to 100 nanometers that are applied to other materials, altering their properties and characteristics.

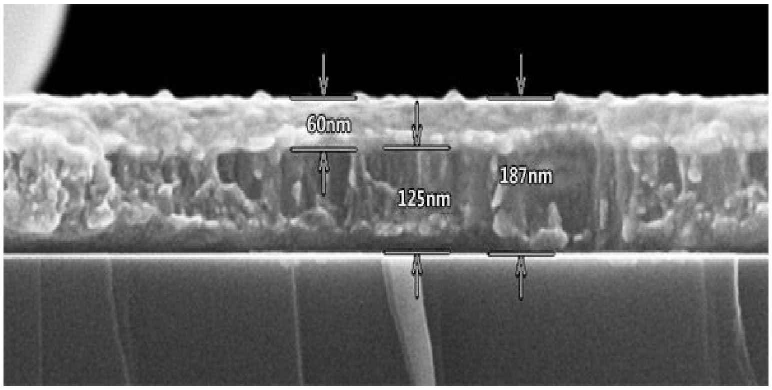


Figure 9: Examples of two-dimensional nanostructures.

### 1.4.2.4 Three-Dimensional Nanomaterials (3D)

Three-dimensional nanomaterials are materials in which all three dimensions are free-scale. As you can see, this definition contradicts the definition of nanostructured materials, because none of its three dimensions are in the nanoscale. This category includes nanocomposites (materials made from multiple components) and bulk nanostructured materials (or bulk nanostructured solids). Figure 8 shows examples of three-dimensional nanostructures. Bulk nanostructured materials have at least one of their constituent unit sizes smaller than 100 nanometers. For instance, some materials may not conduct electricity, but if we add conductive nanoparticles to them, the resulting composite can become conductive. These are called nanocomposites. If at least one component of the composite is in the nanoscale, the material is called a nanocomposite. Another example of 3D nanomaterials are porous nanomaterials, or materials that have pores less than 100 nanometers in size.

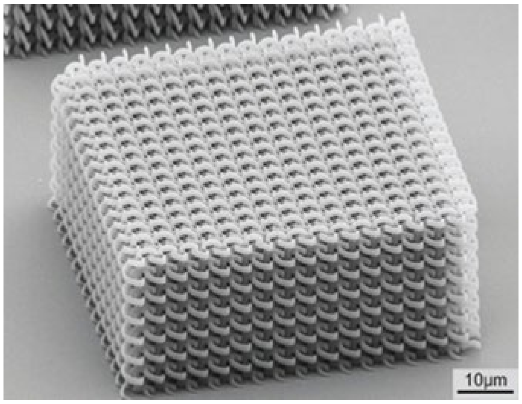


Figure 10: Examples of three-dimensional nanostructures.

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Introduction to Nanoscience and Technology ۱ - Farzad Hosseini Nasab, Mohsen Afsari Velayati, Seyed Masoumeh Ghasemi-Nejad Lichani - Koochak Amooz Publications

# Crystal Networks

## Abstract

Crystal systems can be categorized into two-dimensional and three-dimensional systems. In two dimensions, four crystal systems are introduced. In three dimensions, 14 Bravais crystal lattices are introduced. The unit cells of these 14 lattices differ in the sizes of their sides and the angles between them. Among them, cubic and hexagonal lattices are particularly important because many crystalline materials in nature have these structures. Therefore, knowing the properties of these crystal systems is essential. This article introduces two-dimensional and three-dimensional crystal systems and discusses the key characteristics of the most important crystal lattices.

Keywords: Crystallography, Bravais lattices, simple cubic, body-centered cubic, face-centered cubic, atomic packing factor

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## 1. Introduction

Crystallography studies (mathematical models and experimental investigations) have shown that different crystal systems can be defined and studied in two and three dimensions. The key to this study is the symmetry present in these structures and the types of symmetries involved. This article does not aim to discuss these symmetries but focuses on explaining the result: the two-dimensional and three-dimensional crystal systems.

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## 2. Crystal Systems

Atoms in crystal structures are arranged in different ways. The arrangement of atoms in these crystal structures plays a crucial role in determining the material's properties. Crystal systems can be broadly classified into two categories: two-dimensional and three-dimensional. This section will introduce and review these systems in which atoms can arrange themselves in an orderly manner.

### 2.1 Two-Dimensional Crystal Systems

The simplest shape that can fill a plane is a parallelogram. To define a parallelogram, it’s enough to know two vectors for its sides and the angle between them (Figure 1).

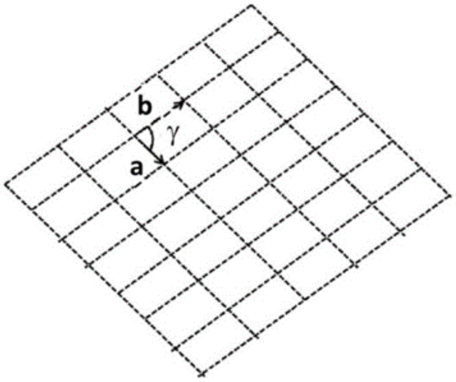


Figure 1: Defining a two-dimensional system with two vectors and the angle between them.

These two vectors and their angle can have different values. The different combinations of these three variables (two vectors and their angle) lead to four two-dimensional crystal systems, as shown in Figure 2. These four systems are: oblique, rectangular, hexagonal, and square.

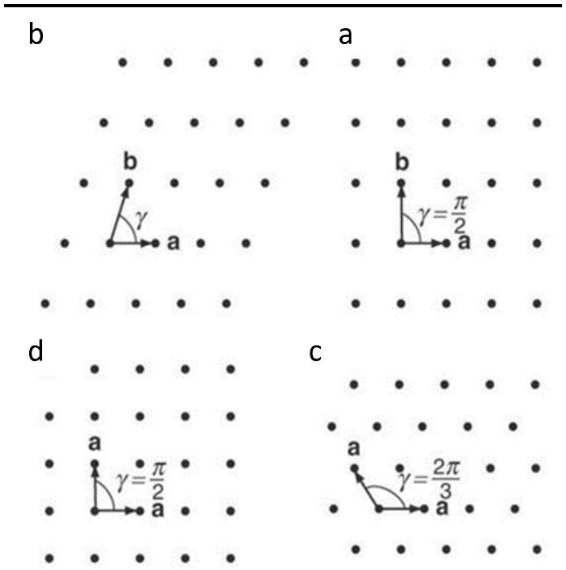


Figure 2: Four different two-dimensional crystal systems: (a) rectangular, (b) oblique, (c) hexagonal, (d) square. [1].

As shown in Figure 2, the oblique system has no specific relationship between the sides and the angle between them. In the rectangular system, the angle between the two vectors is 90 degrees. In the hexagonal system, the two vectors are equal in length, and the angle between them is 120 degrees. In the square system, the angle between the two vectors is 90 degrees, and the lengths of the two vectors are also equal.

A unit cell can be defined in each of these systems under the given conditions, and this unit cell represents each of the two-dimensional crystal systems. By repeating the unit cells, we can create these crystal structures.

One famous nanostructure that has a two-dimensional structure is graphene. Graphene is a honeycomb structure of carbon atoms, where the distance between each pair of atoms is about 0.142 nanometers. Figure 3 shows the two-dimensional structure of graphene. As seen in Figures 2 and 3, the crystal structure of graphene corresponds to the hexagonal system. This description applies to the ideal case with no impurities or defects.

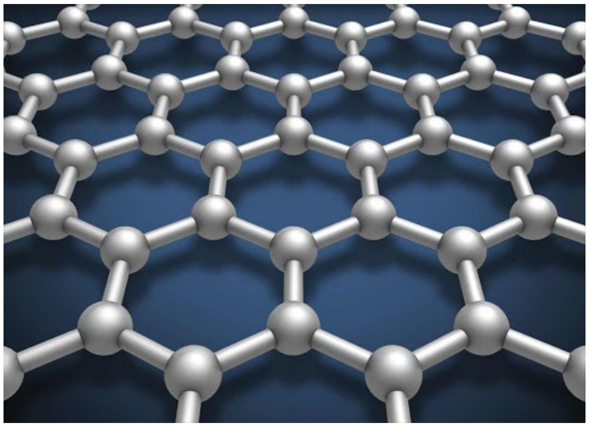
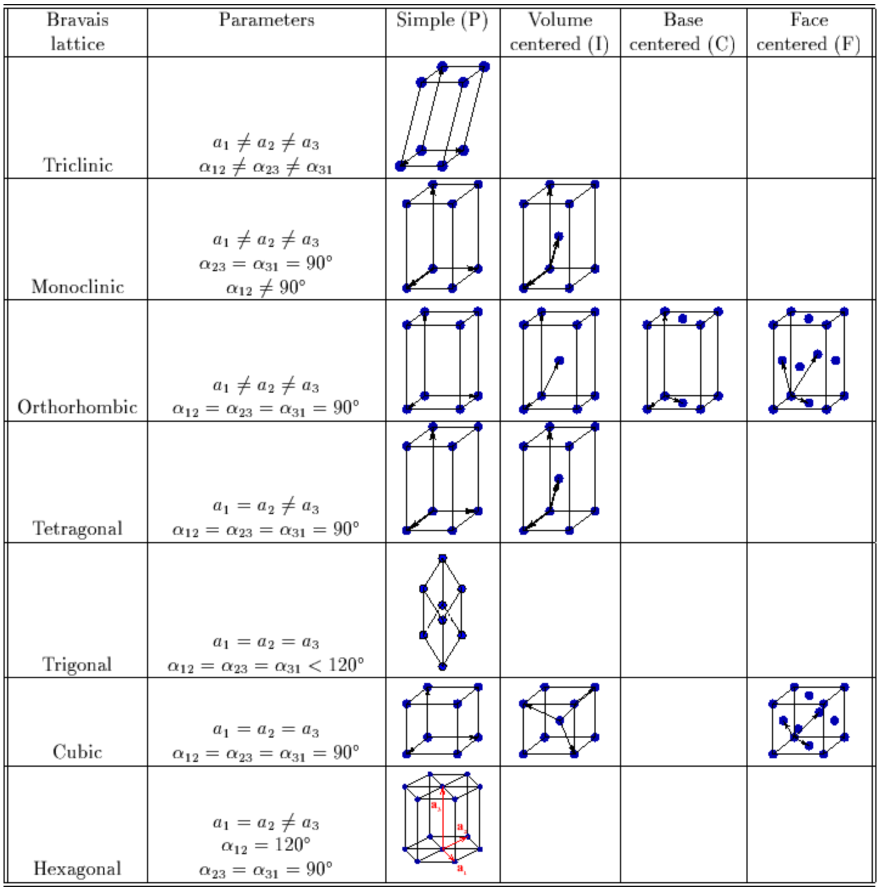


Figure 3: Two-dimensional structure of graphene.

## 2.2 Three-Dimensional Crystal Systems



| Bravais lattice | Parameters | Simple (P) | Volume centered (I) | Base centered (C) | Face centered (F) |
|---|---|---|---|---|---|
| Triclinic | $a_1 \neq a_2 \neq a_3$<br>$\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$ | | | | |
| Monoclinic | $a_1 \neq a_2 \neq a_3$<br>$\alpha_{23} = \alpha_{31} = 90°$<br>$\alpha_{12} \neq 90°$ | | | | |
| Orthorhombic | $a_1 \neq a_2 \neq a_3$<br>$\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$ | | | | |
| Tetragonal | $a_1 = a_2 \neq a_3$<br>$\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$ | | | | |
| Trigonal | $a_1 = a_2 = a_3$<br>$\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$ | | | | |
| Cubic | $a_1 = a_2 = a_3$<br>$\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$ | | | | |
| Hexagonal | $a_1 = a_2 \neq a_3$<br>$\alpha_{12} = 120°$<br>$\alpha_{23} = \alpha_{31} = 90°$ | | | | |

Figure 4: Fourteen Bravais lattices. In the parameters shown in the figure, the parameters a1, a2, a3 are the same as a, b, c, and α12, α23, α13 are the same as α, β, γ, as explained in the article. The only difference is the symbols used. [1].

These fourteen lattices have been identified through mathematical modeling and experimental research, and none of them are identical. Also, there is no other structure that fulfills the required conditions and is not similar to one of these 14 lattices. For example, if it is asked why the " base centered tetragonal" is not included in this list, the answer is that if viewed from another side, the base centered tetragonal is exactly the same as the simple tetragonal lattice. [2].

According to Figure 4, the fourteen Bravais lattices consist of seven primary lattices and seven secondary lattices. The seven primary lattices include simple cubic, tetrahedral (quadratic), orthorhombic, rhombohedral (triangular), hexagonal, monoclinic, and triclinic. The seven secondary lattices are formed by adding different types of centered atoms to the seven primary lattices, such as body-centered, face-centered, or base-centered lattices. To define each of these 14 Bravais lattices, it is necessary to specify the three vectors forming the unit cell and the angles between them (a total of three angles). Figure 4 shows these angles and vectors for each of the seven primary structures [2].

As stated, these 14 Bravais lattices assume identical motifs, meaning they are used for crystalline materials with one type of atom. For crystalline materials with two or more types of atoms (such as ceramics), non-Bravais lattices exist, which are combinations of several Bravais lattices. Here, we will only display the crystal structures of well-known ceramics (Figure 5). Many other ceramic materials have similar crystal structures and are named accordingly.

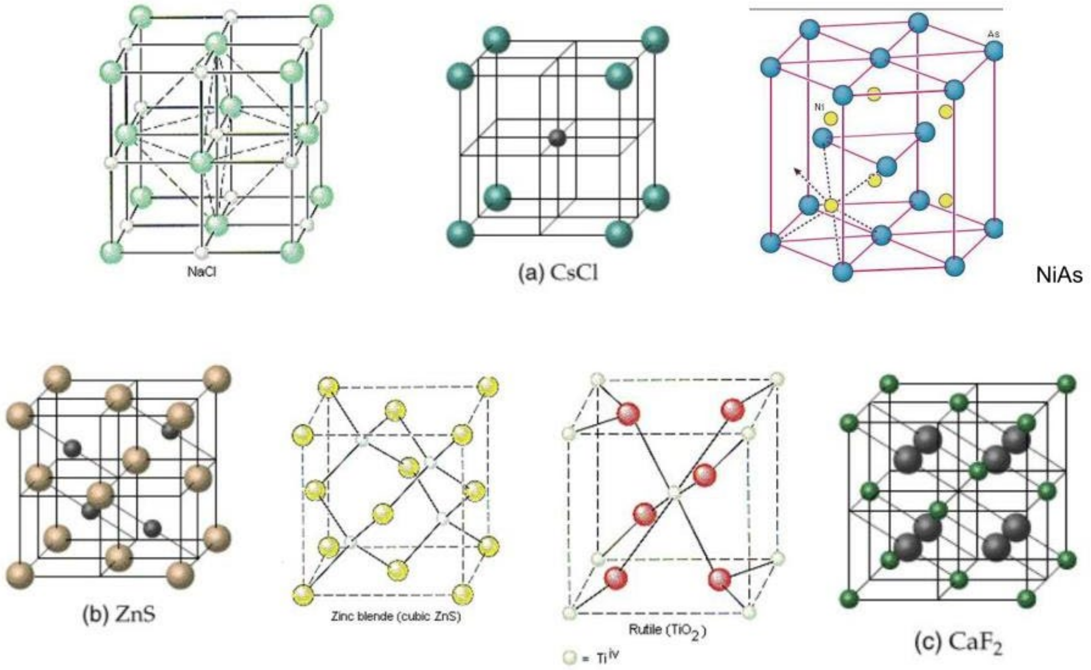


Figure 5: Well-known crystalline structures of ceramics (non-Bravais lattices).

Among the Bravais lattices mentioned above, the cubic and hexagonal lattices are of greater importance, as most common crystalline materials have cubic or hexagonal structures. Therefore, we will examine these lattices in more detail.

### 2.2.1 Cubic Lattices

As mentioned earlier, cubic lattices are divided into three types: simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC). These lattices are typically represented using the abbreviations mentioned, and it is important to remember these terms. Figure 6 shows these three lattices.

As shown in Figure 6, in the body-centered cubic lattice, one atom is placed in the center of the cube, and eight atoms are located at the corners of the cube. In the face-centered cubic lattice, six atoms are located at the faces of the cube, and eight atoms are at the corners. Conventionally, the first row of Figure 6 is shown to represent these cubic networks, which is easier to understand and simpler to display, but it should be noted that in reality these networks are in the form of the third row of Figure 6. The second row of Figure 6 also helps to calculate the number of pure atoms in each network, which we will discuss below.

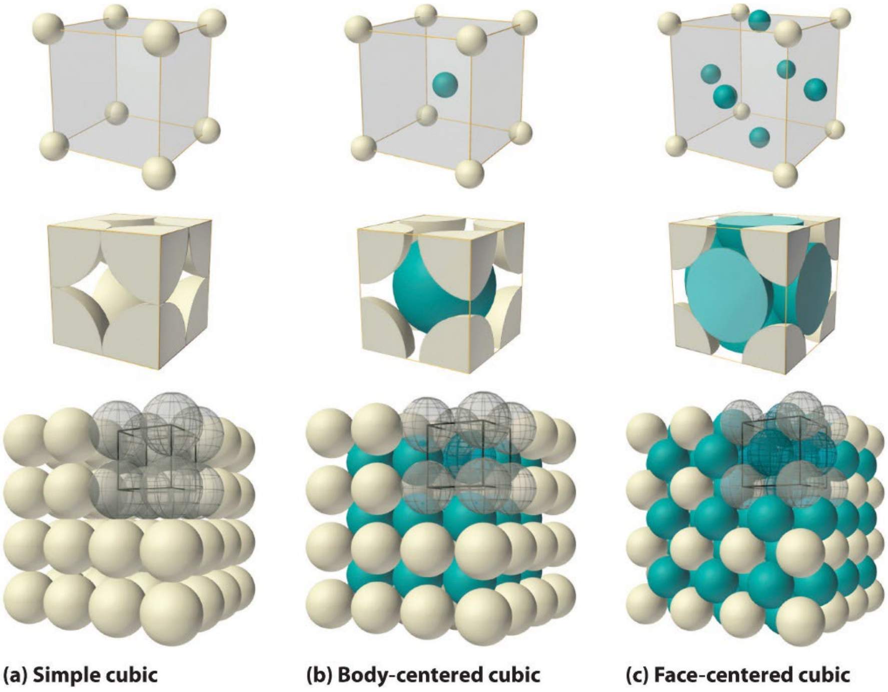


Figure 6: Schematic representation of the three cubic lattices: a) simple cubic, b) body-centered cubic, and c) face-centered cubic.

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#### 2.2.1.1 Simple Cubic Lattice

Several important factors need to be considered when studying this lattice: the number of atoms in the unit cell, the Packed vector , the atomic packing factor (APF), and the coordination number.

To calculate the number of atoms in the unit cell of a simple cubic lattice, refer to the second row of Figure 6. As shown, the unit cell consists of eight atoms at the corners of the cube. Since one eighth of each atom belongs to a unit cell (because each corner atom is shared by eight unit cells), the total number of atoms in the unit cell is:

(8 × 1/8) = 1 (the number of atoms in a simple cubic unit cell).

The lattice parameters in crystal lattices are the quantities specifying a unit cell or the unit of the periodicity of the atomic arrangement.. The packed vector (packed direction) in this lattice is the direction in which the atoms are tangent to each other. In fact, the value of the lattice parameter is always equal to the distance between two atoms in the packed direction. There is no distance between atoms along the packed direction. The packed direction in each cubic structure is different from the other and depends on the way the atoms are arranged next to each other. As can be seen in Figure 7-a, the packed direction in a simple cubic lattice is along the cube edges. Determining the packed vector is very important for the calculations that follow.

The coordination number, as shown in Figure 7-b, is the number of atoms that are in the neighborhood of each atom in the lattice. It is difficult to determine the coordination number in some crystal structures due to the complexity of the structure. The coordination number for a simple cubic lattice is 6 (2 neighboring atoms in each of the three directions of the x, y, and z axes).

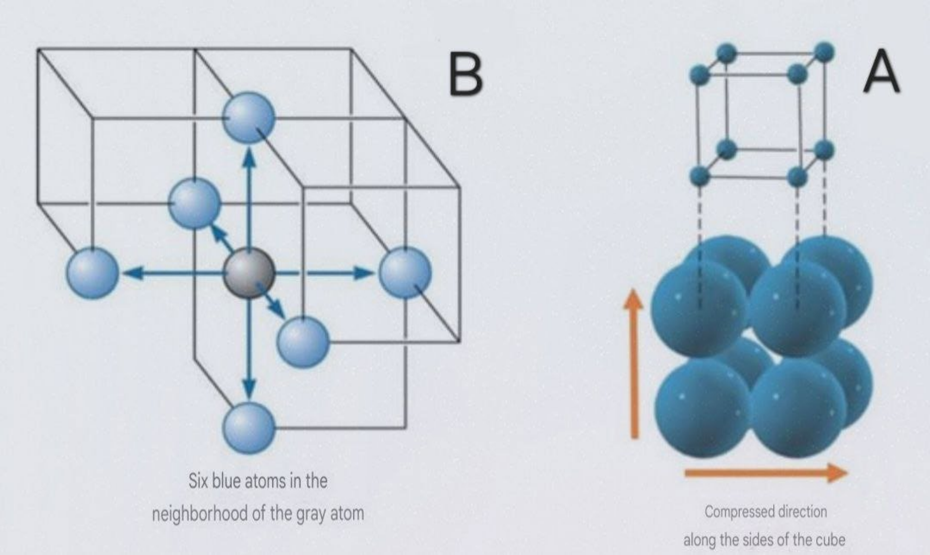

Figure 7 - Representation of a) Packed vector and b) coordination number in a simple cubic lattice

Another very important characteristic of a crystal is the atomic packing factor. The atomic packing factor indicates how much of the volume of a unit cell is occupied by atoms, and the higher it is, the more tightly packed the atoms are in that unit cell. The calculation of the packing factor is given in Equation 1:

Equation 1:

$$APF(atomic\ packing\ factor) = \frac{the\ net\ numbers\ of\ atoms\ in\ unit\ cell * volume\ of\ a\ single\ atom}{volume\ of\ unit\ cell}$$

As mentioned, in a simple cubic lattice, each unit cell contains 1 atom; also, to calculate the volume of atoms, we assume them to be spheres; in this case, the volume of an atom is equal to:

$$\frac{4}{3}\pi R^3$$

The volume of a unit cell is also equal to the cube of the length of each of its sides, that is: $a^3$.

Also, considering the determination of the Packed vector, we know that in the simple cubic crystal lattice, the lattice parameter is twice the atomic radius: (a=2R)

As a result, we have:

$$\frac{1 \times \frac{4}{3}\pi R^3}{(2R)^3} = \frac{\frac{4}{3}\pi R^3}{8R^3} = \frac{\pi}{6} = 0.524 = 52.4\%$$

Therefore, the atomic packing factor in the simple cubic lattice is equal to 52%.

### 2.2.1.2 Body-Centered Cubic (BCC) Lattice

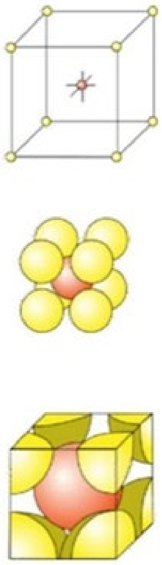

Figure 8: Schematic representation of a body-centered cubic lattice.

Similar to the simple cubic lattice, we will calculate the coordination number, packed vector, and atomic packing factor for the body-centered cubic lattice. According to the third row of Figure 8, it can be seen that in the unit cell of this lattice, one atom is completely in the center, and eight atoms, each contributing one-eighth to the unit cell, are at the corners. Therefore, the total number of atoms in the unit cell is:

$1 + (8 \times 1/8) = 2$

The coordination number for this structure is 8. To better understand this, imagine the atom in the center of the structure, surrounded by eight atoms in its neighborhood.

The Packed vector in this lattice is along the diagonal of the cube. To see this clearly, refer to Figure 9.

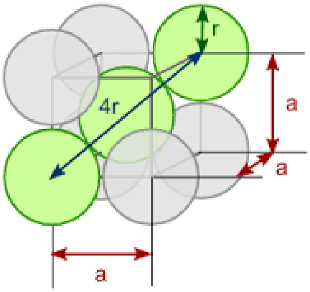

Figure 9: Showing the Packed vector and the relationship between the cube edge length and atomic radius in the body-centered cubic lattice.

According to Figure 9, in the body-centered cubic lattice, the relationship between the lattice parameter and the atomic radius along the cube diagonal is:

$\sqrt{3}a = 4R \rightarrow a = 4R/\sqrt{3}$

Now, we can calculate the atomic packing factor for this lattice:

$$\frac{2\times\frac{4}{3}\pi R^3}{a^3}=\frac{\frac{8}{3}\pi R^3}{(\frac{4R}{\sqrt{3}})^3}=\frac{\frac{8}{3}\pi}{\frac{64}{3\sqrt{3}}}=\frac{\sqrt{3}\pi}{8}=0.68=68\%$$

### 2.2.1.3 Face-Centered Cubic (FCC) Lattice

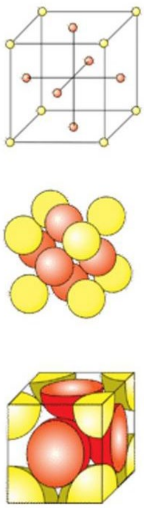

Figure 10: Schematic representation of a face-centered cubic lattice.

In the unit cell of the face-centered cubic lattice (Figure 10), six atoms are located at the faces, with half of each atom contributing to the unit cell, and eight atoms at the corners, with one-eighth of each atom belonging to the unit cell. Therefore, the number of atoms in the unit cell is:

$$(6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 4$$

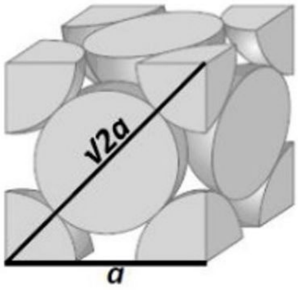

Figure 11: Showing the Packed vectors and the relationship between the cube edge length and atomic radius in the face-centered cubic lattice.

The coordination number for this structure is 12. To determine the Packed vector, refer to Figure 11. It shows that the diagonal of the faces (equal to the edge length multiplied by √2) is the Packed direction in this structure. The relationship between the edge length and atomic radius in this structure is:

$$a\sqrt{2} = 4R \rightarrow a = \frac{4R}{\sqrt{2}}$$

Now, we can calculate the atomic packing factor for this lattice:

$$\frac{4 \times \frac{4}{3}\pi R^3}{a^3} = \frac{\frac{16}{3}\pi R^3}{\left(\frac{4R}{\sqrt{2}}\right)^3} = \frac{\frac{16}{3}\pi}{\frac{64}{2\sqrt{2}}} = \frac{\sqrt{2}\pi}{6} = 0.74 = 74\%$$

As seen in these calculations, the FCC lattice has the highest atomic packing factor, while the SC lattice has the lowest among the cubic lattices.

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### 2.2.2 Hexagonal Close-Packed (HCP) Lattice

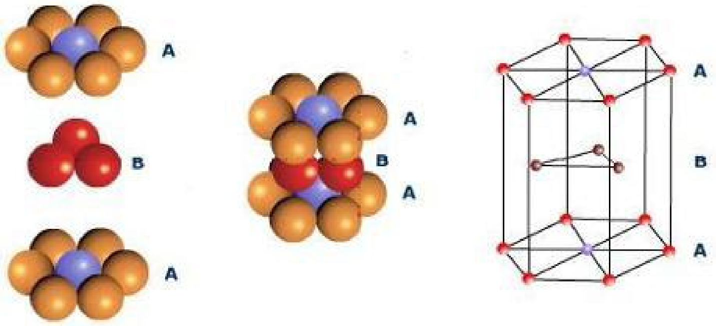


Figure 12: Showing the hexagonal close-packed lattice.

In the hexagonal close-packed lattice, three atoms are completely inside the unit cell; two atoms are at the top and bottom bases with half of each atom belonging to the unit cell, and twelve atoms at the corners contribute one-sixth of each atom to the unit cell. Therefore, the number of atoms in the unit cell is:

$$3+\left(2\times\frac{1}{2}\right)+\left(12\times\frac{1}{6}\right)=6$$

The coordination number in this structure is also 12, similar to the face-centered cubic lattice. The Packed vector can be any of the edges of the hexagonal base, as the atoms on these edges are in contact with each other. According to this, each edge length is equal to two atomic radii.

The atomic packing factor in this lattice is also 74%, similar to the FCC lattice.

It's important to note that another unit cell for this lattice can be considered. To do this, the unit cell shown in Figure 12 can be divided into three equal rectangles, which would also serve as the unit cell. However, the atomic packing factor and coordination number remain unchanged, as these are properties of the entire network, and defining different unit cells does not affect them.

Exercise 1

If we call the size of each hexagonal side of the bases (a) and the height of the unit cell (c), to calculate the density factor of the HCP lattice we have:

$$\frac{6\times\frac{4}{3}\pi R^3}{\frac{3\sqrt{3}}{2}a^2c}$$

The denominator of this expression is equal to the volume of the unit cell. To calculate it, we must find a relationship between the height of the unit cell and the size of each hexagonal side of the bases. Find a relationship between them and calculate the atomic packing factor of the HCP lattice as stated above.

## 3. Directions and Planes in Crystals

Miller indices are used to define and specify directions and planes in crystals. This section will introduce these indices. Given the greater importance of cubic crystal systems over other Bravais lattices, this section will focus on determining directions and planes in cubic crystal networks. First, a suitable right-handed coordinate system is selected for these calculations.

### 3.1 Miller Indices for Directions

To specify a Miller direction, subtract the coordinates of the starting point in the lattice from the coordinates of the endpoint. If the resulting number is not an integer, multiply it by the smallest possible multiple to make all the components integers. Also, no negative signs are used in Miller indices; instead, a bar (over the number) is used. For a better understanding, refer to Figure 13.

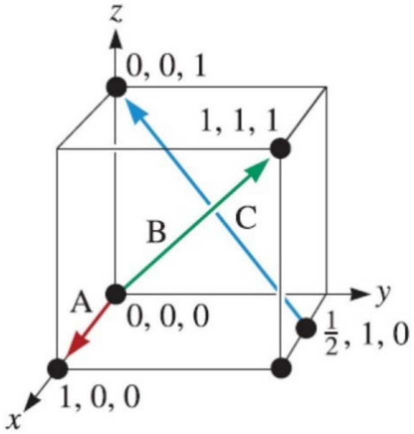


Figure 13: Showing some Miller directions in a cubic lattice.

For example, in Figure 13, the green arrow represents the [111] direction, as this vector moves one unit along each of the x, y, and z axes. The blue arrow represents a direction where the x-component is -0.5, the y-component is -1, and the z-component is +1. To make these components integers, we multiply by 2, giving the Miller index of $[\overline{12}2]$. The red arrow also shows the [100] direction because it has only moved in the x direction.

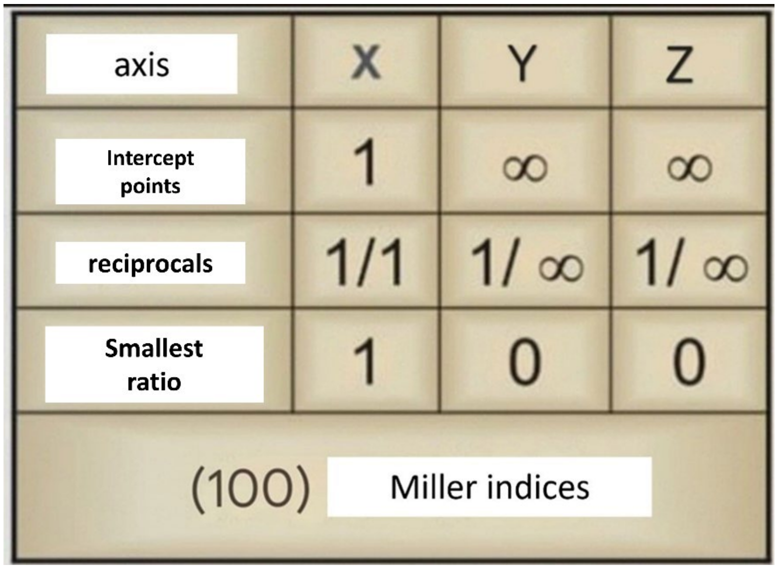
As you saw above, directions are given in brackets. Also, families of directions are indicated by <>. For example, in cubic lattices, the family <100> includes all directions [100] [010] [001] $[\bar{1}00]$ $[0\bar{1}0]$ $[00\bar{1}]$. The reason for stating a family of directions is that in many cases, different properties are the same within a family of directions. Also, an important characteristic such as the linear compression factor (the length of the atoms in that direction divided by the length of the direction) is the same across a family of directions [2].

Exercise 3

Now, by learning the Miller index of the crystal directions, determine the compact vectors in SC, BCC, and FCC lattices.

## 3.2 Miller Indices for Planes

A plane in a crystal refers to all the parallel planes in the crystal that are equally spaced. Each set of parallel planes in a crystal has its own Miller index. Some Miller planes and their indices are shown in Figure 14. The notation for Miller planes is represented by parentheses () and the family of planes by curly braces {}. To determine the Miller index of a plane, first find the points where the plane intersects the three axes, then take the reciprocals of these values and simplify them to the smallest possible integers. For example, for the (100) plane we have:



| axis | X | Y | Z |
|---|---|---|---|
| Intercept points | 1 | $\infty$ | $\infty$ |
| reciprocals | 1/1 | $1/\infty$ | $1/\infty$ |
| Smallest ratio | 1 | 0 | 0 |
| (100) | Miller indices | | |

Note that the meaning of infinity is that this plane is parallel to the y and z axes and therefore intersects them at infinity. The inverse of infinity is also equal to zero. Here, too, the sign of the bar is used instead of the negative.

If, similar to the table above, we determine the intersection points with the three axes for the (111) plane, the point of contact will be 1 on all three axes. The inverse of 1 is also equal to 1. As a result, the Miller index of this plane, shown in Figure 14, is equal to (111).

You can find the other three planes shown in Figure 14 yourself as an exercise.

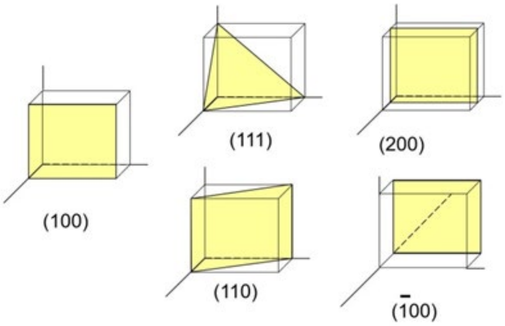


Figure 14 - A number of Miller planes of the cubic lattice and their Miller plane indices [2]

As mentioned at the beginning, in these investigations, appropriate and rectilinear coordinates are first selected. If the desired plane passes through the origin, it is sufficient to transfer the origin to another suitable point.

## 4. Conclusion

Three-dimensional crystal systems are divided into two categories: Bravais lattices and non-Bravais lattices. Bravais lattices consist of identical atoms, while non-Bravais lattices include two or more types of atoms (such as ceramics). Bravais lattices have 14 different configurations, with some of the most important being simple cubic (SC), body-centered cubic (BCC), face-centered cubic (FCC), and hexagonal close-packed (HCP). Understanding the characteristics of these lattices, such as the number of atoms in the unit cell, the coordination number, and the atomic packing factor, is crucial. By knowing these variables, it is possible to determine the properties of materials that have these crystal systems. Miller indices are used to define and specify directions and planes in crystals. X-ray diffraction analysis provides valuable information about the crystal structure of materials, which will be discussed in the article on X-ray diffraction analysis.

## 5. References

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## Defects in Crystals

### Abstract

The structure of a crystal is not always ideal and flawless. Various types of defects, including zero-dimensional, one-dimensional, two-dimensional, and three-dimensional defects, can be found in crystals. These defects are classified based on their size and shape. Some defects, like vacancies, naturally occur in crystals thermodynamically, while others, such as pores, cracks, and even grain boundaries, can be prevented through different methods. This paper introduces and explains each of these defects.

Keywords: Crystal defects, vacancy, interstitial, substitution, dislocation, grain boundary

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### 1. Introduction

The previous articles on crystal structures assumed ideal, perfect conditions, but such structures do not exist in nature. Crystalline materials naturally have various defects, such as point defects, line defects, surface defects, and even bulk defects. These defects will be explained in the following sections.

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### 2. Defects in Crystals

As mentioned earlier, crystalline structures can have various defects, or "imperfections." These defects and their size ranges are shown in Figure 1. Below, each of these defects will be introduced and discussed.

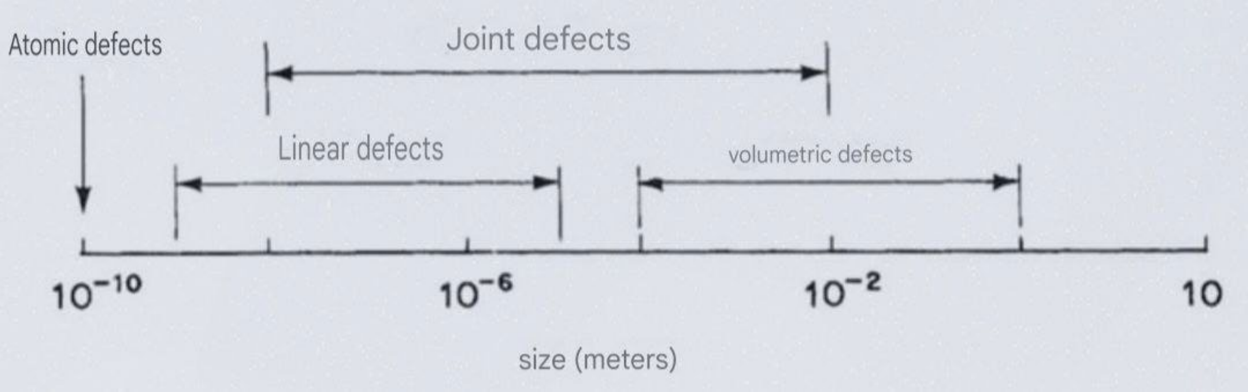

Figure 1: Various defects in a crystal and their size ranges.

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### 2.1 Point Defects (Zero-Dimensional)

#### 2.1.1 Vacancy Defect

Vacancies naturally occur in all crystalline solids. As the temperature increases, the number of vacancies also increases, continuing until the melting point of the material is reached, as the crystal structure itself breaks down at this point.

Vacancies greatly assist the diffusion process in crystalline materials. In fact, it is with the help of vacancies that atoms can diffuse from one location to another within the crystal. These diffusing atoms may be of the same type as the crystal's atoms or could be different types. A vacancy defect in a crystal structure is shown in Figure 2.

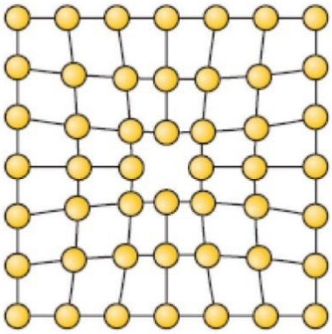

Figure 2: Representation of a vacancy defect in a crystal structure.

As seen in the figure, the size of the vacancy defect is atomic (angstrom scale). With vacancies in the crystal structure, the surrounding atoms tend to move toward the vacancy.

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### 2.1.2 Interstitial Defect

An interstitial defect occurs when an atom enters the crystal lattice at a position that is not its regular lattice site, causing distortion in the lattice. Due to the limited space between atoms, only atoms with small atomic radii can fit into the crystal lattice as interstitials. Therefore, only atoms like carbon, hydrogen, oxygen, nitrogen, and fluorine can act as interstitial atoms.

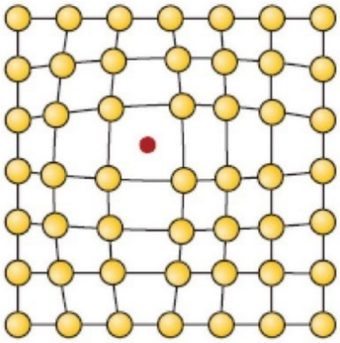

Figure 3: Representation of an interstitial atom in a crystal structure.

In addition to the case above, an interstitial defect can also occur when an atom from the crystal lattice moves to another position, creating a vacancy and acting as an interstitial atom in the new location. This situation is shown in Figure 4.

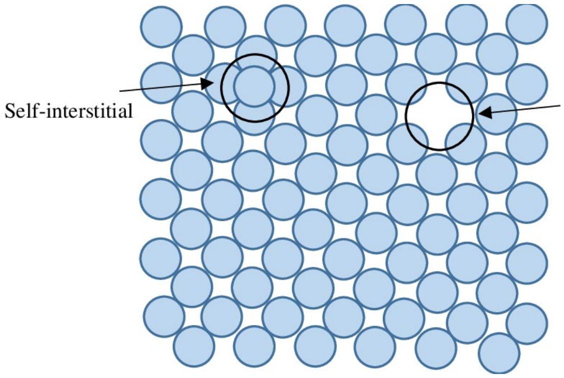

Figure 4: Self-interstitial defect in a crystal lattice, creating a vacancy.

However, self-interstitials are rare in a crystal lattice because removing an atom from its lattice position and moving it to a new position (especially causing large distortion at the new interstitial site) requires a significant amount of energy. Therefore, self-interstitials usually only occur at high temperatures, near the material's melting point. Even when this energy is available, it creates significant local strain at the interstitial position.

It’s worth noting that the presence of an interstitial atom always creates compressive local stresses at that location.

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### 2.1.3 Substitutional Defect

In this defect, an atom from outside the crystal lattice replaces one of the atoms in the lattice, as shown in Figure 5. For example, copper atoms can replace nickel atoms in the face-centered cubic (FCC) lattice of nickel.

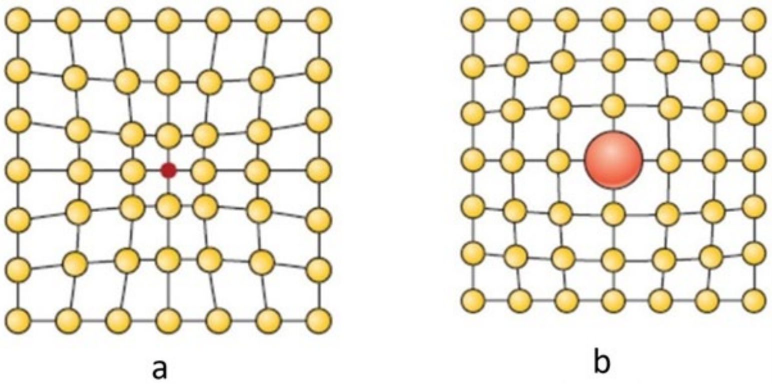

Figure 5: Representation of a substitutional atom in two cases: (a) larger than the host atoms, (b) smaller than the host atoms.

As shown in the figure, whether the substitutional atom is larger or smaller than the host atoms, it causes distortion in the lattice, resulting in local strain at the substitution site. If the substitutional atom is larger than the host atoms, it creates compressive strain. If the substitutional atom is smaller, it causes tensile strain at that point.

---

### 2.1.4 Defects in Electrically Charged Lattices

In lattices such as sodium chloride (NaCl), which contains sodium cations and chloride anions, defects in one of the components disrupt the charge balance in the crystal lattice, and the system seeks to compensate for it.

For example, if there is a vacancy related to the cation in a system, the overall charge becomes negative. In this case, electrical balance is achieved when a vacancy related to the anion appears next to the cation vacancy. This type of defect, where a cation vacancy and an anion vacancy occur together, is called a Schottky defect, as shown in Figure 6.[۲]

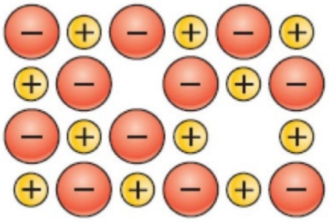

Figure 6: Representation of a Schottky defect.

In another case, when there is a cation vacancy, an interstitial cation can enter the lattice to balance the charge. This defect is called a Frenkel defect, shown in Figure 7. Also, in Figure 7, you can compare the Frenkel and Schottky defects.

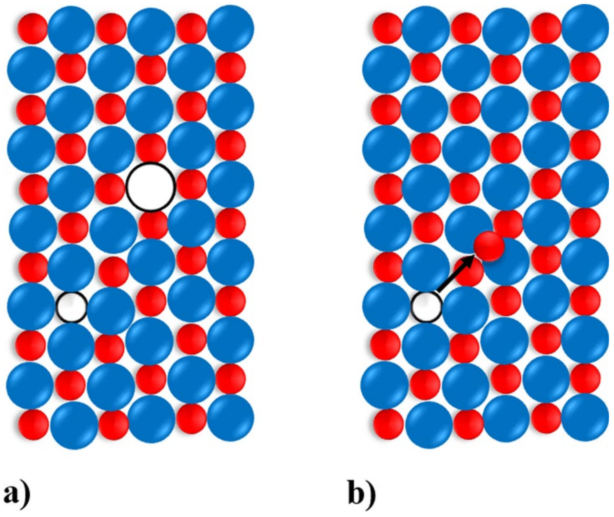

Figure 7: Representation of both Schottky(a) and Frenkel(b) defects occurring together in an ionic compound.

---

## 2.2 Linear Defects (One-Dimensional)

Linear defects in a crystal lattice are called dislocations, which significantly impact the material’s properties, particularly its mechanical properties. In many materials, especially metals, plastic deformation and yield points are directly influenced by dislocations. Therefore, understanding dislocations and their characteristics is crucial for the mechanical properties of materials.

Dislocations can be of two types: edge dislocations and screw dislocations, or a combination of both. These dislocations are shown in Figure 8.

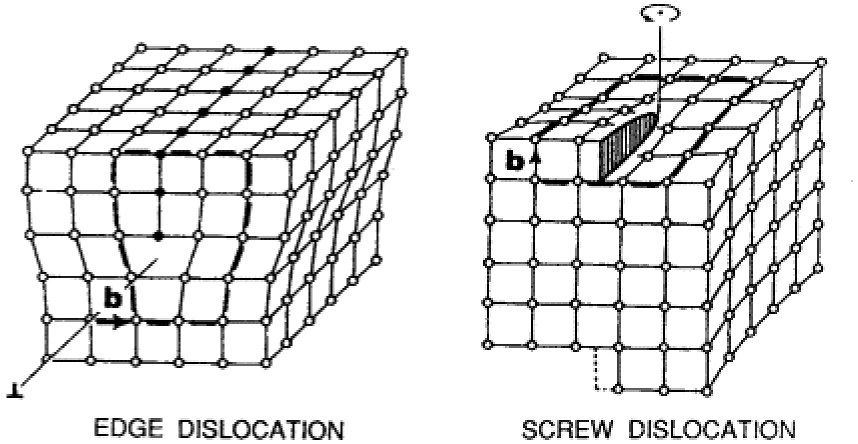

Figure 8: Representation of edge and screw dislocations.

An edge dislocation is caused by the presence of an extra half-plane of atoms in the crystal structure. A screw dislocation occurs when shear stress is applied to the lattice, as shown in Figure 8, where the right side shifts downward by one atomic distance, creating a screw dislocation.

Dislocations are observed using transmission electron microscopes due to their very small size.

---

## 2.3 Surface Defects (Two-Dimensional)

As the size of a defect increases, we move to two-dimensional defects, which can be much larger than zero-dimensional and one-dimensional defects (which are at the atomic scale) and can even reach the centimeter range. Some examples of two-dimensional defects, which are typically surfaces or interfaces, include the free surface of a crystal, grain boundaries, phase boundaries in a crystal, and twin boundaries. A twin boundary is a boundary where there is a mirror symmetry between the atoms on either side, as shown in Figure 9.

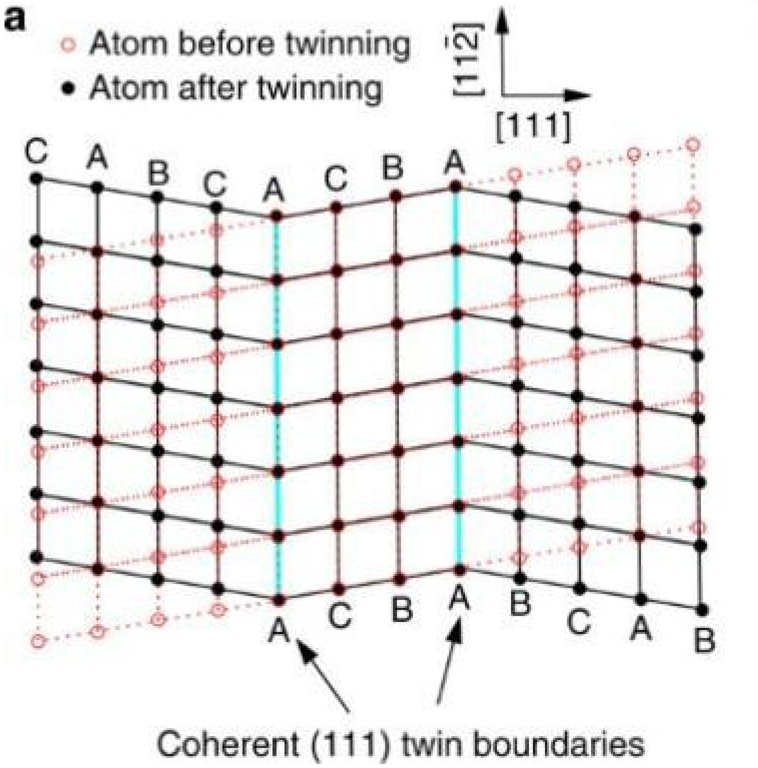

Figure 9: Representation of a twin boundary in a crystal, showing mirror symmetry on both sides.

In material science, a grain boundary is the interface between two grains, or crystallites, in a polycrystalline material. Grain boundaries are defects that significantly affect the physical and chemical properties of a material. For example, grain boundaries are sites where corrosion can initiate. Additionally, at room temperature, grain boundaries increase material strength by preventing plastic deformation (by restricting dislocation movement). On the other hand, at high temperatures, grain boundaries cause plastic deformation (due to creep). Because of the change in atomic orientation at the grain boundaries, they also have a detrimental effect on electrical and thermal conductivity. Therefore, controlling the amount of grain boundaries is crucial in the manufacturing of crystalline materials, especially metals. Many processes are used to control the grain size and amount of grain boundaries due to their impact on the physical and chemical properties of crystalline materials..

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## 2. 4 Bulk Defects (Three-Dimensional)

These defects have large dimensions and are more easily prevented during crystal production by controlling the conditions. Examples of three-dimensional defects include the presence of voids or cracks in the crystalline material and impurities. It’s important to note that these impurities are large-scale, unlike atomic impurities that might act as interstitials or substitutionals. These are bulk impurities made up of a large number of atoms.

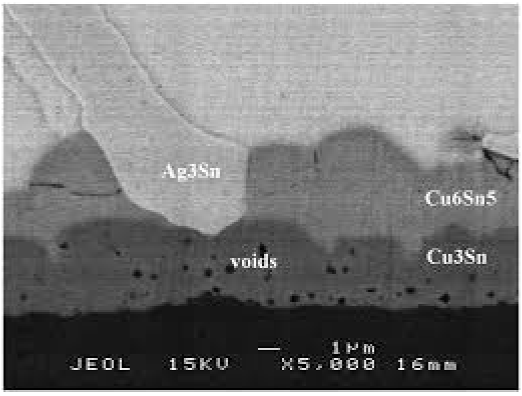

Figure 10: Representation of voids (three-dimensional defect) in an SEM image.

Figure 10 shows voids within the material's structure. As seen in the image, the size of these voids is about half a micrometer. In comparison, a vacancy is atomic in size and about a thousand times smaller than the voids shown here.

## 3. Summary and Conclusion

Various defects can exist within a crystal lattice. These defects are classified into zero-dimensional, one-dimensional, two-dimensional, and three-dimensional defects based on their size and geometry. Each of these defects affects the physical and chemical properties of the crystal in its unique way. Zero-dimensional defects include vacancies, interstitials, and substitutions. One-dimensional defects are dislocations (edge and screw dislocations). Two-dimensional defects include free surfaces, grain boundaries, and twin boundaries. Three-dimensional defects include impurities, voids, and cracks in the crystal material.

## 4. References

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## Types of Nanomaterials

- **Carbon Nanomaterials: Carbon Structures**
- **Carbon Nanomaterials: Carbon Nanotubes and Graphene**
- **Nanocomposites**

## Carbon Nanomaterials 1: Carbon Structures

Abstract

Carbon is one of the essential elements for life on Earth. This element is used in a wide range of industries, from pharmaceuticals to the manufacture of products. Carbon's key role in life on Earth and living organisms stems from its ability to bond with almost all elements, creating an infinite variety of compounds. Carbon structures, or carbon compounds, refer to chemical materials containing carbon. After hydrogen, carbon compounds are more abundant than any other chemical element in nature. The number of organic carbon compounds is much higher than that of inorganic carbon compounds. Carbon atoms are held together by various bonds and form plenty of allotropes, such as diamond, carbon black, graphite, graphene, carbon nanotubes, carbon fibers, fullerenes, and others. The size of the structures and the arrangement of atoms in each of these allotropes vary. In recent years, research related to carbon materials, especially graphene and carbon nanotubes, has significantly increased, and these materials have found widespread use in various industries. This article introduces the different types of carbon structures such as diamond, graphite, fullerene, carbon black, and carbon fibers and discusses the applications of each of these materials.

Keywords

Carbon structures, diamond, graphite, fullerene, carbon black, and carbon fibers.

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### 1. Introduction

Carbon is a non-metal element in the periodic table with atomic number 6 and atomic mass 12. One of its main uses is as an alloying element in steel production. Before delving into carbon bonds and the study of its allotropes, it's essential to first review the electronic structure of the carbon atom. The carbon atom has six electrons in its energy levels ($1s^2\ 2s^2\ 2px^1\ 2py^1$). When excited, one of the two 2s orbital electrons moves into the empty 2pz orbital (see Figure 1). In such a state, the carbon atom will have four unpaired electrons available to form bonds ($1s^2\ 2s^1\ 2px^1\ 2py^1\ 2pz^1$). In the electron configuration of the carbon atom, the energy gap between the 2s and 2p levels is very small. This feature allows the overlap of orbital energies, a process called hybridization. In simple terms, hybridization occurs when, in a compound, the central atom forms more bonds than the capacity of its half-filled orbitals.. For example, when methane ($CH_4$) is formed, the carbon atom has two unpaired electrons in the 2px and 2py orbitals. Thus, by exciting the carbon and transferring one electron from the 2s orbital to the 2pz orbital, the carbon atom forms four bonds.

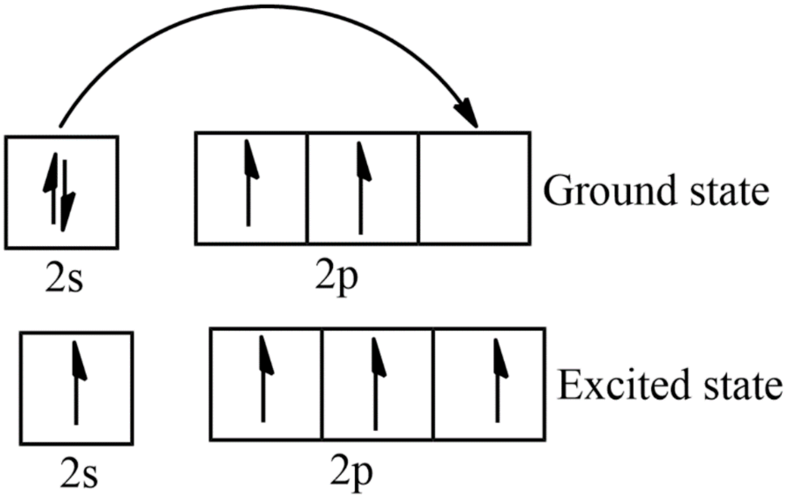

Figure 1: Electron configuration in the 2s and 2p levels of a carbon atom.

Various types of hybrids exist with different bond angles, including:

sp hybrid with a 180° bond angle, as in $C_2H_2$;

$sp^2$ hybrid with a 120° bond angle, as in $C_2H_4$;

$sp^3$ hybrid with a 109.5° bond angle, as in $CH_4$.

Figure 2 shows a diagram of the different hybridizations with varying bond angles. The formation of different hybrids with varying bond angles allows carbon to exist in different forms in nature. Since all carbon structures are made of the same element, studying the differences in how the atoms are arranged in these structures and the types of bonds formed in them is essential to understanding the differences between carbon compounds.

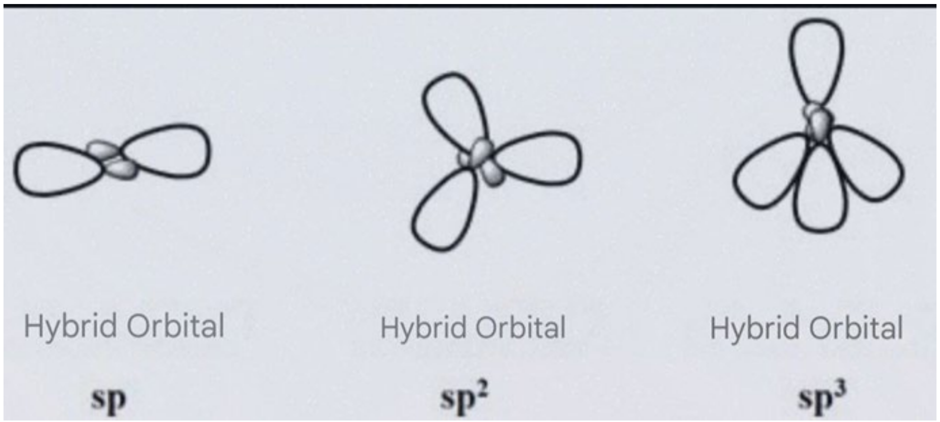

Figure 2: Diagram showing the different types of hybrids with varying bond angles.

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2. Prerequisites

Before discussing the various carbon structures, it is essential to familiarize oneself with a few concepts that are discussed below:

The smallest repeating unit of a crystal lattice is called the unit cell.

Thermal conductivity is a phenomenon that occurs due to interactions between neighboring atoms and molecules, during which part of the energy/heat is transferred to the neighbors. Thermal conductivity is the most important mechanism for heat transfer in a solid material and between solid materials in thermal contact.

A composite material consists of two or more building materials. These materials, with different physical and chemical properties, combine to form a material with different properties than the individual materials. The two main parts of a composite are the matrix and the reinforcement.

In crystallography, semi-crystalline materials are those that have a short-range or medium-range ordered lattice structure (similar to liquid crystal phases). Long-range order is not observed in these materials' crystal lattices.

Isomers are compounds with the same chemical formula but different structural formulas.

Diamagnetic materials are those that create an opposing magnetic field when exposed to an external magnetic field, hence being repelled by it. All materials with atoms that contain paired electrons exhibit diamagnetism.

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## 3. Carbon Allotropes

Due to the presence of a valence shell with unpaired electrons, carbon can form various allotropes. These allotropes can be categorized based on their dimensionality or hybridization. Figure 3 shows a diagram of the unit cells for one-dimensional, two-dimensional, and three-dimensional carbon compounds.

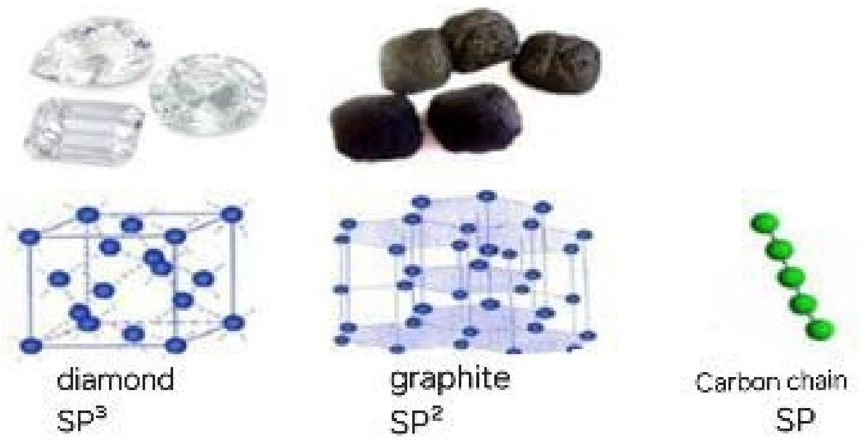

Figure 3: unit cells of one-dimensional, two-dimensional, and three-dimensional carbon compounds.

A carbon chain with sp hybridization has a one-dimensional structure, where each carbon atom is bonded to two neighboring carbon atoms through covalent bonds. Two-dimensional carbon structures, like graphite, graphene, carbon nanotubes, and fullerenes, have $sp^2$ hybridization, where the carbon atoms in the plane are bonded to other carbon atoms via three covalent bonds. Three-dimensional carbon structures, like diamond, have $sp^3$ hybridization, where each carbon atom is bonded to its neighboring atoms via four covalent bonds.

Here's a simplified version of the text in English:

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Displaying Points on a Carbon Sheet with Regular Arrangement

One important point about carbon nanostructures is how the points are displayed on the carbon sheet. This is crucial in determining the type and properties of carbon nanotubes. To get an idea of how to find the position of a point on a carbon sheet, refer to Figure 4 and its explanation. In this figure, a carbon sheet with a regular arrangement is shown, along with two indices to define the points.

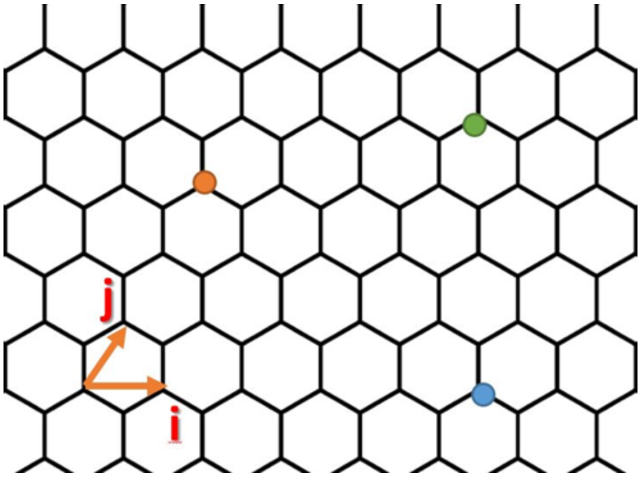

Figure 4: A carbon sheet with a regular arrangement and indices used to display points on the sheet.

To determine the position of each point on the carbon sheet, you first need to check how much the point has moved from the origin (starting point). Since each sheet has two dimensions, you should use vectors i and j to measure the movement. Below, the coordinates of three points—orange, blue, and green—on the carbon sheet in Figure 4 will be determined:

Blue point: It is 5 units away from the origin in the direction of i, and there is no movement in the direction of j. So, the coordinates of this point on carbon sheet are (5, 0).

Orange point: There is no movement along the i direction, but it is 3 units away in the j direction. So, the coordinates of this point are (0, 3).

Green point: It is 3 units away along the i direction and 4 units away in the j direction from the origin. So, the coordinates of this point are (3, 4).

The components of i and j used to determine the coordinates of points on the carbon sheet are called "chiral components." Sometimes, the letters m and n are also used to name these components.

To find the chiral angle (shown as "ϴ" in Figure 4), simply draw a line from the point to the origin. The angle between this line and the i vector is the chiral angle of the point on the carbon sheet.

Calculation of the Diameter and Chiral Angle

Nanotube Diameter

The diameter d of a carbon nanotube can be calculated using the chiral indices (m, n) and the graphene lattice constant a, which is approximately 2.46 Å(figure5):

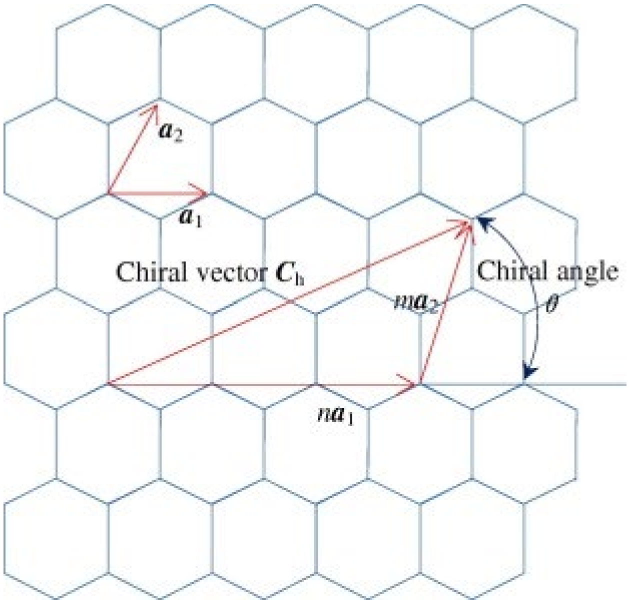

Figure5: Schematic diagram of the chiral vector and the chiral angle

$$d = \frac{a}{\pi}\sqrt{\left(n^2 + nm + m^2\right)},$$

Chiral Angle

The chiral angle θ determines how the graphene sheet is rolled up and is given by:

where:

$\theta = 30°$ for armchair nanotubes.

$\theta = 0°$ for zigzag nanotubes.

$0° < \theta < 30°$ for chiral nanotubes.

Geometric Relationship Between (m, n) and the Chiral Vector Length

Through certain geometric calculations in the carbon coordinate system, a direct relationship between m, n, and the chiral vector length can be derived. It is important to note that the length of the chiral vector is equal to the circumference of the nanotube's cross-section.

## 4. Introduction to Carbon Structures

Below are descriptions of some important carbon structures. Note that not all of the following are nanostructures, but they have been included due to their significant importance and widespread applications in various industries.

### 4.1 Diamond

As mentioned earlier, in the unit cell of diamond, carbon atoms are strongly bonded together with four covalent bonds. Carbon atoms in diamond's crystal lattice form a regular tetrahedral structure, with bond angles of 109°. The unit cell of diamond is cubic and similar to the ZnS structure. The key difference is the presence of carbon atoms at all points in the diamond unit cell.

Diamond has unique mechanical properties, making it one of the hardest materials known in the world. This feature makes diamond useful in applications requiring high abrasion resistance, such as metal cutting tools with diamond-coated surfaces. Additionally, diamond is one of the most popular materials in jewelry applications. Larger diamonds are used in jewelry, while smaller diamonds are used for cutting. In addition to its hardness, diamond has a very high thermal conductivity (five times higher than copper). Figure 6 shows a cutting tool with a diamond-coated surface.

Figure 6: Image of a cutting tool with a diamond-coated surface.

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## 4.2 Graphite

Graphite is a crystalline form of carbon. It has a layered structure made up of six-membered carbon rings. These rings are arranged in horizontal planes with a distance between each layer. The unit cell of graphite is hexagonal. Graphite forms naturally and is the most stable form of carbon under standard thermodynamic conditions. Figure 7 shows a diagram of graphite's layered structure, the type of bonds between the atoms, and how the layers are stacked relative to each other.

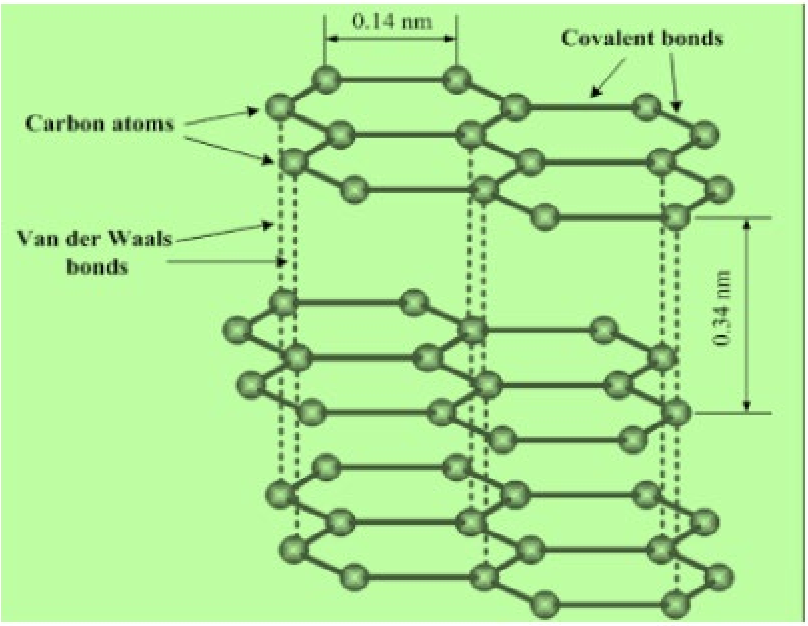

Figure 7: Diagram showing the layered structure of graphite, the type of bonds, and how the layers are arranged.

Each layer in graphite is called a graphene sheet. Within each sheet, carbon atoms are connected to each other by covalent bonds. Weak van der Waals forces hold the layers together. Important applications of graphite include pencils, lubricants, refractory materials, and batteries. The weak interlayer interactions allow the graphene sheets to easily slide over each other. This is why graphite is used in pencils—when the pencil tip is rubbed on paper, the graphene layers peel off, leaving a black mark. Unlike diamond, which is an electrical insulator due to its filled valence shell, graphite has free electrons in its layers, making it a good conductor of electricity.

## 4.3 Carbon Fibers

Carbon fibers were first created by Thomas Edison in the 1880s. Commercial production of these fibers began in Japan in 1970. Carbon fibers have a diameter of around 5-10 micrometers and are made up of carbon atoms. These fibers have high stiffness, excellent tensile strength, a high strength-to-weight ratio, and exceptional corrosion resistance. These properties make carbon fibers ideal for reinforcing composite materials. Carbon fiber-reinforced composites are very strong yet lightweight and are used in the production of car bodies, boats, missiles, and sports equipment (such as tennis rackets). For example, using carbon fiber composites in car bodies increases vehicle speed and reduces fuel consumption. Figure 8 shows an image of carbon fibers and their application in the automotive industry.

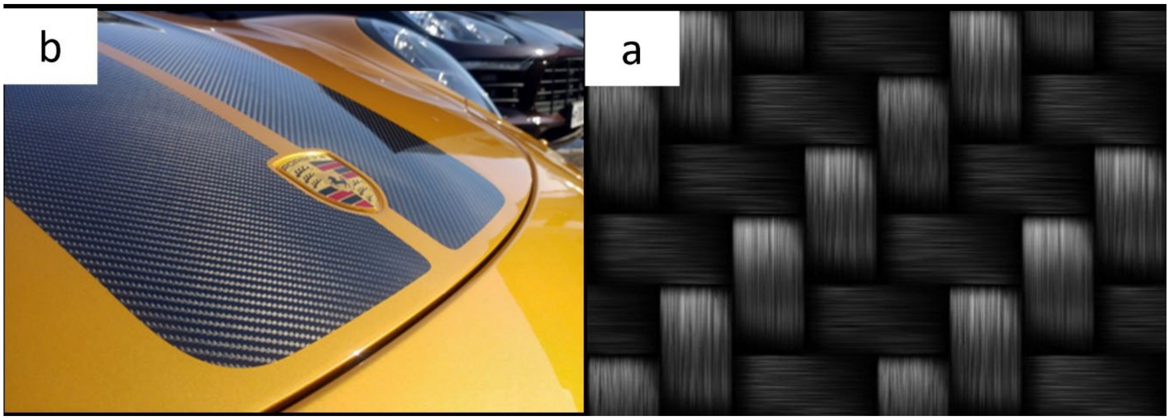

Figure 8: Image showing (a) carbon fibers and (b) their use in the automotive industry.

## 4.4 Carbon Black

Carbon black is a material produced from the incomplete combustion of coal, coal tar, plant materials, or petroleum products. Carbon black contains more than 95% pure carbon, with trace amounts of oxygen, hydrogen, nitrogen, and sulfur. It is a semi-crystalline form of carbon with a high surface-to-volume ratio. This ratio is higher in activated carbon compared to carbon black. Carbon black is typically found as aggregates of particles and is rarely seen as a single particle. Figure 9 shows various forms of carbon black along with the size range of each.

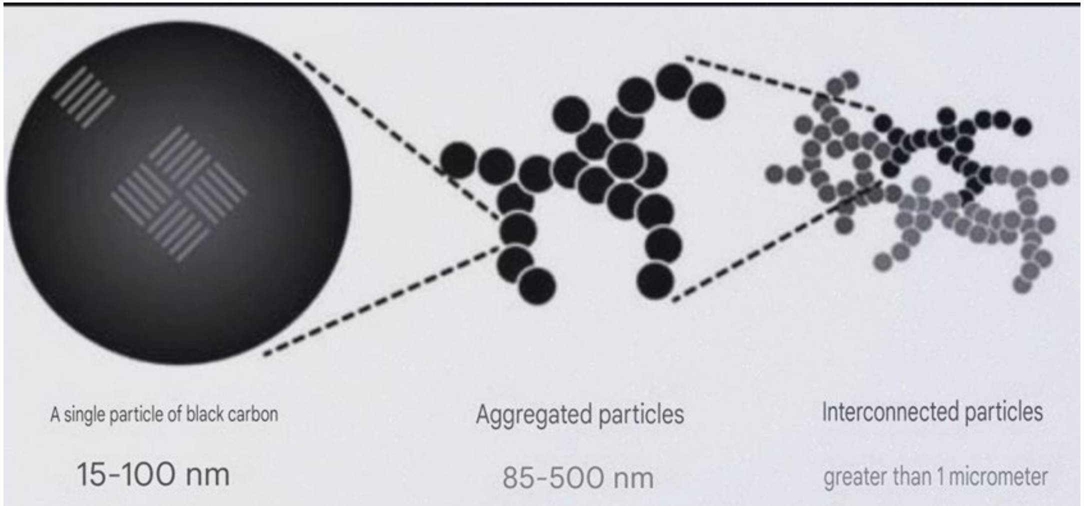

Figure 9: Diagram showing different forms of carbon black with their size ranges.

As shown in Figure 9, carbon black in its bonded form has the largest size. If the individual carbon black particles are prevented from clumping together and bonding, carbon black can be classified as nanoparticles. However, in practice, doing this is very difficult due to the high surface-to-volume ratio of carbon.

Carbon black is used in various applications, such as a filler to improve mechanical properties, to create black color in rubber and plastics, and to provide electrical conductivity (only a specific type of carbon black has electrical conductivity). About 90% of the carbon black produced worldwide is used in the tire industry.

## 4.5 Fullerene

Fullerenes are carbon allotropes where the molecules consist of carbon atoms. These carbon atoms in fullerene structures are bonded with single and double bonds to form a closed or semi-closed network of rings containing five to seven atoms. Fullerenes are known by the empirical formula Cn, where n is the number of carbon atoms. Fullerenes are considered nanoparticles. The most famous member of the fullerene family is C60, which has a structure with 20 hexagonal rings and 12 pentagonal rings. This carbon allotrope is shaped like a soccer ball and is also known as "buckyball." In the fullerene crystal lattice, each carbon atom is covalently bonded to three other carbon atoms in the sphere ($sp^2$ hybridization). Since fullerene has a hollow spherical structure, drugs can be loaded into the hollow section and used for targeted (smart) drug delivery to damaged tissues. Other applications of fullerenes include hydrogen storage, biosensors, and catalytic processes. Figure 10 shows a diagram of the crystal lattice of fullerenes with varying numbers of carbon atoms.

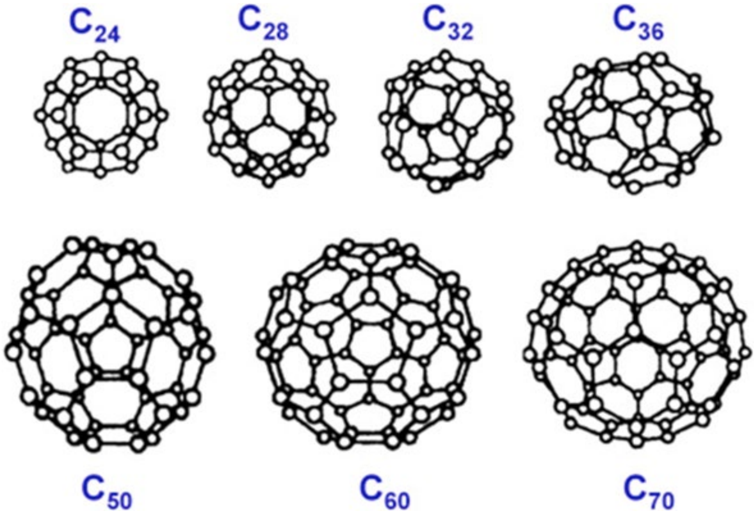

Figure 10: the crystal lattice of fullerenes with varying numbers of carbon atoms.

Fullerenes have a size in the nanometer scale. For example, the diameters of the C60 and C70 fullerenes are 0.7 nm and 0.8 nm, respectively. In general, the diameter of fullerenes is considered to be 1 nanometer. An important point is that in all fullerene molecules, the number of pentagonal rings is always 12. Each pentagon creates a 60-degree angle. The presence of these 12 pentagonal rings in fullerenes is the main reason their structure is spherical. As the size of the fullerenes increases (meaning the number of carbon atoms increases), the number of hexagonal or heptagonal rings also increases.

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## 6. Conclusion

Carbon is an essential element for life on Earth and is used in a wide range of industries. Carbon atoms bond in different ways to form various allotropes like diamond, carbon black, graphite, graphene, carbon nanotubes, carbon fibers, fullerenes, and others. This article introduced different types of carbon structures, including diamond, graphite, fullerene, carbon black, and carbon fibers, and discussed their applications. It was highlighted that due to the presence of a valence shell with unpaired electrons, carbon can form various allotropes. Also, it was emphasized that one of the important aspects of carbon nanostructures is how to represent points on a carbon plane, which is crucial for determining the properties of carbon nanotubes.

It was mentioned that in the diamond unit cell, carbon atoms are strongly bonded to each other with four covalent bonds. It was emphasized that the graphite unit cell is hexagonal. Graphite forms naturally and is the most stable form of carbon under standard thermodynamic conditions.

Unlike diamond, which is an electrical insulator due to its full valence shell, graphite has free electrons in this shell, making it a better electrical conductor than diamond.

Carbon fibers are fibers with a diameter of about 5-10 micrometers, made from carbon atoms. They have advantages such as high stiffness, excellent tensile strength, high strength-to-weight ratio, and chemical resistance.

It was emphasized that if the clumping and bonding of individual carbon black particles can be prevented, carbon black can be classified as nanoparticles. However, in practice, this is very difficult due to the high surface-to-volume ratio of carbon.

It was mentioned that fullerene is another allotrope of carbon, where molecules are made of carbon atoms. The carbon atoms in the fullerene structure are connected with single and double bonds. Fullerene applications include hydrogen storage, biosensors, and catalytic processes.

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## Carbon Nanomaterials 2: Carbon Nanotubes and Graphene

### Abstract

Carbon nanotubes and graphene are the most important and widely used allotropes of carbon. Carbon nanotubes have a crystal structure and unique properties, such as a large surface area, hollow structure, high mechanical strength, and excellent electrical properties. These features make them suitable for various applications, such as energy storage, nanocomposite materials, and the synthesis of nanoelectronic devices like nanosensors. Graphene, a two-dimensional sheet of carbon atoms arranged in a hexagonal (honeycomb-like) structure, has also received significant attention in nanoelectronics and nanocomposites, similar to carbon nanotubes. This paper provides a detailed introduction to carbon nanotubes and graphene, including their synthesis methods and applications.

### Keywords

Carbon nanostructures, carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, nanoelectronic devices.

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### 1. Introduction

Carbon nanostructures like carbon nanotubes and graphene have unique properties due to the chemical nature of carbon atoms, which form the basic building blocks of these structures. The arrangement of carbon atoms in these nanostructures also contributes to their distinct properties. From a crystallographic perspective, carbon nanotubes are cylindrical tubes made from graphene sheets. The behavior of these nanomaterials can be controlled by changing their structure, diameter, and orientation. The size, crystalline structure, and surface topography of carbon nanotubes significantly affect their mechanical and microstructural properties. The term graphene was first introduced in 1986. Graphene is a two-dimensional sheet of carbon atoms arranged in a hexagonal pattern, and it is the latest member of the multi-dimensional family of carbon materials. Each carbon atom in a graphene sheet forms bonds with three other carbon atoms, with all these bonds lying within the same plane. The bond angle between carbon atoms is 120°.

Both carbon nanotubes and graphene have excellent mechanical, electrical, thermal, and optical properties, making them ideal for applications in nanoelectronic devices and nanocomposites. Various methods for synthesizing these nanomaterials have been studied. When choosing the best synthesis method, factors such as cost, time, and the alignment of the synthesis method with the desired final properties should be considered.

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### 2. Prerequisites

Before discussing various carbon structures, it's important to understand some basic concepts that will be covered below:

A composite material is made from two or more constituent materials. These materials, which have different physical and chemical properties, combine to form a material with properties distinct from the individual components. The two main components of a composite are the matrix and the reinforcement.

Electronic packaging involves the design and manufacture of enclosures for electronic devices, ranging from small semiconductors to computers. The packaging of an electronic system should protect it from mechanical damage, electrostatic discharge, electromagnetic interference, and other hazards.

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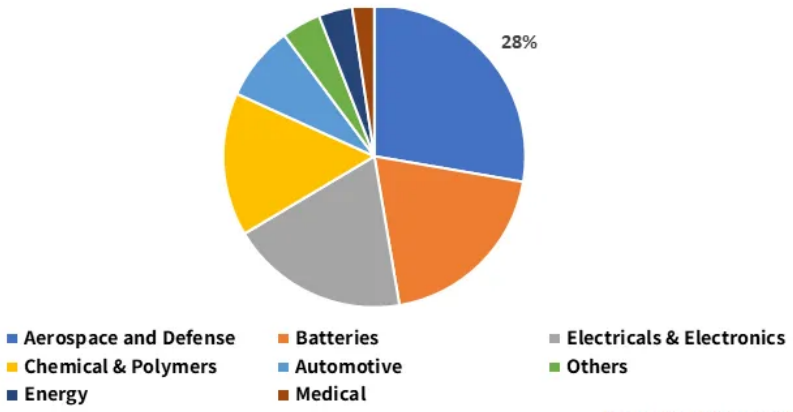
## 3. Carbon Nanotubes

Carbon nanotubes are formed from carbon sheets that are one atom thick and shaped into hollow cylinders. The unique geometric structure ($sp^2$ hybridization of carbon atoms in the nanotube structure) and their very low weight give them remarkable mechanical properties. In the crystalline structure of carbon nanotubes, carbon atoms form three bonds with their neighboring atoms, and the fourth electron is free around the atom. The elastic modulus of carbon nanotubes is 1 terapascal (TPa), and they can remain stable at temperatures up to 2800°C in a vacuum (they have very high thermal stability). Their tensile strength and elastic modulus are 100 and 7 times greater than steel, respectively. In terms of weight, carbon nanotubes are lighter than aluminum. Their thermal conductivity is twice that of diamond, and their electrical conductivity is up to 1000 times greater than copper. These properties make carbon nanotubes highly attractive for the synthesis of nanoelectronic devices, batteries, and nanocomposites. Carbon nanotubes are often used as a reinforcement or filler in polymeric and metallic composites. Figure 1 shows the global carbon nanotubes market share, by application in 2022.



Source: www.gminsights.com

Figure 1: global carbon nanotubes market share, by application 2022[1].

Depending on the number of walls, carbon nanotubes are classified into three categories: single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and multi-walled carbon nanotubes (MWCNTs). Single-walled carbon nanotubes are made from a single graphene layer rolled into a tube, with a diameter of about 1-2 nanometers. These single-walled carbon nanotubes have very high electrical and thermal conductivity. However, synthesizing them is challenging, and their final price is quite high. Double-walled carbon nanotubes are coaxial structures made of two single-walled carbon nanotubes nested together. Multi-walled carbon nanotubes consist of densely packed graphene tubes with a gap between the layers. These nanotubes have a hollow core with an external diameter between 2-25 nanometers, and the distance between the graphene sheets in the tube is about 0.34 nanometers. Figure 2 illustrates different types of carbon nanotubes based on the number of walls.

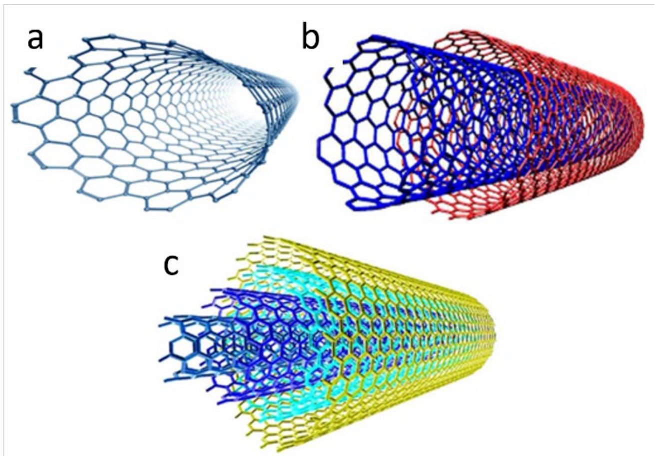


Figure 2: Types of carbon nanotubes based on the number of walls: (a) Single-walled carbon nanotubes, (b) Double-walled carbon nanotubes, and (c) Multi-walled carbon nanotubes [2].

In terms of chirality and component angles in a graphene sheet, carbon nanotubes are classified into three types: zigzag, armchair, and chiral. Figure 3 shows a schematic of these three different types of carbon nanotubes based on their chirality and component angles.

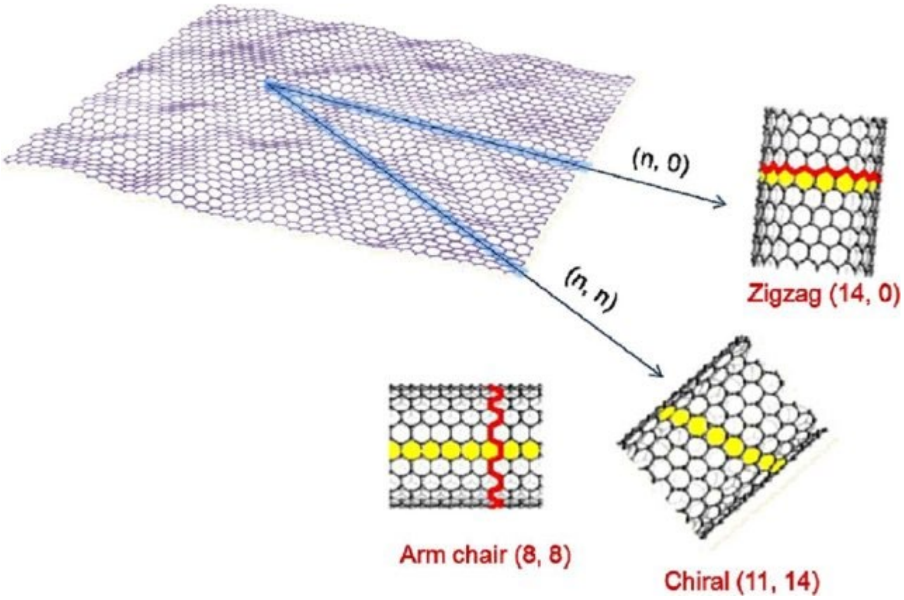


Figure 3: Types of carbon nanotubes based on chirality and angle [2].

Zigzag carbon nanotubes have a zigzag pattern along their width. Armchair carbon nanotubes have a regular pattern along their width or can be oblique. Carbon nanotubes that do not follow either of these patterns are classified as chiral. Calculating the chirality and angle of a carbon nanotube allows you to determine its type. Figure 4 shows a graphene sheet with three different points, each corresponding to a different type of carbon nanotube.

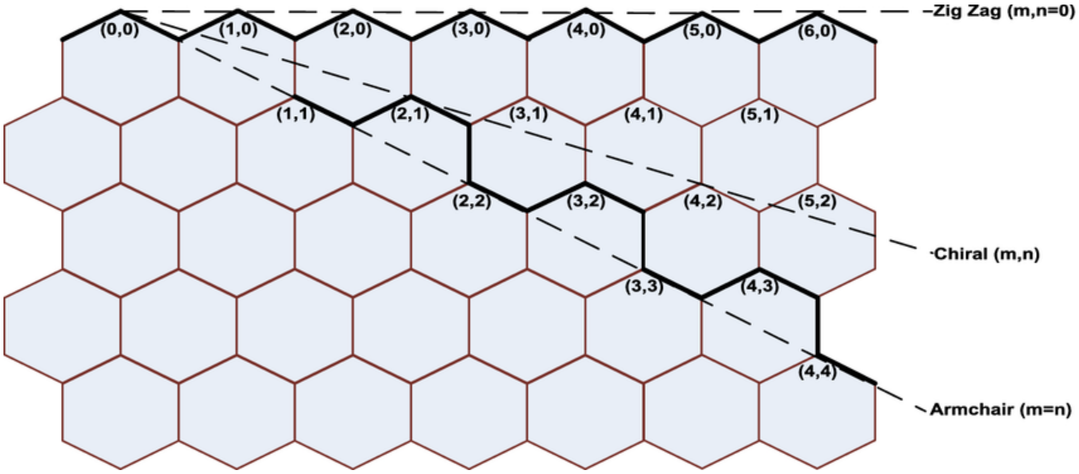


Figure 4: A graphene sheet with three different points, each corresponding to a different type of carbon nanotube.

The way to determine the coordinates of a point and chirality angle is explained in detail in the article "Carbon Nanomaterials 1: Carbon Structures" . If the component j or n of a point on the graphene sheet is zero, the carbon nanotube is classified as zigzag. If both components i and j or m and n are equal, the carbon nanotube is of the armchair type. If neither of these conditions is met, the carbon nanotube is classified as chiral.

To identify the type of carbon nanotube using the chirality angle, the chirality angle must first be calculated. If the chirality angle is 0 degrees, the carbon nanotube is of the zigzag type, and if the chirality angle is 30 degrees, the nanotube is of the armchair type. If the angle is between 0 and 30 degrees ($0 < \Theta < 30$), the nanotube will be of the chiral type.

One important application of the chirality components (i, j) is determining whether a carbon nanotube is conductive or semiconductive. If the difference between the chirality components is a multiple of 3, the carbon nanotube is conductive. The mathematical expression for this condition is as follows:

$$m-n=3k$$

where k is an integer. If this condition is met, the nanotube is metallic (conductive); otherwise, it is semiconducting. For example, a carbon nanotube with chirality components (6, 6) is conductive because the difference between the chirality components is zero. Similarly, a carbon nanotube with chirality components (4, 10) is conductive because the difference is 6. If the chirality components are (5, 10), the nanotube is considered semiconductive. Therefore, it can be concluded that armchair carbon nanotubes are always conductive due to their identical chirality components, while zigzag and chiral nanotubes can be either conductive or semiconductive.

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## Applications of Carbon Nanotubes

The unique features of carbon nanotubes make them useful in a wide range of applications, some of which are listed below:

Transportation: Body and components of fuel systems and engines (internal combustion engines) in cars, airplanes, and boats. The use of carbon nanotubes in fuel systems and engines increases fuel efficiency and lubricating properties.

Electronics: Electronic packaging, protection from electromagnetic interference, synthesis of transistors, p-n diodes, and increasing the performance speed of electronic components like CPUs in computers and sensors.

Energy: Manufacturing lithium batteries and fuel cells, as carbon nanotubes, due to their free electron, have hydrogen storage capabilities.

Medical Treatment: Assisting in brain injury treatment, drug delivery to damaged cells, removing cancerous tumors, gene therapy.

Industrial Applications: Oil and gas (as nanosensors for detecting sulfur-containing gases), rubber parts, protective coatings, conductive paints, sports equipment, and thermal devices.

Figure 5 illustrates the drug loading inside the hollow core of a single-walled carbon nanotube for targeted drug delivery applications.

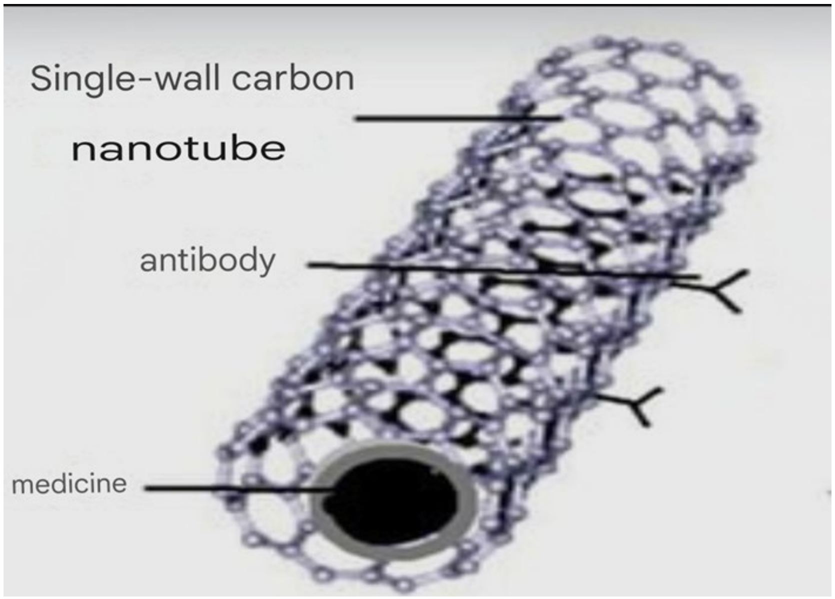

Figure 5: Drug loading inside the hollow core of a single-walled carbon nanotube for targeted drug delivery [3].

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Synthesis Methods for Carbon Nanotubes

Various methods for synthesizing carbon nanotubes have been proposed, with some of the most important methods being:

Laser Ablation

Catalytic Decomposition of Hydrocarbons

Electric Arc Discharge

Chemical Vapor Deposition (CVD)

In laser ablation, a graphite target is vaporized using pulsed laser energy in a high-temperature chamber under a flow of inert gas like argon or helium. In catalytic decomposition of hydrocarbons, hydrocarbons like acetylene ($C_2H_2$) decompose at low temperatures with a palladium/alumina catalyst. The palladium catalyst activates the acetylene and creates nucleation sites for carbon nanotube growth. The electric arc discharge method applies a direct current arc voltage to two graphite electrodes in an inert gas environment like helium.

The most common and effective method for synthesizing carbon nanotubes is Chemical Vapor Deposition (CVD). This method involves the decomposition of a hydrocarbon gas at temperatures ranging from 500 to 1100°C. The carbon atoms generated in the chamber deposit onto a substrate with catalysts like iron, nickel, or cobalt, which help in the formation of nanotubes. To move carbon atoms to a substrate with a catalyst, gases like hydrogen, nitrogen, and acetylene are used. Important factors that affect the purity, quality, and efficiency of this method in making carbon nanotubes include the type and combination of hydrocarbons used, as well as the temperature of the chamber. Figure 6 shows a diagram of the chemical vapor deposition process for making carbon nanotubes and the mechanisms that help them grow.

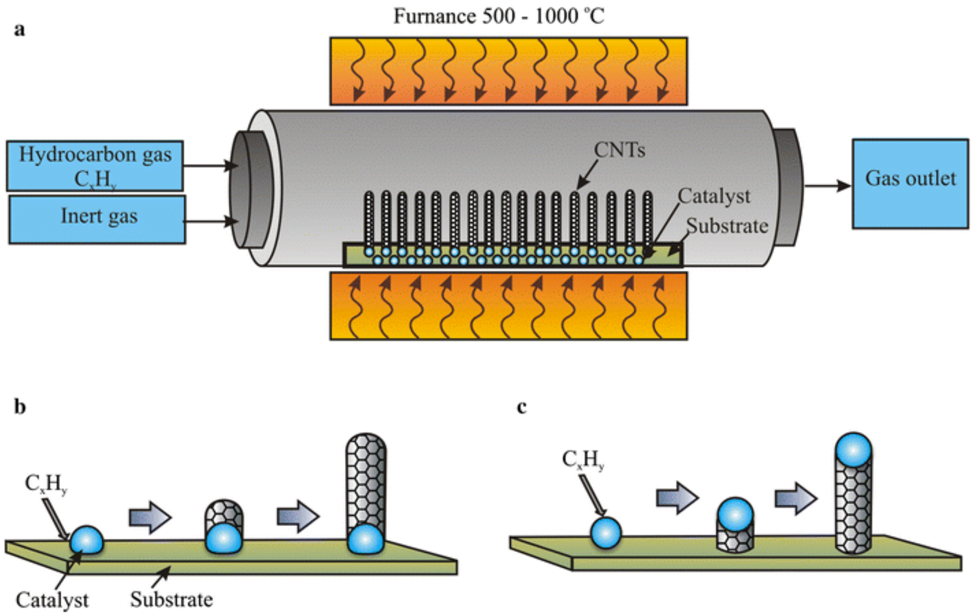

Figure 6: (a) A schematic of the Chemical Vapor Deposition process for synthesizing carbon nanotubes, (b) and (c) mechanisms for nanotube growth [4].

The use of alternative methods such as electric arc discharge for synthesizing carbon nanotubes results in the production of other carbon allotropes like fullerene and graphene alongside carbon nanotubes, leading to lower purity of the synthesized nanotubes. Another challenge in successfully synthesizing carbon nanotubes is the variation in the structures of the nanotubes. In other words, the synthesized nanotubes consist of a mixture of zigzag, armchair, and chiral types, which leads to some nanotubes being conductive while others are semiconductive. To overcome this challenge, methods such as alternating current electrophoresis, electric current-induced oxidation, and chemical separation are employed to isolate different nanotube structures. These processes increase the time and cost of production.

Figure 7 shows a Transmission Electron Microscopy (TEM) image of carbon nanotubes synthesized by the CVD method. As shown, the nanotubes are intertwined and tangled.

Figure 7: TEM image of carbon nanotubes synthesized by the CVD method [5].

4- Graphene

The term graphene was first introduced in 1986. The word is a combination of "graphite" and the suffix "en," which refers to aromatic polycyclic hydrocarbons. Graphene is the latest member of the family of multi-dimensional carbon materials. It is a two-dimensional sheet of carbon atoms arranged in a hexagonal or honeycomb pattern, where the carbon atoms are bonded with $sp^2$ hybridization. These sheets are formed by the arrangement of carbon atoms. In a graphene sheet, each carbon atom forms bonds with three other carbon atoms. All these bonds lie within the same plane, and the bond angle between them is 120 degrees. The bond length between carbon atoms in graphene is approximately 0.142 nanometers.

The delayed discovery and introduction of graphene was due to the energetic instability of a flat carbon sheet, according to theoretical studies and simulations. Continued research revealed that graphene sheets experience numerous distortions due to thermal fluctuations. The presence of these distortions provided a solution to overcome the challenge of the instability of graphene sheets, as indicated by simulation results. Figure 8 shows a schematic of the distortions in a graphene sheet.

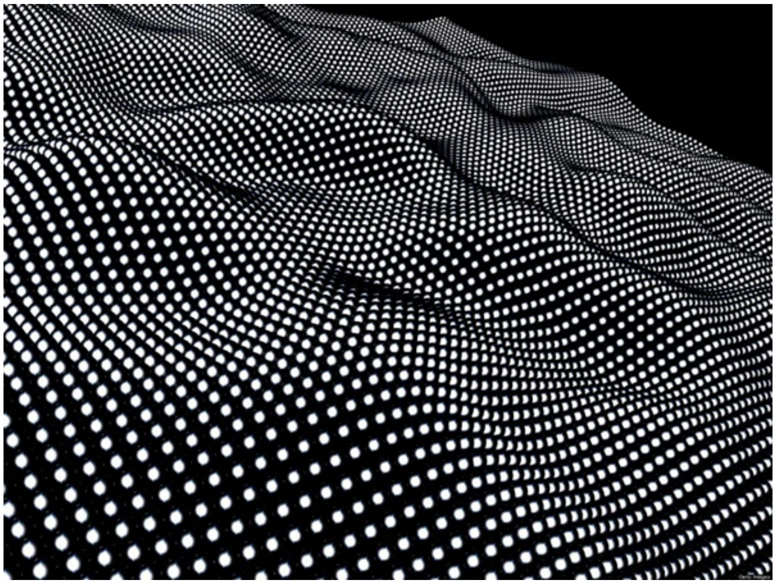

Figure 8: Schematic representation of the distortions in a graphene sheet.

Single-layer graphene serves as the precursor for various carbon allotropes. By stacking graphene sheets, graphite is formed; by rolling it around an axis, carbon nanotubes are formed; and by twisting it into a sphere, fullerenes are formed. Figure 9 shows the geometric shapes of various carbon allotropes.

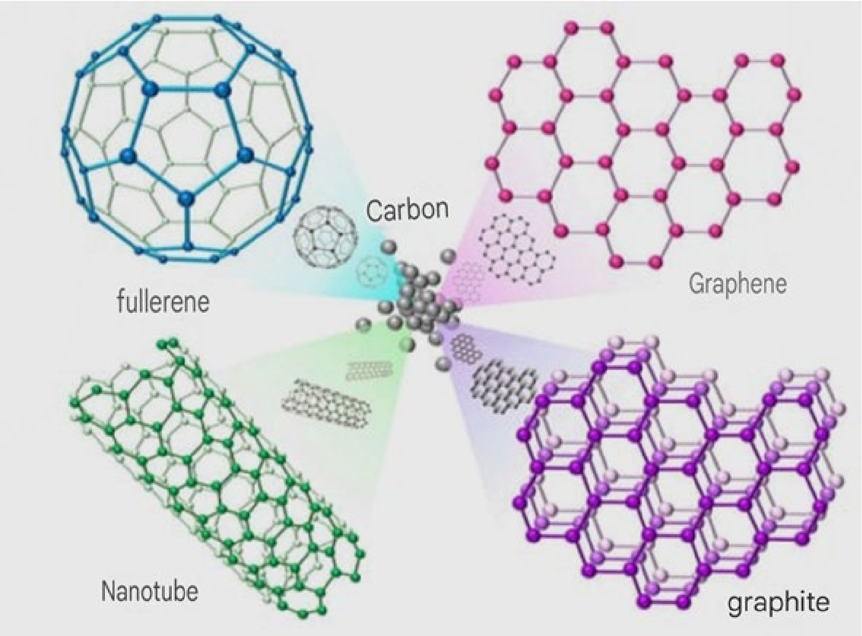

Figure 9: Geometric shapes of different carbon allotropes [6].

Like carbon nanotubes, graphene also has excellent mechanical properties and good electrical and thermal conductivity. The mechanical properties of single-layer graphene, such as Young's modulus and fracture strength, have been studied using numerical simulations and molecular dynamics. Research results indicate that the Young's modulus of a defect-free graphene sheet is one terapascal (TPa), and its fracture strength is 130 gigapascals. Carbon atoms have six electrons, two of which are in the inner shell, while the remaining four are in the outer shell, participating in the formation of chemical bonds. However, in graphene, each carbon atom, due to $sp^2$ hybridization, can form bonds with three other atoms, leaving one electron free. The electron mobility in graphene is so high that it can be considered independent of temperature, even at room temperature.

Single-layer or bilayer graphene exhibits very high transparency across a wide range of spectra (from ultraviolet to infrared). This property makes it ideal for use in the fabrication of transparent electrodes for solar cells. Single-layer graphene absorbs only 2.3% of white light, transmitting the rest.

Graphene composed of 3 to 10 layers is called "few-layer graphene," and nanostructures of graphene with 10 to 30 layers are referred to as "multi-layer graphene" or "thin graphite nanocrystals." Therefore, graphene nanostructures are not necessarily single-layered, and it is possible to synthesize graphene by stacking a limited number of single graphene sheets. The applications of graphene depend significantly on the number of layers. For example, in applications based on the electrical and thermal properties of graphene, single-layer graphene or graphene with a very limited number of layers should be used.

## 1-3 Characterization Methods for Graphene Properties

Various tools are used for characterizing the properties of synthesized graphene. Each of these tools is used to characterize a specific feature, as outlined below:

Morphological properties, size, and number of layers can be analyzed using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

Surface chemistry and functional surface groups can be studied using Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

The phase structure can be analyzed using X-ray diffraction (XRD).

## 2-3 Applications of Graphene

The unique properties of graphene have led to its use in various applications, such as the synthesis of composites (as a reinforcement) and electronic applications like transistors, transparent electrodes for solar cells, and supercapacitors. In the synthesis of polymer-based composites, adding graphene as a reinforcement significantly improves the electrical and thermal conductivity of the composite.

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## 3-3 Graphene Production and Synthesis Methods

Graphene was first synthesized in 2004 using the mechanical exfoliation method, in which a sticky tape was used to peel graphene layers from high-crystalline graphite. In this method, graphene layers are peeled off the surface of graphite and stick to the tape (see Figure 10). To achieve low-layer graphene, another layer of tape is applied on top of the previous tape. By peeling the new layer, fewer graphene layers remain on it. By repeating this process, the number of graphene layers is reduced.

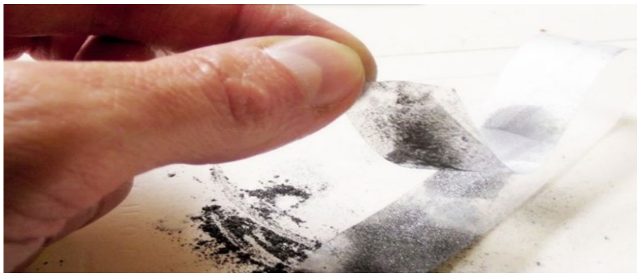

Figure 10: The mechanical exfoliation method for synthesizing graphene from high-crystalline graphite.

Various physical and chemical methods have been developed for synthesizing single-layer and multi-layer graphene, with some of the most important methods listed below:

Bottom-up methods:

- Chemical vapor deposition (CVD)
- Epitaxial growth
- Thermal cracking
- The Hummers method

Top-down methods:

- Atomic force microscopy (AFM)
- Mechanical exfoliation
- Reduction (or chemical reduction)
- Chemical synthesis

The two main methods for synthesizing graphene are chemical vapor deposition (CVD) and Hummers' method. The basis of the CVD method for synthesizing graphene is similar to that for carbon nanotubes, with the difference being that copper is used as the catalyst in graphene synthesis. The reaction in Hummers' method for synthesizing graphene is based on the oxidation of graphite, during which oxygen molecules enter the pure carbon graphene structure. This reaction occurs between graphite and concentrated sulfuric acid, with potassium permanganate and sodium nitrate acting as catalysts. The Hummers method is much cheaper than the CVD method and is capable of large-scale production. The main drawback of this method is the higher number of defects on the synthesized graphene, which results in reduced electrical conductivity. To overcome this challenge, a modified Hummers method is used. Figure 11 shows the steps of the modified Hummers method for synthesizing graphene oxide and reduced graphene oxide.

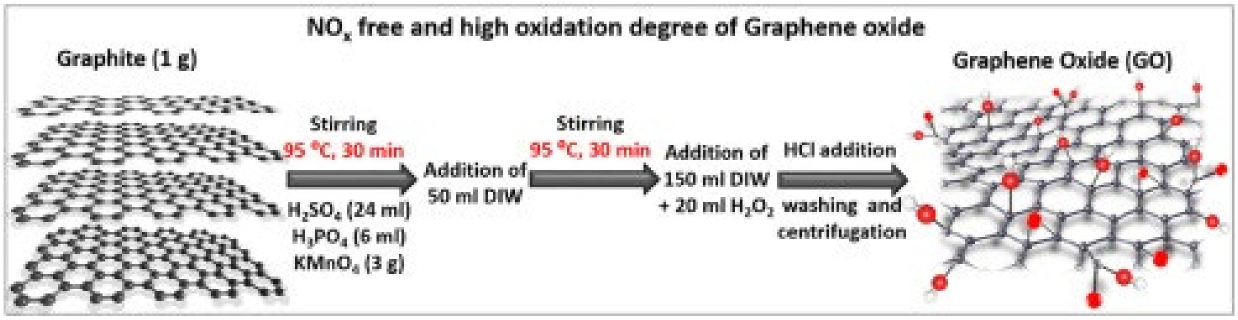

Figure 11: Steps of the modified Hummers method for synthesizing graphene oxide and reduced graphene oxide.

As shown in Figure 11, graphite reacts with acid and oxidizing agents, creating acidic groups between the graphite layers, which increases the distance between the layers. Then, applying ultrasonic waves or thermal expansion exerts a force on the layers, ultimately separating them from one another. The main factor causing the separation of graphite sheets is the increase in the distance between the layers due to the infiltration of oxidizing groups. Additionally, as the acidic groups exit the material during thermal expansion, they exert a force on neighboring sheets, helping to separate them. The material obtained after opening the graphite sheets is graphene oxide. The crystalline structure of graphene oxide has $sp^3$ hybridization because, in addition to the three covalent bonds between the carbon atoms in the sheet, a covalent bond is formed outside the sheet with the oxidizing groups. Therefore, graphene oxide does not conduct electricity due to the absence of free electrons. The presence of oxidizing groups on the surface of this material also makes it polar. Thermal and chemical processes are used to reduce graphene oxide. During reduction, a significant portion of the oxidizing groups on the surface of graphene oxide is removed, restoring $sp^2$ hybridization. The material obtained after the reduction of graphene oxide is called reduced graphene oxide, which is electrically conductive. However, the removal of a significant portion of the oxidizing groups reduces the polarity of the final product, making reduced graphene oxide a non-polar material. It is noteworthy that reduced graphene oxide has more crystal defects compared to graphene oxide synthesized by the CVD method.

## 4- Conclusion

Carbon nanotubes and graphene are the most important and widely used carbon allotropes. From a crystallographic point of view, carbon nanotubes are cylindrical tubes made of graphene sheets. Graphene is a two-dimensional sheet of carbon atoms arranged in a hexagonal pattern, and it is the latest member of the multi-dimensional carbon materials family. This article introduced carbon nanotubes and graphene, discussing their synthesis methods and applications. It was mentioned that in the crystalline structure of carbon nanotubes, carbon atoms form three bonds with neighboring atoms, and the fourth electron remains free around the atom. Depending on the number of walls, carbon nanotubes are classified into single-walled, double-walled, and multi-walled carbon nanotubes. The calculation of chirality components and angles helps in identifying the type of carbon nanotube. Laser ablation, catalytic decomposition of hydrocarbons, electric arc discharge, and chemical vapor deposition are common methods for synthesizing carbon nanotubes. Graphene was introduced as a two-dimensional sheet of carbon atoms arranged in a hexagonal pattern, with carbon atoms bonded through $sp^2$ hybridization. It was noted that graphene nanostructures are not necessarily single-layered, and graphene can be synthesized by stacking a limited number of single graphene sheets. The applications of graphene depend significantly on the number of layers. The article emphasized that the unique properties of graphene lead to its use in various applications, such as the synthesis of composites (as a reinforcement) and electronic applications such as transistors, transparent electrodes for solar cells, and supercapacitors. The two main methods for synthesizing graphene are CVD and the Hummers method. It was noted that the Hummers method is much cheaper than CVD and suitable for mass production. The main disadvantage of this method is the higher number of defects on the synthesized graphene, which reduces its electrical conductivity.

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## Nanocomposites

### Abstract

Composites are materials made by combining a reinforcing substance (like fibers or particles) with a matrix (like plastic or metal) to create a material with improved strength, flexibility, or durability. Nanocomposites are a special type of composite where the reinforcing particles are at the nanoscale, making the material even stronger, lighter, and more efficient. These materials are used in construction, transportation (like cars and airplanes), electronics, and medical devices. For example, nanocomposites improve the performance of batteries, create lightweight car parts, and enhance drug delivery systems. They are key to making advanced, high-performance materials for modern technology.

All the mentioned advantages of nanocomposites and their attractive applications are based on ideal conditions. However, in most cases, conditions are not ideal, and solutions are needed to improve these conditions. Some of the key factors to consider in nanocomposite production include the uniform distribution and dispersion of the nanofillers in the matrix, compatibility, and avoiding unwanted reactions between the components. There are different methods for producing nanocomposites, depending on the type of matrix phase. If the matrix phase is polymeric, the main methods are solvent-based (solution mixing), melt mixing, and in situ polymerization. If the matrix is metallic, the two main methods are Stir Casting and Liquid Metal Infiltration . This paper discusses the methods for producing nanocomposites, important properties, and their applications.

Keywords: uniform distribution, dispersion, methods of nanocomposite production, applications of nanocomposites

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### 1-Introduction

Composites are engineered materials made by combining two or more distinct components to achieve superior mechanical, thermal, or electrical properties. They consist of a matrix (continuous phase) and a reinforcement (dispersed phase) that enhances the material's performance.

Classification Based on Matrix Material:

Polymer Matrix Composites (PMCs): Lightweight and corrosion-resistant, commonly used in aerospace and automotive industries.

Metal Matrix Composites (MMCs): Offer high strength and thermal resistance, used in structural and aerospace applications.

Ceramic Matrix Composites (CMCs): Provide excellent heat and wear resistance, ideal for high-temperature environments.

Classification Based on Reinforcement Type:

Particle-Reinforced Composites: Contain dispersed particles that enhance stiffness and wear resistance.

Fiber-Reinforced Composites: Utilize fibers (glass, carbon, aramid) for high strength-to-weight ratio.

Structural Composites: Include laminates and sandwich panels designed for load-bearing applications.

Composites are widely used in aerospace, automotive, construction, and biomedical industries due to their customizable properties and high-performance characteristics.

A composite becomes a nanocomposite when at least one of its components (either the matrix or the reinforcement) has at least one dimension in the nanometer scale (below 100 nanometers).(Figure1)

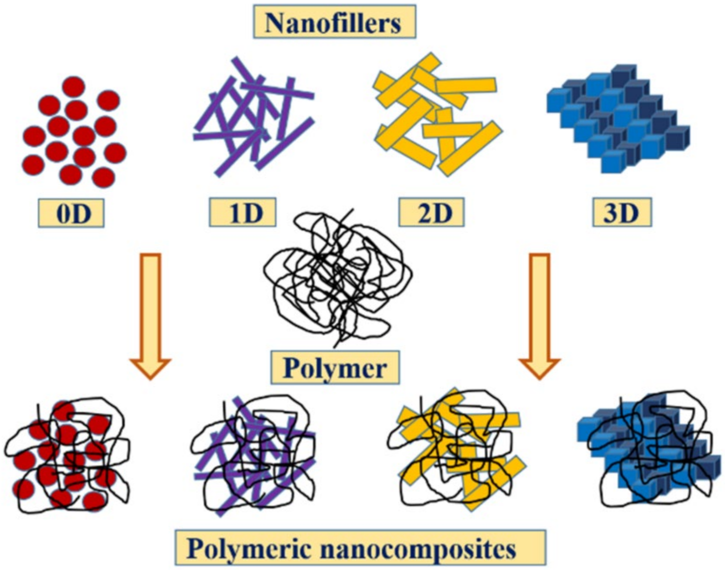

Figure 1: different kind of nanomaterial can be used as nanofillers in nanocomposites

In nanocomposite production, several factors must be considered. One of the most important factors is the conditions under which the nanocomposite is made. These conditions must be set up in a way that nanomaterials used as reinforcers can show their reinforcing properties in the best possible way. The required conditions are listed below, and various methods for producing nanocomposites are explained based on the type of matrix. Finally, some important applications of nanocomposites are discussed.

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## 2-Important Considerations in Nanocomposite Production

All the advantages of nanocomposite production and improvements that happen in the matrix can only be achieved if a true nanocomposite is made. This is very difficult to achieve, and in most cases, it doesn't happen! There are three very important aspects in nanocomposite production, which are explained below.

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## 2-1- Uniform Distribution and Dispersion of Nanofillers in the Matrix

The most important factor in nanocomposite production is the uniform distribution and dispersion of nanofillers in the matrix. This is very challenging because nanomaterials tend to aggregate due to their high surface energy. If these aggregates cannot be separated and kept in a uniform distribution, a true nanocomposite is not formed, and only aggregates of nanomaterials are added to the matrix. In this case, none of the expected improvements mentioned earlier will occur.

To achieve uniform dispersion of the fillers, two steps are necessary. First, the nanomaterials that form aggregates must be separated. These aggregates are called primary aggregates. For example, Figure 2 shows primary aggregates of carbon nanotubes.

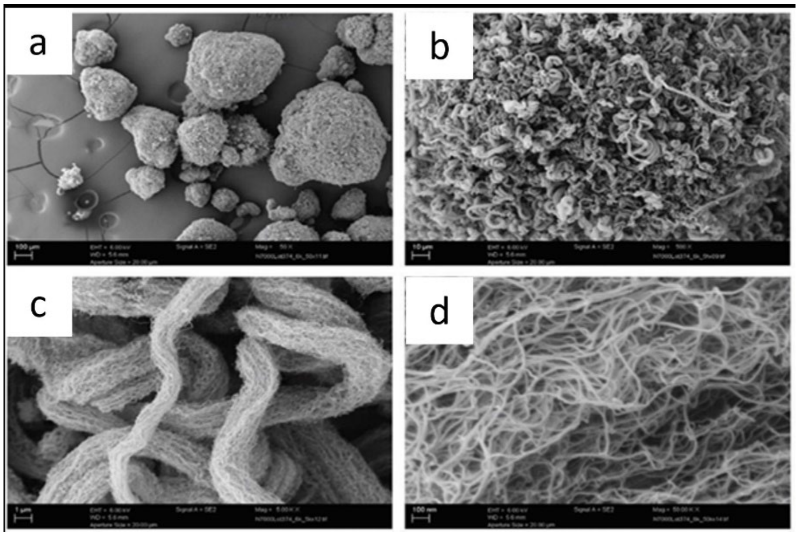

Figure 2: SEM image of carbon nanotube aggregates at different magnifications (from (a) to (t) magnification increases) [2].

In Figure 2, we can see that carbon nanotubes are tangled together, forming a rope-like structure, and these rope-like structures themselves are twisted together to form a large aggregates. The first step in nanocomposite production is to separate these aggregates and untangle the ropes to get individual nanotubes distributed in the matrix.

Similarly, in Figure 3, a schematic and SEM image of nanoclay sheets are shown. For nanoclay, the distance between the sheets needs to be increased sufficiently, or ideally, the sheets should be fully separated. If the distance between the sheets cannot be increased, a true nanocomposite is not created.

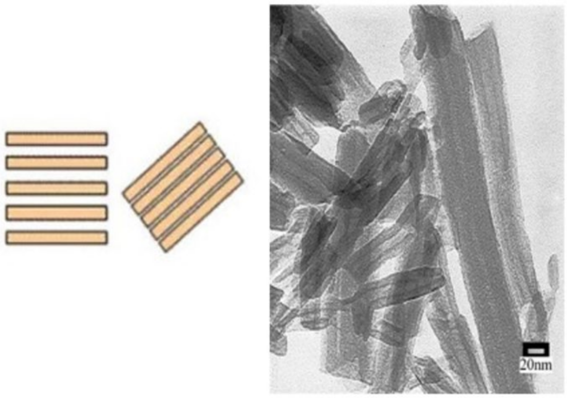

Figure 3: SEM and schematic image of nanoclay sheets [1].

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2-1-1- What is the difference between Distribution and Dispersion?

As mentioned, in nanocomposite production, both uniform distribution and uniform dispersion are needed. However, what is the difference between distribution and dispersion? This difference is shown in Figure 4. As shown in Figure 4, if the reinforcing components are present in most areas of the matrix, it is called a suitable distribution, whether the reinforcing components are separate nanoparticles or still in aggregates. However, dispersion means the separation of the nanostructures from each other and turning the aggregates into individual nanostructures

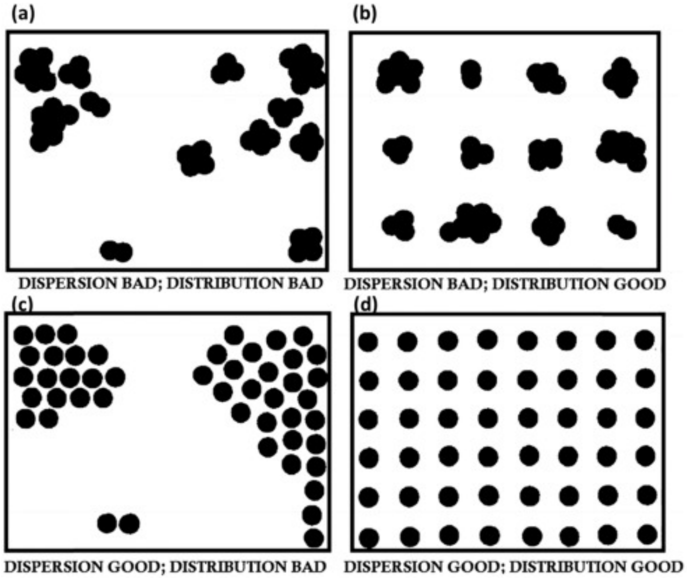

Figure 4: The concept of distribution and dispersion of reinforcing components in the matrix phase.

## 2-2- Compatibility Between Nanomaterials and the Matrix

Another important issue in nanocomposite production is the need for compatibility between the nanomaterials and the matrix. For the nanomaterials to remain uniformly dispersed in the matrix and not form aggregates again, both the nanomaterial and the matrix must be compatible from a chemical point of view. For example, carbon nanotubes and graphene, which are commonly used in nanocomposites, are nonpolar in their pure form. If the matrix is also nonpolar (for example, polyethylene), they will be compatible. However, if the matrix is polar (e.g., polyamide), surface modification of the nanomaterial is needed. This can be done by adding functional groups such as carboxyl or hydroxyl groups on the surface of the nanomaterials to make them compatible with the polar matrix. Additionally, dispersing agents such as surfactants or copolymers with both hydrophilic and hydrophobic sides can be used to improve compatibility.

## 2-3- Avoiding Unwanted Reactions Between Nanomaterials and Matrix

Another factor that can affect the final result of nanocomposite production is the potential for unwanted reactions between the reinforcing nanomaterial and the matrix, especially in metallic matrices. This is because metallic matrices often require high temperatures and pressures during the production process. At these high temperatures and pressures, there is a high possibility of a chemical reaction between the metal and the nanomaterial, which could be undesirable. For example, if single-walled carbon nanotubes are used in an aluminum matrix, a reaction might occur between the carbon nanotubes and aluminum at high temperatures and pressures, leading to the

$$4Al + 3C \rightarrow Al_4C_3$$

formation of aluminum carbide instead of maintaining the carbon nanotubes.

When a carbon nanotube is single-walled, it is almost entirely destroyed during the reaction. However, if the carbon nanotube is multi-walled, only the outer walls are damaged, and the inner walls remain intact. Nevertheless, even in the case of multi-walled carbon nanotubes, the formation of aluminum carbide significantly reduces the deformation capability and impact resistance of the resulting nanocomposite, which limits its applications.

The only advantage of this unwanted reaction is the formation of an aluminum carbide interface between the aluminum and the carbon nanostructure. This interface improves compatibility between them and increases yield strength and tensile strength. However, the reduction in plastic deformation capability is so significant that this reaction is rarely desirable.

Although the above discussion focused on carbon nanostructures, especially carbon nanotubes, similar reactions may occur with other nanostructures as well.

Another important factor that may lead to the destruction of the nanomaterial's structure is the intense processing conditions during nanocomposite fabrication. This is particularly significant for nanostructures with special shapes, such as nanotubes or nanosheets. For instance, if high shear stresses are applied to carbon nanotubes or graphene during the nanocomposite production process, their structure may break down, causing them to fragment. As a result, their aspect ratio (the ratio of the largest dimension to the smallest dimension) is significantly reduced.

A decrease in the aspect ratio of these nanostructures severely reduces improvements in properties such as thermal conductivity, electrical conductivity, and mechanical properties. Therefore, it is essential to control the processing conditions during nanocomposite fabrication and avoid damaging the nanostructures to maintain their functionality. [1]

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## 3- Methods of Nanocomposite Production

The methods for fabricating nanocomposites depend on the matrix material. In the case of polymer matrices, there are three main fabrication methods: the solution method, in situ polymerization, and melt mixing.

In the solution method, the nanomaterial and polymer are dissolved in a suitable solvent and then mixed together. Afterward, the solvent is evaporated, resulting in a polymer-based nanocomposite. The advantage of this method is the ease of dispersing nanomaterials within the polymer matrix due to the presence of the solvent. However, it is primarily a laboratory-scale method. The choice of solvent depends on the type of polymer and reinforcing nanomaterial.

In the in situ polymerization method, the nanomaterial is mixed with a monomer, and then an initiator is added along with appropriate temperature conditions. The monomer polymerizes, forming the polymer matrix with the nanomaterials dispersed within it. This method is not considered industrial and is more suitable for polymers that do not dissolve in appropriate solvents or have poor thermal stability.

The final method, melt mixing, is a fully industrial technique capable of large-scale production. In this simple and fast process, a thermoplastic polymer and reinforcing nanomaterial are introduced into an extruder. By applying heat and shear stress, the polymer melts, and the nanomaterial is dispersed within it. [3]

Figure 5 schematically illustrates the methods for producing polymer matrix nanocomposites reinforced with clay nanosheets.

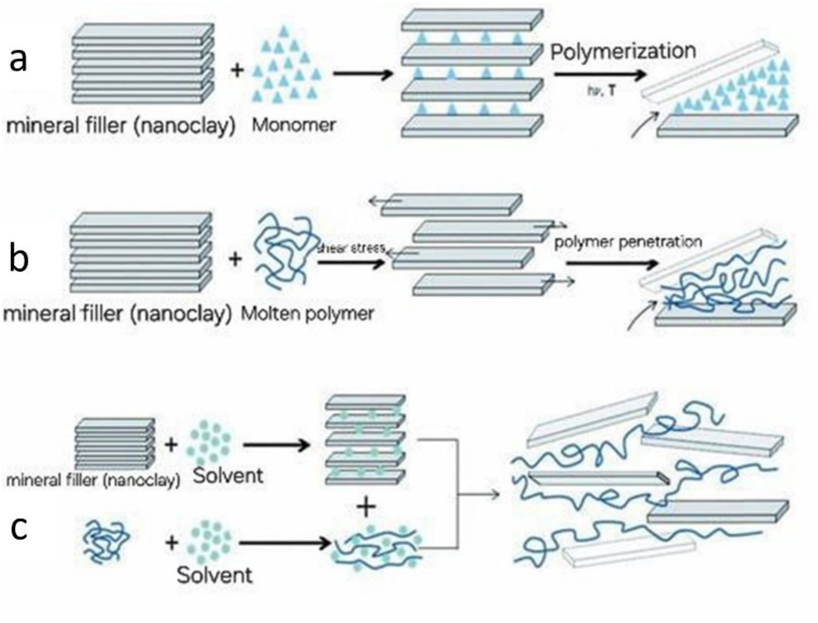

Figure 5: Schematic of methods for producing polymeric nanocomposites with nanoclay [3].

As shown in Figure 5, each of these methods uses a specific approach to separate the clay nanosheets. These approaches include the penetration of monomers between the clay sheets, increasing their spacing through polymerization, applying shear stress to the clay sheets using an extruder, and increasing the spacing between the sheets by infiltrating a polymer-containing solvent.

For fabricating metal matrix nanocomposites, various methods are also available, one of which is stir casting. This method, illustrated in Figure 6, involves adding the nanomaterial to the chamber while the metal is in a molten state. The stirring mechanism inside the chamber helps disperse the nanomaterial into the molten metal phase. Additionally, the stirring process applies shear stress, which breaks apart the initial agglomerates of the added nanomaterials.

To improve the mixing process, inert argon gas is also injected into the chamber. However, due to potential density differences between the nanomaterial and the molten metal, the nanomaterials often either float on the surface of the melt or settle at the bottom of the chamber, resulting in non-uniform dispersion. Despite this limitation, stir casting is a simple and fast method that is considered suitable for industrial applications. [4]

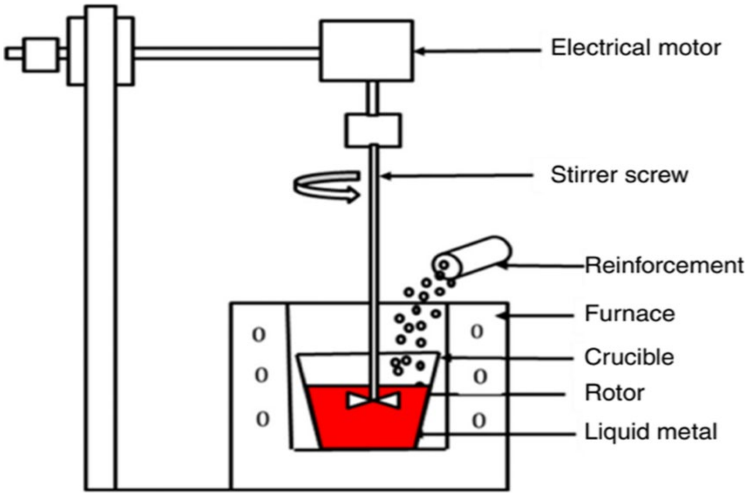

Figure 6: Production of Metal Matrix Nanocomposites via Stir Casting

Another common method is melt infiltration (liquid metal infiltration). In this method, the nanomaterial is prepared as a pre-shaped porous structure. To create this preform, an organic binder can be added to the carbon nanostructures, followed by sintering or pressing them. The preform is then placed in a chamber, and molten metal is poured over it. Various techniques are used to apply pressure to the molten metal to ensure it fully infiltrates the porous preform, resulting in a uniform piece.

In this process, since the preform is already uniformly distributed, and the molten metal only infiltrates it (with the binder evaporating during infiltration), a structure with excellent uniformity is achieved. This makes it highly suitable for specialized applications of metal matrix nanocomposites. This process is illustrated in Figure 7. [4-5]

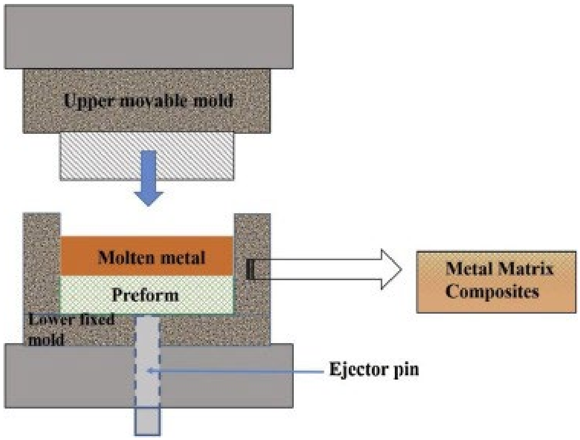

Figure 7: Schematic of the Melt Infiltration Process for Metal Matrix Nanocomposites

## 4- Applications of Nanocomposites

Due to the numerous benefits of nanocomposites, this field has attracted a lot of attention in industry. Below are some of the important applications of nanocomposites.

### 4-1- Smart Food Packaging

By using nanomaterials like nanoclay in polymeric food packaging, the shelf life of food products can be significantly increased. Nanoclay's barrier properties help to reduce the amount of oxygen entering the packaging, thus slowing down food spoilage. Figure 8 shows an example of this function.

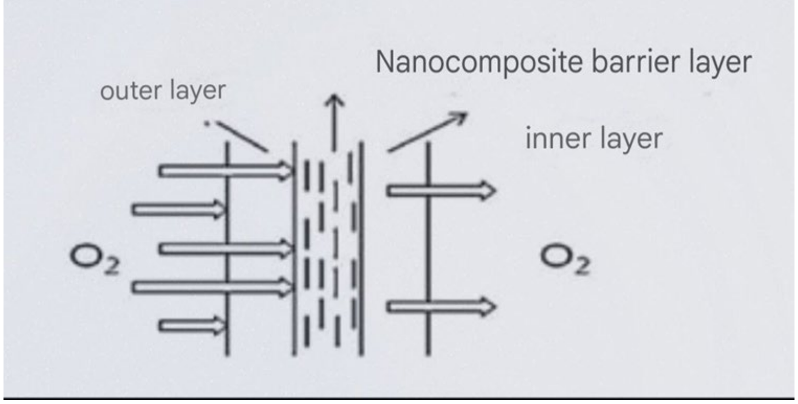

Figure 8: Use of nanoclay as a barrier to prevent oxygen from entering food packaging [6].

### 4-2- Producing Polymer Parts with High Electrical or Thermal Conductivity

Polymers are an attractive alternative to metals in some applications due to their lightweight and excellent moldability. For instance, using polymers in fuel storage tanks can simplify their production and make transportation easier. However, fuel tanks need to be somewhat electrically conductive to prevent the accumulation of surface charges, as surface discharge could lead to explosions. Most conventional polymers are electrical insulators, and conductive polymers are often very expensive. A practical solution is to produce electrically conductive polymer matrix nanocomposites reinforced with nanostructures like carbon nanotubes or graphene .Other applications of these nanocomposites include LED lamp holders, which need to be thermally conductive to protect the semiconductor inside from damage. Another example is polymer parts that require electrical conductivity for electrostatic painting, such as car fuel tank caps. [7]

### 4-3- Using Metal Matrix Parts in Aerospace and Automotive Industries

In the aerospace and automotive industries, the need to reduce weight for increasing speed and reducing fuel consumption is significant. One solution is replacing heavy metals like steel with lighter metals such as aluminum. However, aluminum lacks the required mechanical properties, so nanomaterials like silicon or carbon nanotubes are used to enhance its strength. [4]

### 4-4- Producing Ceramic Parts with High Plasticity

By using nanomaterials like silica in ceramic matrices, it is possible to improve the toughness and plasticity of ceramics, allowing them to be shaped. This has applications in manufacturing ceramic knives and other complex shapes for use in harsh environments. [8]

### 4-5- Other Applications

Nanocomposites also have many other applications, such as improving wear resistance in tires, producing flame-retardant polymers, UV-resistant polymers, noise-reducing pipes, antibacterial pipes, and self-healing polymeric nanocomposites.

## 5- Conclusion

As discussed, to create successful nanocomposites, it is essential to focus on achieving uniform distribution and dispersion of nanofillers, ensuring compatibility between the nanomaterials and matrix, and preventing unwanted reactions. Various methods for producing nanocomposites were outlined, and key applications in industry were highlighted.

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## Properties of Nanomaterials

- **Thermal Properties**
- **Mechanical Properties**
- **Optical Properties**

# Thermal Properties of Nanomaterials

## Abstract

Research findings show that when bulk materials are transformed into nanoscale, their physical properties undergo significant changes. One of the key physical properties of materials is their thermal properties. Thermal properties include thermal conductivity, thermal expansion coefficient, specific heat capacity, melting point, and other related factors. It has been observed that when materials are converted from bulk to nanoscale, their thermal properties change considerably. The reasons for this could include an increase in surface atom contributions, reduction in lattice constants, an increase in defects and vacancies, enhanced vibrations, and thermal instability. This article reviews the concepts of each of these thermal properties and describes how these properties change when materials transition from bulk to nanoscale.

Keywords: thermal expansion coefficient, specific heat capacity, heat carriers, thermal instability, melting point

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## Introduction

One important physical property of materials is their thermal properties. The study of thermal properties includes examining factors like thermal conductivity, thermal expansion coefficient, specific heat capacity, and melting point. Like many other characteristics, nanomaterials exhibit special thermal properties influenced by various factors. This paper briefly discusses some of these properties and examines the unique thermal properties of nanomaterials.

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## 2. Reasons for Differences in Thermal Properties in Different Materials

As you know, the thermal properties of metals, polymers, ceramics, and composites differ significantly from each other. But what factors account for these differences? Many factors affect the thermal properties of materials, the most important of which include atomic structure, electronic structure, and chemical bonds. The primary reason for differences in the thermal properties of materials is these factors. When materials from each category enter the nanoworld, their thermal properties undergo considerable changes. It's important to note that studying these changes is challenging due to the numerous influencing factors and their complexity. One of the factors that change significantly in nanomaterials compared to bulk materials, and that greatly affects thermal properties, is the role of defects and vacancies, which have not been well studied. The following sections delve deeper into each of these thermal properties.

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## 3. Thermal Expansion in Nanomaterials

Bulk materials typically expand when heat is applied due to two reasons: thermal vibrations and the increase in porosity.
Atoms are always vibrating in close proximity to each other. The extent of these vibrations depends on their structure and energy. As atoms vibrate, the bonds between them can contract, causing them to come closer at times, and at other moments, atoms move apart. To understand this, imagine a spring placed between two atoms, with the atoms constantly moving back and forth (Figure 1).

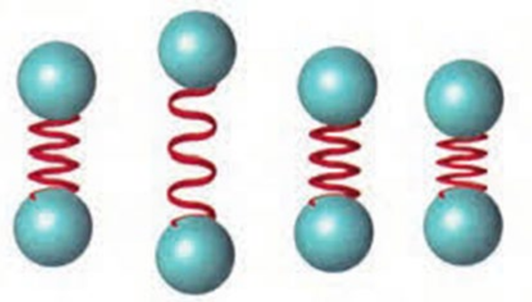


Figure 1: Representation of atomic distance changes assuming a spring exists between two atoms (the spring repeatedly compresses and extends).

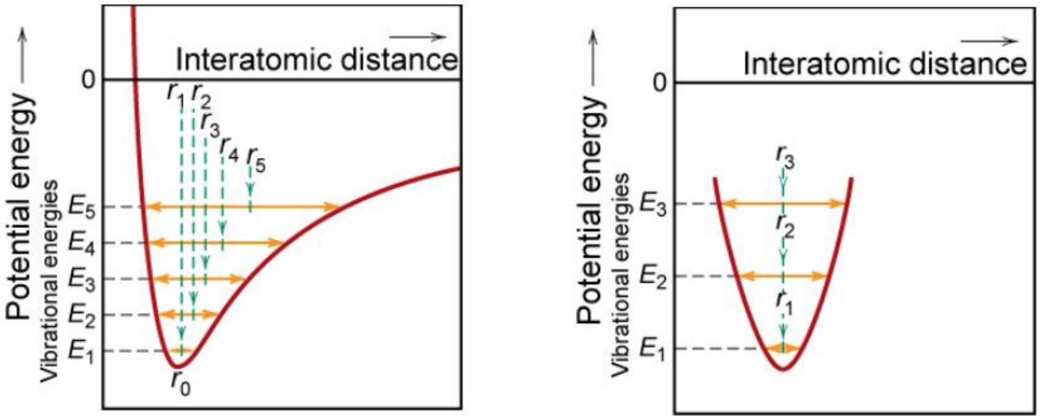


Figure 2: Potential energy diagrams (vertical axis) as a function of interatomic distance (horizontal axis) at various vibrational energies of a material (due to increased temperature). a) For a material with symmetric potential wells, b) For a material with asymmetric potential wells [1].

As the temperature increases, the vibrational energy of atoms increases, and the vibrations become more intense. In Figure 2, the changes in interatomic distance due to the increase in vibrational energy are shown. As seen in Figure 1, with increased vibrational energy, both the compression and expansion of the atoms increase. However, not all materials respond the same way in this case. Figure 2-a shows materials that are said to have symmetric potential wells. In these materials, the amount of compression and expansion of atoms due to increased vibrational energy (due to the increase in temperature) is the same. As a result, the equilibrium interatomic distance does not change, and the increase in temperature does not affect the interatomic distance. Such materials do not show thermal expansion. These materials are rare, and most materials have asymmetric potential wells.

Figure 2-b shows an asymmetric potential well. Most materials exhibit this behavior. As shown, in these materials, when the vibrational energy increases, the increase in interatomic distance due to bond expansion is greater than the decrease in interatomic distance from bond compression. Therefore, it is observed that an increase in temperature leads to an increase in the equilibrium interatomic distance. This increase in interatomic distance due to temperature increase leads to thermal expansion.

Thermal expansion can be expressed by the following equation:

$$\Delta L = L0 \cdot \alpha \cdot \Delta T \qquad \text{equation1}$$

In this equation1, L0 is the initial length, $\alpha$ is the linear thermal expansion coefficient, $\Delta L$ is the change in length, and $\Delta T$ is the temperature change. Additionally, $\beta$ is the volumetric expansion coefficient, which is approximately three times the linear expansion coefficient.

However, nanomaterials show differences in thermal expansion compared to bulk materials. This could be due to various reasons such as changes in thermal vibrations in the nanoscale, reduction in lattice constants, increased defects and vacancies in nanomaterials, and an increase in the proportion of surface atoms [1].

For example, Figure 3 shows the changes in the lattice parameter and the thermal expansion coefficient with temperature changes in gold nanoparticles

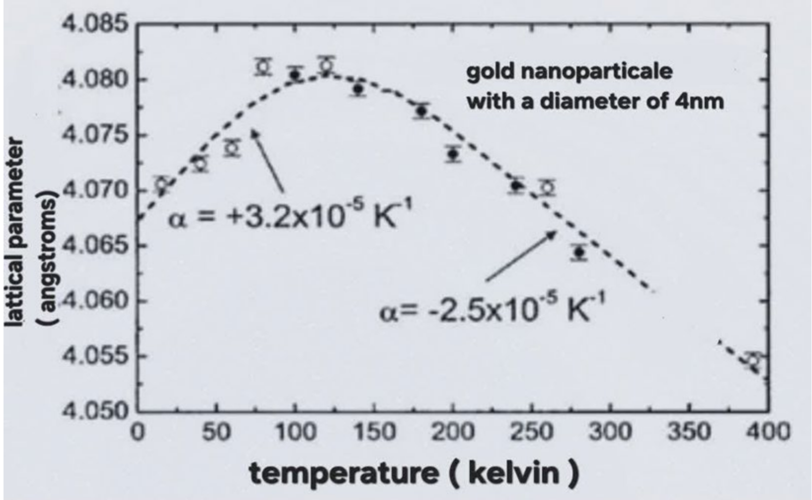


Figure 3: Changes in the lattice parameter and thermal expansion coefficient with temperature in gold nanoparticles [3].

As shown in Figure 3, at very low temperatures (below about 125 Kelvin), the behavior of the nanoparticle is almost the same as that of the bulk material, and the thermal expansion coefficient is positive. However, at temperatures above that, the thermal expansion coefficient becomes negative. The exact physical reason for this is not definitively clear, but some believe it is due to the effect of the valence electrons' potential on the lattice constant changes. The decrease in thermal expansion coefficient in nanomaterials can improve the material's performance. For example, ceramic nanomaterials can be used as thermal shields because their thermal expansion coefficient is lower than their bulk counterparts. It should be noted that there are different results in various studies on this topic, and sometimes these results contradict each other. The reason for this lies in the complexity and variety of factors affecting the thermal properties of materials [3].

## 4. Specific Heat Capacity of Nanomaterials

The specific heat capacity (C) of a substance is the amount of energy required to raise the temperature of the substance by one degree Celsius. The specific heat capacity per unit mass (usually taken as one gram) is referred to as specific heat capacity. The specific heat capacity at constant volume is denoted by $C_V$ and at constant pressure by $C_P$.

Figures 4 and 5, as well as Table 1, show the impact of converting bulk material into nanoparticles on specific heat capacity.

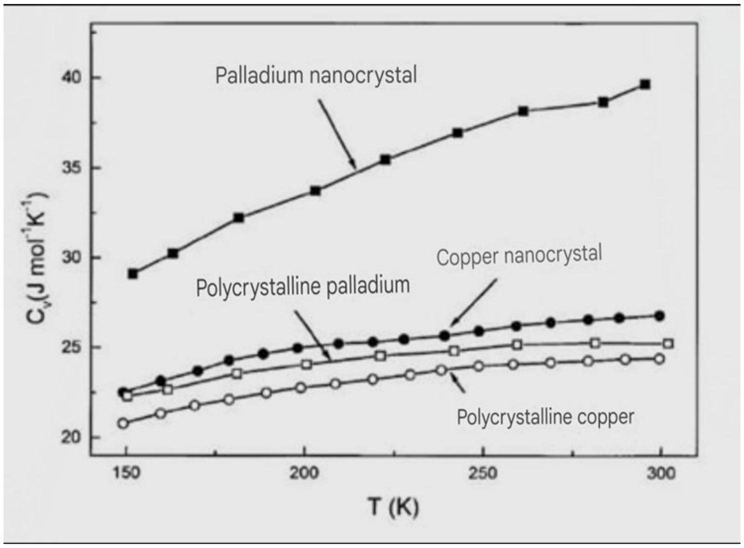


Figure 4: Impact of temperature on the specific heat capacity in nanocrystals and polycrystals (bulk) for palladium and copper [4].

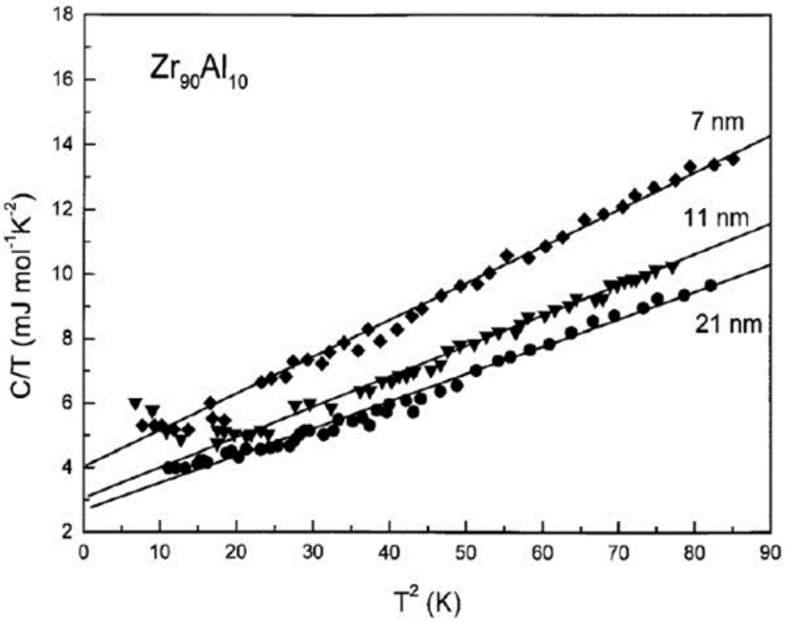
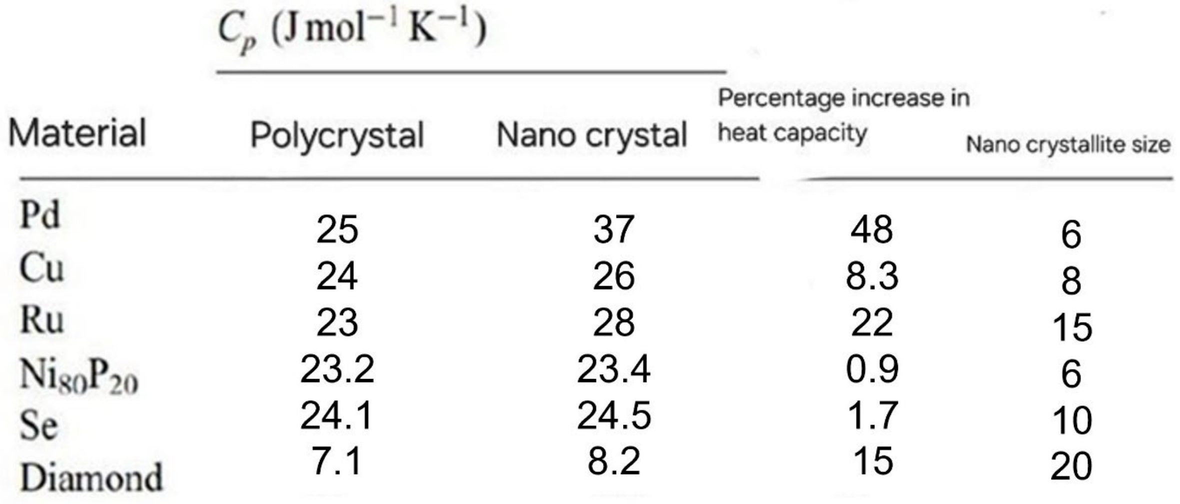


Figure 5: Impact of temperature on the specific heat capacity in ceramic nanoparticles of different sizes [4].

Table 1: Impact of converting bulk to nano on the specific heat capacity of various materials [4].



| | $C_p$ (J mol$^{-1}$ K$^{-1}$) | | | |
|---|---|---|---|---|
| Material | Polycrystal | Nano crystal | Percentage increase in heat capacity | Nano crystallite size |
| Pd | 25 | 37 | 48 | 6 |
| Cu | 24 | 26 | 8.3 | 8 |
| Ru | 23 | 28 | 22 | 15 |
| $Ni_{80}P_{20}$ | 23.2 | 23.4 | 0.9 | 6 |
| Se | 24.1 | 24.5 | 1.7 | 10 |
| Diamond | 7.1 | 8.2 | 15 | 20 |

As seen in Figure 4 and Table 1, the specific heat capacity in nanomaterials is higher compared to their bulk counterparts. Additionally, it can be observed that the increase in specific heat capacity due to the transition from bulk to nanoscale varies for different materials, being significant for some materials and negligible for others [2,4]. Figure 5 also shows that for Zr90Al10, the smaller the nanoparticle size, the higher the specific heat capacity. Moreover, the increase in specific heat capacity due to temperature rise is more noticeable in nanoparticles with smaller sizes. It is important to note that due to the many complex influencing factors, as previously mentioned, there is no clear and definite explanation for these changes.

---

## 5. Thermal Conductivity

Thermal conductivity is another important physical property. Heat carriers are responsible for transferring heat in different materials. Depending on the material type, heat carriers can be one or more of the following [1]:

Electrons: The primary heat carriers in metals and electronic conductors are electrons.

Phonons: The primary heat carriers in ceramics and polymers are phonons, which are elastic vibrations in the atomic network. This is shown in Figure 6.

Photons: Both in metals and ceramics at high temperatures, photons are heat carriers. This type of heat transfer happens through radiation from a material that has been heated.

As seen, depending on the material, the main heat carriers can vary. For example, in metals, both electrons and phonons contribute to heat conduction, but electrons play a much larger role. Various factors affect thermal conductivity, including the material's specific heat capacity, the type of heat carrier, the speed of the heat carrier, and the mean free path length of the heat carriers.

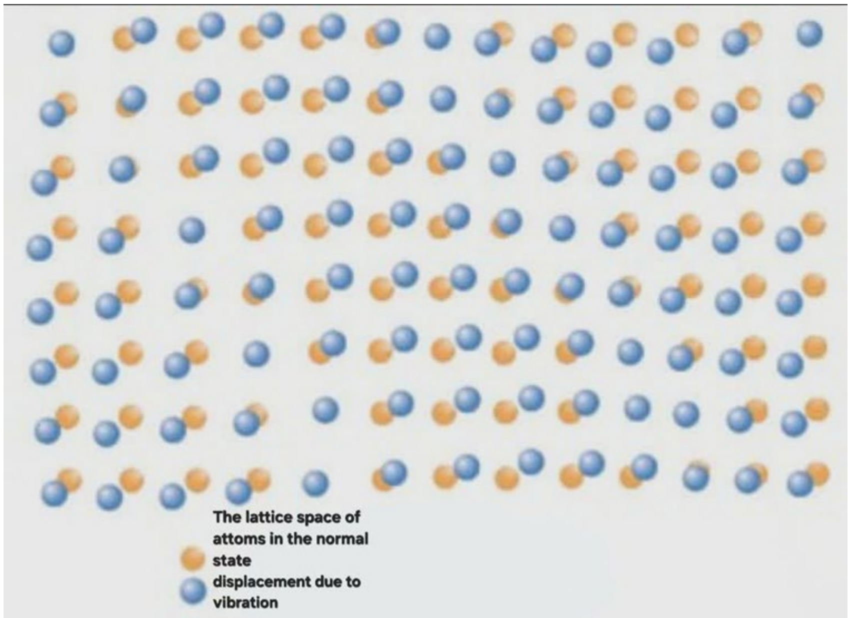


Figure 6: Schematic of atomic vibrations in a material due to atomic oscillations caused by heat application [1].

In some specific nanomaterials, we observe exceptionally high thermal conductivity. One such example is graphene. In graphene, it is said that ballistic transfer of heat carriers occurs, meaning the heat carriers can move through graphene without encountering resistance, and the mean free path length of these heat carriers is equal to or greater than the size of the graphene sheet. The mean free path refers to the average distance that a heat carrier moves between two obstacles in graphene without encountering any barriers. It should be noted that not all nanomaterials show increased thermal conductivity compared to their bulk state, and it is not possible to make a general conclusion in this regard. However, in several cases, an increase in thermal conductivity has been reported as a result of transitioning from bulk material to nanoscale.

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## 5.1. Nanofluids

By using nanoparticles in common heat-transfer fluids, nanofluids with higher thermal conductivity can be made. In addition to higher thermal conductivity, nanofluids offer other benefits such as greater stability, no sedimentation, reduced corrosion, and improved pressure drop issues. As a result, one of the outcomes of higher thermal conductivity in certain nanomaterials, compared to their bulk form, is the creation of nanofluids with enhanced properties compared to conventional fluids. Heat transfer in nanofluids occurs due to the nanoparticles sticking together and creating pathways for heat transfer, as the nanomaterials used have higher thermal conductivity than the fluid itself. However, for this to work, a conductive path must be created in the fluid, and the nanoparticles must not aggregates together. Furthermore, the Brownian motion of nanoparticles inside the fluid and the increased mixing improve heat transfer [5]. Nanofluids are not only used for heat transfer but also have applications in important fields such as medicine, although the primary focus remains on their use in heat transfer. It should be noted that, as mentioned earlier, the use of nanomaterials in these fluids is not solely for the purpose of improving thermal conductivity. Other advantages, particularly the increased stability, are of great importance.

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## 6. Melting Point of Nanomaterials

In bulk materials, the melting point is the temperature at which, during heating, the structural arrangement in the material breaks down, converting long-range order into short-range order, and the solid turns into a liquid. It should be noted that melting starts at the surface of the material and gradually spreads to the interior.

In nanomaterials, due to the high surface-to-volume ratio, a large percentage of atoms are located at the surface. These surface atoms have higher energy levels compared to the atoms inside the material, meaning they have more freedom to vibrate than the bulk atoms. This causes nanomaterials to melt or become liquid with much less thermal energy. As a result, it has been observed that the melting point in nanomaterials decreases compared to their bulk counterparts. This decrease in the melting point becomes especially noticeable for very small sizes (around 10 nanometers or below). Figure 7 shows the decrease in the melting point for gold nanoparticles [2,6].

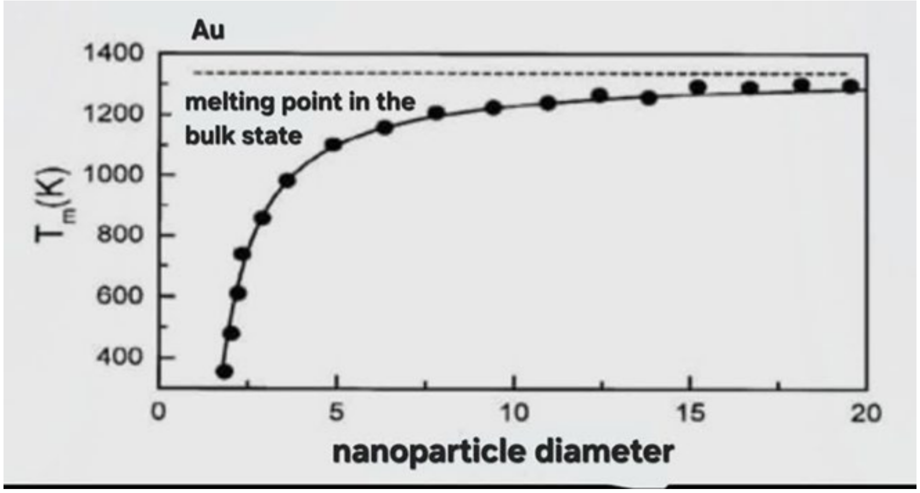

Figure 7: The effect of reducing nanoparticle size on the melting point of gold nanoparticles. The bulk melting point is shown as a dashed line; note the sizes [6].

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7. Thermal Instability

When materials are placed in an environment, they can gain energy from the heat in that environment. This energy is equal to KBT, where KB is the Boltzmann constant ($1.38 \times 10^{-23}$ J/K), and T is the temperature in Kelvin. If the temperature is not very high, this energy transferred to bulk materials is negligible. However, for nanomaterials, due to their small size, this energy becomes significant. For example, if this energy is converted into potential energy caused by the increase in the nanoparticle's height, the nanoparticle can rise to distances on the scale of meters. Due to the significant thermal energy in the environment for nanoparticles, they constantly move and do not remain stationary, creating thermal instability [6].

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Exercise

Based on the above explanation, how high can a nanoparticle with a diameter of 1 nanometer be lifted by the thermal energy at room temperature (27°C)? For this calculation, ignore air resistance.

Density of the nanoparticle: 5.6 g/cm³

The Boltzmann constant is provided above.

---

8. Conclusion

Studying the changes in thermal properties as a result of converting bulk material into nanomaterials is a challenging task due to the many complex influencing factors. Important factors that lead to changes in thermal properties in the nanoscale include the increased proportion of surface atoms, reduction in lattice constants, presence of more defects and vacancies, and enhanced vibrations and thermal instability.

To examine thermal properties, factors such as thermal expansion coefficient, heat capacity, heat carriers, thermal conductivity, melting point, and thermal instability must be studied. These factors should first be analyzed in bulk material and then evaluated for their changes as the material is converted to nanoscale.

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## Mechanical Properties of Nanomaterials

### Abstract

Stress and strain are fundamental concepts in studying the mechanical properties of materials. The force applied to the cross-sectional area of a material is called stress, and the change in length of a material relative to its initial length is called strain. For most materials, at low stresses, there is a linear relationship between stress and strain, known as Hooke's law. In this region, the change in stress relative to strain is linear, and the sample is in the elastic region. As the force increases, at a certain point, the relationship between stress and strain deviates from linearity, and the material enters the plastic region. In the plastic region, the deformation of the material becomes permanent and irreversible. The stress at which the material transitions from the elastic region to the plastic region is known as the yield stress. In nanomaterials, where the grain size is in the nanometer scale, the yield stress and strength show a significant increase.

Keywords: Stress, Strain, Yield Stress, Tensile Strength, Hooke’s Law, Elastic Region, Plastic Region, Nanostructures

### Introduction

The production of metals and alloys with a grain size smaller than 100 nanometers has led to the development of materials with extremely high strength. In fact, reducing the grain size in materials is a powerful tool for producing structures with excellent mechanical properties. To better understand the mechanical properties of nanomaterials, it's essential first to be familiar with some basic concepts related to the mechanical behavior of materials, such as stress, strain, and definitions of material properties like strength. In this section, we will first introduce the fundamental concepts needed for studying the mechanical properties of nanomaterials and then discuss the mechanical properties of nanostructured materials in the next section.

### Stress

Stress is the force applied per unit area of a material. In other words, stress is the ratio of the total applied forces on a surface to the area of that surface. The formula for stress on a surface (Equation 1) is given as:

$$\sigma = \frac{P}{A} \qquad \text{(Equation 1)}$$

Where σ (sigma) is the stress, P is the applied force, and A is the cross-sectional area under stress (Figure 1).

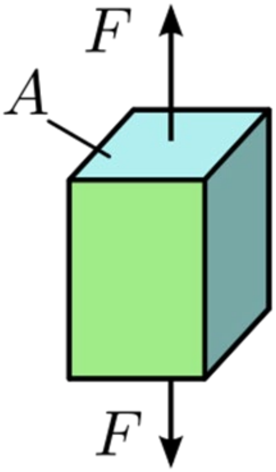

Figure 1: Stress caused by applying force to a surface.

The greater the surface area on which a force is applied, the lower the stress, as the force is distributed across a larger surface. Stress is commonly measured in units such as N/cm², N/mm², or kg/cm².

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Strain

When a material is subjected to stress, it undergoes deformation in the direction of the applied force. The ratio of the change in shape of the material to its original length is called strain. In other words, strain is the ratio of the change in length due to stress to the original length before stress is applied. The strain equation (Equation 2) is expressed as:

$\varepsilon = \Delta L / L$ where $\Delta l = L' - L$ (Equation 2)

Where ε (epsilon) is the strain, L is the initial length of the material, L' is the length of the material after applying stress, and Δl is the change in length caused by stress (Figure 2). Strain is essentially the percentage change in length of a material due to the applied stress and does not directly relate to the final length of the material. Strain is the material's response to applied stress. The smaller the strain, the harder the material, and the less flexible it is. Since strain is the ratio of two lengths, it is dimensionless.

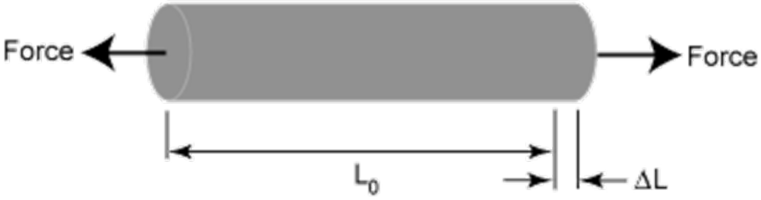

Figure 2: Deformation of a material due to applied stress.

## Hooke's Law

The relationship between stress and strain in a material is always direct, meaning as stress increases, strain also increases. Stress and strain for any type of material produce a two-dimensional curve, known as the "stress-strain curve," where changes in strain with respect to changes in stress are plotted (Figure 3). In the stress-strain curve, stress is always plotted on the vertical axis, and strain is plotted on the horizontal axis. This curve may be linear, curved, or a combination of both, depending on the material.

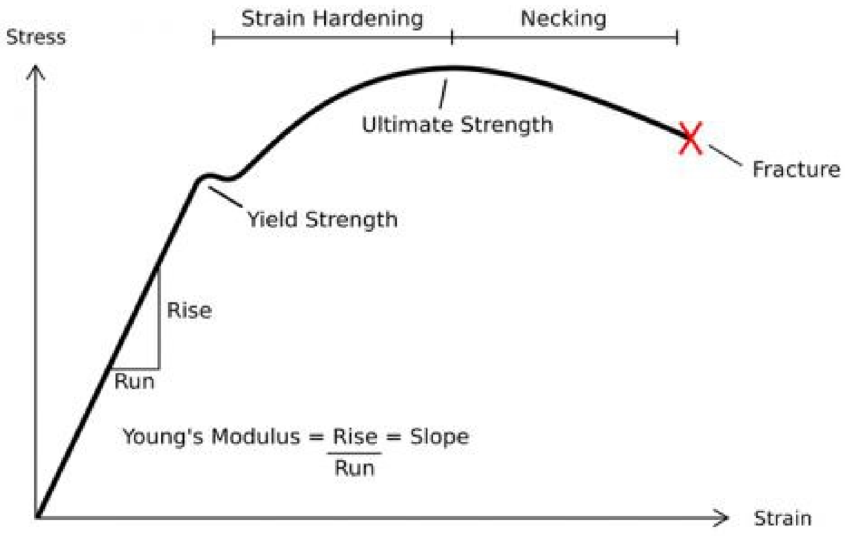

Figure 3: Stress-strain curve for materials, showing the direct relationship between stress and strain in the linear region.

In the stress-strain curve, the first part of the curve is typically linear. In this section, the relationship between stress and strain behaves linearly. The deformation in this region is elastic, meaning it is reversible. This means that if a limited force is applied to a solid, it will return to its original dimensions after the force is removed. The limit of the force beyond which the material no longer behaves elastically is called the elastic limit. The slope of this linear region is known as Young's modulus, or the modulus of elasticity. Young's modulus is measured in units of stress ($N/cm^2$, $N/mm^2$, or $kg/cm^2$).

If we use Young's modulus to express the equation of the linear region of the stress-strain curve, we find that the modulus of elasticity has a direct relationship with stress and an inverse relationship with strain. This is known as Hooke's Law and is expressed as follows (Equation 3):

$$E = \frac{\sigma}{\varepsilon} \quad \text{(Equation 3)}$$

The elastic deformation of metals is very small, and to measure it, very precise instruments are required. When the force applied to the material exceeds the elastic limit, the deformation becomes permanent, and the material enters the plastic region. Plastic deformation is irreversible and occurs beyond the yield point. To obtain the mechanical properties of materials, they are subjected to tensile or compressive forces, and their stress-strain curve is obtained. Figure 4 shows a typical stress-strain curve obtained from a tensile test until failure of a sample.

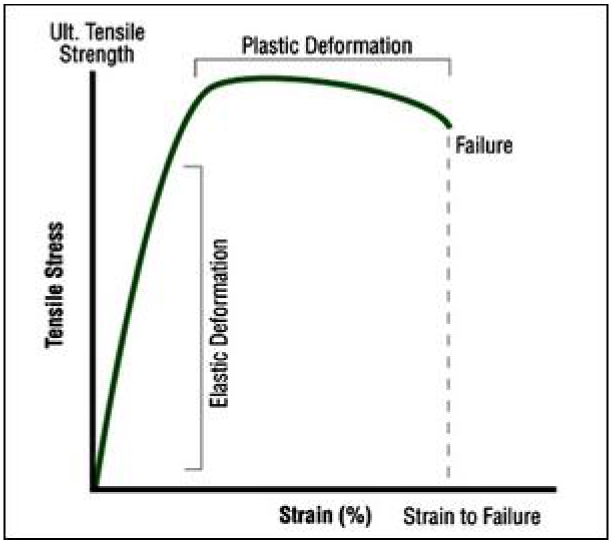

Figure 4: Stress-strain curve obtained from a tensile test of a sample.

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Important Mechanical Properties for Studying Nanostructures:

Proportional Limit: The point at which the stress-strain curve deviates from linearity. This value is very close to the elastic limit or yield stress, but since determining the elastic limit is difficult, the proportional limit is usually calculated.

Young’s Modulus (Elastic Modulus): The ratio of stress to strain in a material, defined by Young's modulus.

Yield Stress: The stress at which permanent deformation occurs and the strain reaches 0.002.

Tensile Strength: When the stress exceeds the elastic limit, plastic deformation occurs. As the plastic deformation increases, the material's strength (usually in metals) increases, and the force required to continue the deformation steadily increases. The maximum load a metal can withstand is called its tensile strength.

Fracture Stress: In ductile metals, if the applied load exceeds the maximum force, the sample's diameter decreases rapidly, and the force required to continue deformation decreases quickly, leading to sample failure.

Percent Elongation and Reduction in Cross-sectional Area: It is essential to note that tensile strength and yield stress represent the strength of a material, while the percent elongation and reduction in cross-sectional area represent the material's ductility.

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Nanostructured Materials and Their Mechanical Properties

After understanding the concepts of mechanical properties and the influence of grain size and crystallographic defects, let's continue with the details. In Figure 5-a, we see the microstructure of a material (considered two-dimensional for simplicity) consisting of six grains, each with its unique structure. The orientation and order of atoms change abruptly as you move from one grain to another. At the grain boundaries (the intersections of grains), there are a few atoms with no clear order, and these atoms do not belong to any neighboring grains (Figure 5-b). These regions, only a few atomic diameters wide, are called grain boundaries. Grain boundaries, which are crystallographic defects, significantly affect the mechanical properties of crystalline materials and especially nanocrystalline materials.

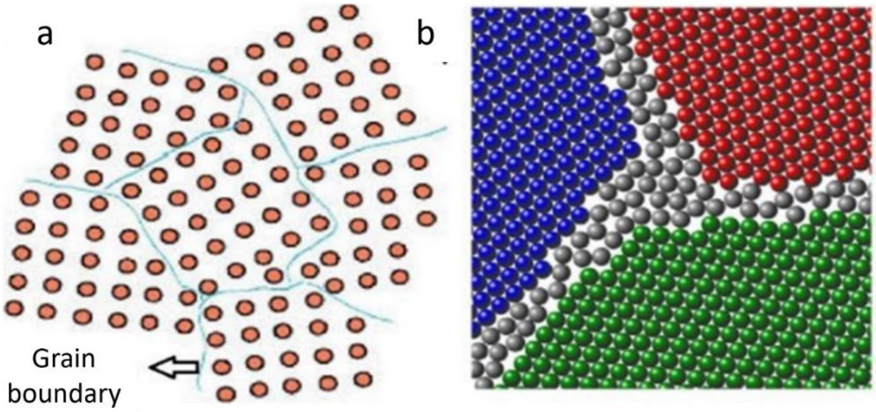

Figure 5: a) Grain boundaries as disordered regions separating grains in a polycrystalline material. b) Disordered arrangement at grain boundaries.

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What are Nanocrystalline Materials?

Consider a polycrystalline material (a material that is not single-crystal or single-grain) as shown in Figure 6. Each polygon represents a grain, and the lines shown represent the grain boundaries. If we apply physical methods to this material that result in breaking up the grains, turning each into smaller grains, the number of grains increases, and the average size of the grains decreases.

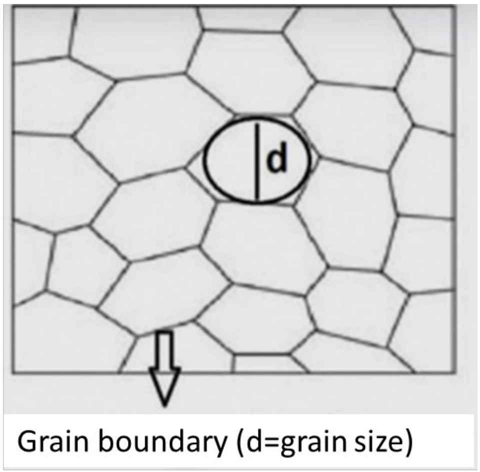

Figure 6: A polycrystalline material, with grain boundaries shown inside the square. The approximate size of a grain is the diameter of the hypothetical circle within it.

If this process continues until the grains reach the nanometer scale, the resulting material is called a nanocrystalline material, or nanostructured bulk material. These materials are also referred to as bulk nanostructured materials or 3D nanomaterials. In the section on introducing types of nanomaterials based on the number of free dimensions, this category of nanostructures has been briefly mentioned.

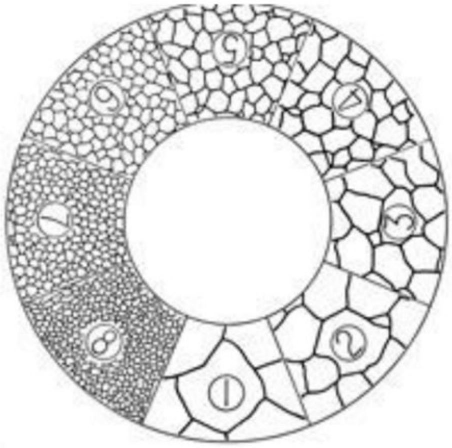

Figure 7: The eight stages of grain refinement due to the application of mechanical forces on a material. As the process progresses, the number of grains increases while their size decreases.

Take another look at Figure 7. As the grains become smaller, how has the total grain boundary area (or its overall length) changed? As you likely correctly deduced, the amount of grain boundaries has significantly increased. As previously stated, grain boundaries significantly influence the mechanical properties of nanocrystalline materials. These properties differ from those of materials with conventional grain sizes but the same chemical composition. Although all the diagrams provided are two-dimensional for simplicity, the same trend of increasing grain boundaries with decreasing grain size applies to real, three-dimensional objects.

The effect of grain boundaries is more pronounced in nanocrystalline materials because a high percentage of atoms in nanocrystalline substances reside at the grain boundaries. Generally, nanocrystalline materials exhibit remarkable hardness, high strength, and excellent wear resistance, which makes these features advantageous for various applications.

Apart from mechanical properties, the increase in grain boundaries in nanocrystalline materials also alters other properties, such as magnetic characteristics and corrosion resistance. In many cases, the very high hardness, strength, and wear resistance of nanocrystalline materials are attributable to the grain boundaries.

Although detailed discussions about material deformation mechanisms are beyond our scope, the effect of grain boundaries can be summarized as follows: Grain boundaries act as strong barriers to the sliding and movement of certain crystalline defects (dislocations), which are primarily responsible for material deformation and failure.

The general relationship between yield stress (a measure of material strength) and grain size was developed by scientists Hall and Petch and is known as the Hall-Petch relationship:

Equation 4:

$$\sigma_0 = \sigma_i + KD^{\frac{-1}{2}}$$

Where:

σ0: Yield stress,

σi : Frictional stress, representing the overall resistance of the crystal lattice to defect movement (responsible for material deformation),

K: a constant,

D: Grain size.

This relationship clearly demonstrates that reducing grain size increases the material's strength and yield stress. For instance, researchers compared the yield strength of palladium at grain sizes of 50 micrometers and 14 nanometers. The 14-nanometer nanocrystal had a yield strength of 259 GPa, significantly higher than the 52 MPa yield strength of the 50-micrometer grain-sized palladium.

However, it is worth noting that increasing material strength generally reduces ductility and malleability. Instead of yield stress, hardness (resistance to indentation or scratching) and wear resistance can also be considered. Similarly, as with strength, the hardness and wear resistance of materials increase as the grain size decreases.

Nevertheless, the increase in strength due to grain size reduction continues only up to a critical grain size (approximately 10 nanometers). Beyond this size, further grain size reduction results in a decrease in material strength or hardness. This phenomenon occurs due to changes in deformation mechanisms (the explanation of deformation mechanisms is beyond the knowledge requirements of students).

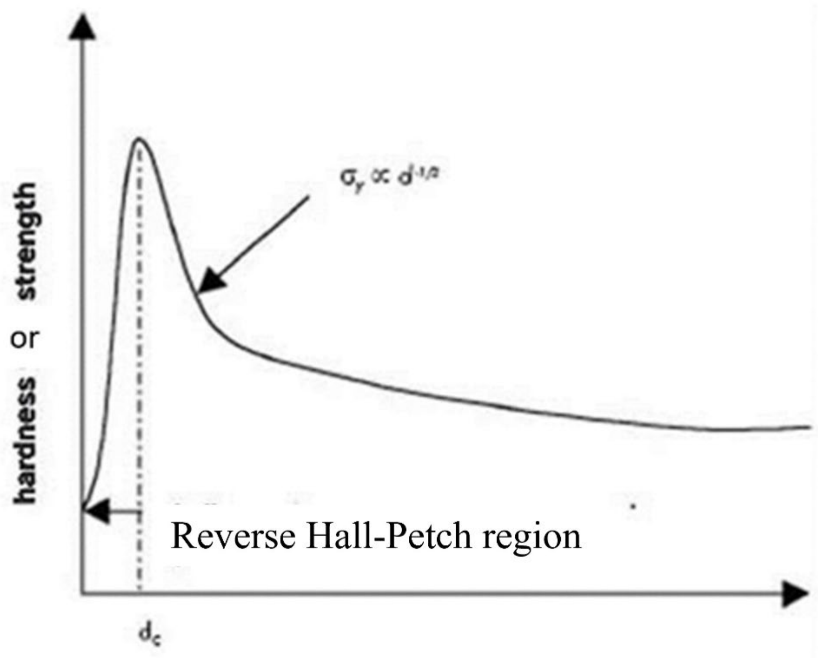

Figure 8: The graph illustrates the changes in material strength or hardness with variations in grain size.

Generally, according to the Hall-Petch relationship, the strength and hardness of materials increase as grain size decreases. However, when the grain size becomes smaller than a critical limit (dc ), the strength or hardness abruptly decreases. This region is referred to as the reverse Hall-Petch region.

Investigating the mechanical properties of nanostructured materials presents numerous challenges, such as:

The inability to prepare ideal samples,

The presence of porosity and microcracks,

High internal stresses,

Trapped impurities and gases,

The inability to evaluate certain quantities (e.g., strain measurements) due to the small sample size.

These challenges have limited the availability of experimental data regarding the mechanical properties of this class of materials.

### Nanostructures with Extraordinary Intrinsic Mechanical Properties

Some nanostructures possess extraordinary intrinsic mechanical properties due to the unique nature of their structure. A prime example is carbon nanotubes. These structures, formed by rolling up single layers of graphite (graphene), exhibit exceptional properties such as high strength and adequate flexibility (generally, as the strength of a material increases, its flexibility decreases). The strength of carbon nanotubes can be up to 100 times greater than that of steel. Remarkably, these structures can also be up to six times lighter than steel.

Materials with poor mechanical properties (such as most polymers) can be enhanced through composite formation with nanostructures. These nanostructures may include various nanoparticles, such as carbon nanotubes. Filling polymers with nanoparticles, nanorods, or nanotubes leads to significant improvements in their mechanical properties.

Nanomaterials also exhibit other intriguing mechanical properties. For example:

Superplasticity: A unique behavior of nanomaterials where they can undergo extremely large deformations without failure.

Creep and fatigue properties: Nanomaterials display different creep (deformation under sustained stress) and fatigue (resistance to repeated stress) behavior compared to conventional bulk materials.

Conclusion and Summary

Reducing the grain size in nanostructured materials increases the number of grains and the area of grain boundaries. Since grain boundaries act as barriers to dislocation movement, they increase the material's strength. Nanostructures with a high proportion of grain boundaries exhibit excellent mechanical properties such as high strength, hardness, and wear resistance, making them highly useful for various applications.

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## Optical Properties of Nanomaterials

Abstract: The behavior of nanoparticles when exposed to light waves is different from that of bulk materials. This difference is another key distinction between bulk materials and nanoparticles. In nanoparticles, changing their size alters the spacing between energy levels, which affects their light absorption. As a result, nanoparticles of the same material can appear in different colors depending on their size. In this article, we will study topics such as the interaction of light with matter and the optical properties of nanoparticles and quantum dots.

Keywords: Nanoparticles, Optical Properties, Energy Levels

## Introduction

Some nanomaterials show different optical properties, such as color or transparency, compared to bulk materials. From an industrial perspective, the optical properties of nanoparticles and nanocomposites are very important. To better understand the optical properties of nanomaterials, we will first review some key principles about light and then explore the optical properties of nanoscale materials.

## Interaction of Light with Matter

The color of a material is due to the interaction between light and the object. We see objects in a room when the light is turned on because the light spreads throughout the room, reflects off objects, and reaches our eyes. When light with a specific wavelength hits an object, some of it is absorbed while some is reflected. The reflected light determines the color we see. For example, leaves appear green because they contain chlorophyll, which absorbs red and blue light and reflects green light.

In general, light that strikes a material can pass through (T), be absorbed (A), or be reflected (R). The following equation always holds:

$T + A + R = 1$

where T is the transmitted light, R is the reflected light, and A is the absorbed light, all expressed as percentages.

Reflection (R) occurs when light hits a smooth surface and bounces back without scattering. Examples include polished metal surfaces like nickel or silver and mirrors with a silver-coated back.

Absorption (A) is a process that involves energy transfer. The energy levels of materials, which are formed by the accumulation of atomic energy levels, absorb specific wavelengths of light waves. This process is a molecular phenomenon that depends on the chemical nature and structure of materials (not on molecular size or clusters) and involves the transfer, vibration, and rotation of electrons. Fluorescent materials are examples of substances that absorb light at specific wavelengths. In chemistry, we learned about the cathode ray tube, which works by applying a strong voltage between two electrodes, causing rays to flow from the negative electrode to the positive electrode. When these rays hit a fluorescent material, they produce a green light. In reality, fluorescence is one of the physical properties of certain chemical substances (such as zinc sulfide). These materials absorb light of a specific wavelength and then emit light with a longer wavelength.

Transmission (T) refers to light passing through a material. This process is the opposite of absorption. Depending on the material's structure, different wavelengths of light are transmitted while others are absorbed.

Scattering (S) occurs when a beam of light hits a structure that is similar in size to its wavelength. This is a physical process that depends on the size of the cluster, the refractive index of the cluster, and the refractive index of the suspension medium. As mentioned earlier, scattering is a physical interaction, meaning that, unlike absorption, no energy transfer occurs during scattering. Instead, the energy is redirected in specific directions. The wavelength of the incoming light and the scattered light remains the same. When light hits clusters in a colloidal environment, it changes direction. After the initial change in direction, the light can hit other clusters and change direction again. This process is called multiple scattering. The scattered beam can either return along the path it came from (backscattering) or continue moving forward (forward scattering). The maximum scattering occurs at wavelengths that are twice the size of the cluster. So, if a cluster is about 200 nanometers, the maximum scattering happens at 400 nanometers (which is in the visible light range). In equations, scattering is divided into reflection (backscattering) and transmission (forward scattering). Light that is absorbed cannot be scattered.

## Optical Properties of Nanoparticles and Quantum Dots

As you may know, when the size of particles decreases to the nanoscale, their energy levels change from continuous to discrete. If the energy of an incoming photon (electromagnetic waves) is equal to the energy gap between atomic energy levels, the electrons in those levels absorb the light energy and move to higher energy levels. On the left side of Figure 1, the excitation of electrons in an atom is shown.

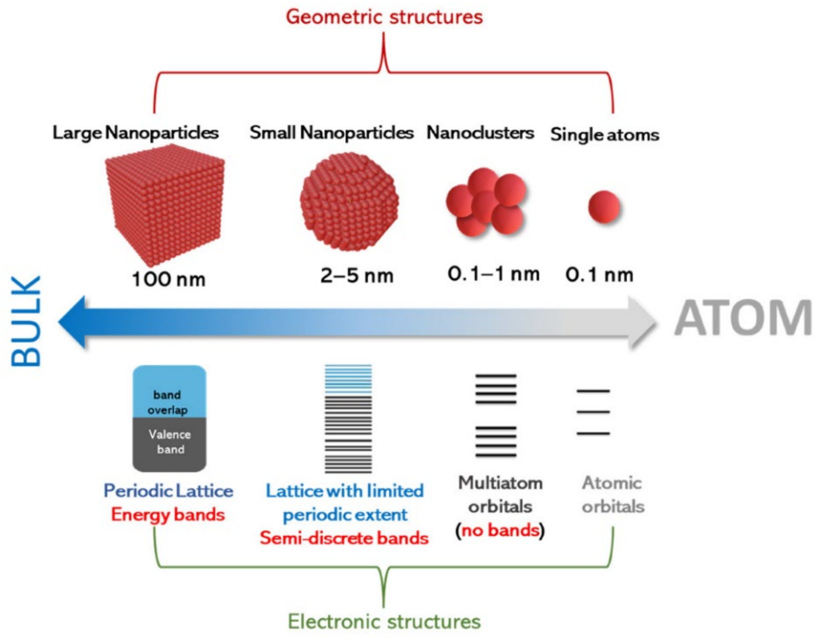

Figure 1: Excitation of electrons in atoms, bulk materials, and nanoparticles

As shown in the left side of Figure 1, light absorption also occurs in bulk materials with continuous energy bands. In these materials, electrons move from the valence band to the conduction band. (In this case, thermal energy can also excite electrons to the conduction band.) The middle part of of the figure 1, illustrates the mechanism of light absorption by nanoparticles. As seen in the image, nanoparticles, like atoms, have discrete energy levels. Therefore, nanoparticles are sometimes called "artificial atoms."

Furthermore, semiconductor nanoparticles smaller than 10 nanometers are referred to as **quantum dots**. Changing the size of semiconductor nanoparticles alters their energy level spacing. The smaller the nanoparticle, the greater the energy gap, and the larger the nanoparticle, the smaller the energy gap. This property allows scientists to adjust the size of nanoparticles to absorb specific wavelengths of light. For example, nanoparticles of a particular material can be sized to absorb infrared, ultraviolet, or radio waves. This characteristic is widely used in military and electronics industries. The different colors of CdSe nanoparticles in Figure 2 reflect variations in their energy levels.

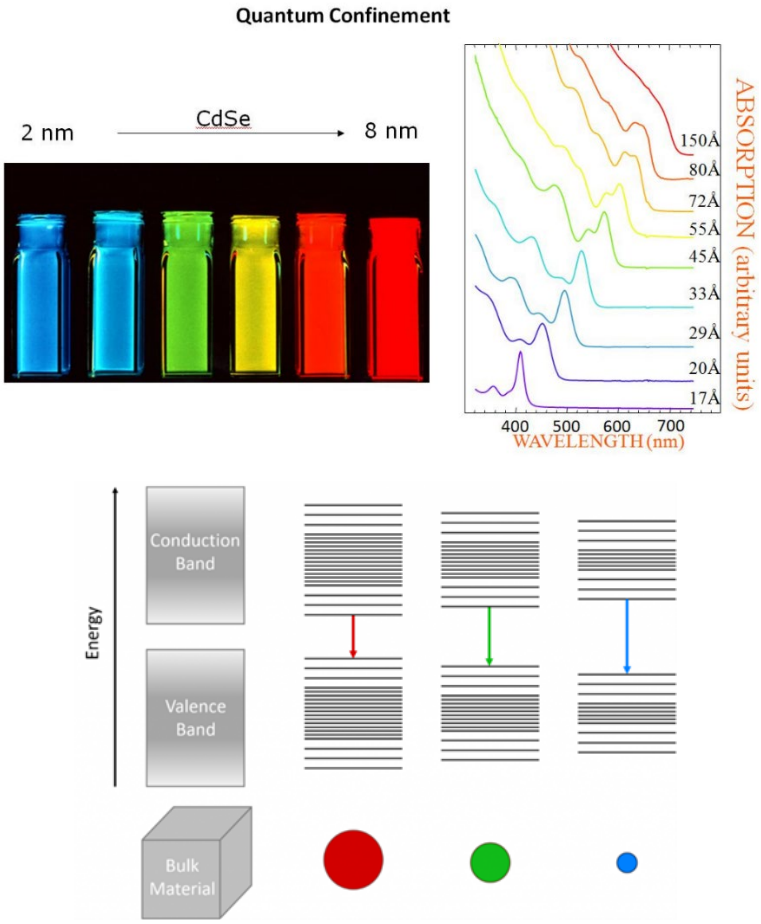

**Figure 2**: Top: Colors and absorption spectra of CdSe nanoparticles of different sizes. Bottom: The relationship between the electronic structure of quantum dots and their color at different sizes."

You have probably seen broken glass shards many times. No matter how small the glass pieces are, they remain transparent and colorless, just like the original glass. However, at the nanoscale, this rule does not apply. Some materials have nanoparticles whose color changes depending on their size. Gold and silver are the most well-known examples. Figure 3a shows how the color of gold nanoparticles changes with their size. This phenomenon is unusual in our macroscopic world, but an even more surprising effect is that silver nanoparticles can change color based on their shape. Figure 3b displays the colors of gold and silver nanoparticles with different geometric shapes. The reason behind this color change in metallic nanoparticles is a phenomenon called **localized surface plasmon resonance (LSPR),** which will be discussed in the next section.

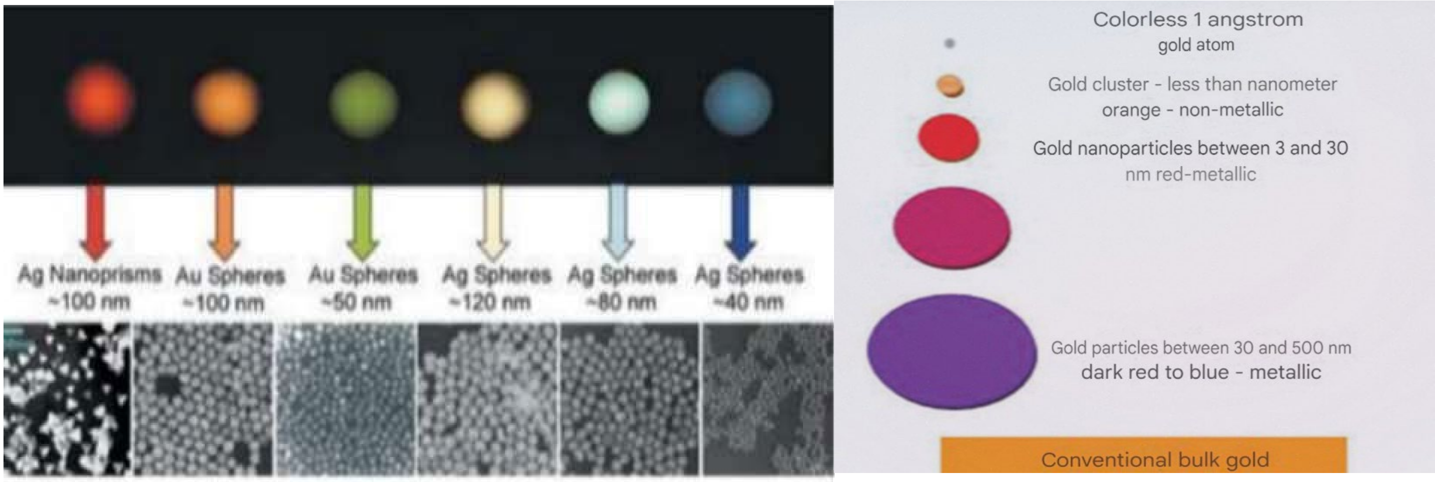

Figure 3: (a) Colors of gold nanoparticles at different sizes, (b) Colors of gold and silver nanoparticles with different shapes and sizes

One of the useful properties of some nanomaterials is their transparency. The scattering of visible light is what causes sunscreen creams to appear white. These sunscreens contain zinc oxide and titanium dioxide clusters about **200 nanometers** in size. Visible light interacts with these clusters, causing all wavelengths to scatter. Since the visible spectrum consists of multiple wavelengths, the combined effect results in a white appearance. However, if the cluster size is reduced, for example, from 200 nanometers to **100 nanometers**, the maximum scattering shifts to **200 nanometers**, which is outside the visible range. This shift makes the material appear transparent rather than white. (See Figure 4.)

Figure 4: Color changes of titanium dioxide particles based on size (right: bulk particles, left: nanoparticles)

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## Color in Metallic Colloids (Surface Plasmon Resonance)

One of the key differences between metallic nanoparticles and bulk materials is their optical properties. This difference arises due to localized surface plasmon resonance (LSPR). In simpler terms, when light strikes metal surfaces (of any size), some light waves are scattered along metal surfaces by generating surface plasmons (in fact, these waves transfer part of their energy to the surface electrons, causing them to oscillate)

In bulk metals, these oscillations are free to move through the material without leaving a noticeable effect. However, in nanoparticles, surface plasmons are confined to a limited space. As a result, the electrons oscillate back and forth within a small region. This effect is called localized surface plasmon resonance (LSPR). When the frequency of these oscillations matches the frequency of the incoming light, the plasmon is said to be in resonance with the incident light.

The energy of LSPR is sensitive to the dielectric properties of the material and its surroundings, as well as the shape and size of the nanoparticles. If a ligand, such as a protein, binds to the surface of metal nanoparticles, it alters the LSPR energy. Similarly, LSPR effects are sensitive to changes in the distance between nanoparticles, which can be influenced by the presence of surfactants or ions.

One important result of LSPR in metallic nanoparticles is their strong absorption of visible light due to coherent plasmon oscillations. Studies show that metallic nanoparticle colloids, such as silver or gold, can display colors such as red, purple, or orange, which are not seen in their bulk form. The observed color changes depend on the shape, size, and surrounding environment of the silver nanoparticles.

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## Summary and Conclusion

The color of a material results from the interaction between light and the material. Although color is an inherent property of a material, at the nanoscale, the color of nanoparticles depends on their shape and size. In metallic nanoparticles, reducing the particle size changes the range of electron oscillations at the surface, thereby altering the color of the nanoparticle. Similarly, in other nanoparticles, changing particle size modifies the spacing between energy levels, which affects light absorption and consequently changes the color.

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**Reference**

**Nanoscience and Nanotechnology Book 1**

## Production and Synthesis of Nanomaterials

- **Main Approaches in Nanomaterials Fabrication**
- **Nucleation and Growth**
- **Chemical Reduction: A controllable method for synthesizing nanoparticles**
- **Principles and Fundamentals of Nanoparticle Synthesis by Chemical Precipitation Method (1)**
- **Principles and Fundamentals of Nanoparticle Synthesis by Chemical Precipitation Method (2)**
- **Preparation of Nanomaterials by Sol-Gel Method**
- **Synthesis of Nanomaterials by Hydrothermal Method**
- **Mechanical Milling**

## Main Approaches in Nanomaterials Fabrication:

Abstract: Nanomaterials can be made using two main approaches: top-down and bottom-up. In the top-down approach, larger bulk materials are broken down into smaller parts through processes like cutting, grinding, or etching, often requiring significant energy. This method is scalable for industrial production but can be less controlled, leading to a wider range of nanoparticle sizes. Advanced techniques such as lithography and etching fall under this category.

In contrast, the bottom-up approach involves assembling nanomaterials from smaller units like atoms or molecules. This method often relies on self-assembly and can produce high-quality, uniform nanoparticles, but it may have lower yield and is typically used for specific applications. Techniques like Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), and Sol-Gel are common bottom-up methods. Both approaches can sometimes be combined to produce complex nanomaterials, offering flexibility and control depending on the desired product.

Keywords: Nanomaterials, top-down approach, bottom-up approach, nanoparticle synthesis, bulk materials, self-assembly, chemical vapor deposition (CVD), physical vapor deposition (PVD), sol-gel method, lithography

Introduction:

Imagine you want to build a cube with a side length of 10 cm using LEGO bricks. If the bricks available to you are like the ones shown in Figure 1, how would you achieve your desired cube? Clearly, you would build the cube brick by brick, constructing your desired shape from smaller pieces.

Figure 1 - Disorganized LEGO bricks

But what if the bricks you have are like the ones shown in Figure 2 and are already arranged into a larger cube? How would you reach a smaller cube?

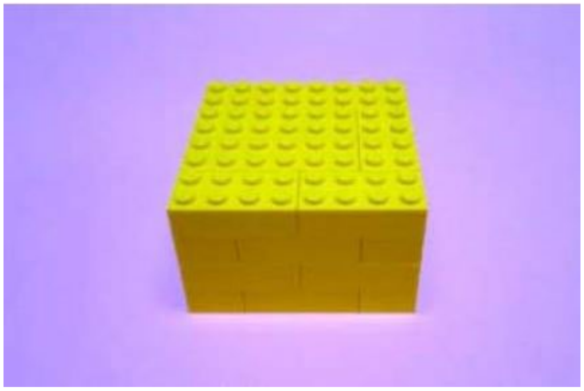

Figure 2 - A larger cube

You might think that you could remove the bricks one by one from the larger cube to get to the smaller cube, as though it were embedded inside the larger one (Figure 3).

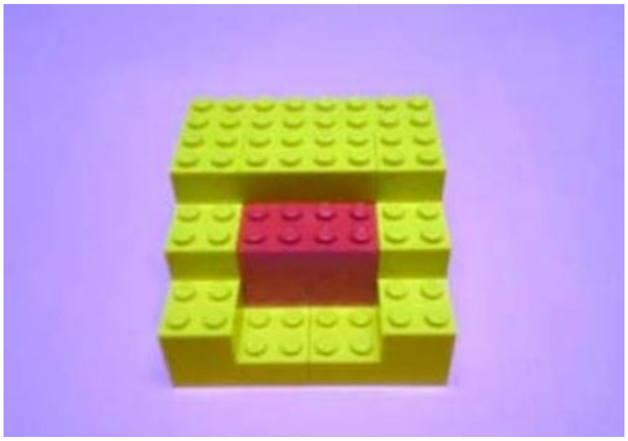

Figure 3 - A smaller cube gradually emerges from the larger cube.

The first method, where we built from a smaller to a larger shape, is called a "bottom-up" approach. The second method, where we removed extra pieces from a larger structure to reach the desired one, is called a "top-down" approach.

---

## 1. Top-down Methods

Top-down methods involve using larger bulk materials and reducing them through processes like breaking, cutting, or separating parts. During these processes, a significant amount of mechanical, thermal, or chemical energy is required to reduce the material into nanoparticles. These methods can often be used for large-scale production of nanoparticles, but they are typically less controlled compared to bottom-up approaches. This can lead to a wider range of nanoparticle sizes in comparison to bottom-up methods. However, top-down methods are often highly scalable and can be used for industrial production.

There are many diverse methods within the top-down category, some of which are more advanced than others. Various lithography techniques, etching, and advanced methods can not only be used to remove excess parts (sometimes with the help of masks) but also for patterning nanoparticles (and other nanomaterials).

For older technologies that rely mainly on physical mechanisms, there are various methods in which materials are broken down using mechanical energy, sunlight, corrosive chemicals, or high heat. Methods like grinding, cutting, and ball milling are common physical techniques to break down bulk materials and create nanoparticles. Another method is exfoliation, which is used for materials that have separate, removable layers (like graphite). Thermal energy, acidic chemicals, solar radiation, or mechanical energy can be used to separate layers from bulk structures.

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## 2. Bottom-up Methods

Bottom-up methods are those that build the atomic structure from the ground up, atom by atom, through the aggregation of atoms under specific conditions. These methods often involve self-assembly, where growth occurs in a repetitive manner, leading to the formation of crystalline networks. Many of these methods follow a nucleation-growth mechanism, starting with the formation of a small nucleus that then grows to form the rest of the structure. The formation of crystals is an example of self-assembly.

Although there are commercially viable bottom-up methods for producing nanoparticles, their yield is often much lower than top-down methods and they are typically used for specific, limited applications or to solve a particular problem. Even though large-scale production of nanomaterials may not be achievable through these methods, they offer better control over the process, often leading to uniform (monodisperse) and high-quality products. Common bottom-up methods include Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), and Atomic Layer Deposition (ALD). Additionally, there are various chemical methods, such as the Sol-Gel process, that can be used to create nanomaterials.

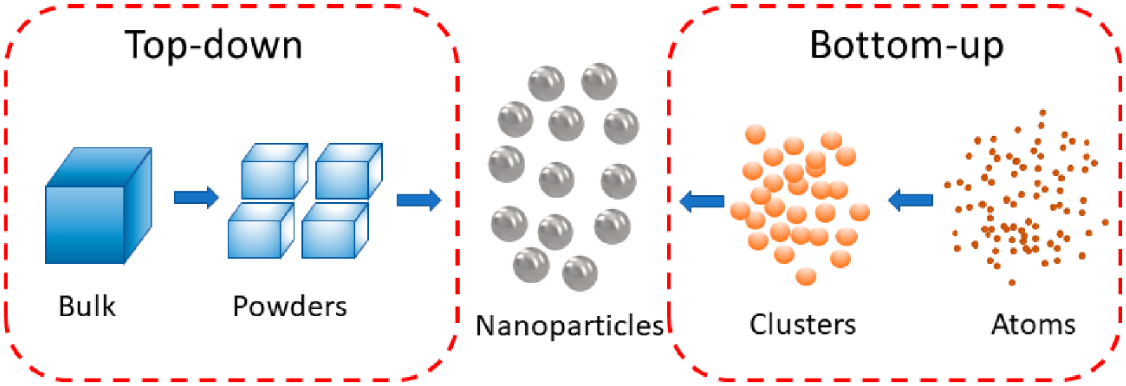

Figure 4- Diagram of Top-Down and Bottom-Up Approaches to Nanomaterials Production

Now, imagine you want to create a structure similar to the one shown in Figure 5, which is a bit more complex than the cube we initially created. What can you do this time?

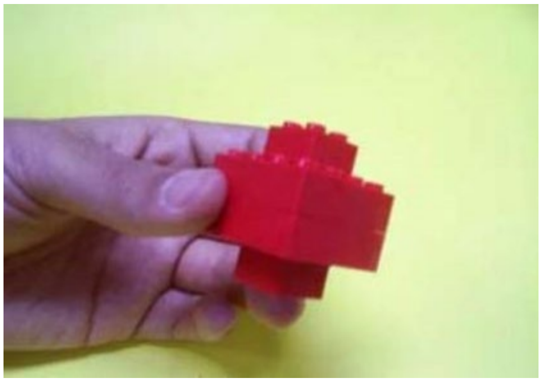

Figure 5 - A more complex structure

You could use the LEGO bricks like the ones in Figure 1 and construct the entire structure using a bottom-up approach. Alternatively, you could use a pre-made larger cube, available to you, and create the structure using a top-down approach. However, this may become more challenging, and you may not even be able to achieve the desired structure. So, what is the solution? Perhaps you could initially use the larger cube to create part of the structure and then use the bottom-up approach to add two more pieces on either side to complete the desired structure.

In nanotechnology, this is how it works too—both bottom-up and top-down approaches are used to produce nanoparticles, and sometimes both approaches are combined to create a single product.

## Nucleation and Growth

### Abstract

One of the key concepts in understanding and studying bottom-up methods for nanomaterial fabrication is the concept of nucleation and growth. Nucleation and growth can occur in two forms: homogeneous and heterogeneous. In homogeneous methods, there is no external surface, while in heterogeneous methods, external surfaces such as nucleuss are used. Nucleation and growth via the heterogeneous method are simpler and faster, which is why this method is commonly employed for synthesizing nanomaterials in some bottom-up approaches. This paper explains the concepts of supersaturation, nucleation, and growth, and compares and analyzes homogeneous and heterogeneous nucleation and growth from the perspective of free energy.

Keywords: Supersaturation, Nucleation, Growth, Homogeneous Growth, Heterogeneous Growth

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### Introduction

One of the key principles in bottom-up methods for the synthesis and production of nanomaterials is the understanding of nucleation and growth. For example, in chemical reduction (and some other methods) to create nanoparticles, three stages occur: supersaturation, nucleation, and growth, all of which influence the size, shape, and distribution of the final nanoparticles. These three stages are explained and reviewed in the following sections.

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### Supersaturation

The first step in the process is supersaturation. To better understand supersaturation, imagine a glass of hot water to which you are adding sugar. As you know, only a certain amount of sugar can dissolve in the water, and if too much sugar is added, it will precipitate out. In this scenario, supersaturation occurs. You also know that increasing the temperature of the water allows more sugar to dissolve. In nanomaterial synthesis, the same principle applies. By dissolving a certain amount of precursor in a solvent, supersaturation can be created. To achieve this, the solvent's temperature can be increased so that more precursor dissolves into it.

After supersaturation, the next step is nucleation. To begin nucleation, the solution must exit the supersaturated state. This can be achieved in several ways, one of them is increasing the precursor concentration beyond the supersaturation concentration, and the other is lowering the temperature after reaching supersaturation. This is because solubility decreases at lower temperatures, and by reducing the temperature, the solution exits the supersaturated state. Another method is to induce a chemical reaction within the solution, which produces a product or products that are less soluble, thus leading the solution out of the supersaturated state, initiating nucleation [1].

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Exercise

For a better understanding of supersaturation, consider the process of making rock candy. Search for more information online about how this process works.

---

Nucleation

The next step is nucleation. As mentioned earlier, after reaching supersaturation, the solution exits this state due to a decrease in temperature, an increase in precursor concentration, or the formation of a new compound with lower solubility. Once this happens, the solution no longer wants to keep the precursor in its dissolved state and prefers to convert it into a solid. As a result of this tendency, primary nuclei gradually form in the solution. These primary nuclei are called " nuclei " or " nucleus." Depending on the solution conditions and their size, these nuclei can grow and become nanoparticles or may dissolve back into the solution. This process is shown in Figure 1 [2].

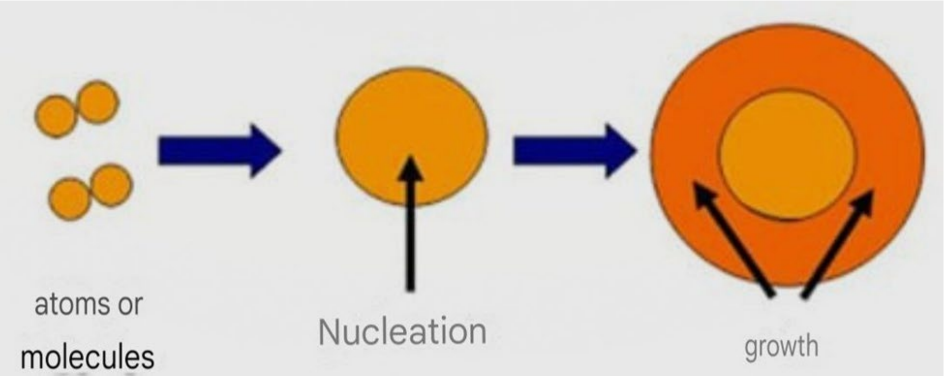

Figure 1: nucleation and growth

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Growth

The third stage after nucleation is growth. During this stage, if the formed nuclei remain stable, other atoms or molecules present in the solution join these nuclei, enlarging them and forming nanoparticles. If growth is uncontrolled and does not stop at the desired size, the nanoparticles may grow large enough to become microparticles. To control this growth, methods of stabilizing nanomaterials are used. Next, nucleation and growth will be introduced in two forms: homogeneous and heterogeneous. Their principles will be analyzed based on energy changes.

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## Homogeneous Nucleation and Growth

Homogeneous nucleation and growth refer to the process of nucleation and growth occurring within a solution without the presence of any external surface. In contrast, when an external surface is present, nucleation and growth are considered heterogeneous. Heterogeneous nucleation and growth are faster and easier to achieve. To better understand this concept, consider the process of making rock candy. This process is an excellent example of heterogeneous growth, as after supersaturation is created, a wooden stick (or string) is placed into the solution, and the sugar crystals form around it. The stick serves as the external surface or "nucleus," and the formation of sugar crystals around this surface is faster and easier.(figure2)

Figure 2 - Production of rock candy through the heterogeneous method.

In homogeneous nanomaterial synthesis, no external surfaces are present in the solution. Therefore, nucleation and growth are evaluated based on free energy changes. To explain this, refer to Figure 3.

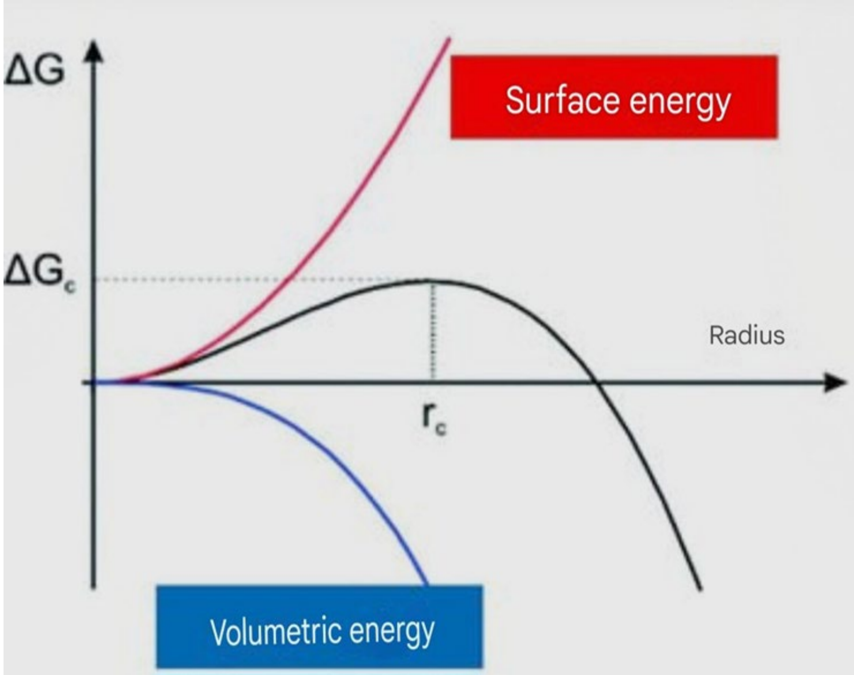

Figure 3: Changes in free energy based on the radius of the created nucleus [2].

In Figure 3, changes in surface energy are shown in red, changes in volume energy are shown in blue, and total changes in free energy (resulting from the combination of surface and volume energies) are shown in black. The natural tendency is to minimize free energy. Therefore, increasing the radius of the formed nucleus is undesirable in terms of surface energy but desirable in terms of volume energy. The undesirability of surface energy arises because forming a nucleus creates a surface between the liquid (solution) and the solid (nucleus), which the system does not prefer, increasing its free energy. On the other hand, as the nucleus radius increases, volume energy decreases.

Thus, as observed, the system does not prefer to increase the nucleus size, and even larger nuclei are considered undesirable. The total free energy (black curve) represents the sum of both surface and volume energies. It is observed that increasing the radius of the nucleus up to a critical radius (denoted as $r_c$) leads to an increase in free energy, and thus, the system does not prefer this. However, if the radius exceeds the critical radius, the system prefers further growth, and the nucleus will grow into a nanoparticle.

Now, let’s revisit nucleation and growth based on the black curve. After supersaturation and nucleation, nucleuss form in the solution. If the radius of these nucleuss is smaller than the critical radius, they will dissolve back into the solution. However, if their radius exceeds the critical radius, they will grow and eventually form a nanoparticle.

The next question arises: what happens that allows nuclei with a radius greater than the critical radius to form?

This occurs when, due to the random collision of several small nuclei or a large number of atoms/molecules, a nucleus with a critical radius or larger is formed. Otherwise, the formation of a nucleus with a radius smaller than the critical radius and its gradual growth is not possible. These random collisions result from the Brownian motion of particles and the relatively high concentration in the solution.

Another point to consider is the change in free energy at the critical radius. This amount of free energy is the energy the system requires to form a critical nucleus. The lower this energy, the easier and faster nucleation and subsequent growth will occur [1,2].

---

Heterogeneous Nucleation and Growth

As stated earlier, when there is an external surface present in the solution, nucleation and growth are considered heterogeneous. This external surface is usually a nucleus, which is added to the solution. It is worth noting that most nanomaterials are synthesized using this method.

In Figure 4, the formation of a nucleus on the external surface is shown. The radius of this nucleus is also illustrated in the figure. It is worth noting that in the homogeneous method, the formed nucleus takes the shape of a perfect sphere, as there is no external surface present.

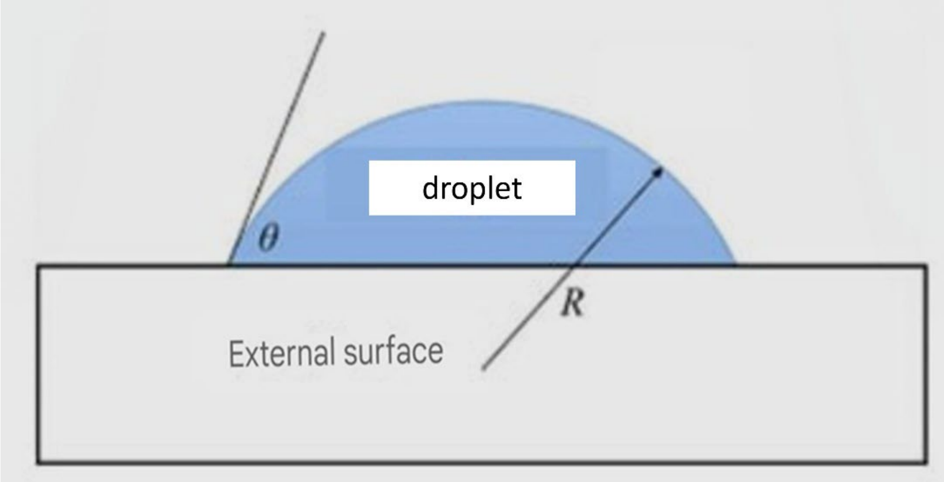

Figure 4: Formation of a nucleus on the external surface and its radius [2].

In Figure 5, a comparison is made between the free energy diagrams for homogeneous and heterogeneous nucleation and growth.

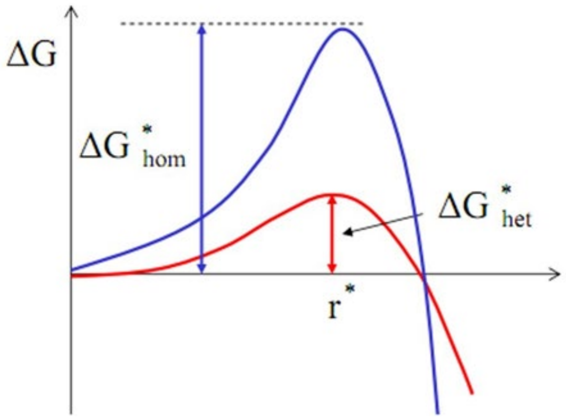

Figure 5: Comparison between free energy in homogeneous (blue) and heterogeneous (red) nucleation and growth [1].

From Figure 5, two important conclusions can be drawn. First, the free energy required to form a critical nucleus in the heterogeneous process is lower than in the homogeneous process (because the red curve is lower than the blue curve). This shows that nucleation and growth are much easier and faster in heterogeneous processes. Second, the critical radius for both homogeneous and heterogeneous processes is the same. However, in the heterogeneous case, fewer atoms are needed to reach the critical radius, as in the homogeneous process, a full sphere is needed, while in the heterogeneous case, a portion of the sphere suffices to reach the critical radius, which requires fewer atoms. Therefore, nucleation and growth are faster and simpler in the heterogeneous process.

---

Exercise

What can be done to produce nanoparticles with a uniform size?

Answer: If conditions are controlled such that nucleation occurs first and growth starts afterward, the size distribution of nanoparticles becomes narrower, and their size becomes uniform. It is worth noting that nucleation and growth usually occur simultaneously, which is why the size distribution of final nanoparticles can be broad. However, by separating the nucleation and growth steps, uniform-sized nanoparticles can be obtained.

---

Exercise

What effect does increasing the nucleation rate have on the final nanoparticle size?

Answer: It leads to smaller final nanoparticles. Increasing the nucleation rate means creating more nuclei in the solution, and more nuclei result in less growth for each particle, making the final nanoparticles smaller. The reason is that the amount of precursor in the solution is limited, and if the number of nuclei is small, all the precursor will join the limited number of nuclei, causing them to grow larger. However, if the number of nuclei is increased, the precursor is spread among the nuclei, and each one grows more slowly.

## Conclusion and Summary

The three key stages in nanomaterial synthesis via bottom-up methods are supersaturation, nucleation, and growth. Nucleation and growth can occur in both homogeneous and heterogeneous forms. In the heterogeneous method, unlike the homogeneous one, external surfaces such as nucleuss are present, making the process easier and faster. Although the critical radius is the same in both methods, fewer atoms are needed in the heterogeneous method to reach the critical radius. Furthermore, the free energy required to reach the critical radius is lower in the heterogeneous method, making nucleation and growth easier and faster.

## 8. References

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Abbaschian, Reza, and Robert E. Reed-Hill. Physical Metallurgy Principles. Cengage Learning, 2008.

# Chemical Reduction: A Controllable Method for Nanoparticle Synthesis

## Abstract

Chemical reduction is a bottom-up approach for synthesizing metallic nanoparticles, such as gold, silver, platinum, and palladium. This method allows for the synthesis of metallic nanoparticles with narrow size distributions and desired morphologies. The three main components of this method are the metal precursor, reducing agent, and stabilizing agent. The type of each component can be selected depending on the intended application and solvent type. Some key factors that affect the properties of nanoparticles synthesized by chemical reduction include temperature, process time, metal precursor type and concentration, the reducing power of the reducing agent, and the type of stabilizing polymer. In this paper, we provide a brief overview of the concepts of oxidation and reduction and introduce the fundamentals of the chemical reduction process. We then study the main components of the method and the influence of various parameters on the characteristics of the nanoparticles synthesized by chemical reduction in detail.

Keywords: Chemical reduction, oxidation, reduction, bottom-up synthesis, metallic nanoparticles.

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## 1. Introduction

Bottom-up synthesis methods are key approaches for producing nanomaterials, where the constituent atoms and molecules of the desired material come together to form the nanomaterial. By controlling the arrangement and assembly of atoms and molecules, the desired product can be obtained. Sol-gel methods, chemical vapor deposition, and chemical reduction are the most commonly used bottom-up techniques for synthesizing nanomaterials. Chemical reduction is one such bottom-up method for synthesizing metallic nanoparticles like gold. The three main components of this method are the metal precursor, reducing agent, and stabilizing agent. Modifying each of these components and controlling the synthesis conditions allows for the variation of the size distribution and morphology of the synthesized metallic nanoparticles. This paper discusses the basics of the chemical reduction method and the role of each component in a simple manner.

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## 2. Oxidation and Reduction Concepts

Before delving into the fundamentals of the chemical reduction method, it is important to understand the basic concepts of oxidation and reduction. Oxidation-reduction reactions (redox) refer to chemical reactions in which the oxidation state of an atom changes. Simply put, oxidation is the process of losing electrons, and reduction is the process of gaining electrons. During oxidation, an atom or ion loses electrons and, as a result, becomes a cation or a more positively charged ion. On the other hand, during reduction, an atom or ion gains electrons and becomes an anion or a neutral atom. Therefore, the atom loses electrons during oxidation, and the cation gains electrons during reduction.

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## 3. Chemical Reduction Method

After understanding the basic concepts of oxidation and reduction, we will now explain the fundamentals of the chemical reduction method. As the name suggests, this method involves reduction (electron gain). In the chemical reduction method, a metal precursor is first dissolved in an appropriate solvent. As the metal precursor dissolves, metal cations are dispersed in the solvent. A reducing agent is then added to the solution to provide electrons for the reduction of the metal cations. The reason for adding the reducing agent is that metal cations need to be converted into metal atoms to form nanoparticles. This is because electrostatic repulsion prevents the metal cations from attaching to one another. To synthesize nanoparticles, the atoms produced by the reduction of cations first come together and form a nucleus. These nuclei then grow and form nanoparticles. If the growth of the nuclei is not controlled, the nanoparticles may grow larger than 100 nm, and according to the definition of nanoparticles, they will no longer be considered nanoparticles. To prevent excessive growth of nanoparticles, stabilizing agents are used. Stabilizing agents are usually polymers that surround the nanoparticles and prevent their further growth. A schematic of the chemical reduction process is shown in Figure 1.

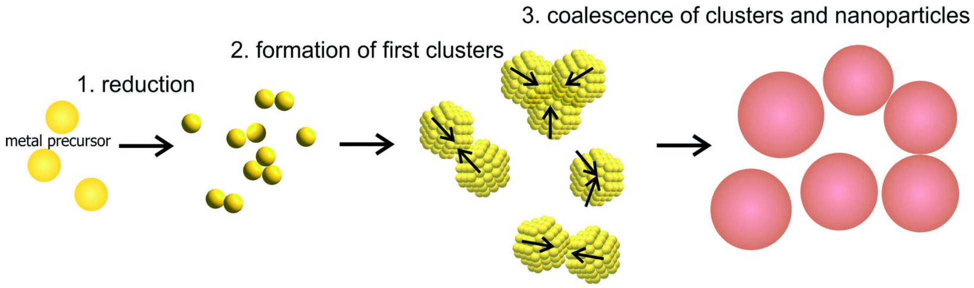

Figure1: A schematic of the chemical reduction process

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## 4. Main Components of Chemical Reduction Method

### 4.1. Metal Precursor

Metal precursors used in the chemical reduction method can be metallic anodes or metal salts. In cases where metallic anodes are used to supply metal cations, an electrical potential must be applied to the anode to release the cations. However, the use of metallic anodes is not very common. Typically, metal salts are dissolved in an appropriate solvent to supply the metal cations. Water is a commonly used solvent for this process. For example, by dissolving silver nitrate (a suitable salt for supplying silver cations) in water, an appropriate precursor can be obtained for synthesizing silver nanoparticles. Table 1 lists some common metal precursors used in the chemical reduction method.

Table1: Common metal precursors used in the chemical reduction method

| Metal Precursor Name | Chemical Formula |
|---|---|
| **Metal Anodes (Cobalt, Nickel, Palladium)** | Pd, Ni, Co |
| **Palladium Chloride** | $PdCl_2$ |
| **Hexachloroplatinate Hydrogen** | $H_2PtCl_6$ |
| **Potassium Hexachloroplatinate** | $K_2PtCl_6$ |
| **Silver Nitrate** | $AgNO_3$ |
| **Silver Tetraoxychlorate** | $AgClO_4$ |
| **Gold Chloride** | $HAuCl_4$ |
| **Rhodium Chloride** | $RhCl_3$ |

### 4.2. Reducing Agent

Various reducing agents are used to reduce the metal cations in the liquid medium. The reducing power of each of these agents varies. The choice of reducing agent has a significant impact on the properties of the nanoparticles, such as their size, shape, particle size distribution, and production cost. Table 2 lists some common reducing agents used in the chemical reduction method.

Table2: Some common reducing agents used in the chemical reduction method

| Chemical Formula of the Agent | Name of the Agent |
|---|---|
| $H_2$ | Hydrogen |
| $Na_3C_5H_5O_7$ | Sodium Citrate |
| $NH_4OH + HCl$ | Ammonium Hydroxide + Hydrochloric Acid |
| $C_6H_8O_7$ | Citric Acid |
| $CO$ | Carbon Monoxide |
| $P$ | Phosphorus |
| $CH_3OH$ | Methanol |
| $H_2O_2$ | Hydrogen Peroxide |
| $Na_2CO_3$ | Sodium Carbonate |
| $NaOH$ | Sodium Hydroxide |
| $HCHO$ | Formaldehyde |
| $NaBH_4$ | Sodium Borohydride |
| $^{-}NH_4$ | Ammonium Ion |

Some reducing agents like sodium borohydride are highly reducing and can rapidly provide the electrons needed to reduce metal cations. On the other hand, some agents, such as plant-based reducing agents, have lower reducing power and require more time to provide the necessary electrons. The use of plant-based reducing agents like Rumex hymenosepalus in silver nanoparticle synthesis is an example of using plants as reducing agents in chemical reduction. It is worth noting that plant-based reducing agents are environmentally friendly and inexpensive, which is why there has been significant research in recent years on their use in synthesizing metal nanoparticles. (These methods are known as green synthesis methods.)

### 4.3. Stabilizing Agent

To stabilize the metallic nanoparticles, prevent their excessive growth, and avoid aggregation, stabilizing agents, which are typically polymeric, are used. Since the solvents used in this method are usually polar solvents like water, it is better to use polar polymers as stabilizing agents so that they can dissolve in the polar solvent and surround the nanoparticles. Overall, the choice of polymer depends on the polarity of the solvent and the intended application. Table 3 lists some common stabilizing agents used in the chemical reduction method.

Table3: Some common stabilizing agents used in the chemical reduction method

| Name of the Agent |
|---|
| Polyvinylpyrrolidone |
| Polyvinyl alcohol |
| Polyethyleneimine |
| Sodium polyphosphate |
| Sodium polyacrylate |
| Tetraalkylammonium halogenides |

## 5. Case Studies of Nanoparticle Synthesis via Chemical Reduction

### 5.1. Silver Nanoparticles

The chemical reduction method is widely used to synthesize silver nanoparticles. To synthesize silver nanoparticles via this method, a solution with a specific molarity of a silver-containing precursor (such as silver nitrate) is prepared in deionized water. Then, a solution with a specific molarity of the reducing agent (such as sodium borohydride) is prepared in deionized water. The reducing agent solution is added to the precursor solution, initiating nucleation and growth. After mixing the solutions, an appropriate stabilizer such as polyvinyl alcohol is added to control the growth of the metallic nanoparticles and prevent aggregation. The reduction of silver ions to silver atoms can take place over a wide range of temperatures, from -4°C to +90°C. The appropriate temperature for the reaction depends on experimental conditions such as the reducing agent's power. At higher temperatures, the reduction of metal cations and the processes of nucleation and growth occur more rapidly. Under these conditions, if a strong reducing agent is used, control over the final nanoparticle properties may be reduced.

Various parameters influence the size and shape of metal nanoparticles synthesized through the chemical reduction method. These parameters include:

#### 5-1-1. Type (Strength) of Reducing Agent

The higher the concentration or reducing strength of the agent used, the greater the number of neutral atoms formed, leading to an increased nucleation rate. High nucleation rates result in limited growth of the nuclei (due to the presence of numerous nuclei), leading to smaller nanoparticles. Thus, an effective strategy to reduce the size of metal nanoparticles synthesized via the chemical reduction method is to increase the reducing agent concentration or to use agents with higher reducing power.

### 5-1-2. Metal Precursor Concentration

Figure 2 illustrates the effect of metal precursor concentration on the number of nuclei formed at different times and the size distribution of metal nanoparticles synthesized through the chemical reduction method. A brief analysis of the graphs reveals that increasing the metal precursor concentration enhances nucleation within shorter times, resulting in smaller nanoparticles.

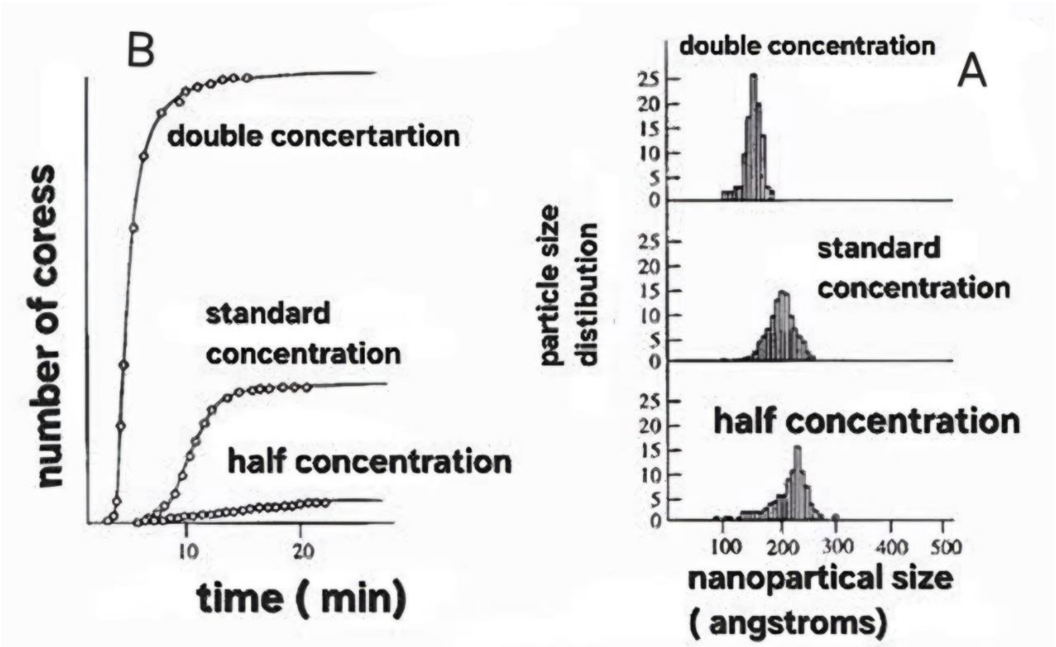

Figure 2: Effect of metal precursor concentration on (a) the number of nuclei formed at different times and (b) size distribution of metal nanoparticles synthesized via the chemical reduction method.

Another observation from the graphs is that increasing the metal precursor concentration narrows the size distribution of synthesized nanoparticles. A narrower size distribution means that the majority of nanoparticles are within a small size range, implying minimal size variation among them. As shown in Figure 2(b), decreasing the metal precursor concentration broadens the size distribution, resulting in nanoparticles within the size range of 80–300 nm.

### 5-1-3. Rate of Reducing Agent Addition

If the reducing agent is added suddenly to the aqueous solution containing the metal precursor, a large number of metal cations are reduced within a short time. This increase in metal atoms leads to a higher nucleation rate. As mentioned earlier, a higher nucleation rate limits nanoparticle growth, leading to smaller synthesized nanoparticles. However, the sudden addition of the reducing agent can result in the formation of non-uniformly shaped nanoparticles, as a large number of reduced metal atoms are formed simultaneously, leaving nuclei insufficient time to find suitable sites for uniform growth. It is important to note that the rate of reducing agent addition is only one of the parameters affecting the properties of synthesized nanoparticles, and changes in size and shape cannot be solely attributed to this factor.

### 5-1-4. Number of Reduction Steps

The reduction of metal cations into metal atoms may occur in one or multiple steps. For instance, the metal precursor may first react with a specific compound to form another intermediate, such as metal hydroxide. The metal hydroxide may then react with a secondary reducing agent, such as hydrogen, to form metal atoms. In general, the number of reduction steps influences the size and shape of the synthesized nanoparticles.

Other factors influencing the properties of nanoparticles synthesized through the chemical reduction method include impurities (such as chlorine), the type of stabilizing agent, and reaction temperature.

## 6. Applications of Chemical Reduction Method in Nanoparticle Synthesis

As mentioned earlier, the chemical reduction method is used to synthesize metallic nanoparticles. It is also possible to synthesize composite nanoparticles by adding reinforcing particles such as ceramic nanoparticles. Since the principles of the method for synthesizing both metallic and composite nanoparticles are the same, the synthesis of composite nanoparticles is not discussed in this paper. However, here are a few examples of nanoparticles synthesized via chemical reduction and their applications:

Synthesis of silver nanoparticles for biomedical applications due to their antibacterial properties.

Synthesis of copper nanoparticles for biomedical applications due to their antifungal properties

Synthesis of silver/zinc oxide composite nanoparticles for catalytic applications.

Synthesis of iron-platinum alloy nanoparticles for catalytic applications.

## 7. Conclusion

Chemical reduction is a bottom-up method for synthesizing metallic and sometimes alloy and composite nanoparticles. This method allows for the synthesis of metallic nanoparticles with narrow size distributions, desired morphologies, and shapes. The main components of the method are the metal precursor, reducing agent, and stabilizing agent. This method is based on the process of electron gain (reduction). The metal precursor is first dissolved in an appropriate solvent, and metal cations are dispersed in the solution. Then, a reducing agent is added to provide electrons for reducing the metal cations. To prevent excessive growth of the nanoparticles, stabilizing agents are used. The effects of various factors such as the reducing agent power, metal precursor concentration, and others on the properties of nanoparticles were discussed. Several applications of the nanoparticles produced by this method were also highlighted.

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# Principles and Fundamentals of Synthesizing Nanoparticles Using the Chemical Precipitation Method (1)

## Abstract

Chemical precipitation is a process where a solution (containing precursor materials) turns into a solid. To achieve this, the soluble material is either made insoluble or brought to a supersaturated state. The reactants in precipitation reactions are usually ionic compounds that dissolve in water. When these compounds dissolve, they separate into anions and cations. Precipitation happens when a cation from one compound combines with an anion from another compound to form an insoluble compound. Applications of this method include synthesizing metal oxide nanoparticles, semiconducting metal compounds, removing heavy metals and anions from wastewater, reducing water hardness, and recovering metals. This article introduces the chemical precipitation method and thoroughly explains the main mechanisms of nanoparticle precipitation, including substitution reactions, oxidation-reduction, thermolysis, hydrolysis, polymerization, and condensation.

Keywords

Nanoparticles, chemical precipitation, oxidation-reduction, hydrolysis, thermolysis, condensation.

---

## 1. Introduction

Depending on the application, the size of synthesized nanoparticles can either be very uniform (almost the same size) or vary significantly. In most cases, it is crucial to synthesize nanoparticles with sizes that are very similar, with size variations of less than 5%. This is important because nanoparticles with similar sizes will have consistent properties. Therefore, developing large-scale methods to synthesize nanoparticles with nearly the same size, also called "monodisperse nanoparticles," is of great importance. For example, in the powder metallurgy industry, particles with a wide size distribution are useful. Smaller particles fill the empty spaces between larger particles, increasing the density of the material.

Various chemical methods like chemical precipitation, sol-gel, microemulsion synthesis, and solvothermal/hydrothermal processes are used to synthesize nanoparticles. These methods are also known as wet synthesis methods or solution-phase synthesis methods. Chemical methods are considered part of the "bottom-up" approach to nanoparticle synthesis, as they allow precise control over the arrangement of atoms. The main advantage of chemical methods is their ability to produce a wide range of materials (metallic, ceramic, and composite) with uniform properties. They are also cost-effective.

Chemical precipitation is a process where a solution containing precursor materials turns into a solid. This is done by making the soluble material insoluble or bringing it to a supersaturated state. The reactants in precipitation reactions are typically ionic compounds that dissolve in water, separating into anions and cations. Precipitation occurs when a cation from one compound reacts with an anion from another compound to form an insoluble compound. In addition to synthesizing metal oxide nanoparticles and many semiconducting metal compounds, chemical precipitation is also used to remove heavy metals and anions from wastewater, reduce water hardness, and recover metals.

## 2. Prerequisites

Before diving into the basics of the chemical precipitation method and its mechanisms, it’s important to understand a few concepts, which are discussed below:

Composite: A composite is a non-uniform solid made of two or more different materials. Each component retains its own properties, and the boundary between components is distinct. The composite has properties that none of the individual components have on their own.

Ceramic: A ceramic is a non-metallic inorganic material. Oxides, nitrides, and carbides are examples of ceramics.

Supersaturated Solution: A solution is called supersaturated when more solute is added than the solvent can dissolve. In this condition, the excess solute precipitates out.

Amorphous Solid: An amorphous solid lacks the long-range order found in crystalline materials. Its structure is only ordered over short distances.

Scanning Electron Microscope (SEM): SEM is a powerful tool used to image surfaces and analyze their chemical composition. Unlike optical microscopes that use light, SEM uses focused, high-energy electrons to create images.

Slightly Soluble Materials: These are materials with solubility between 0.01 and 1 gram per 100 grams of water.

Lewis Acid: In acid-base theory, a Lewis acid is a molecule that can accept a lone pair of electrons from another molecule.

Viscosity: Viscosity is the resistance of a fluid (liquid or gas) to flow. Fluids with low viscosity flow more easily. For example, water has lower viscosity than honey.

Doping: Doping involves introducing impurities into a material to achieve a specific property that the material does not have on its own.

## 3. The Chemical Precipitation Method

The chemical precipitation method is one of the most important and widely used methods for synthesizing nanoparticles. As mentioned earlier, this method is based on converting a solution into either a supersaturated solution or an insoluble state. The chemical precipitation process involves two main stages: nucleation and growth. Synthesizing nanoparticles with specific sizes, size distributions, and properties requires precise control over both stages.

Most nanoparticles synthesized through chemical precipitation, especially at low temperatures, are amorphous (non-crystalline). To achieve a crystalline material with a desired structure, heat treatment of the synthesized nanoparticles is required. However, heat treatment can lead to particle aggregation and reduced quality of the nanoparticles.

For example, to synthesize ceramic nanoparticles using the chemical precipitation process, a solution containing a precipitating agent (such as hydroxide, ammonium acid carbonate, or oxalic acid) is added to another solution containing the cations of the desired material.

The chemical precipitation method includes direct precipitation, co-precipitation, and homogeneous precipitation:

Direct Precipitation: In this process, only one type of cation is present in the solution. For example, yttria nanoparticles ($Y_2O_3$) can be synthesized by adding a solution containing ammonium hydrogen carbonate to a solution of yttrium nitrate.

Co-precipitation: In this process, multiple cations are present in the solution. For instance, yttrium-aluminum garnet nanoparticles with an average size of 60 nanometers can be synthesized through co-precipitation. In this case, a combination of solutions containing $NH_4Al(SO_4)_2$ and $Y(NO_3)_3$ is mixed with a solution of ammonium hydroxide ($NH_4OH$), which acts as the precipitating agent.

Homogeneous Precipitation: In this process, urea is often used as the precipitating agent. Compared to direct precipitation and co-precipitation, nucleation and growth are more uniform in this method. For example, titanium dioxide ($TiO_2$) nanoparticles with sizes ranging from 15 to 40 nanometers and good crystallinity can be synthesized through homogeneous chemical precipitation at relatively low temperatures (83-100°C). In this method, ammonium fluorotitanate serves as the titanium source, while urea acts as the precipitating agent.

Figure 1 shows SEM images of titanium dioxide nanoparticles synthesized using the homogeneous chemical precipitation method at 80°C and 100°C.

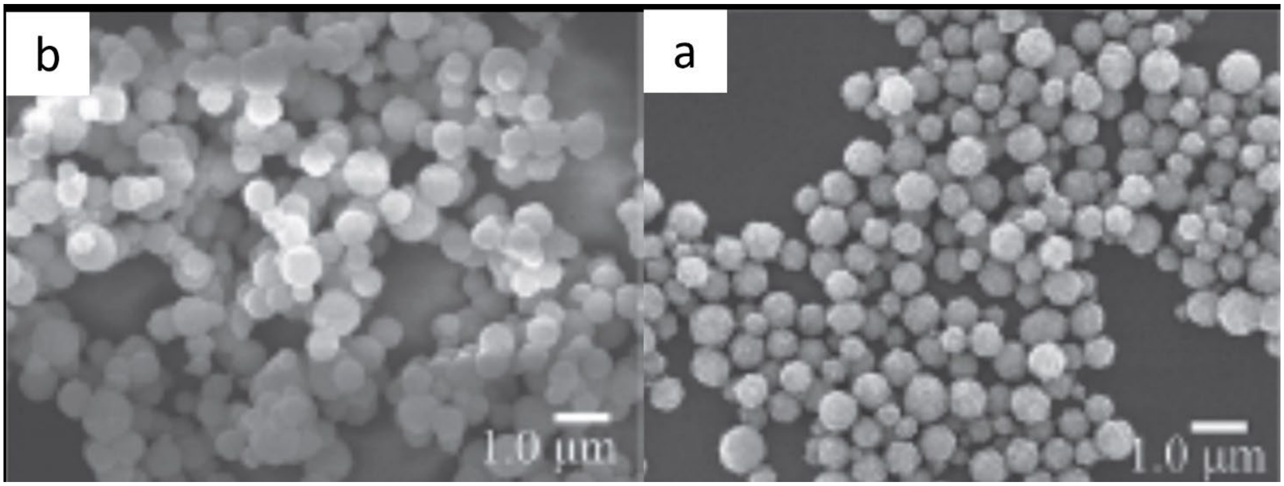


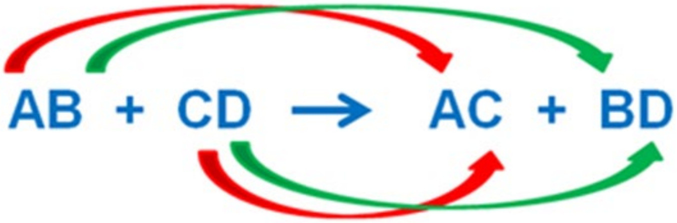
Figure 1. SEM images of titanium dioxide nanoparticles synthesized by homogeneous chemical precipitation at (a) 80°C and (b) 100°C [1].

Chemical Reactions in Nano Synthesis

Chemical reactions are the foundation of chemical methods for synthesizing nanoparticles. As mentioned earlier, many of these reactions ultimately lead to the precipitation of solid particles from a solution phase. These chemical reactions include precipitation reactions, oxidation-reduction (redox) reactions, and processes such as hydrolysis, thermolysis, polymerization, and condensation. The following sections introduce these reactions and processes.

### 4.1 Precipitation Reactions

When the concentration or amount of a solute exceeds the solubility limit of the solvent, the solute begins to precipitate. One way to synthesize nanoparticles using chemical precipitation is to supersaturate the solution. Typically, double replacement reactions can produce slightly soluble ionic solids, which lead to the formation of a precipitate. This reaction is also known as a double displacement reaction. A schematic of a double displacement reaction and an example of a reaction between silver nitrate and sodium chloride are shown below:



$$\boldsymbol{AgNO_3(aq) + NaCl\,(aq) \rightarrow AgCl(s) + NaNO_3(aq)}$$

Before discussing the reaction, it is important to note that in a chemical equation, (s) indicates a solid substance, while (aq) indicates a dissolved substance in solution. In the reaction between silver nitrate and sodium chloride, both substances are dissolved in the solution, resulting in the formation of solid silver chloride. Silver chloride is poorly soluble, so it immediately precipitates when formed. The other product, sodium nitrate, remains dissolved in water as separate $Na^+$ and $NO3^-$ ions. These ions do not participate in the reaction and are called spectator ions. By removing the spectator ions, the overall reaction can be written as:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl\,(s)$$

Unlike sodium and nitrate ions, silver and chloride ions can only coexist in solution at extremely low concentrations. The above reaction quickly leads to the formation of a precipitate. On the other hand, considering the reverse reaction, it can be stated that silver chloride is almost insoluble in water (having very low solubility), releasing only a tiny amount of silver and chloride ions into the solution. A simple precipitation reaction considering stoichiometric coefficients is represented as follows:

$$A_xB_y(s) \leftrightarrows XA\,(aq) + yB\,(aq)$$

The thermodynamic equilibrium between reactants and products in the above reaction, based on concentration (instead of activity), can be expressed using the solubility product constant:

$$K_{sp} = [A]^x[B]^y$$

The brackets indicate the concentration of species A and B. Ksp is the solubility product constant. The Ksp values for certain compounds, such as hydroxides, carbonates, oxalates, and chalcogenides, are small in aqueous solutions. As a result, these compounds have low solubility and tend to precipitate in aqueous solutions.

### 4.2 Oxidation-Reduction Reactions

In addition to double displacement reactions that form slightly soluble compounds, oxidation-reduction (redox) reactions can also produce insoluble compounds. Redox reactions involve chemical changes where the oxidation number of an element changes. Simply put, oxidation refers to the loss of electrons, while reduction (or reduction reaction) refers to the gain of electrons. To make a metal ion insoluble in an aqueous environment, reduction reactions are typically used. The half-reaction for metal reduction is shown below:

$$\mathrm{M^{n+}(aq) + ne^- \rightarrow M^0(s)}$$

In the above reaction, M represents a metal. The oxidation of a reducing agent releases electrons. These electrons ($ne^-$) originate from the oxidation of another substance, which is not mentioned here. In any redox process, oxidation and reduction occur together. The substance that undergoes oxidation releases electrons and is called the reducing agent. On the other hand, the substance that undergoes reduction is called the oxidizing agent. In the reaction above, the metal ion ($M^{n+}$) gains electrons to become a neutral metal (M), making it the oxidizing agent. The standard electrode potential (E0) of a substance determines whether it acts as an electron donor or acceptor in a redox reaction. This value is an indicator of a chemical species' tendency to gain or lose electrons.

### 4.3 Hydrolysis Process

In hydrolysis, the addition of a water molecule to a chemical structure breaks a specific bond within the original molecule. Simply put, hydrolysis is a reaction in which chemical bonds break due to water addition. In many cases, the water molecule itself breaks apart, with its fragments attaching to different parts of the initial molecule. During hydrolysis, a water molecule dissociates into hydroxyl ($OH^-$) and hydronium ($H_3O^+$) ions. Instead of hydronium, hydrogen ions are sometimes written in reaction products. The hydrolysis of a water molecule is represented as follows:

$$\mathrm{H_2O + H_2O \rightleftarrows H_3O^+ + OH^-}$$

The ions generated by the hydrolysis of water can participate in other reactions. Figure 2 illustrates the hydrolysis of a fullerene (C60) molecule.

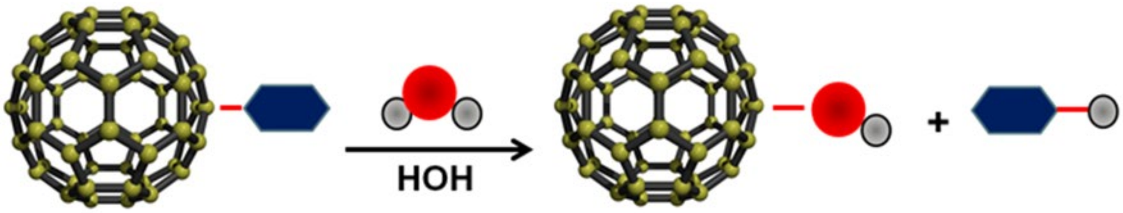


Figure 2 - A schematic representation of the hydrolysis of a fullerene (C60) molecule.

The hydrolysis process is also used in the sol-gel method for nanoparticle synthesis. Additionally, hydrolysis can lead to the decomposition of metal cations. Figure 3 provides a schematic of the hydrolysis of metal cations. In aqueous solutions, metal ions behave similarly to Lewis acids. The positive charge on the metal ion withdraws electrons from the O-H bond in water, increasing its polarity and making it easier to break. When the O-H bond breaks, a hydronium ion is released, acidifying the solution.

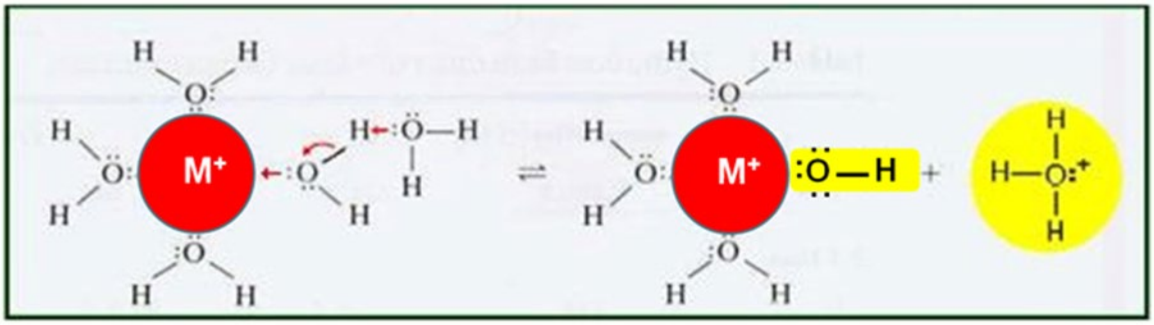


Figure 3 - A schematic representation of the hydrolysis process of metal cations.**

The hydrolysis reaction of a hydrated metal ion (M) is as follows:

$$[M(H_2O)_n]^{z+} + H_2O \leftrightarrows [M(H_2O)_{n-1}(OH)]^{(z-1)} + H_3O^+$$

For nanoparticle synthesis, metal ions usually convert into metal hydroxides depending on the pH of the environment. In many cases, metal hydroxides serve as precursors for metal oxides. The conversion of hydroxides to metal oxides typically occurs through thermal decomposition. However, hydrolysis can directly synthesize metal oxide nanoparticles from their hydroxides. For example, titanium chloride ($TiCl_3$) can be converted to titanium oxide ($TiO_2$) through hydrolysis in the presence of $NH_4OH$.

### 4.4 Thermolysis Process

Thermolysis, or thermal decomposition, refers to the irreversible chemical breakdown of a substance at high temperatures. Simply put, thermolysis is a type of chemical decomposition caused by heat. This process is used for nanoparticle synthesis when the remaining product forms a solid precipitate. Thermal decomposition of metal-organic carbonyl complexes is an example of applying this process in nanoparticle synthesis. Figure 4 shows an SEM image of zinc sulfide (ZnS) nanoparticles synthesized by thermolysis of the precursor Zinc (II) bis (N,N-diallyl dithiocarbamate) in hexadecylamine.

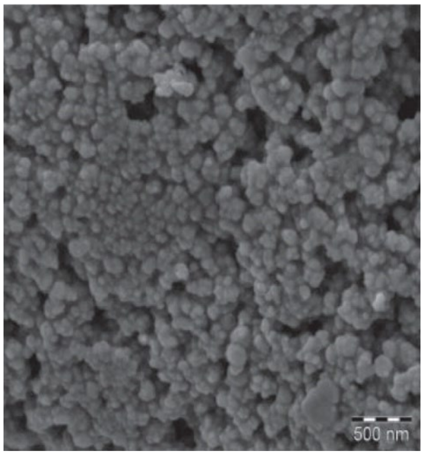


Figure 4 - SEM image of zinc sulfide (ZnS) nanoparticles synthesized by the thermolysis of the precursor Zinc (II) bis (N,N-diallyl dithiocarbamate) in hexadecylamine [2].

4-5. Polymerization Process

In the polymerization process, small molecules (monomers) chemically bond together to form a large molecule (polymer). Polymerization processes are divided into two main types: addition polymerization and condensation polymerization. In addition polymerization, monomers simply join together without producing any byproducts. In condensation polymerization, monomers bond while releasing small molecules such as water or alcohol. Figure 5 illustrates different types of polymerization processes.

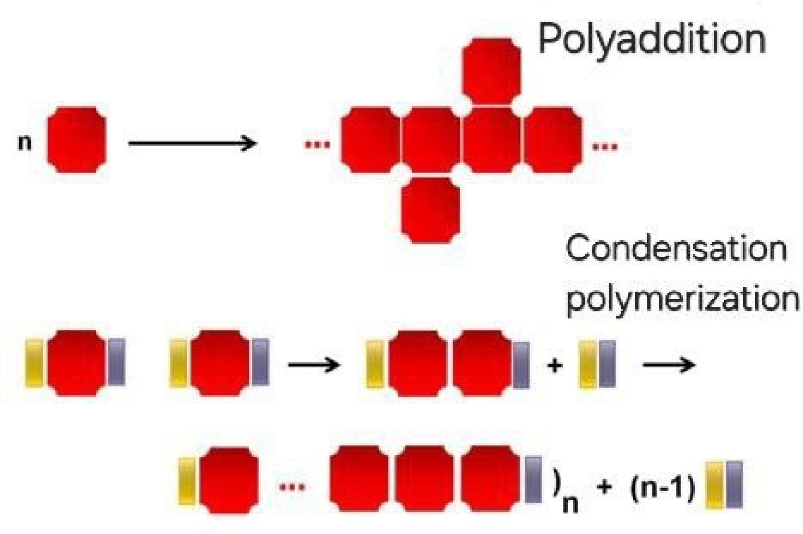


Figure 5 - Schematic representation of different polymerization processes.

Polymeric nanoparticles synthesized by this method have various applications, especially in biomedical fields. Recently, they have gained significant attention due to their non-toxic nature in the body and their effectiveness in drug delivery processes.

### 4-6. Condensation Process

In the condensation process, monomer molecules bond together, forming a polymer while also generating a byproduct. If the released molecule is water, this process is the reverse of the hydrolysis reaction. In hydrolysis, chemical bonds break upon absorbing water. Conversely, in the condensation process, bond formation leads to the release of a water molecule. This process is a key step in the sol-gel method. Typically, condensation occurs simultaneously with or after hydrolysis, leading to the formation of macromolecular structures as the final product. As a result, the viscosity of the initial solution (sol) gradually increases, eventually turning into a solid (gel).

A common example of this process in nanoparticle synthesis is the condensation of silanol groups (Si-OH) to form silica ($SiO_2$) nanoparticles. It is important to note that silanol groups themselves originate from the hydrolysis of alkoxide groups (Si-OR). Figure 6 illustrates the hydrolysis and condensation reactions involved in nanoparticle synthesis.

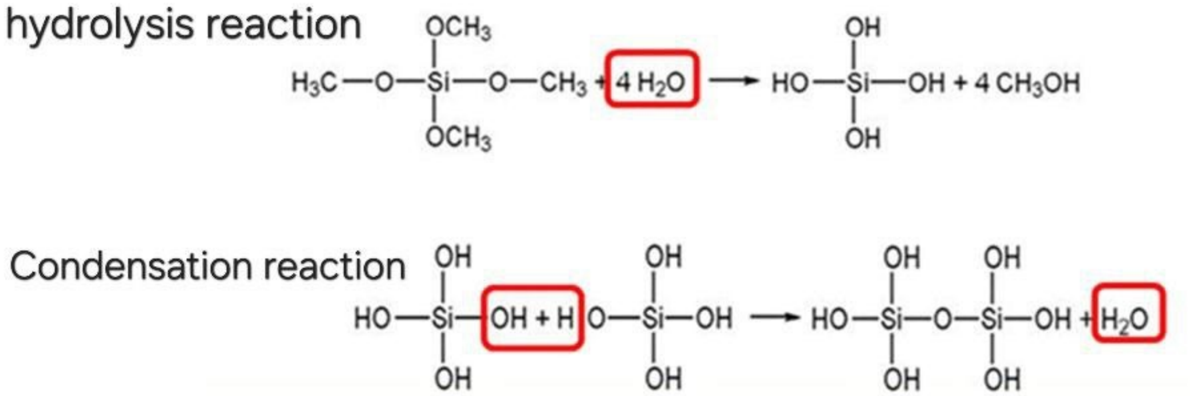


Figure 6 - Schematic representation of hydrolysis and condensation reactions for nanoparticle synthesis.

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### 5. Examples of Nanoparticles Synthesized by This Method

The chemical precipitation method is widely used to synthesize ceramic nanoparticles and metal-doped ceramic nanoparticles. Below are some examples of nanoparticles synthesized using this method and their applications:

Cadmium Oxide (CdO) and Silver-Doped Cadmium Oxide Nanoparticles: Used in solar cells, gas sensors, low-emission glass coatings, and biomedical applications.

Zinc Sulfide (ZnS) Nanoparticles: Applied in optical and optoelectronic devices, sensors, lasers, photocatalysts, and display technologies.

Cadmium Sulfide (CdS) Nanoparticles: Used in optoelectronic applications, photocatalysts, solar energy conversion, and X-ray detectors.

Carbon Nanotubes: Applied in solar cells, biomedical applications, scanning probe sensors, and nanoelectronics.

Magnetite ($Fe_3O_4$) Nanoparticles: Used in biomedical and medical applications.

Zinc Oxide (ZnO) and Cerium-Doped Zinc Oxide (Ce-ZnO) Nanoparticles: Used in photocatalytic applications.

Maghemite ($Fe_2O_3$) Nanoparticles: Applied in catalysis, medicine, heavy metal removal, data storage, gas sensors, and audio/video recording.

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## 6. Conclusion

Chemical precipitation is a process in which a solution containing precursor materials transforms into a solid. This is achieved by making the dissolved material insoluble or supersaturating the solution. The reactants in precipitation reactions are typically water-soluble ionic compounds.

This article reviewed the principles and fundamentals of the chemical precipitation method. It was explained that the precipitation process consists of two stages: nucleation and growth. Controlling both stages precisely is essential for synthesizing nanoparticles with the desired size, size distribution, and properties.

The different types of chemical precipitation, including direct precipitation, coprecipitation, and homogeneous precipitation, were also discussed. Additionally, the article emphasized that chemical reactions are the foundation of wet chemical methods for nanoparticle synthesis. Many of these reactions ultimately lead to the precipitation of solid particles from a solution.

These chemical reactions include precipitation reactions, redox reactions, and processes such as hydrolysis, thermolysis, polymerization, and condensation. The fundamentals of these reactions and processes were examined in detail. Finally, some nanoparticles synthesized via the chemical precipitation method and their applications were introduced.

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# Principles and Fundamentals of Nanoparticle Synthesis by Chemical Precipitation (2)

## Abstract

Chemical precipitation is a process in which a solution (containing a precursor) turns into a solid. To achieve this, the soluble material is either made insoluble or converted into a supersaturated solution. The reactants in precipitation reactions are usually water-soluble ionic compounds. Nanoparticle synthesis by chemical precipitation occurs in two stages: nucleation and growth. Synthesizing nanoparticles with the desired size, size distribution, and properties requires precise control over both the nucleation and growth stages. This article introduces and examines the mechanisms of nucleation and growth in the chemical precipitation process. It also explores practical methods for controlling the size of synthesized nanoparticles, including controlling synthesis-related variables, stabilizing the nanoparticle surface, and applying post-thermal treatments.

## Keywords

Synthesis, chemical precipitation, nucleation, growth, size, and size distribution.

## Introduction

The size of nanoparticles synthesized using different processes and methods varies significantly. Depending on the type of process, process parameters, and whether post-thermal treatments are applied, the size can range from a few angstroms to several hundred nanometers. Colloidal precipitates are solid aggregates that form in colloidal suspensions. A colloidal suspension consists of particles with diameters ranging from 1 to 100 nanometers, which are too small to be seen with the naked eye(unaided eye). Due to Brownian motion, nanoparticles in a colloidal suspension do not settle and can remain stable for a very long time. In contrast, larger precipitates settle quickly and spontaneously. Unlike nanoparticles in colloidal suspensions, larger precipitates can be easily separated from the solution using processes such as filtration, centrifugation, or decantation.

The synthesis process of nanoparticles through chemical precipitation follows a complex mechanism that is still not fully understood in many aspects. This article provides a detailed and simplified explanation of the governing mechanisms in the chemical precipitation process. Proper selection and control of reaction variables can help researchers obtain nanoparticles with the desired chemical composition, shape, size, and size distribution.

## Prerequisites

Before discussing the fundamentals of the chemical precipitation method and its governing mechanisms, it is necessary to understand some key concepts, which are explained below.

Brownian motion refers to the random movement of particles suspended in a fluid (liquid or gas) due to collisions with atoms or molecules of the fluid. Figure 1 illustrates the Brownian motion of a particle in a fluid.

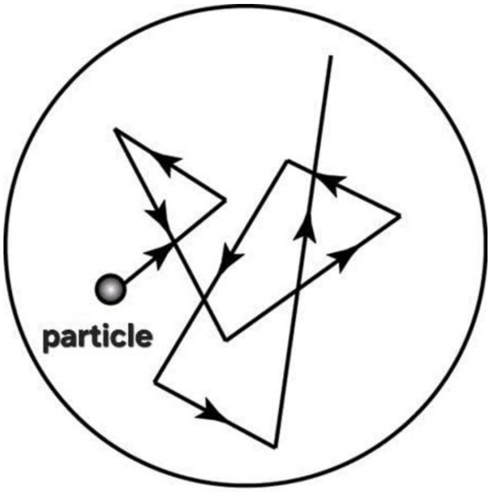

Figure 1 - Schematic representation of the Brownian motion of a particle in a fluid.

Supersaturated solution: A solution in which more solute has been added than the solvent can normally dissolve. In this condition, the excess solute precipitates.

Slightly soluble substances: These are substances with solubility ranging from 0.01 to 1 gram per 100 grams of water.

Crystal: A solid material where atoms, molecules, or ions are arranged in a repeating, ordered pattern.

Transmission electron microscope (TEM): A type of electron microscope that accelerates electrons at high speeds to pass through a sample. The interaction of electrons with the sample produces highly magnified images (up to one million times) and provides information about structure, crystal orientation, and element composition.

Amorphous solid: A solid in which the constituent particles lack long-range order, unlike crystalline materials.

Calcination: A process where a material is heated to remove moisture or decompose the substance.

Mechanisms of Precipitation Processes

As mentioned earlier, the complex mechanism of chemical precipitation from solution is not yet fully understood. However, chemical precipitation, as a bottom-up approach in nanoparticle synthesis, consists of two main stages: nucleation and growth.

3.1. Nucleation

Nucleation refers to the formation of new crystalline nuclei in a supersaturated solution. These nuclei are the first particles of a specific material phase formed during the synthesis process.

During nucleation, a small number of ions, atoms, or molecules come together to form an initial nucleus. Nucleation can occur from both gaseous and solution (melt) environments.

The nucleation process is categorized into two types: homogeneous nucleation and heterogeneous nucleation.

Homogeneous nucleation does not require a specific site for nuclei to form. Many initial nuclei are simultaneously created due to significant physical changes, such as temperature variations.

Heterogeneous nucleation occurs when nuclei form on specific surfaces present in the reaction environment, such as container walls, dust particles, or impurities. In simple terms, heterogeneous nucleation happens due to external influences. It is more likely to occur than homogeneous nucleation because it requires lower energy.

To better understand nucleation, consider the example of solid-phase nucleation from the liquid phase during the freezing of a melt. In homogeneous nucleation, the temperature must drop enough for nuclei to form from less mobile atoms binding together. In this case, the melt itself provides the atoms needed to form nuclei. In contrast, in heterogeneous nucleation, the nuclei form on container walls or existing impurities.

Precipitation from a solution typically occurs under supersaturation conditions. Initially, the liquid phase becomes saturated due to a progressing reaction that produces a poorly soluble product. Then, the newly formed product directly converts from the solution phase to the solid phase and precipitates. This means that converting the solution into a supersaturated solution is the first step in initiating nucleation. The higher the supersaturation level, the faster the precipitation process.

The concept of relative supersaturation is used to describe the precipitation rate from a solution, as shown below:

$S=(C-Cs) / Cs$

where:

$C$ = actual concentration of the solute in the solution

$Cs$ = equilibrium solubility of the solute in the solvent

Relative supersaturation has an inverse relationship with the size of synthesized particles. When the relative supersaturation is high, colloidal precipitation occurs, and when it is low, crystalline (large) precipitation occurs. Regarding the effect of relative supersaturation on nucleation rate, an increase in supersaturation causes the nucleation rate to change exponentially.

3.2. Growth

The growth process is more complex than nucleation. Growth occurs when structural units (atoms, molecules, or ions) attach to existing nuclei and align in preferred orientations. Since crystal growth happens rapidly, added atoms may not always find optimal positions, leading to defects such as dislocations in the crystal structure. Figure 2 presents a TEM image and a schematic representation of a dislocation defect.

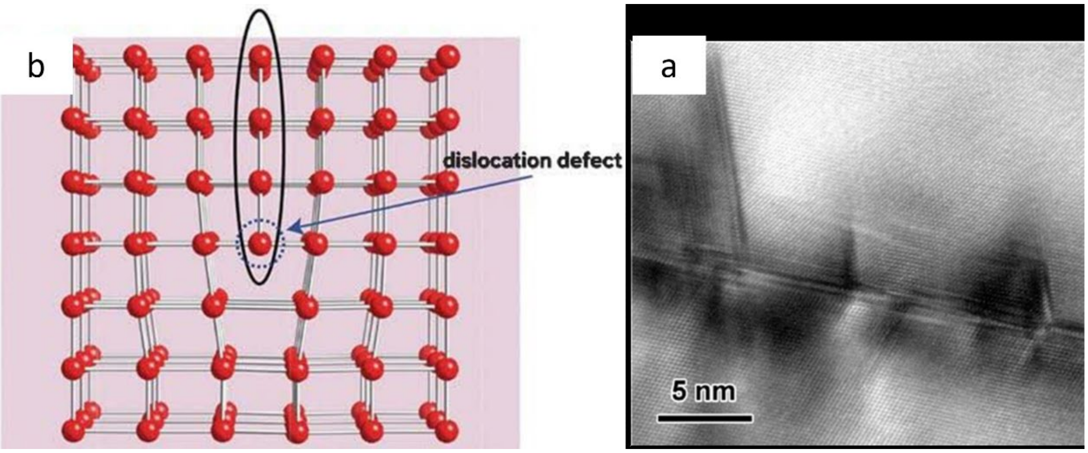

Figure 2 - (a) TEM image and (b) schematic representation of a dislocation defect [1].

Crystal growth differs from the growth of liquid droplets because molecules or ions must align in the correct positions. Depending on the conditions, nuclei growth can occur in one or multiple directions. When growth happens in a single direction, the resulting crystal exhibits unique properties in different directions.

Various mechanisms, such as mass transfer or diffusion, influence growth. For example, according to Fick's first law of diffusion, molecules or ions move from areas of high concentration to low concentration until equilibrium is reached. In most cases, diffusion controls the growth rate. This causes crystal edges to become more supersaturated than their faces, leading to increased nucleation at the edges, preventing a polyhedral structure from forming. With further growth, dendritic (branching) crystals may form, as shown in Figure 3.

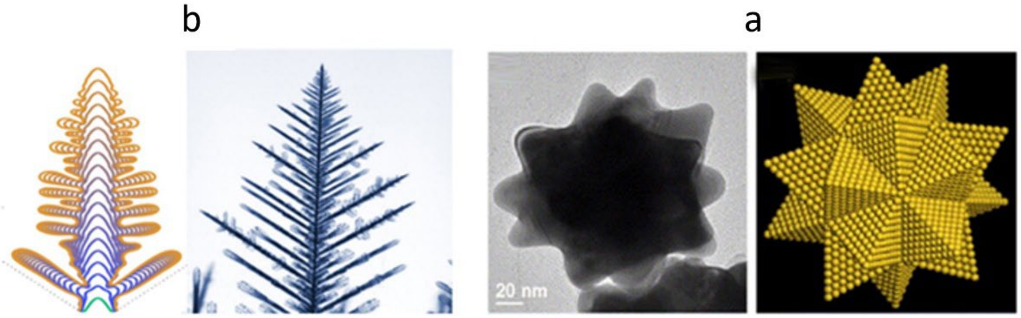

Figure 3 - Microscopic images and schematics of (a) polyhedral and (b) dendritic crystals.

Ostwald Ripening and Control of Nanoparticle Size

3. Ostwald Ripening

Controlling the processes of nucleation and growth does not always guarantee precise control over the size of crystals. This is because crystal size can change due to different mechanisms. When a colloidal solution is left undisturbed for some time under controlled conditions, the smaller particles gradually disappear while the larger ones grow. This process is called Ostwald ripening, which means that larger particles grow at the expense of smaller ones. The digestion process of a precipitate is also based on Ostwald ripening. Therefore, when the goal is to synthesize larger crystals, colloidal solutions can be left undisturbed under heat for several hours. Figure 4 illustrates the stages of Ostwald ripening.

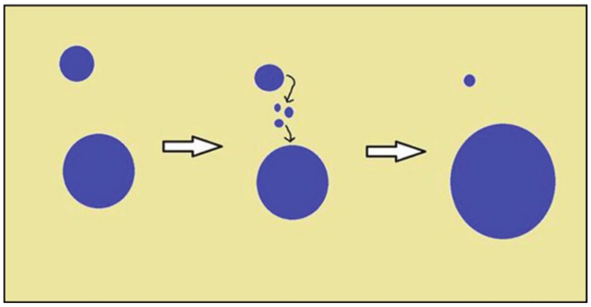

Figure 4 - A schematic of the Ostwald ripening process, where smaller particles dissolve, and larger ones grow.

Ostwald ripening happens because dissolved particles naturally try to form a more thermodynamically stable structure. The main reason for this process is the energy instability of molecules on the surface of particles compared to those inside. In simple terms, surface molecules are less stable than inner molecules. As a result, the unstable molecules on the surface gradually dissolve into the solution, making the small particles shrink. At the same time, the concentration of free molecules in the solution increases. When the solution becomes supersaturated with these free molecules, they start attaching to the larger particles. Consequently, the smaller particles shrink further, while the larger particles continue to grow.

This phenomenon not only changes the size of nanoparticles from the desired size but also affects their size distribution. If the solution remains undisturbed for too long, two distinct groups of particles—small and large—may form. Figure 5 shows TEM images of the Ostwald ripening process in palladium nanoparticles dissolved in formaldehyde over different time periods.

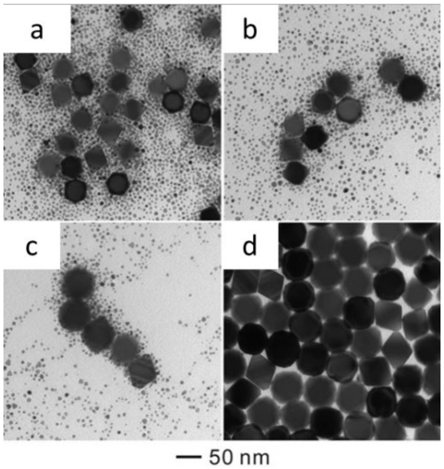

Figure 5 - TEM images showing Ostwald ripening in palladium nanoparticles dissolved in formaldehyde at different time intervals: (a) 6 hours, (b) 24 hours, (c) 48 hours, and (d) 72 hours [2].

## 4. Practical Control of Particle Size

### 4.1. Controlling Synthesis Variables

Almost all particles are formed during the nucleation process, and their initial size is very small. The most critical stage in controlling particle size is the growth phase. As mentioned earlier, processes such as agglomeration and Ostwald ripening, which occur during the growth phase, can significantly affect the size and distribution of synthesized particles. Since the processes of nucleation, growth, and agglomeration happen almost simultaneously (with minimal time gaps), synthesizing particles with a very narrow size distribution is highly challenging and requires precise control over each step.

One way to control the size of synthesized particles is to complete the nucleation process before the growth phase starts. This ensures that all particles form at the same time and have a similar size. If these processes overlap, the size distribution will be broader. A method to achieve rapid and complete nucleation is to create conditions of high supersaturation so that nucleation finishes quickly. Then, the conditions should be controlled to limit further nucleation while allowing the growth phase to dominate. In this way, the initially formed nuclei grow uniformly, resulting in particles of nearly the same size.

In precipitation reactions, supersaturation plays a key role in initiating and advancing nucleation and growth processes, as well as determining the size of synthesized nanoparticles. For nanoparticle synthesis, the goal is to create very small colloidal particles through precipitation reactions. In general, any factor that increases supersaturation reduces the size of the synthesized particles. This occurs because high supersaturation increases nucleation. Several factors significantly affecting nanoparticle size include solubility, temperature, reactant concentration, stirring intensity, and the presence of complexing or stabilizing agents.

If a material is insoluble in water, it will have a high supersaturation level. On the other hand, when using partially soluble compounds, special control is needed to synthesize particles of the desired size. For example, adjusting the pH and temperature of the solution can change the solubility of the dissolved substance, allowing precise control over particle size. To obtain smaller particles, which result from higher supersaturation, temperature and pH can be adjusted to minimize the solubility of the dissolved substance. Although it may seem that lowering temperature always decreases solubility, sometimes increasing temperature can speed up precipitation and increase supersaturation, leading to smaller particles. In general, nucleation rate is highly dependent on supersaturation, whereas the growth process is less affected by it.

### 4.2. Surface Stabilization of Nanoparticles

Nanoparticles have high surface energy, making them highly prone to sticking together and forming clusters and agglomerates. However, stable colloidal solutions are needed in nanoparticle synthesis. Two main approaches help prevent agglomeration and stabilize nanoparticles:

Adding Certain Chemicals: Some compounds, such as surfactants, polymers, or organic molecules, can be added to create repulsion between nanoparticles. These compounds, known as capping agents, give the nanoparticles a uniform surface charge, preventing them from coming close and forming clusters.

Electrostatic Repulsion: This occurs when nanoparticles adsorb charged ions, such as hydroxyl (OH-) or hydrogen (H+), on their surfaces. When nanoparticles have the same surface charge, they repel each other. This repulsion is stronger in highly acidic or highly basic solutions. Figure 6 shows a schematic representation of these stabilization methods.

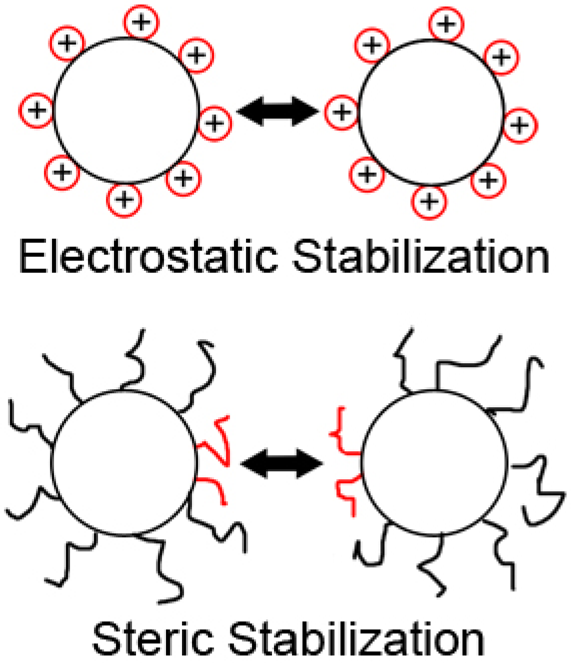

Figure 6 - A schematic of stabilization methods for preventing nanoparticle agglomeration.

### 4.3. Secondary Thermal Processes

Many particles synthesized through chemical precipitation, especially at low temperatures, are amorphous. To obtain crystalline nanoparticles, post-synthesis thermal treatments such as calcination or annealing are necessary. In oxide nanoparticle synthesis, thermal decomposition of the precipitate is often required. However, thermal processes can cause particle agglomeration and reduce size control. Alternative synthesis methods, such as hydrothermal and solvothermal techniques, which do not require thermal post-treatment, can provide better size control.

## Conclusion

Chemical precipitation is a process in which a solution containing precursor materials transforms into a solid. This occurs by either making the dissolved material insoluble or creating a supersaturated solution. The complex mechanism of chemical precipitation is not yet fully understood. However, it is recognized as a bottom-up approach for nanoparticle synthesis, involving nucleation and growth. Several practical methods for controlling nanoparticle size were explored, including synthesis variable adjustments, surface stabilization techniques, and post-synthesis thermal treatments.

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## Preparation of Nanomaterials by Sol-Gel Method

Abstract

The sol-gel process is a bottom-up method for producing nanoparticles. In this process, raw materials are initially dissolved in a solution, and in the next step, the solution turns into a wet gel. The next stage of the sol-gel process is drying the wet gel. If the drying process is done in an autoclave, a highly porous structure with very low density called an aerogel is formed. However, if drying is done through conventional methods, the final product will be nanoparticles.

Keywords: Nanomaterial synthesis, sol-gel, factors affecting the sol-gel process, aerogel

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### Introduction

The sol-gel method is a simple and inexpensive process that can be used to synthesize various nanoparticles. This method starts by forming a homogeneous sol from precursors, which is then chemically triggered to form a gel. After that, the solvent is removed from the gel structure using one of the conventional methods and dried. Depending on the drying method, the final product will have different morphologies and properties. The products obtained have various applications in surface coatings, building insulation, optical devices, and more. In this section, the sol-gel method and the factors influencing it will be introduced.

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### Sol-Gel Process

The sol-gel process is a bottom-up synthesis method. In this process, the product results from a series of irreversible chemical reactions. These reactions convert the homogeneous molecular sol (initial solution) into an indefinite, heavy, three-dimensional polymeric molecule (gel). For example, the hydrolysis reaction followed by condensation that leads to the final product can be summarized as follows (Figure 1).

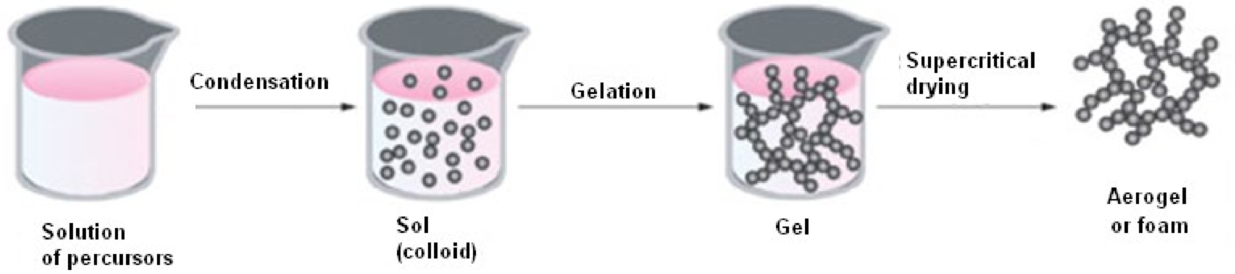

Figure 1 - Overview of different stages in the sol-gel reaction.

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### Stages of the Sol-Gel Process

To produce a product via the sol-gel method, the necessary conditions for the reactions must first be prepared. The stages of the sol-gel method are schematically shown in Figure 2. These stages are:

Preparation of a homogeneous solution

Formation of sol

Formation of gel

Drying

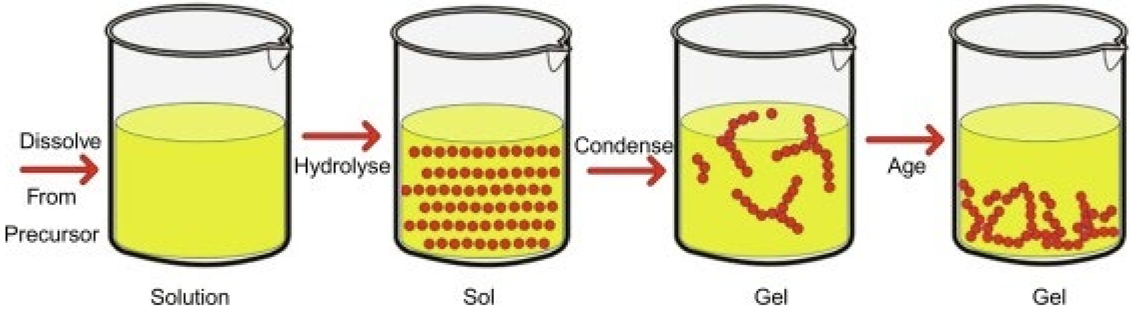

Figure 2 - Overview of all stages in the sol-gel process.

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### 3.1. Preparation of Homogeneous Solution

The first step is to prepare a homogeneous solution consisting of a solvent and precursors that will shape the final product during the process. For this, the solvent (water, alcohol, organic solvents, or a combination of them) and precursor are dissolved in a container to form a homogeneous solution. Sometimes, it is necessary to combine two solvents in specific ratios so that the precursors dissolve completely, and the homogeneous solution is obtained. For example, some organic metal precursors should first be dissolved in an organic solvent that is soluble in water, and then the resulting solution is dissolved in water. However, when the precursor is a metal salt, it is directly soluble in water, and no organic solvent is needed.

Alkoxylated precursors are often used, but the sol-gel process can also proceed via a colloidal pathway.

Metal alkoxides are chemical compounds in which a metal atom is bonded to an alkoxy group (R-O). The alkoxy group consists of an oxygen atom bonded to an alkyl group (R). In other words, metal alkoxides are composed of a metal (usually transition metals or rare metals) and an alkoxy group. These compounds are typically liquid-soluble and are used in various processes such as the synthesis of metal nanoparticles and the production of thin films and ceramics.

An example of a metal alkoxide is tetraethyl orthosilicate (TEOS), which is used as a precursor for the production of silica and silicate ceramics in sol-gel processes.

The general formula of metal alkoxides is $M(OR)_n$, where:

M represents the metal.

R is the alkyl group (such as methyl, ethyl, etc.).

n represents the number of alkoxy groups bonded to the metal.

Metal alkoxides are commonly employed in hydrolysis and condensation reactions in sol-gel processes to create ceramic materials or metal nanoparticles.

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### 3.2. Formation of Sol

After creating a homogeneous solution, it must be converted into a sol. The hydrolysis reaction forms the basis of this step. Hydrolysis refers to the breakdown of a compound by water. In chemistry, water can break down a molecule into simpler components. In brief, hydrolysis refers to reactions in which water breaks down a molecule into simpler molecules.

The hydrolysis reaction is not complex. To begin this process, some water is added to the reaction environment (if the homogeneous solution is prepared in a water-free solvent). The presence of water causes the hydrolysis reaction to occur on the precursor, activating it so that metal oxide particles cluster together and form small solid particles dispersed in the solvent. This mixture is called a sol (an intermediate product in the process). An overview of the hydrolysis reaction is shown in Figure 3.

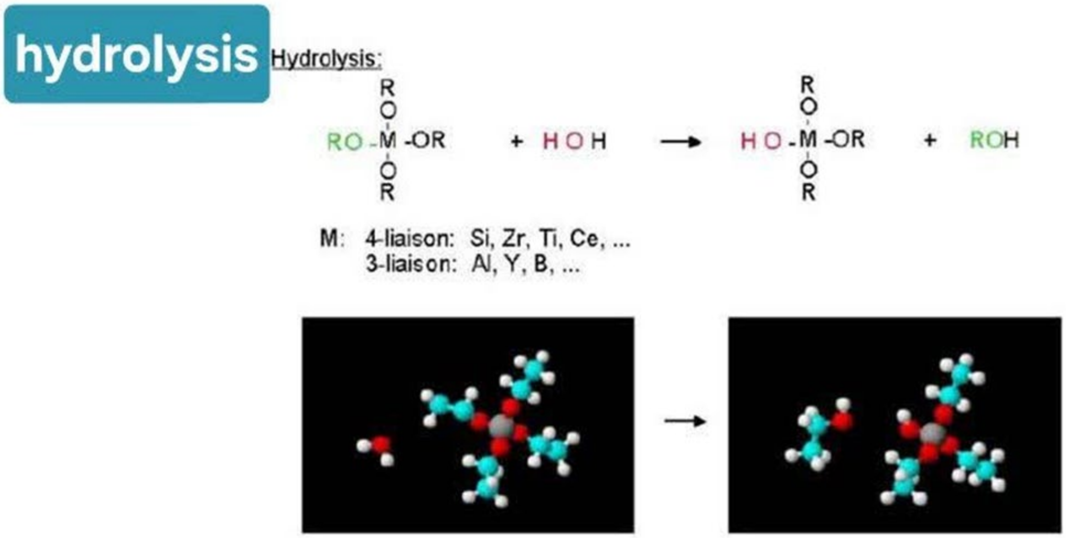

Figure 3 - Overview of the hydrolysis reaction for a metal alkoxide

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A sol (derived from the English word "Solution") is a colloidal solution made from various reactants (such as precursors, solvent, acid or base catalysts, and other necessary additives) that will eventually form a gel through hydrolysis and condensation. It should be noted that sols are slightly different from true solutions. In a true solution, the solute is uniformly dispersed in the solvent as atoms, molecules, or ions, with particle sizes not exceeding 1 nm. However, if the particle size exceeds 100 nm, the particles gradually settle (forming a suspension). If the particles range from 1 to 100 nm, they remain dispersed throughout the mixture, forming a colloidal mixture. Sols contain very fine particles (less than 100 nm) dispersed in the solvent, essentially forming a colloidal solution.

The key feature of a good, acceptable sol is that it should remain stable for months without settling. This means the particles should be small enough for Brownian motion to counteract gravity, preventing settling and maintaining homogeneity over time. If a sol has this characteristic, we can expect a homogeneous, pure product with high yield.

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### 3.3. Formation of Gel

To form a gel, the sol solution must be triggered in such a way that the dispersed particles (each consisting of a few to several dozen molecules or atoms of the respective precursors) start to aggregate. Through physical and chemical interactions between the dispersed particles in the sol, they cluster into units of tens of thousands of molecules and form a giant three-dimensional molecule that typically occupies the entire volume of the reaction vessel.

This giant molecule, which has many pores, traps the solvent inside, forming a wet gel. To produce a wet gel, it is necessary to trigger the sol solution to form a gel. This triggering can be done using an appropriate reagent (pure water or water with NaOH, HCl). In fact, during the conversion from sol to gel, which is controlled by condensation reactions, a mineral polymerization reaction occurs, and the final product is an oxide network containing M-O-M metal oxide clusters. An overview of the condensation reaction is shown in Figure 4.

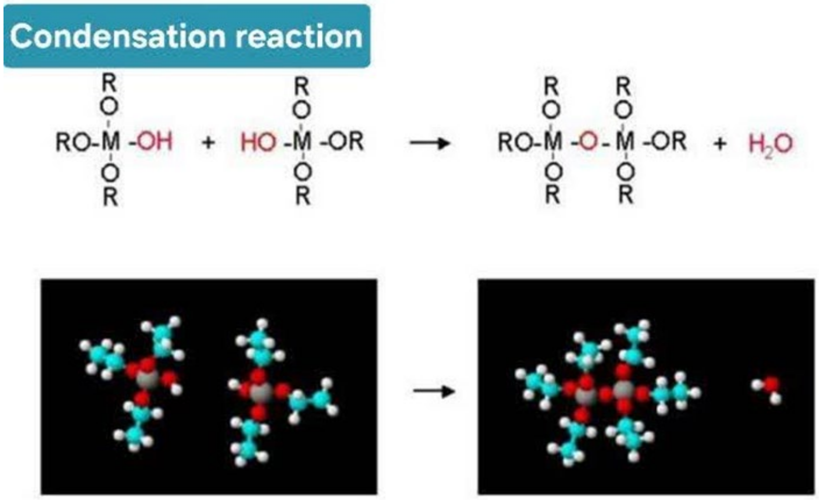

Figure 4 - 3D model of the condensation reaction.

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Condensation reactions are the reverse of hydrolysis reactions. In hydrolysis, a large molecule is broken down into simpler components by consuming water, while in condensation, two simple molecules combine to form a more complex molecule. During this process, a small molecule, like water, is released. A condensation reaction occurs when two metal hydroxides (or one metal hydroxide and one alkoxide) combine to create a metal oxide (M-O-M). The gel is eventually formed as a solution. In the next stage, the solvent must be removed to complete the process. Gels come in various types, each with its own specific properties and applications. Depending on the solvent used or the drying method, the names, characteristics, and applications of these gels will vary.

By mixing different primary salts, binary or ternary systems can be produced. Each of the primary salts has its own reaction rate, which depends on factors such as pH, concentration, solvent, and temperature. The polymeric gel formed creates a three-dimensional scaffold, which leads to the merging of pores. After drying, the structure shrinks and condenses, resulting in a solid, rigid material. It can be said that the final materials and products can be designed in such a way that nano-scale porosity is created, leading to a much higher specific surface area.

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### 3.4. Drying

Gels have the characteristic of taking the shape of the container in which they are produced. Depending on the strength of the gel structure, a separate piece with large pores can be obtained. Since the solvent is one of the internal components of the gel (helping to keep the structure stable), maintaining the stability of the pore structure by removing the solvent is challenging. The gel structure must usually be allowed to age (sit for a while) before drying so that the bonds between the particles become stronger. This aging process can last from several hours to several days. During aging, the gel continues to change, forming new bonds and increasing the strength of its structure.

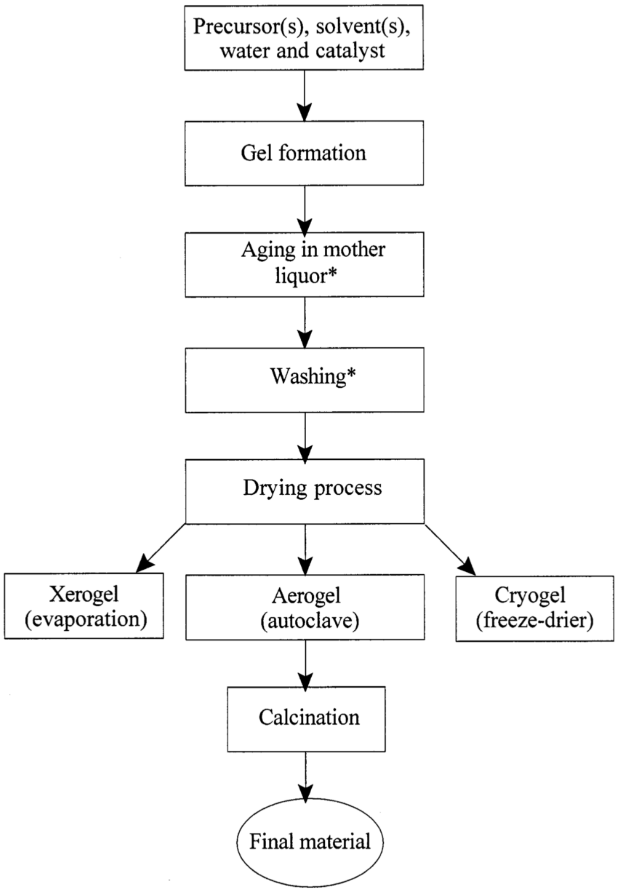

Figure 5 - Various stages of the sol-gel process and the aging stage.

After aging and preparing the gel, the liquid phase (solvent) is removed by various methods. This drying or solvent removal process can be done in two main ways:

Allowing the material to dry naturally, resulting in xerogel, which has fewer pores and is more compact. Xerogel refers to gel in which all the liquid inside the pores has been removed, causing the structure to become denser and more compressed. The shrinkage compared to the wet gel is clearly visible (Figure 6).

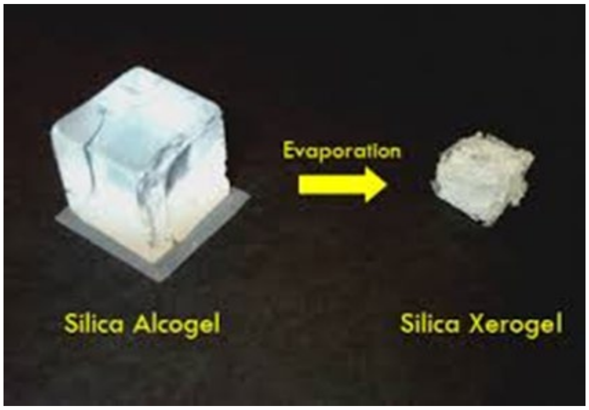

Figure 6 - Simple evaporation drying and the creation of xerogel.

The second method is supercritical drying, in which the changes in the solid network are minimized. The resulting material has a porous, hollow network called aerogel. Aerogel is a type of dry gel, meaning the solvent has been removed from it. In this process, the solvent is removed in such a way that no compression or change occurs in the gel structure. Aerogel is typically produced by heating the gel to the solvent's critical temperature, where there is no phase equilibrium between liquid and vapor. This results in an aerogel with a high surface area and preserved structure, compared to the wet gel. Unlike xerogel, aerogel maintains its pore structure and does not compress.

Drying can also be achieved via simple evaporation or solvent removal under vacuum. During evaporation, capillary forces between the solvent and the walls of the material may reduce porosity. If this happens, the change is irreversible after the gel dries. One way to address this issue is by eliminating the contact surface between the gas and liquid phases in the system. This can be achieved by removing solvents when they are in their supercritical state. The supercritical point on the phase diagram is where gas and liquid no longer exist as separate phases (see Figure 7).

Thus, the solvent is removed without the need for a phase change. In other words, the solvent does not need to transition from the liquid phase to the gas phase and then be removed. In this condition, the solvent exists in the supercritical phase (where it is neither liquid nor gas!). In Figure 7, the arrows and numbers indicate the possible paths to reach this point. Initially, in a completely sealed chamber, the temperature is raised above the critical point (Tc), which increases the pressure above the critical pressure (slightly higher than Pc), resulting in a supercritical state.

In the pressure-temperature phase diagram, Pc and Tc refer to the critical pressure and temperature, respectively. Arrows 1 and 2 show the supercritical drying paths. At first, the liquid is converted into a supercritical fluid by increasing the temperature. The pressure also increases simultaneously. Then, by maintaining the temperature constant, the pressure is reduced. As a result, the supercritical fluid transitions into the gas phase and is expelled from the system.

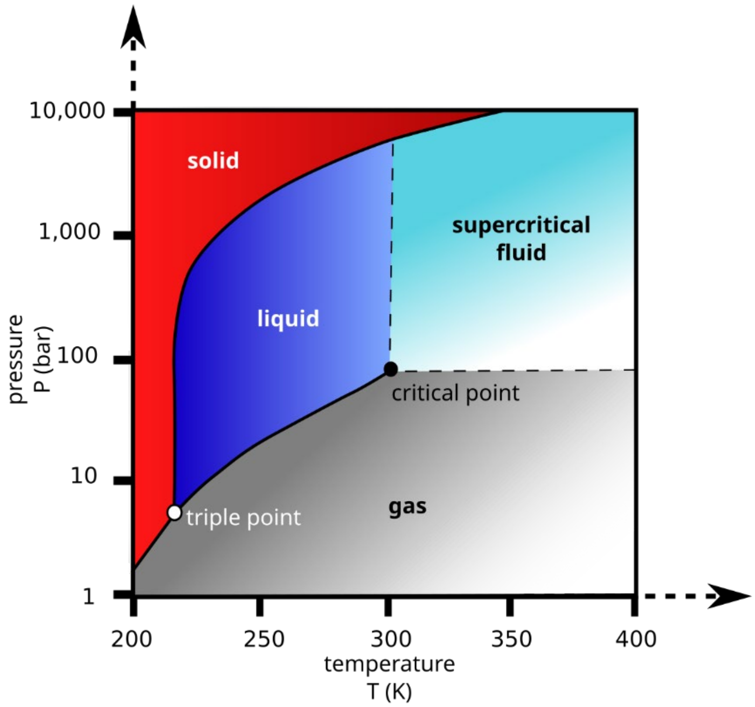

Figure 7 - Pressure-temperature phase diagram for reaching critical conditions.

In this case, the solvent is removed without changing phase. This requires an autoclave since the pressure needed to achieve supercritical conditions is higher than 6 MPa. For example, ethanol requires high temperatures to reach its critical point (around 234°C), while CO2 reaches its critical point at around room temperature (31°C).

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## Properties of Sol-Gel Products

The main reasons for using the sol-gel process include producing high-purity products, achieving a narrow particle size distribution, and obtaining uniform nanostructures at low temperatures. The sol-gel method is commonly used for synthesizing metal oxide nanoparticles. The sol-gel process involves changing the sol to a gel using various techniques, most of which use slow and gentle drying methods to remove the solvent.

It should be noted that due to shrinkage during gel drying, precautions must be taken to prevent cracks during drying. The gel produced can be molded into shapes, and by drying these shapes, a solid, integrated piece can be obtained. These molded pieces can be used as filters or membranes.

As shown in Figure 8, thin films with thicknesses ranging from 50 to 500 nm can be produced on a substrate by using spin coating or dipping methods. These thin films have a wide range of applications, including electronic, abrasive, and chemical uses, and they can also influence optical properties.

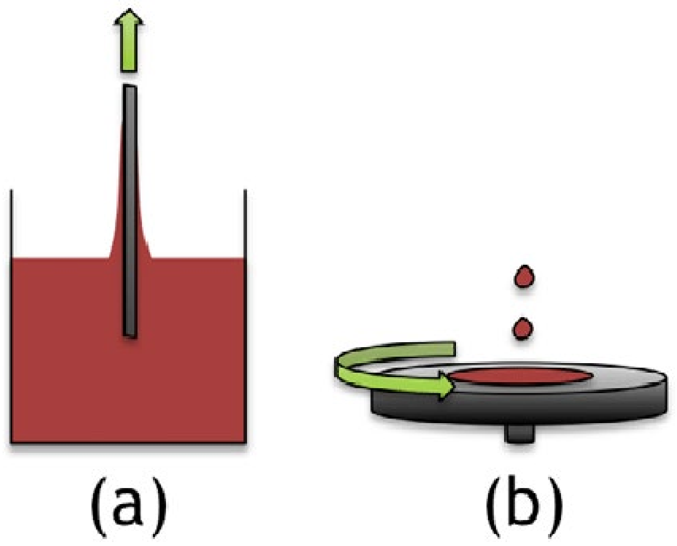

Figure 8 - Overview of coating methods: a) dip coating, b) spin coating.

Continuous nanometer-scale pores in the material can be filled with secondary materials, creating nanocomposites. These materials are useful in various applications, including catalytic reactions, where their high surface area improves catalytic efficiency and reduces the cost of production.

To create more compact parts, heat treatment must be used. The high surface area increases the speed of compaction (densification), but it should be noted that higher temperatures for sintering can cause grain growth. Figure 9 shows a detailed diagram of this process.

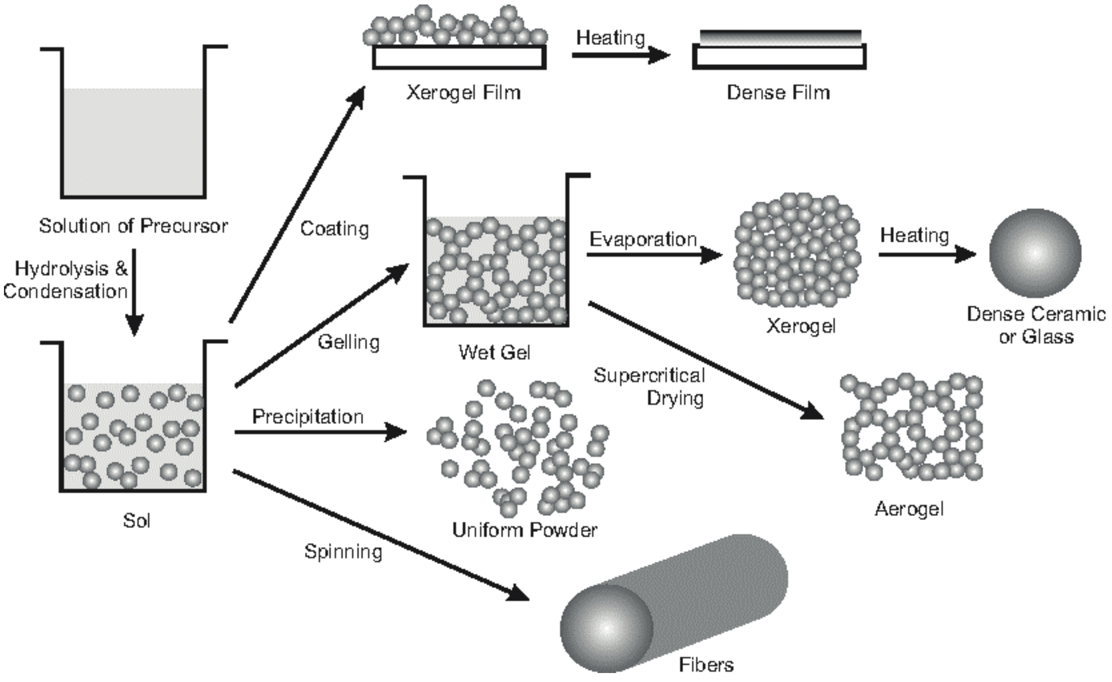

Figure 9 - Types of processes that can be performed in the sol-gel method and the products resulting from each process.

## 5- Conclusion

Sol-gel is one of the most important methods for preparing metal oxide nanoparticles. In this article, we reviewed the different stages of the sol-gel process for synthesizing nanoparticles. These stages include preparing a suitable sol from the raw materials, converting the sol into a gel, aging, conventional drying, autoclave drying, and finally calcination. The nanoparticles obtained from the sol-gel process exhibit high purity and a narrow particle size distribution. The sol-gel method is one of the key techniques for producing nanopororous materials, such as aerogels.

## 6- References

http://edu.nano.ir/

# Hydrothermal Synthesis of Nanomaterials

## Abstract

The hydrothermal method is one of the common techniques for nanomaterial production and falls under the category of bottom-up synthesis methods. Nanomaterial synthesis using the hydrothermal method is carried out over a wide range of temperatures, from room temperature to high temperatures. In this method, the raw materials are first dissolved in an aqueous or organic solution and then placed into an autoclave. The function of the autoclave is to increase the temperature and pressure to the desired levels, allowing the solution to enter the critical region and causing the reactants to interact. This leads to supersaturated conditions, where precipitates are formed in the solution, and nanoparticles are synthesized from these precipitates. This article provides a general introduction to the hydrothermal process, discussing the principles, mechanisms of nanoparticle synthesis, various hydrothermal methods, and heating techniques in detail.

## Keywords

Synthesis, Nanoparticles, Hydrothermal, Bottom-up Synthesis, Autoclave.

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## Introduction

The hydrothermal method is a well-established process for nanomaterial synthesis, offering a simple execution process and economic feasibility. It is a bottom-up synthesis approach that allows the preparation of various nanoparticles across a broad temperature range. One of the main advantages of this method is its ability to synthesize nanomaterials that are not stable at high temperatures. Additionally, materials with high vapor pressures can be synthesized effectively using the hydrothermal technique. The method also allows for control over the chemical composition of the synthesized material. These advantages make the hydrothermal method widely used in various industries.

The term hydrothermal refers to heterogeneous reactions conducted in an aqueous solvent under high pressure and temperature to dissolve materials that are nearly insoluble under normal conditions and promote their recrystallization. In simpler terms, hydrothermal conditions allow two reactants, which are difficult to dissolve in each other, to form a solution in the presence of solvents and mineralizers. Figure 1 shows an image of a hydrothermal device used for nanomaterial synthesis.

Figure 1 - An image of the hydrothermal device used for nanomaterial synthesis.

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## Fundamentals of the Hydrothermal Method

Among the advanced nanoparticle synthesis methods, the hydrothermal approach has received significant attention. The term "hydrothermal" has geological origins, where it was initially used by an English geologist to describe the role of water at high temperatures and pressures in creating changes in the Earth's crust that lead to the formation of rocks and minerals. The hydrothermal process has been responsible for the creation of the largest natural single crystals as well as large amounts of synthetic single crystals in laboratories.

Initially, the hydrothermal process referred to chemical reactions (either homogeneous or heterogeneous) in the presence of a solvent under high temperature and pressure. Over time, as thermodynamic information about the process improved, the temperature and pressure were reduced significantly, and the method moved toward green chemistry. Today, the hydrothermal method accounts for about 6% of advanced nanomaterial synthesis. This method allows the production of a wide range of metal oxides, hydroxides, silicates, carbonates, phosphates, sulfides, and nitrides in various shapes such as nanotubes, nanowires, nanorods, etc. Furthermore, the hydrothermal method is not only limited to the synthesis and growth of advanced materials but also has interdisciplinary applications such as waste treatment.

The hydrothermal method involves a chemical reaction in an aqueous environment within a sealed vessel, typically an autoclave. This reaction occurs at high temperatures (130–250°C) and high vapor pressures (0.3–4 MPa). Figure 2 illustrates a schematic of the hydrothermal process used to synthesize molybdenum sulfide ($MoS_2$) nanostructures, which are used for photocatalytic applications in energy production.

Figure 2 - Schematic of the hydrothermal process for synthesizing MoS2 nanostructures.

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## Mechanism of Nanoparticle Synthesis by the Hydrothermal Method

The main mechanism in the hydrothermal process is the nucleation and crystal growth resulting from chemical reactions and changes in the solubility of materials in an aqueous solution under the desired temperature and pressure conditions. Initially, high temperatures and pressures were used in the process. However, with the discovery of appropriate solvents and advanced energy delivery methods, such as microwave and magnetic field techniques, this process can now be carried out at lower temperatures and pressures.

In the general procedure, the reactants (precursors) are dissolved in a suitable solvent. To enhance the dissolution of precursors or to achieve a more uniform distribution of reactants in the solution, ultrasonic waves can be used. The solution is then introduced into an autoclave, which is sealed. The temperature of the autoclave is then raised to the required level. As the temperature increases, the pressure inside the autoclave rises, creating suitable conditions for the chemical reactions to take place. After sufficient time for the reaction(s), heating is stopped, and the products are extracted from the autoclave. Often, the reaction is stopped by quenching the autoclave. If necessary, the products from the hydrothermal process can be dried by heating. The autoclave contents are then washed with acetone or water several times to remove potential impurities. After washing and prior to calcination, the obtained powder mixture is dried at lower temperatures (60–80°C). Figure 3 shows an image of a typical autoclave used in the hydrothermal process.

Figure 3 - An image of an autoclave used in the hydrothermal process.

Types of Hydrothermal Methods

The environmental conditions and types of reactions in the hydrothermal process greatly influence the progress of the reaction and the resulting products. To control the size and morphology of the products, various additives, templates, or substrates can be used in the hydrothermal process. Depending on the materials used and the system and environmental conditions, the hydrothermal process can be divided into several categories. The impact of the chemical composition of materials used and various heating techniques on the properties of the nanomaterials produced through hydrothermal synthesis will be discussed.

Thermal treatment (calcination) is one of the common processes to enhance the properties or achieve specific characteristics in nanomaterials derived from the hydrothermal process. For example, calcination can be used to crystallize nanoparticles synthesized in the hydrothermal process. It is important to optimize the temperature and time conditions for calcination. If the calcination time is too long, nanoparticles may agglomerate and form clumps after crystallization.

Therefore, careful control of the calcination conditions is necessary to obtain nanoparticles with the desired size.

Other factors influencing the properties of nanomaterials obtained from the hydrothermal process include reaction chamber conditions, precursor concentration, pH, reaction time, pressure, organic additives, and the type of template.

## 4.1 Methods Using Organic Additives

To control the morphology of nanoparticles and the progress of reactions in the hydrothermal process, organic additives can be used. Depending on the chemical nature of the additives and the solution, these additives can play roles such as reducing agents, absorbents, etc., in the chemical reactions between the reactants. Surfactants, biomolecules, ionic liquids, organic acids, and organic solvents are among the most commonly used organic additives in the hydrothermal process.

Surfactants are organic compounds that have both hydrophilic and hydrophobic ends. When surfactants are introduced into a solution, the two ends align in different directions, with the hydrophilic head facing the aqueous solution and the hydrophobic tail directed towards the reactants, leading to the formation of aggregates known as micelles. The shape of the micelles strongly depends on the surfactant concentration and can be spherical, cylindrical, etc. Figure 4 shows a schematic of the orientation of surfactants in a solution.

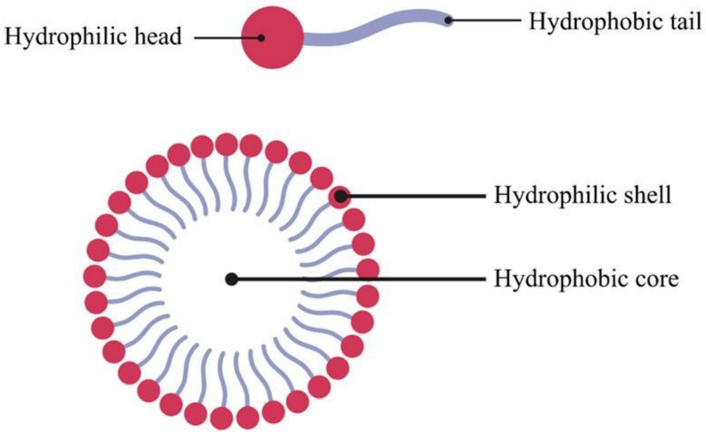

Figure 4 - Schematic showing the orientation of surfactants in a solution.

## 4.2 Methods Using Templates

In some cases, particles are added to the system to act as templates to precisely control the dimensions and shape of the synthesized nanoparticles. Theoretically, it has been demonstrated that it is possible to synthesize nanoparticles with desired sizes and shapes using templates. However, practical challenges exist in template usage. The template material must be selected in such a way that it not only provides a suitable platform for the synthesis and formation of nanoparticles but also remains compatible with the reactants and can be easily separated from the synthesized nanoparticles after the reaction. Depending on the method of template removal and the manner of template use in the reaction, hydrothermal methods using templates can be divided into the following four categories:

Adding and Removing the Template: In this method, the template is introduced into the chamber at the start of the reaction, and after the hydrothermal process is complete, it is separated from the product either by calcination or by dissolution.

Adding and Self-Removing the Template: In this method, the template is introduced into the chamber before the reaction begins, and during the hydrothermal process, it reacts with the reactants and is removed after the product is produced.

Self-Adding and Removing the Template: In this method, the template is generated during the hydrothermal process and is separated from the product after the process is complete by calcination.

Self-Adding and Self-Removing the Template: In this method, the template is formed during the process and is removed after reacting with other reactants.

"For example, carbon spheres are used as templates for the synthesis of iron oxide nanocages (see Figure 5). In such conditions, the carbon spheres are first added to the hydrothermal reaction solution, and then the functional groups present on the surface of the carbon spheres cause the adsorption and formation of iron oxide on the surface. After the reaction is completed, the carbon spheres are removed from inside the iron oxide nanocages through calcination."

This process highlights the use of carbon spheres as templates to create hollow structures, in this case, iron oxide nanocages, by removing the template after the synthesis is complete.

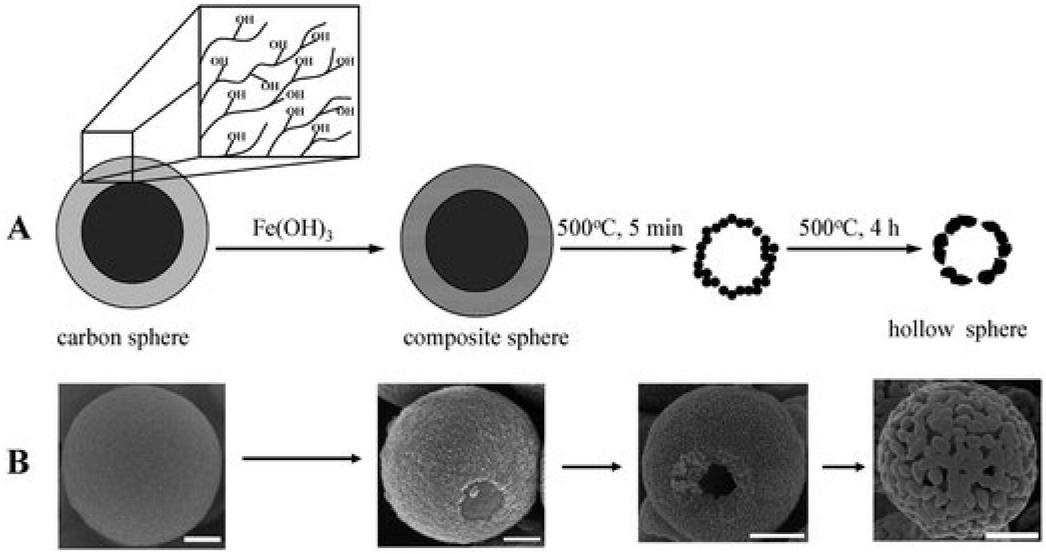

Figure 5 - (a) A schematic of the synthesis of iron oxide nanocages, and (b) scanning electron microscope (SEM) images of the product at each stage.

### 4-3. Substrate-Based Methods

The hydrothermal method based on substrate use is a cost-effective alternative to physical and chemical vapor deposition methods. The main condition for synthesizing nanostructure arrays with this method is selecting an appropriate substrate and placing it in the reaction chamber. The role of the substrate in this process depends on its type and can be one of the following three:

Substrate as reactant growth; SARG: In this case, a metal foil substrate is used. The substrate not only acts as a foundation for the growth of nanostructure arrays but can also serve as a reactant.

Homo-epitaxy growth; HoEG: In this method, no chemical reaction occurs between the substrate and precursors. Particles of the precursor are sprayed onto the substrate, and these particles act as seeds for the growth of the desired nanostructures. The nanostructure arrays form on these seeds.

Hetero-epitaxy growth; HEEG: This method is similar to homogeneous co-growth, but the nanostructures directly settle on the substrate, without using seeds.

Figure 6 shows a schematic of the different types of hydrothermal methods based on substrate use.

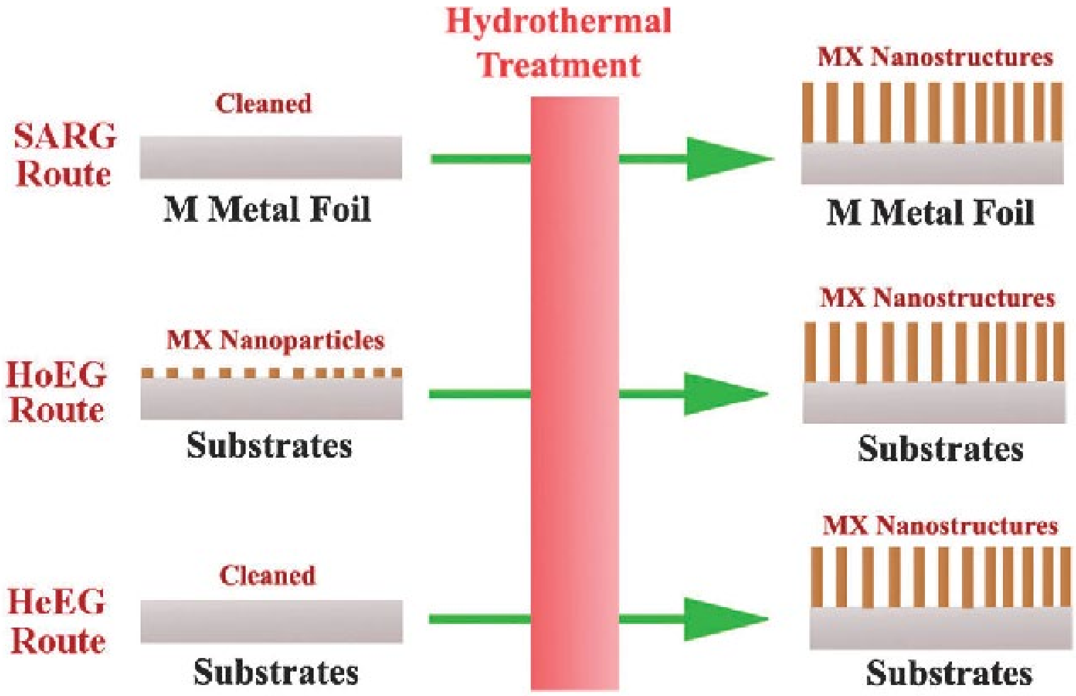

Figure 6: A schematic of the types of substrate-based hydrothermal methods.

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### Heating Methods in Hydrothermal Process

The heating method used for the system is one of the critical parameters in the hydrothermal process as it significantly affects the reaction rate and the properties of the final synthesized product. In the early stages of hydrothermal process development, furnaces were typically used for heating. The use of furnaces and conductive heat transfer caused significant temperature gradients in different parts of the reaction chamber, resulting in uneven reaction conditions and, thus, nanoparticles with varying sizes. Therefore, today, alternative methods, such as microwave heating and heating using magnetic fields, are employed to ensure uniform heating throughout the system. Figure 7 illustrates the heating methods using microwave and magnetic fields.

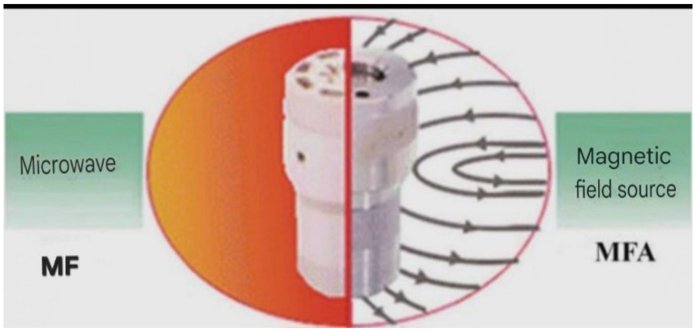

Figure 7 - Schematic of heating methods using microwave and magnetic fields.

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Conclusion

The hydrothermal method is a widely used technique for the production of nanomaterials and falls under the category of bottom-up synthesis methods. It is a simple yet effective technique for synthesizing nanoparticles with different chemical compositions, crystal structures, and shapes. By utilizing high temperatures, high pressure, and various additives, it is possible to control the growth and morphology of nanoparticles. The use of templates and different heating methods can further enhance the properties of the synthesized nanomaterials. The versatility of the hydrothermal method makes it an essential technique for the development of nanomaterials in various applications, including energy production, electronics, and nanomedicine.

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## Mechanical Milling

### Abstract

Milling has been used for many years in various industries, including cement production and mineral processing, to crush raw materials. However, this section discusses the use of milling methods to achieve nanomaterials. In top-down synthesis approaches, bulk material with a size larger than the nanometer range is reduced to a material where at least one dimension falls within the range of 1 to 100 nanometers. Specialized mills, laser beam irradiation, and high-power electric current are some of the tools used for particle size reduction. Another top-down approach is lithography, which operates with a different mechanism.

### Introduction

In various nanomaterial synthesis processes, different methods can be used to reduce the dimensions of the target material to achieve a final, efficient product. The approach where a large bulk material is converted into a smaller-sized product is known as the top-down approach. In these synthesis methods, bulk material with a size larger than the nanometer scale is reduced to at least one dimension within the range of 1 to 100 nanometers. Specialized mills, laser beam irradiation, and high-power electric current are commonly used tools for crushing and downsizing particles. Another top-down method is lithography, which functions differently. For further understanding of the lithography method, you can refer to available articles on the internet or standard reference books.

Given the nature of the top-down approach, it can be concluded that these methods provide the simplest path to achieving nanoscale products. This is a significant advantage in synthesis. However, it is important to note that top-down methods generally lack control over the atomic or molecular arrangement and the microstructure of the final product. Instead, the final product often retains a microstructure similar to that of the initial material.

### Types of Milling Methods

Milling has been used for many years in various industries, including cement production and mineral processing, for crushing raw materials. However, this section focuses on the use of milling methods to obtain nanomaterials. One of the methods for obtaining nanoparticles is milling raw materials. Different types of mills are used for this purpose. In most cases, raw materials are placed in the mill along with several metal or ceramic[1] balls inside the chamber. Ultimately, the movement and impact of the balls on the raw material lead to the formation of the final product. Thus, milling methods follow a top-down approach. Figure 1 shows a simple illustration of the inside of a ball mill.

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[1] In engineering and materials science, materials can generally be classified into four categories: metals, ceramics, polymers, and composites. The term "ceramic" is derived from the Greek word "keramikos" (Ķεραμικός), meaning pottery or fired object. Ceramics are composed of a combination of a metal and a non-metal, such as metal oxides and metal nitrides. These materials have a wide range of applications in electrical, magnetic, and optical devices. Their main characteristics include high thermal and electrical insulation as well as surface hardness.

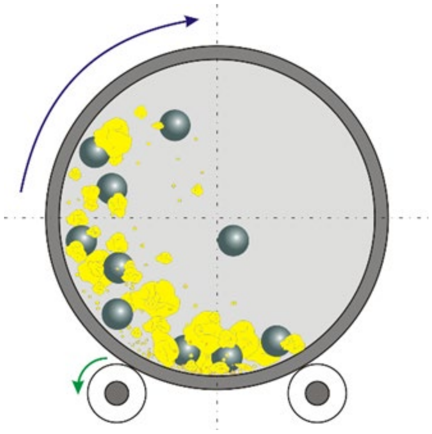

Figure 1 - A simple illustration of the inside of a ball mill.

In milling methods, the initial powder undergoes deformation, breakage, and fragmentation due to the continuous movement of the balls. As shown in Figure 2, the process of fragmentation and size reduction can be divided into three main stages:

Compression and reversible deformation of large particles under ball pressure.

Irreversible deformation of particles due to continued ball pressure.

Collapse and breakage of structures, producing smaller particles.

It is worth noting that if a chemical reaction between the powder components or with the gas inside the mill is possible, this reaction occurs during the third stage.

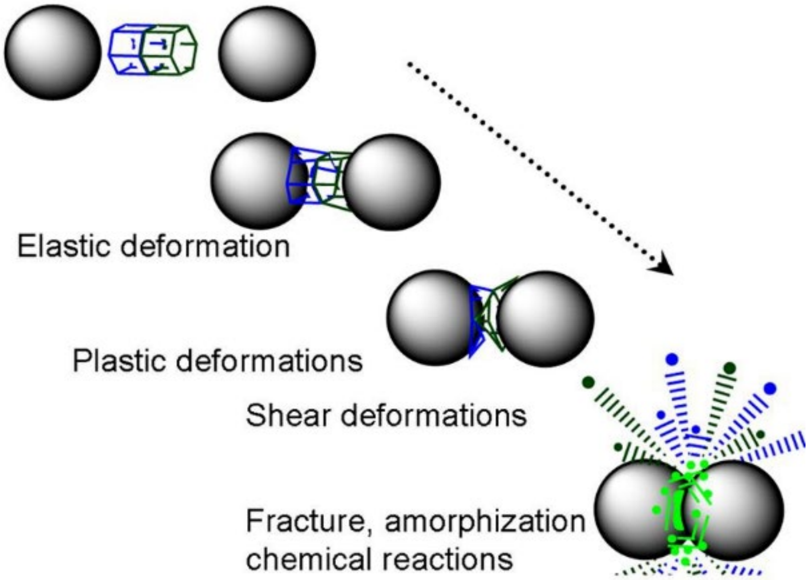

Figure 2 - The three main stages of the initial powder crushing and size reduction process.

Additional events occur during the milling process. For example, due to the pressure and force applied to the initial powder and the clean surfaces formed by material collapse, particles may adhere to each other through cold welding[2] (Figure 3-b). Additionally, the friction and heat generated significantly increase the temperature, leading to a phenomenon known as sintering.

As a result, the materials inside the mill continuously break, fragment (Figure 3-a), and weld (Figure 3-b). This means that the present phases constantly break, weld, and diffuse into one another. These conditions can also be used to produce advanced alloys and composite materials

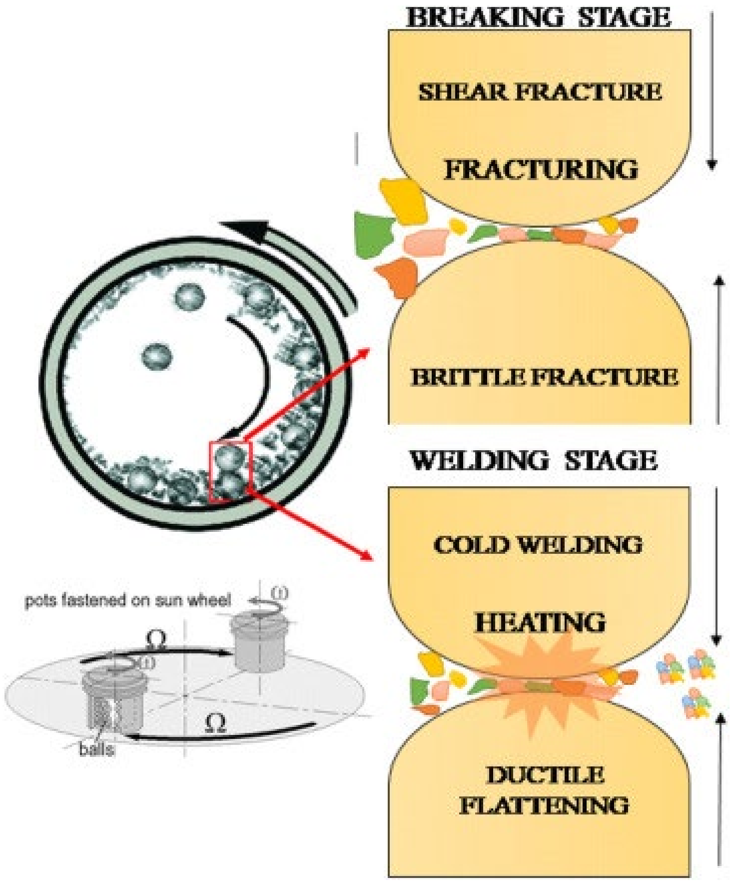

Figure 3 - Breaking and cold welding of particles during the milling process.

Types of Mills Several types of ball mills are used to produce nanomaterials, including attrition mills, horizontal mills, one-dimensional vibratory mills, planetary mills, and three-dimensional vibratory mills. These mills differ in their motion and speed (Figure 4).

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[2] Cold welding is a type of material bonding that occurs without the presence of a molten phase. It happens when there is no contamination or oxide layer between two surfaces.

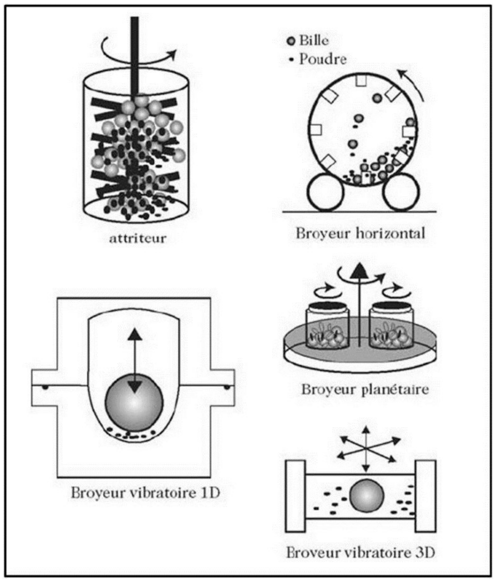

Figure 4 - Types of mills for achieving nanomaterials.

3.1. Role of Speed and Milling Time Speed is one of the most influential factors in determining the shape and size of the particles produced by this method. The motion speed of the balls inside the mill directly affects the energy transferred to the milling particles. As speed increases, the amount of energy transferred to the powder also increases. However, increasing energy does not always mean a reduction in particle size. The change in particle size with ball movement speed follows an initial decreasing trend; as speed increases, particle size decreases. However, after surpassing a critical speed, further increasing the speed leads to larger particle sizes. Thus, the particle size curve has a minimum point (Figure 5). The reason for this size increase at higher speeds is that cold welding of particles becomes dominant over breakage. Additionally, excessive friction-generated heat increases the temperature, leading to sintering and particle growth.

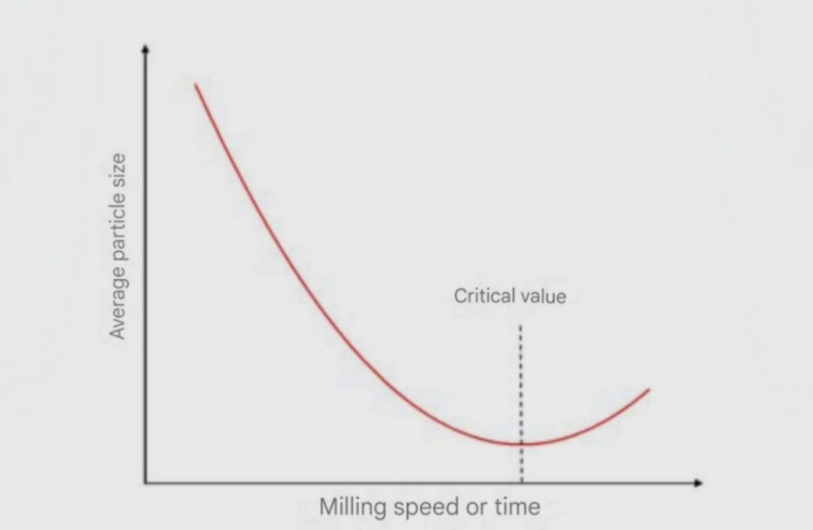

Figure 5 - Curve of average particle size variation as a function of milling speed or time.

The maximum usable speed has two limitations:

Each mill has a maximum speed limit; therefore, the selected milling speed cannot exceed the machine's power.

Beyond a certain speed, centrifugal force dominates gravitational force, causing the balls to stick to the chamber walls, preventing falling and impact of the balls. Thus, in practice, no milling is done.

The effect of milling time on average particle size is similar to the effect of speed. As milling time increases while keeping the speed constant, particle size initially decreases. However, after a critical point, particle size may increase due to the accumulation of heat inside the mill, which leads to sintering.

Properties of Milling Balls

The material, density, size, and mass of milling balls are important factors. Typically, the balls and the mill chamber are made of the same material to minimize wear. The balls are usually made of stainless steel or wear-resistant ceramics. Higher-density balls transfer more energy to the raw materials, resulting in finer particles. Ball diameter also affects the final product's size and shape, with smaller diameters generally leading to finer products. The mass ratio of the initial powder to the milling balls is also important, typically ranging between 1:5 and 1:50.

Types of Additives

As mentioned earlier, friction among the contents inside the mill generates heat and significantly increases temperature. Additives help reduce friction and control temperature. Additionally, processes like sintering and cold welding occur between particles. To control these processes and prevent excessive particle aggregation, additives can be used. Materials such as stearic acid, methanol, and benzene are commonly used to prevent agglomeration and cold welding. It is important to note that after milling, these additives are removed through another process, such as heating.

6. Type of Gas Inside the Chamber Due to the temperature increase during milling, the produced particles may react with the gas inside the chamber. This is a common issue, especially when milling metals. Even a small amount of oxygen, moisture, or nitrogen inside the mill chamber can lead to the formation of metal oxides or nitrides. Therefore, when such sensitivities exist, the chamber must be vacuumed or filled with an inert gas such as argon (Ar). Additionally, ensuring the absence of moisture in this gas is crucial.

Milling methods are beneficial when the primary goal is to achieve a specific particle size. These methods are highly effective for industrial-scale nanoparticle production. The main advantages of milling methods include:

Simple process

Easy control of the process and nanoparticle properties

Capability for large-scale and high-volume production

Ability to produce metallic and non-metallic nanoparticles and advanced alloys

However, these methods also have some limitations and disadvantages:

Time-consuming process (often requiring hours)

Need for additional processes to remove additives

Introduction of impurities from wear of the chamber and balls

Requirement for heat treatment after milling to create crystalline nanoparticles

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# Methods of Characterizing Nanomaterials

- **Scanning Electron Microscope (SEM)**
- **Principles and Components in X-ray Diffraction (XRD)**
- **Analysis and Applications of XRD Diffraction Patterns**

# Principles of Scanning Electron Microscope (SEM)

## 1. Summary

In microscopic methods for observing the nanostructure of nanomaterials, there are three main topics to consider. The first is the source and method of electron production. Electrons are produced using an electron gun, which can work through thermionic emission or field emission. Each method has its own quality and specific features. The second topic is the deflection of the electron beam using electromagnetic lenses. By using a magnetic field, the electron beam can be focused and directed to hit the desired spot on the sample. The third topic is how the electron beam interacts with the sample. This article explains the methods of electron production, focusing and deflecting the electron beam, and finally, the interaction of electrons with the sample.

Keywords: Scanning Electron Microscope, Electron Gun, Electromagnetic Lenses, Electron Interaction Volume

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## 2.Introduction

Today, there are many methods for identifying and analyzing materials, and one of the most well-known is microscopic methods. These methods allow us to obtain magnified images of samples. The Scanning Electron Microscope (SEM), which belongs to the group of electron microscopes, is one of the most famous microscopic techniques. Not only does it provide magnified images, but when equipped with additional tools, it can also be used for chemical analysis and other investigations.

The Scanning Electron Microscope, or SEM for short, is a very popular type of electron microscope that is widely used in nanotechnology today. The first efforts to develop scanning microscopes date back to 1935, when Max Knoll in Germany conducted research on electron optics phenomena and obtained an image of silicon steel. Further development of the SEM was carried out by Professor Charles Oatley and his colleague Gary Stewart at the University of Cambridge in the UK. In 1965, the SEM was commercially introduced to the market for the first time.

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## 3.Components and Functioning of a Scanning Electron Microscope (SEM)

To use a scanning electron microscope, a vacuum environment is required. After placing the sample in the chamber, the air inside the microscope column is removed using pumps to create the necessary vacuum. Once the required vacuum is achieved, an electron beam is produced and focused onto the sample using electromagnetic lenses. Essentially, the electron beam scans the sample to gather information from different points. When the electron beam interacts with the sample, it generates signals that are detected by sensors. These signals are then converted into images or other desired data.

The SEM consists of six main components:

Electron Gun: Produces the electron beam.

Electromagnetic Lenses: Focus and direct the electron beam.

Scanning System: Moves the electron beam across the sample.

Detectors: Capture the signals produced by the sample.

Image Display System: Converts the signals into visible images.

Vacuum System: Maintains the vacuum inside the microscope.

Figure 1 shows the components of an SEM.

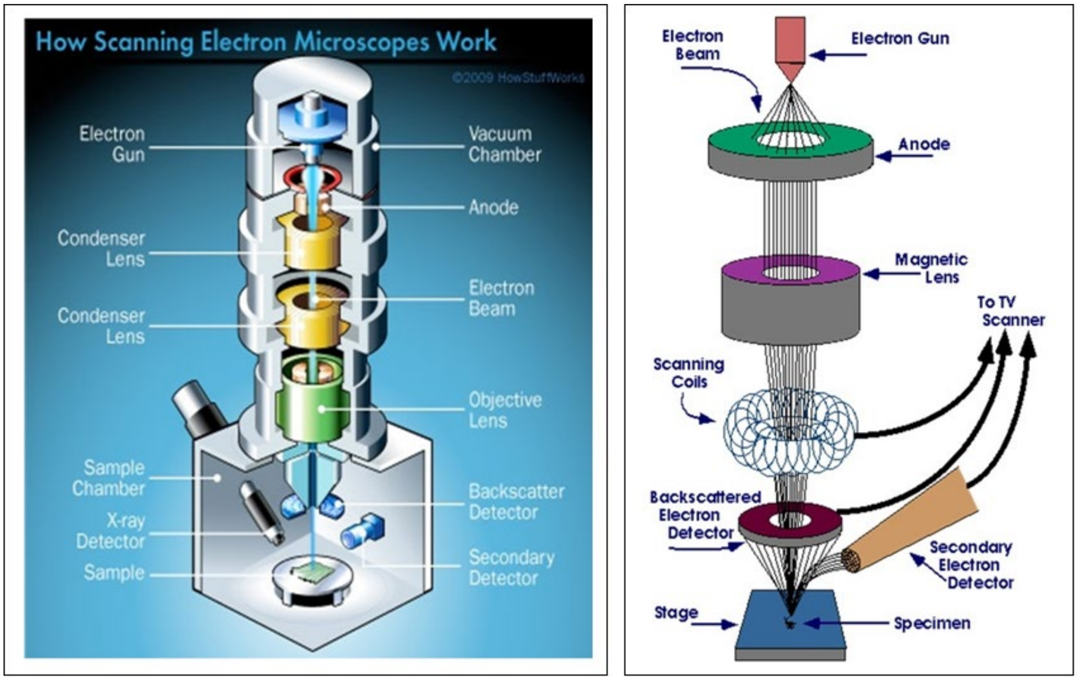

Figure 1 - Schematic of a Scanning Electron Microscope (SEM)

In some microscopic methods for observing nanomaterials, such as SEM (Scanning Electron Microscope) or TEM (Transmission Electron Microscope), it is necessary to produce electrons using an electron gun. As mentioned earlier, these methods use electrons to observe and study nanomaterials. Therefore, the first step in these devices is to produce a suitable electron beam.

There are two main methods for producing electrons:

### 3.1 Thermionic Emission Electron Gun

In this type of electron gun, an electric current is passed through a wire made of tungsten or lanthanum hexaboride ($LaB_6$). As the electric current flows through the wire, the wire heats up due to its electrical resistance. When the wire becomes hot enough and reaches the required work function (the energy needed for electrons to escape), electrons are emitted from the wire. These electrons are then accelerated by the voltage difference between the wire (which acts as the cathode) and a positively charged anode. Finally, the electrons move toward the sample.

Two important characteristics of the metal wires used in thermionic emission are:

Melting Point: The wire must have a high melting point so that it remains solid and does not melt or deform when heated to the required temperature.

Work Function: The work function should not be too high because this would require extremely high temperatures, which could increase costs and potentially damage the structure of the wire.

Work Function of a Metal

The work function of a metal is the minimum energy required to remove an electron from the surface of the metal. In simpler terms, it’s the energy needed for an electron to "escape" from the metal.

### 3.2 Field Emission Gun (FEG)

In this type of electron gun, the surface of a metal (usually a single crystal of tungsten) with a tip sharpened to about 100 nanometers is placed under a very high electric potential. This high potential provides the energy needed to overcome the work function of the metal, allowing electrons to escape from its surface. In this setup, the metal acts as the cathode (negatively charged), and the anode (positively charged) pulls the electrons toward the desired direction. The tip of the metal is extremely sharp in this method.

As shown in Figure 2, after the electrons leave the metal tip, they are guided by the extractor anode into the desired path. The voltage difference between the metal tip (cathode) and the extractor anode is not very high; its main purpose is to direct the electrons. However, after the extractor anode, there is an accelerator anode that applies a much higher voltage. This accelerates the electrons and sends them at high speed toward the sample.

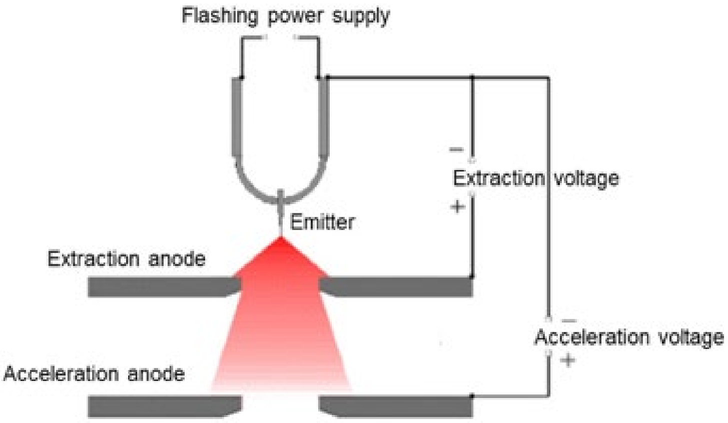

Figure 2 - field-emission electron gun: Electron Emission from the Metal Tip and Guidance by the Extractor Anode, Followed by Acceleration Using the Accelerator Anode

The field emission gun can operate in two modes:

Cold Mode: In this mode, no heat is applied to the sample. Electrons are emitted solely due to the high electric potential applied to the metal tip.

Hot Mode (Schottky Mode): In this mode, heat is applied in addition to the electric potential to help electrons escape from the metal surface. However, the amount of heat used in this mode is much lower compared to the thermionic emission method.

Several key factors are compared when evaluating different types of electron guns:

Operating Temperature: The temperature at which the gun operates.

Current Density: The density of the electron beam produced.

Energy Spread of Electrons: The range of energies of the emitted electrons.

Vacuum Requirement: The level of vacuum needed for operation.

Lifetime: The durability and lifespan of the electron gun.

These factors are summarized in Table 1.

Table 1: Comparison of Electron Guns

| Characteristic | Unit | Thermionic Gun (Tungsten) | Thermionic Gun ($LaB_6$) | Field Emission Gun (Cold Mode) | Field Emission Gun (Hot Mode - Schottky) |
|---|---|---|---|---|---|
| Work Function | Electron Volt (eV) | 4.5 | 2.4 | 4.5 | 3.0 |
| Operating Temperature | Kelvin (K) | 2700 | 1700 | 300 | 1700 |
| Current Density | Ampere per m² (A/m²) | 5 | $10^2$ | $10^6$ | $10^5$ |
| Energy Spread | Electron Volt (eV) | 3 | 1.5 | 0.3 | 0.7 |
| Vacuum Requirement | Pascal (Pa) | $10^{-2}$ | $10^{-4}$ | $10^{-9}$ | $10^{-6}$ |
| Lifetime | Hours | 100 | 1000 | >5000 | >5000 |

As you can see in Table 1, different electron guns have significant differences. The choice of which electron gun to use in a microscope depends on the expected quality, budget, and operating conditions of the microscope. For example: Field Emission Guns (FEGs) are more expensive, but they produce higher-quality images.They have a much higher current density, meaning they produce more electrons in the same amount of time. They also have a narrower energy spread, which means the electrons they produce have almost the same energy. This greatly improves the quality of the final image. However, FEGs require higher vacuum levels, which means more advanced and expensive vacuum equipment is needed. Thermionic Guns also vary depending on the type of metal used (e.g., tungsten or $LaB_6$). Each metal has different requirements and produces different levels of quality.

In Figure 3, images of each type of electron gun are provided for comparison.

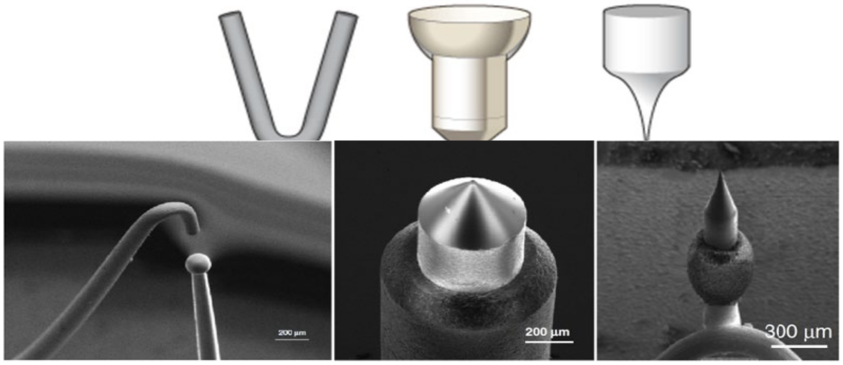

Figure 3 - Images of Common Commercial Filaments

In figure3, you can see examples of commercial filaments used in electron guns. Specifically:

The tungsten hairpin filament is shown, which has melted due to excessive heating. The melted area and the solidified droplet formed after melting are clearly visible.

4. Electromagnetic Lenses

The second component of the SEM is the electromagnetic lenses, which are used to narrow and focus the electron beam. The lenses used in SEM are of two types: condenser and objective lenses, each installed in the system for a specific purpose.

Electromagnetic lenses operate under vacuum conditions. Unlike glass lenses, in these lenses, the incoming beam is not affected by any material medium, and all changes made to it are due to the electromagnetic fields created by the coils. The deflection and focusing of the electrons in electron microscopes are carried out solely by the electromagnetic fields of the coils, and the term "lens" is used merely for ease of understanding. There is no similarity between solid glass lenses with fixed characteristics and coils with fully controllable specifications. The electrons pass through the space between the coils. When an electric current is applied to the coils, a magnetic field is directed toward the center of the electron column in the SEM device. The magnetic field reduces the diameter of the electron beam to achieve the desired magnification and resolution. These processes are shown schematically in Figure 4. A real image of an electromagnetic lens is also provided. The diameter of the electron beam is reduced from an initial value of 100-25 microns (in the electron gun) to a very small diameter of 50 Ångström to 1 micron (depending on the requirement). The strength of the electromagnetic lenses can be adjusted by changing the electric current passing through them. A low electric current reduces the lens strength and increases their focal length, having less effect on reducing the electron beam diameter. The image obtained from such a beam has low noise and appears smooth, but its resolution and magnification are lower. As the electric current passing through the coil increases, the diameter of the electron beam decreases, and the resolution and magnification improve. In addition to the magnetic coils in the optical column, electric coils called astigmators are placed at the end of the optical column. The astigmator's job is to adjust the final shape of the electron beam into a circular shape on the sample. If the electron beam is stretched along a focal axis of a circular shape and perpendicular to the original focal axis, the final image will be blurry. This phenomenon is called astigmatism. The astigmator device creates a magnetic field around the electron beam, shaping it into a perfect circular form on the sample. Typically, there are two types of lenses in the column, each of which can consist of a set of lenses. These lenses are:

Condenser lenses

Objective lenses

The next component of the SEM is the scanning system. After a beam with an appropriate diameter is generated, the scanning phase begins. The operation in this stage is to tilt or deflect the beam emitted from the lenses to enable the surface scanning process. This scanning happens point by point to form a scanning line, and this process continues line by line. In addition to the ability to deflect the beam in two directions, a scanning system must have suitable control capabilities to process the results obtained from the beam scanning. Successful processing of electron beam scanning results is only possible if there is order in the scanning, which is a result of proper control of the scanning system over the beam deflection angles. To tilt the electron beam, two scanning coils are used, each creating magnetic fields perpendicular to the optical axis, deflecting the electron beam to the appropriate angle. The first coil creates the suitable angle with the optical axis, and the second coil brings it back toward the optical axis. This operation is carried out so that the beam can enter the internal area of the objective lens through its entrance aperture (the scanning system is located before the objective lens). In this region, the diameter of the beam is effectively reduced, and as it continues along its path, it is deflected from the optical axis.

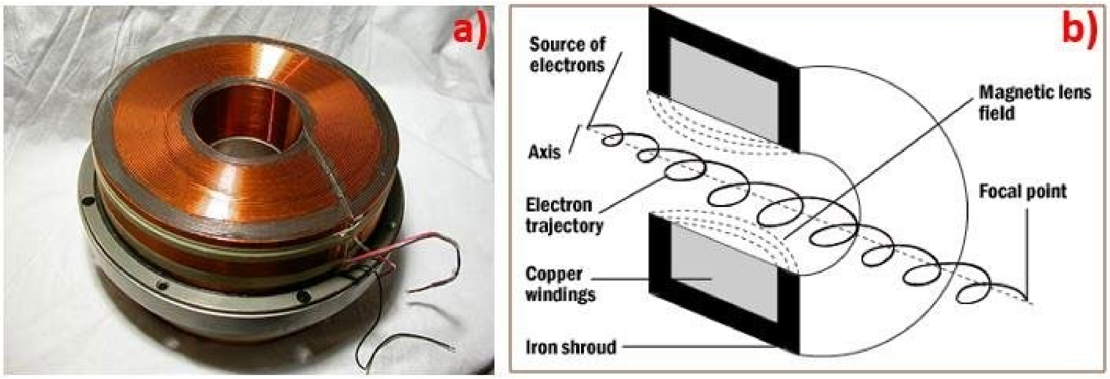

Figure 4 - (a) Schematic of How an Electromagnetic Lens Works, and (b) Real Image of an Electromagnetic Len

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## 5. Electron-Sample Interaction

One of the most important aspects of microscopic methods is understanding how electrons interact with the sample. By studying this interaction and the types of signals or electrons produced, we can understand how images are formed in SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscope) under different operating conditions. Additionally, some of the signals or electrons generated during this interaction are used in non-microscopic methods for characterizing nanomaterials.Figure 5 illustrates how electrons interact with the sample.

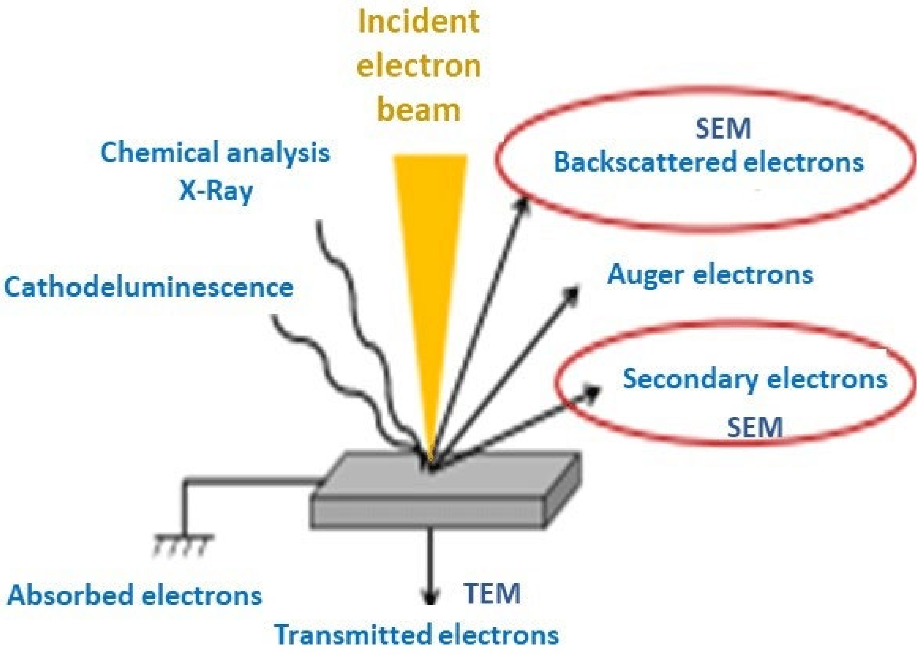

Figure 5 - Electron-Sample Interaction

As shown in Figure 5, when an electron beam hits a sample, two main things can happen:

Transmission of Electrons: For thin samples, electrons can pass through the sample.

Interaction and Reflection: For bulk (thick) samples, electrons interact with the sample, and some may be reflected or produce other signals.

If the sample is bulk (solid), the electrons cannot pass through it. In this case, several different events can occur. One of these is that the electron shot from the electron gun interacts with the nucleus of the sample's atoms and is deflected back. These electrons are called backscattered electrons (BSE), which are the electrons reflected from the electron gun. These electrons are used in SEM in the backscattered mode. Most of the backscattered electrons retain at least 50% of the energy of the incoming electrons (Figure 6). Due to the high energy of backscattered electrons, they can exit the material from a certain depth. Interestingly, the angle change in the elastic scattering of the electron beam when it interacts with the nuclei of heavy atoms is greater than with lighter atoms. Due to the smaller angle change of the electron beam in elastic scattering from nuclei with lower atomic numbers, the probability (or frequency) of backscattered electrons escaping from materials with lower atomic numbers (atoms with lighter nuclei) will be lower. In other words, in atoms with lower atomic numbers, before the electron beam is scattered at angles greater than 90 degrees and has a chance to return, it penetrates deep into the material, and much of it is absorbed. However, in atoms with higher atomic numbers, the possibility of angle changes greater than 90 degrees is higher. In this situation, the amount of backscattered electrons is significantly higher than when the electron beam interacts elastically with a light nucleus. Therefore, the amount of backscattered electrons exiting a material is highly influenced by the atomic number of the material the electron beam enters. More precisely, in the backscattered electron image, phases containing heavy elements appear brighter, and lighter phases appear darker (Figure 7). Figure 5 shows an example of a BSE image from the cross-section of a particle.

If the electron beam interacts with the sample, it can increase the energy of some electrons in the sample. In this case, the outer layer electrons of the sample's atoms can be excited and exit the material's surface. These electrons, belonging to the sample, are called secondary electrons. These electrons are used in SEM to observe the surface of the sample. The energy of secondary electrons is usually around 50 electron volts. However, 90% of these electrons have an energy of less than 15 electron volts (Figure 6). If the depth at which secondary electrons are created is less than 10 nanometers from the sample surface, considering that the surface energy of solids is around 2 to 6 electron volts, their exit as secondary electron beams (SE) from the surface will be feasible. However, if the secondary electrons are generated at a depth greater than 10 nanometers from the surface, they have a very low chance of escaping from the surface due to infinite collisions they may have with electrons and atomic nuclei on their way to the surface. The contrast in images obtained from secondary electrons arises from differences in their energy, number, and paths.

Another situation involves the interaction of the electron from the electron gun with the sample's electrons, leading to the excitation of the sample's atom electrons. In this case, due to the energy transfer from the electron beam to the sample's electrons, an inner orbital electron of the sample is ejected, and the material becomes excited. To return to its initial stability, the material replaces the missing electron in the lower orbit by an electron from a higher orbit. Since higher orbits have higher energy, the energy difference between the two orbits results in the emission of an X-ray with a specific wavelength corresponding to the energy difference between the two atomic orbits. The emitted X-ray is called characteristic X-ray, and its energy is unique for each element. By measuring the energy of the characteristic X-ray, the chemical composition of the sample can be determined. In scanning electron microscopes, an Energy Dispersive X-ray Spectrometer (EDS) is used to measure the energy of the characteristic X-ray spectra emitted from the sample and to identify the elements composing the sample.

Another case involves Auger electrons. These electrons are used for surface analysis in Auger Electron Spectroscopy (AES). This method is also used to determine the elements present on the surface of a sample. Auger electrons that exit the sample's surface are characteristic electrons of the material. By examining their energy, the types of elements present on the sample's surface can be identified. Given the focus of the article on microscopy methods, no further explanation on the AES method is provided.

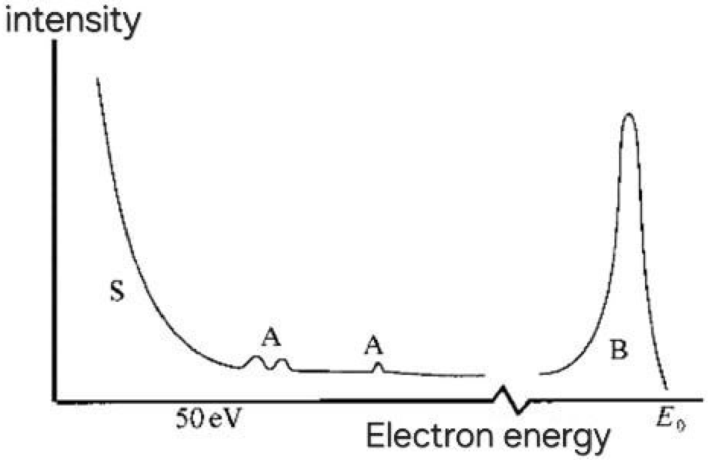

Figure 6 - Electron Spectrum Showing the Relative Abundance of Secondary Electrons (SE), Auger Electrons (A), and Backscattered Electrons (BSE) as a Function of Electron Energy

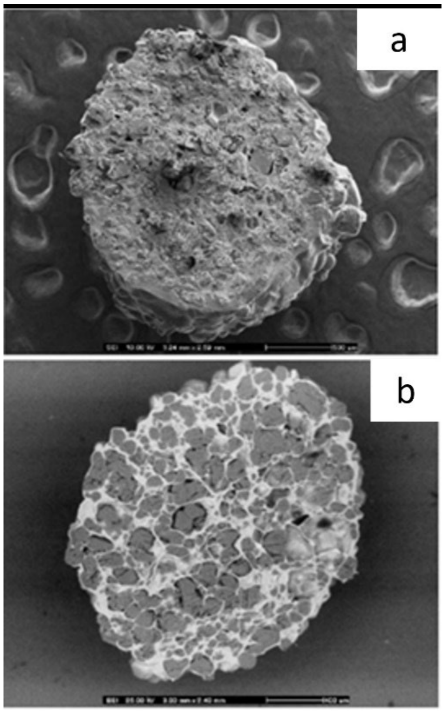

Figure 7 – (a) SE and (b) BSE images of the cross-section of a particle. SE is suitable for topographical and morphological imaging, while BSE is ideal for phase distribution contrast.

5-1 Interaction Volume

Considering scattering mechanisms, it is expected that secondary electrons will exit from a depth of 10 nanometers, and backscattered electrons will exit from a depth of 2 micrometers. These values, of course, vary depending on the conditions of the incoming electron beam and the material. It can be easily imagined that the electron beam hits the surface of the material and affects a certain depth. The terms surface and depth used in the previous sentence clearly indicate the existence of an interaction volume.

Understanding the interaction volume is complex due to the variety and multiplicity of possible collisions. The best way to examine this volume is by using mathematical and statistical principles. Based on calculations made by researchers, it has been shown that the interaction volume is pear-shaped and can be visualized in the region where the beam enters the material. This volume is schematically shown in Figure 8. It should be noted that the depth and extent of the interaction depend on the conditions of the electron beam and the material.

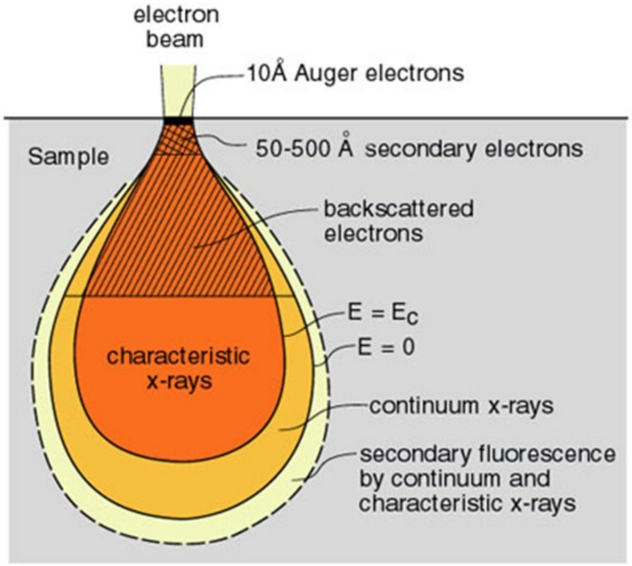

Figure 8 – Depth of penetration of different phenomena resulting from the interaction of the electron beam with the sample.

6- Preparation of SEM Samples

6-1 Cleaning the Sample Any contamination or additional material present on the sample will affect the formation of a proper image. These layers and particles generate unwanted signals and alter the results. Organic solvents like acetone, ethanol, and methanol, or mixtures of them, are used to clean the sample.

6-2 Fixing the Sample Some samples are powdery or brittle (such as soot). If these samples are not securely fixed in place on the sample holder during SEM work, they may cause serious damage to the device and the vacuum system. Sample preparation of powdered materials must be done with great care. Powder sample preparation is typically done using double-sided adhesive tapes. These tapes attach to the sample holder on one side and to the powder on the other. To achieve good dispersion of powders, ultrasonic methods can be used. During SEM operation, samples must be completely fixed, for which dedicated sample holders are used. If the sample cannot be mounted on the holder, conductive vacuum-resistant conductive adhesives are used.

6-3 Establishing Electrical Contact For two reasons, the sample or at least its surface must be electrically conductive: (1) To allow the electron scanning process and enable the movement of electrons in the electron beam across the surface, and (2) To prevent backscattered electrons from accumulating in one area. Thus, the surface of the SEM sample must form an electrical circuit with the sample holder. Therefore, the sample surface must be conductive, and there must be an electrical connection between the sample and the sample holder. If the surface conductivity is not properly established, electrons will accumulate, resulting in the breakdown of the electron beam and the deflection of the electrons. The undesirable outcome of this phenomenon is a white area in the image, where details will not be discernible. This phenomenon is known as electron charging.

To make insulating surfaces conductive, metals such as gold, silver, palladium, platinum, or carbon coatings are typically vapor-deposited onto the surface using physical vapor deposition or sputtering. An example of this device is shown in Figure 9a. The thickness of the coating is very thin and does not affect the surface morphology of the sample. The minimum coating thickness depends on the surface roughness, ranging from 5 angstroms for microscopic surfaces to 100 angstroms for smooth surfaces and 1000 angstroms for rough surfaces. Figure 9b shows a spider coated with gold for SEM analysis.

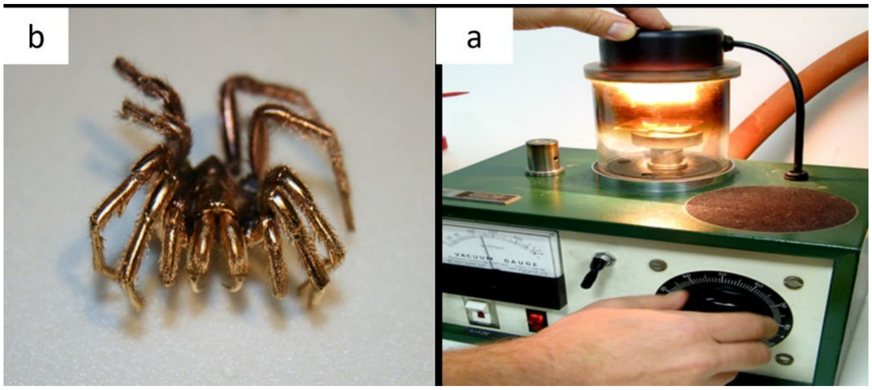

Figure 9 - (a) A schematic of the sputtering device for SEM sample coating. (b) A gold-coated spider prepared for SEM analysis.

7- Vacuum System

In microscopes with large specimen chambers, a rotary vacuum pump and turbo pump are used to create the necessary vacuum. In high-resolution microscopes, turbo vacuum pumps cannot be used due to vibrations they cause in the microscope column. Therefore, in these microscopes, diffusion vacuum pumps replace turbo pumps. In SEMs equipped with LaB6 and FEG electron guns, other vacuum pumps, such as ion pumps, are used to separately evacuate the column and electron gun.

8- Detectors

In scanning electron microscopes, E-T detectors are used to detect secondary electrons. This detector can also be used for backscattered electrons. For detecting backscattered electrons, a variety of detectors, such as scintillation detectors, flat-channel detectors, and solid-state diode detectors, can be used. Due to the complexity of the mechanisms of these detectors, a detailed discussion about their functioning is omitted here.

9- Summary and Conclusion

SEM is a useful tool for generating three-dimensional, high-magnification images of a sample's surface. In SEM, images are formed through interactions between electrons generated by the electron gun and the surface of the sample. The electron gun's function is to produce a stable electron beam for interaction with the sample's surface. Electron guns are classified into thermionic and field emission types. In the first type, as the temperature of the electron gun increases, electrons are emitted from the tungsten or lanthanum hexaboride filament. In the second type, by applying voltage to a tungsten piece, the electrons are emitted through the tunneling effect, and the electron current is formed. The electrons then pass through magnetic coils. By changing the electrical current through the magnetic coils, the magnetic field applied to the electrons changes, reducing the diameter of the electron beam, changing their direction, and scanning the sample's surface. The electrons interact with the sample's surface, causing interactions with the electrons and atoms of the sample. The two main types of electrons used in SEM imaging are backscattered electrons (BSE) and secondary electrons (SE). BSEs are electrons that have interacted with the material and are ejected from the sample's surface due to collisions with atomic nuclei. They have high energy and can escape from deep within the material. On the other hand, if the electron beam interacts with the sample's electrons, causing them to be ejected, these ejected electrons are called secondary electrons. Secondary electrons provide valuable information about the surface topography. Finally, backscattered and secondary electrons are detected by detectors and used to form the final image.

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# Principles and Components of X-Ray Diffraction (XRD)

## Abstract

XRD (X-Ray Diffraction) is a well-established and widely used technique for studying the properties of crystals. In this method, X-rays are diffracted by the sample to analyze its characteristics. XRD is useful for determining various structural properties of crystals, such as lattice constants, crystal geometry, qualitative identification of unknown materials, phase determination, crystal size, single-crystal orientation, stress, strain, lattice defects, and more. In this article, we will first explore the fundamentals of XRD and then discuss its components.

Keywords: X-ray diffraction, Bragg's law, interplanar spacing

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## 1. Introduction

In X-ray diffraction (XRD), when X-rays interact with a crystal, it is observed that the intensity of the reflected X-rays (which are scattered elastically by the atoms, meaning their wavelength remains unchanged) reaches a maximum at specific angles. At other angles, the intensity of the scattered X-rays is negligible. This behavior of X-rays is what we refer to as diffraction.

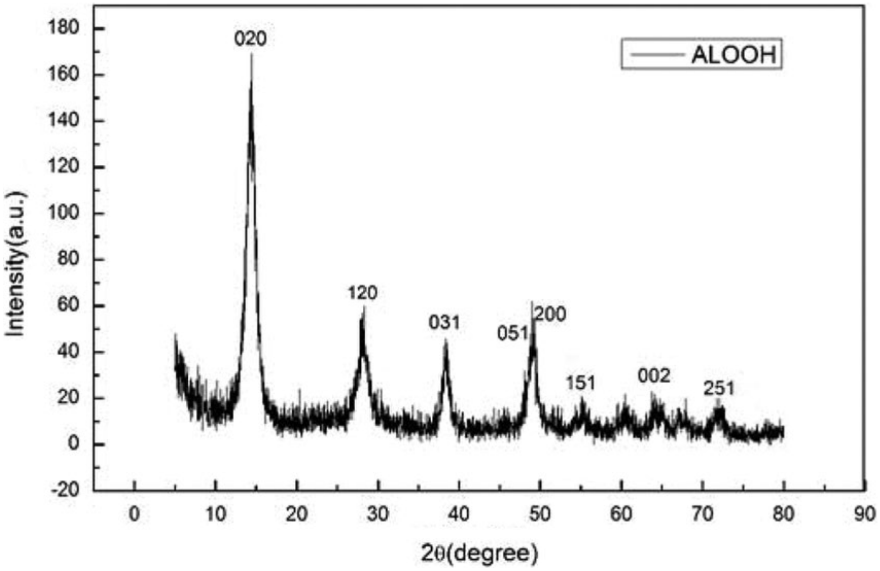


Figure 1 - Example of Data Recorded from Powder Diffraction

Figure 1 shows a graph of the intensity of X-ray reflection from a sample as a function of the angle. This is related to the wave nature of X-rays and the periodic arrangement of the crystal. As seen in the figure, for a crystalline sample, there are multiple peaks at different angles and with varying intensities. Each of these peaks corresponds to a specific crystall plane of the sample. As will be explained later, the angle of each peak depends on the distance between the planes, and the intensity of the peak is related to the arrangement of atoms in the planes.

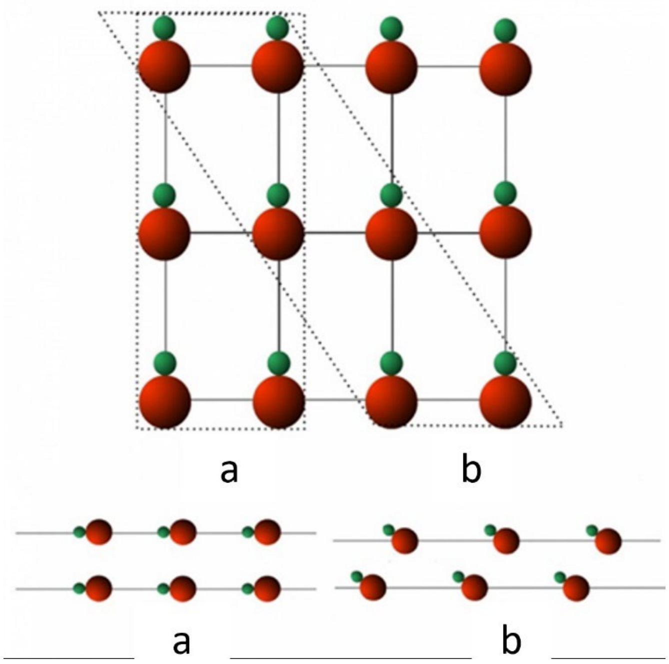


Figure 2 - Different interplanar spacing and the different arrangement of atoms in two planes of a crystal.

Figure 2 shows the difference between two specific planes in a crystal in terms of the interplanar distance and the atomic arrangement in each plane. Two planes, A and B, are cut from the sample and displayed horizontally.

1-1- Interaction of X-rays with Atoms

When X-rays collide with an atom or molecule, they cause the electrons of the atom or molecule to excite and oscillate. As we know, accelerated charged particles emit electromagnetic waves. Thus, these oscillations lead to the emission of new waves. If the frequency of the reflected light is the same as the frequency of the initial light, this phenomenon is called Rayleigh scattering.

From the quantum perspective, electromagnetic waves are made up of photons. The energy of a photon, which is related to the electromagnetic wave, depends on the frequency according to the following equation:

$$E=h\cdot v \qquad \text{equation 1}$$

In this equation, the frequency of the wave and Planck's constant are involved. Since the frequency of light does not change in Rayleigh scattering, according to this equation, the energy of the photons also does not change. The working principle of XRD is based on Rayleigh scattering from the planes of a crystal.

In addition to Rayleigh scattering, atoms also exhibit fluorescence radiation. In fluorescence, an atom absorbs a photon and emits a photon with a lower frequency (longer wavelength). Although fluorescence radiation also exists in X-ray diffraction and provides information about the sample, it is removed using optical filters. Fluorescence radiation is the basis of the XRF technique.

## 2- XRD Principles

The information obtained from X-ray diffraction of a crystal includes the angle of the maximum peak, the relative intensity of the peaks, and the width of each peak. This information forms the basis of XRD and, using this data, there are many applications for XRD. In the following, these details will be discussed.

### 1-2- Bragg's Law

X-ray diffraction was first used by William Henry Bragg and his son William Lawrence Bragg to study the structural properties of crystals. They were awarded the Nobel Prize in Physics in 1915 for this discovery.

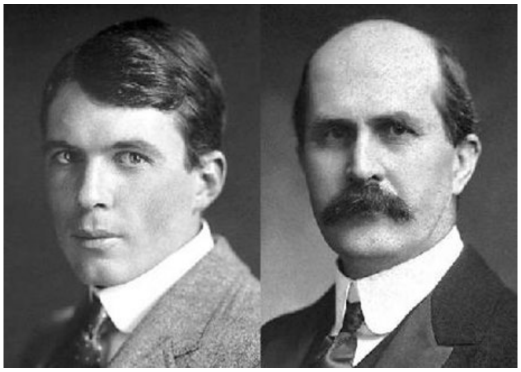


Figure 3 - William Henry Bragg (right) and Lawrence Henry Bragg (left).

As shown in Figure 4, X-rays hit the crystal planes and are reflected. The X-ray beam 1 from the upper surface and X-ray beam 2 from the lower surface are reflected, and they have different paths, which depend on the radiation angle and the distance between the two planes. This difference is determined by the following formula:

$$\Delta x = 2d\sin(\theta)$$

equation 2

Δx=path difference,d=distance between planes,θ=angle between the ray and the plane

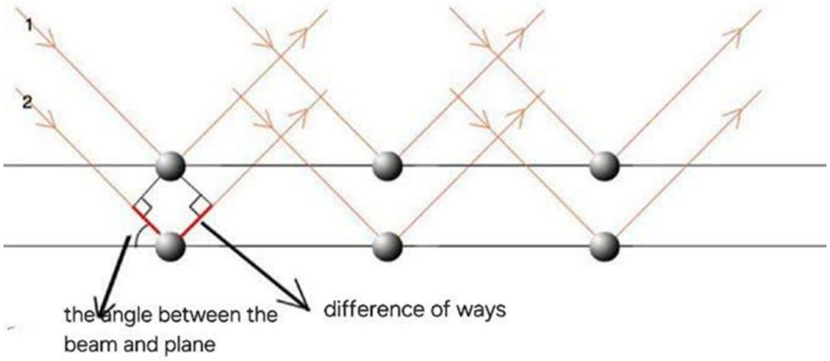


Figure 4 shows X-ray diffraction by a regular array of atoms. The red section represents the path difference between the two rays.

This results in a phase difference between the two rays, which is given by the following formula:

$$\Delta\phi = \frac{2\pi}{\lambda}\Delta x$$ equation3

ΔΦ=phase difference,λ=wavelength of the ray,Δx=path difference

Now, if this phase difference is an integer multiple of 2π, the two rays will combine constructively. In fact, any optical device will average the two rays (1 and 2) as if they were a single ray, even though they have different path lengths. This constructive interference directly corresponds to the maximum intensity of the reflected X-rays in Figure 1. This interference pattern repeats along the entire length of the two planes, and this pattern is repeated between lower planes as well. This condition can be summarized as follows:

$n \cdot \lambda = 2d \cdot \sin(\theta)$ equation4

This is Bragg’s Law, which explains the maxima in Figure 1. For each crystal, there can be multiple planes. These planes differ in their interplanar distances. Bragg’s condition occurs for each plane at a specific angle (assuming the wavelength of X-rays is constant). In Figure 1, each maximum corresponds to a specific plane. In crystallography, planes are labeled with Miller indices. In Figure 1, the Miller indices for each maximum are written above them.

2-2- Differences in Intensity of Maxima

As previously mentioned, the planes differ not only in the Bragg angle (interplanar distance) but also in the relative intensity of the reflected X-rays. The intensity of the diffracted X-rays depends on the type, number, and distribution of atoms in the planes of the sample. To understand how the atomic arrangement affects the intensity of the reflected X-rays, consider the following figure:

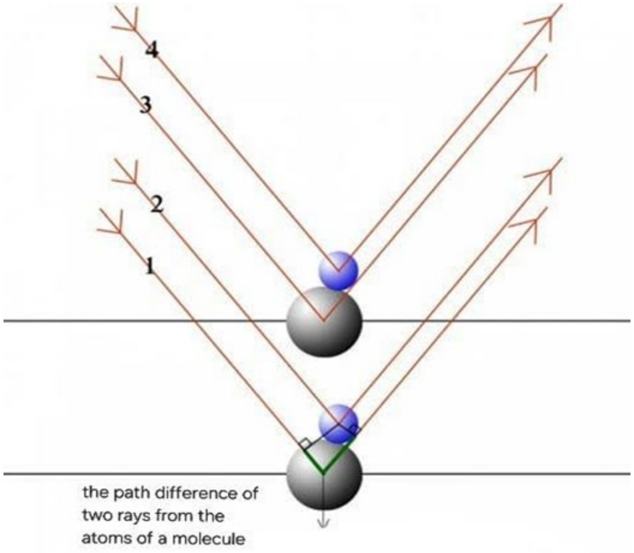


Figure 5 shows the impact of atomic arrangement on the intensity of reflected X-rays. The green section represents the path difference between X-rays 1 and 2.

Suppose in Figure 5, rays 1 and 3, as well as rays 2 and 4, satisfy the Bragg condition. The path difference for these rays is an integer multiple of the wavelength, and they combine constructively. The condition is not the same for rays 1 and 2, as well as 3 and 4. These rays have a path difference (green section in Figure 5) that is not necessarily an integer multiple of the wavelength, so they do not combine constructively. This leads to a decrease in the intensity of the reflected X-rays. Depending on the atomic arrangement in the planes, this effect varies for each plane and causes the maxima intensities to differ from one another. From the Bragg angle and relative intensity of the maxima, a lot of structural information can be extracted.

### 3-2- Peak Widths

The width of each peak also provides information about the sample. There are many factors that affect peak broadening, such as experimental equipment, microstrain, the size of crystalline domains, thermal effects, and the heterogeneity of the solid solution. For more information on how these factors influence the XRD results, refer to the article "X-ray Diffraction: Techniques and Applications."

## 3- Components of the XRD Instrument

The configuration and components of an XRD machine vary depending on the application. In general, the components of an XRD device include the X-ray source, the sample, the detector, and X-ray optics (X-ray filters).

### 1-3- X-ray Source

In XRD, a monochromatic X-ray source is usually needed, and in typical methods, an X-ray tube is used. The X-ray tube is shown in the figure below

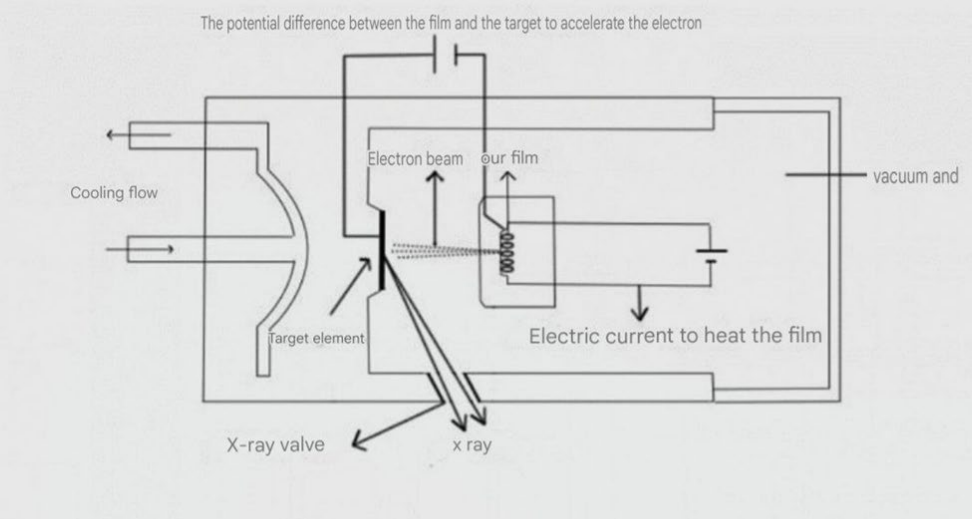


Figure 6 X-ray tube.

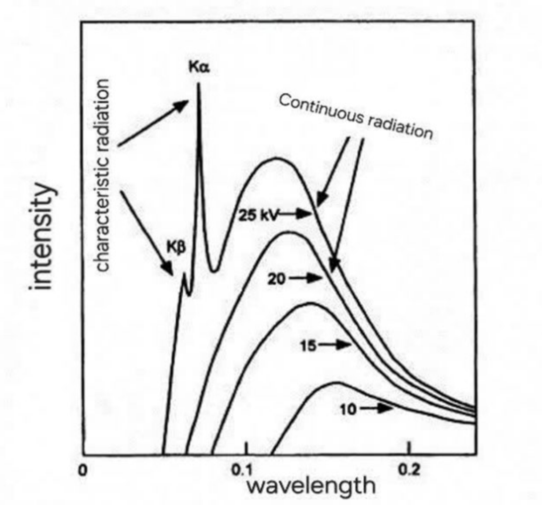


Figure 7 the radiation intensity spectrum of a target bombarded by electron beams as a function of wavelength.

X-rays are produced when high-energy electrons, accelerated in an electric potential, collide with a specific target. In practice, when a specific target is bombarded by high-energy electrons, the target emits a specific spectrum of electromagnetic waves, as shown in the figure below. This spectrum has two main parts: a smooth curve and peaks. The spectrum is continuous and smooth when bombarded by low-energy electrons, as shown in the following three graphs, which represent bombardment with electron energies of 10, 15, and 20 kilo-electron volts, respectively.

When the energy of the electron beam increases, peaks appear in the graph, as shown in the top graph of Figure 7, where bombardment is done with electron energy of 25 kilo-electron volts. These peaks occur at specific wavelengths for each element and are characteristic of the target element. These peaks arise due to electron transitions between the inner layers of the atom. For this transition to happen, a vacancy must first be created in an inner layer, which is done by bombarding the atom with high-energy electrons. This vacancy can be filled by an electron transition from higher layers with more energy.

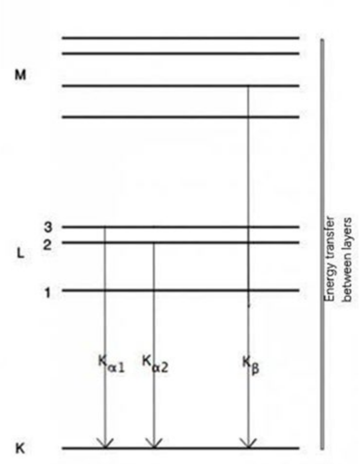
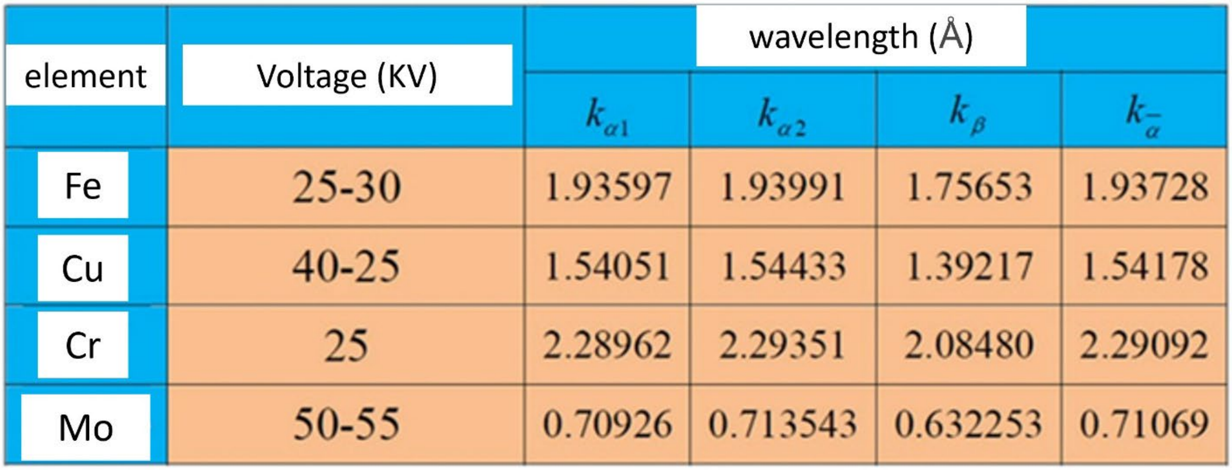


Figure 8 the energy levels of an atom and the associated transitions.

In Figure 8, three radiations to the empty K-layer are shown. Kα radiation results from an electron transition from the L-layer to the K-layer, and Kβ radiation results from an electron transition from the M-layer to the K-layer. The Kα radiation consists of two very close wavelengths (difference of a few ten-thousandths of an angstrom), resulting from transitions from sublevels in the L-layer to the K-layer. In XRD, Kα radiation, which is an average of Kα1 and Kα2, is used. To obtain a monochromatic spectrum of Kα radiation, Kβ radiation is removed using special filters. The table below shows the wavelengths of X-ray radiation and the required voltage for different elements.

Table 1 the characteristic X-ray wavelengths.



| element | Voltage (KV) | wavelength (Å) | | | |
|---|---|---|---|---|---|
| | | $k_{\alpha1}$ | $k_{\alpha2}$ | $k_{\beta}$ | $k_{\bar{\alpha}}$ |
| Fe | 25-30 | 1.93597 | 1.93991 | 1.75653 | 1.93728 |
| Cu | 40-25 | 1.54051 | 1.54433 | 1.39217 | 1.54178 |
| Cr | 25 | 2.28962 | 2.29351 | 2.08480 | 2.29092 |
| Mo | 50-55 | 0.70926 | 0.713543 | 0.632253 | 0.71069 |

Since the Kα wavelength varies for different targets, the voltage must be chosen such that the accelerated electrons have enough energy to generate the Kα radiation in the target element.

It is important to note that, in this method, about 1% of the energy of the electron beam is converted into X-ray radiation, while the rest of the energy heats up the target element. Therefore, the target element must be continuously cooled. In high-resolution XRD (HRXRD), the Kα2 radiation is also removed from Kα1, improving resolution. The HRXRD technique is widely used to examine thin films with epitaxial growth.

Another method for generating X-rays is using synchrotron radiation. A synchrotron is a type of particle accelerator that speeds up particles to very high speeds (close to the speed of light). Through its magnets, a synchrotron forces charged particles into a circular path, and an electric field within this closed path accelerates them. As we know, charged particles that are accelerating emit electromagnetic waves. The phenomenon of synchrotron radiation happens because of the accelerating movement of charged particles in the synchrotron. Using a synchrotron X-ray source allows for much higher X-ray intensity compared to traditional X-ray tubes. Additionally, synchrotron radiation makes it easier to adjust the wavelength of the light.

### 2-3- Sample

In X-ray diffraction (XRD), a sample can be in the form of a thin layer, sheet, or powder. Generally, XRD does not require complicated or hard preparation. Usually, a powdered sample is used in XRD. A powder sample consists of layers of the material that are randomly distributed, which increases the speed of the sample examination. The particles in the powder should be smaller than 50 micrometers. Samples with smaller particles cause broader peaks in the diffraction pattern, which is the basis for certain techniques in XRD. In samples with larger particles, specific orientations of the layers are highlighted, which also leads to specific techniques in XRD. It should be noted that the highlighting of specific orientations increases the intensity of the diffracted X-rays for some planes compared to random orientations.

### 3-3- Optics

In XRD, "optics" refers to the use of optical devices to control and improve the X-rays. Some of these devices are placed between the X-ray source and the sample, aiming to remove unwanted frequencies from the X-rays, produce monochromatic (single-frequency) rays, align the rays, and control their divergence. The second set of optical devices is placed between the sample and the detector. The main goal of these devices is to eliminate background radiation from the diffracted X-rays. In newer methods, a graphite crystal is used between the sample and the detector. This crystal removes unwanted frequencies from both the X-ray source and the background radiation produced by diffraction. Since this crystal replaces optical devices between the source and the sample, as well as between the sample and the detector, it helps reduce costs.

### 4-3- Detector

The detector plays a significant role in the quality of the recorded data. The most common type of detector is the proportional detector. In this type, the X-rays enter a glass chamber and ionize the gas atoms inside. The electrons generated from the ionization of these atoms move towards a conductor connected to a potential difference and create a current. The intensity of this current represents the intensity of the X-rays. Additionally, in XRD, a charge-coupled device (CCD) detector is used, which has higher efficiency, but due to its higher cost compared to the proportional detector, it is used less frequently.

## 4- Advantages and Disadvantages of XRD

XRD is a low-cost and widely used technique because of the simple physical principles it relies on. The data obtained from X-ray diffraction, including the angle of maximum intensity of the diffracted X-rays, the intensity of the diffracted X-rays at each angle, and the width of each maximum, are related to a wide range of properties and quantities of crystals. This makes XRD widely applicable. One of the advantages of XRD is that it does not require a vacuum, which reduces construction costs, making it more accessible than electron-based techniques. XRD is also a non-contact, non-destructive technique, which does not require complicated or difficult sample preparation.

However, some disadvantages of XRD include its lower resolution, limited separation capabilities, and the weaker intensity of diffracted X-rays compared to electron diffraction. The intensity of diffracted electron rays is about 10^8 times greater than diffracted X-rays in XRD. As a result, larger samples are needed for XRD, and the information obtained is averaged. The intensity of diffracted X-rays in XRD also depends on the atomic number. For lighter elements, the intensity is lower, which makes it more challenging for XRD. For example, when a sample consists of a heavy atom and a light atom, XRD has difficulty distinguishing between them. Neutron diffraction is a technique used to overcome this issue. Although XRD works better for heavier elements, it can be used for compounds containing any type of element.

## 5- Refrences

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# Analysis and Application of X-ray Diffraction Patterns

## Abstract

X-ray diffraction (XRD) is a very effective and non-destructive method for characterizing crystalline materials. This method provides information about structure, phase, crystal orientation (texture), and other structural components such as grain size, crystallite size, crystallinity, strain, and crystal defects. In general, the X-ray diffraction pattern is like a fingerprint of the atomic arrangement in a specific material. This paper briefly introduces X-ray diffraction and then goes into detail on analyzing X-ray diffraction patterns for single-crystal and polycrystalline materials, and the information that can be obtained from each pattern.

Keywords: X-ray diffraction pattern, grain size, particle size, Williamson-Hall model

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## 1. Introduction

Many modern characterization methods used in chemistry and physics provide little information about the presence and connection of specific chemical groups and special aspects of a material's physical and chemical properties. In contrast, crystallography is the only method that can provide detailed and accurate information about the approximate positions and movements of atoms in a solid state. Since the physical and chemical properties of a material depend on its structure, obtaining information about these properties is crucial. Therefore, crystallography is considered one of the most valuable characterization methods in modern sciences. X-ray diffraction is one of the most commonly used techniques in crystallography. This method was first used in 1912 by Von Laue. Through multiple studies, he concluded that by studying diffraction behavior, one can understand the crystalline structure of a material. This article focuses on the comprehensive discussion of analyzing X-ray diffraction patterns and explaining what information can be obtained from these patterns.

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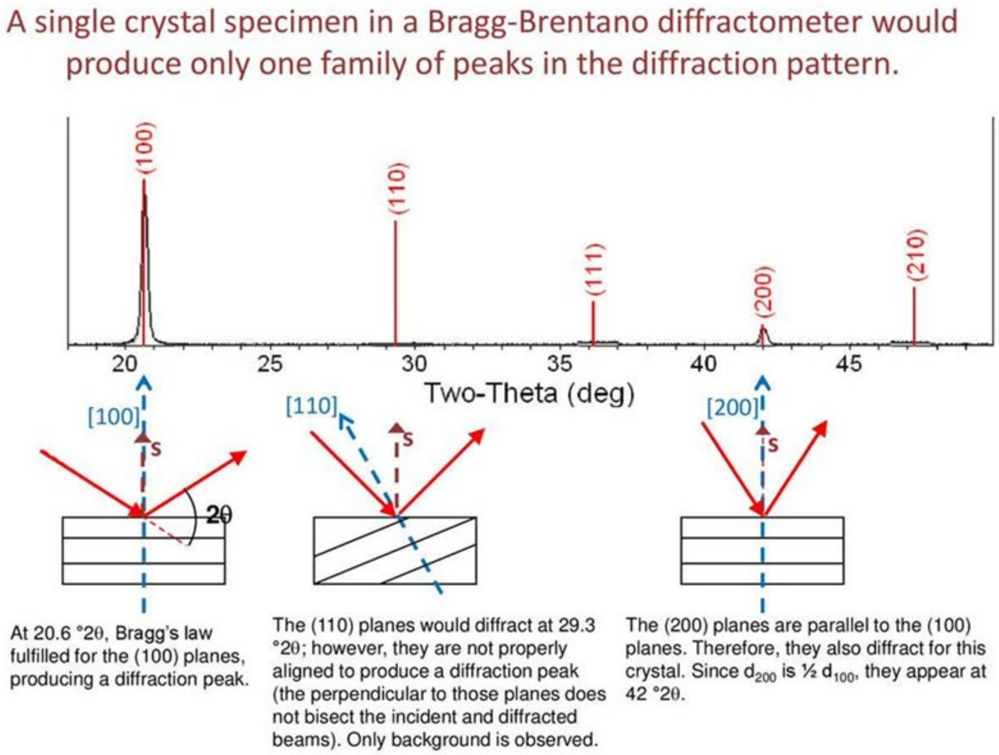
## 2. Types of Information from XRD Patterns

### 2.1. Single Crystals

Single crystals are not limited to research applications, and their use in many electrical and magnetic devices is growing rapidly. Much of humanity's findings regarding polycrystalline materials have been achieved through the study of single crystals, as such studies allow the measurement of the properties of each component of a composite material. Single crystals are anisotropic, meaning that their properties vary depending on the direction. Therefore, studying their properties and behavior requires sufficient information about the direction of the single crystal under investigation. A single crystal sample in a Bragg diffractometer can only create a single set of peaks in the diffraction pattern. Figure 1 illustrates how the alignment of the crystal relative to the incident beam affects the peaks that appear in the X-ray diffraction pattern of a single crystal.



A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since $d_{200}$ is ½ $d_{100}$, they appear at 42 °2θ.

Figure 1: A schematic showing the effect of the crystal orientation on the diffraction peaks observed in the X-ray diffraction pattern of a single crystal.

### 2.1.1. Orientation of Single Crystals

There are three main methods for determining the orientation of single crystals: (1) Back-reflection Laue, (2) Transmission Laue, and (3) Diffractometer. Since the analysis of these methods is not performed using X-ray diffraction patterns, they are not discussed in detail here. For more information on determining the orientation of single crystals, you can refer to the "Elements of X-Ray Diffraction : Cullity, B. D., Stock, S. R." book (refer to the references section).

## 2.2. Polycrystalline Materials

In the previous section, we discussed the orientation of single crystals. Metals and alloys produced under normal conditions are polycrystalline, consisting of a large number of microscopic crystals. Next, we will discuss the types of information that can be obtained from X-ray diffraction patterns of polycrystalline materials.

### 2.2.1. Grain Size

The size of the grains in a polycrystalline metal or alloy significantly affects its properties. Specifically, reducing the grain size increases the strength and hardness. The dependence of a material's properties on grain size has made grain size measurement a crucial factor in many metal-forming processes. The most accurate method for calculating grain size in the range of 10–100 micrometers is through microscopic studies, where grain size is calculated using the number of grains per unit area of a polished cross-section.

In addition to microscopic methods, there are other techniques used to study material properties and measure particle size and crystalline structure. One of these methods is pinhole photography. This technique is especially useful for determining particle size distribution and measuring structural features of different materials. In this method, light passes through a very small hole (pinhole) and is recorded on a light-sensitive surface, such as a film or digital plate. The resulting image is used as a tool to analyze structural characteristics, including particle size distribution. This technique is commonly applied in specific areas such as examining the textures of materials, the structure of nanoparticles, and diffraction processes in crystalline materials. However, this method is not limited to measuring particle size in crystalline materials and can be used in combination with other techniques, like X-ray diffraction (XRD), for more detailed analysis.

A further explanation of these methods is beyond the scope of this article.

2-2-2. Particle Size (Crystallite) and Microstrain

When the size of individual crystals is smaller than 0.1 micrometers, the term "particle size" is typically used. The crystallite size can be calculated using the following equation (Equation 1):

$$D = \frac{0.9\lambda}{t\cos\theta}$$

Equation 1

In this equation, D represents the broadening of the diffraction line at half its maximum intensity, t is the crystallite diameter, and λ is the wavelength. The width of all diffraction lines can be measured if the crystallite size is greater than 1000 angstroms. This equation is also known as the Scherrer equation. In general, according to this relationship, broadening of the diffraction peak indicates a reduction in the size of particles or crystallites. Figure 2 shows X-ray diffraction patterns of cerium oxide in two forms: bulk and nanoparticle. It is clearly seen that as the particle size decreases, the peak broadens.

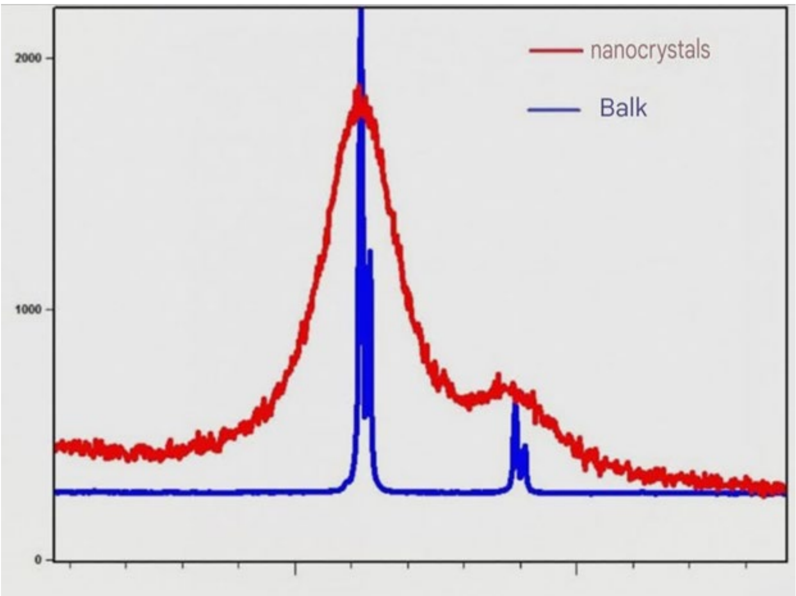


Figure 2: X-ray diffraction patterns of cerium oxide in bulk and nanoparticle forms.

In addition to the Scherrer equation, the Williamson-Hall equation is also used to calculate the particle size (crystallites). Before addressing the Williamson-Hall equation, it should be noted that peak broadening is not solely an indication of reduced particle size; there are other factors that affect peak width. Increased stacking faults, microstrain, formation of inhomogeneous phases in solid solutions with alloys, and the presence of other defects in the crystalline structure also contribute to peak broadening. Additionally, it should be considered that the use of different X-ray diffraction instruments can lead to changes in peak width. Figure 3 shows the diffraction patterns of the same material characterized by two different devices.

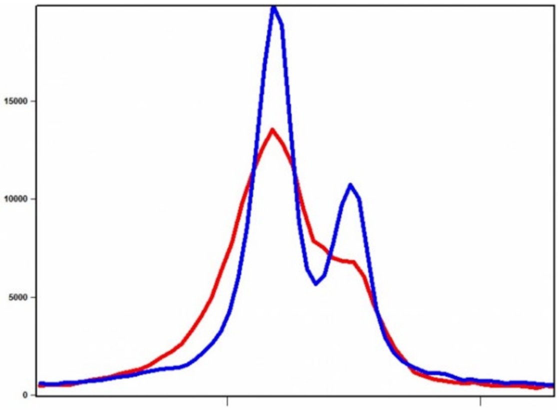


Figure 3: X-ray diffraction patterns of the same material characterized by two different devices.

The main advantage of the Williamson-Hall method over the Scherrer method is that, in addition to the effect of particle size, it also accounts for the effect of lattice strain in the calculations for measuring particle size. According to Williamson-Hall theory, the peak width at half maximum intensity is a function of both particle size and lattice strains.

Williamson-Hall Relationship: $$\beta = \beta_S + \beta_D = \frac{1}{D} + 2\varepsilon K$$

In this relation, $\beta_S$ and $\beta_D$ represent the broadening of the peak due to lattice strain and particle size, respectively. In this equation, $\varepsilon$ represents lattice strain, D is the particle size, and K is a constant.

The main reason for the broadening of peaks due to microstrain is small changes in the lattice parameters caused by defects, impurities, and changes in the crystalline structure. X-ray diffraction patterns of solid solutions typically show broadening due to microstrain. However, calculating the exact amount of broadening due to microstrain is a challenging task. The effect of uniform and non-uniform strains on the X-ray reflection angle is shown in Figure 4.

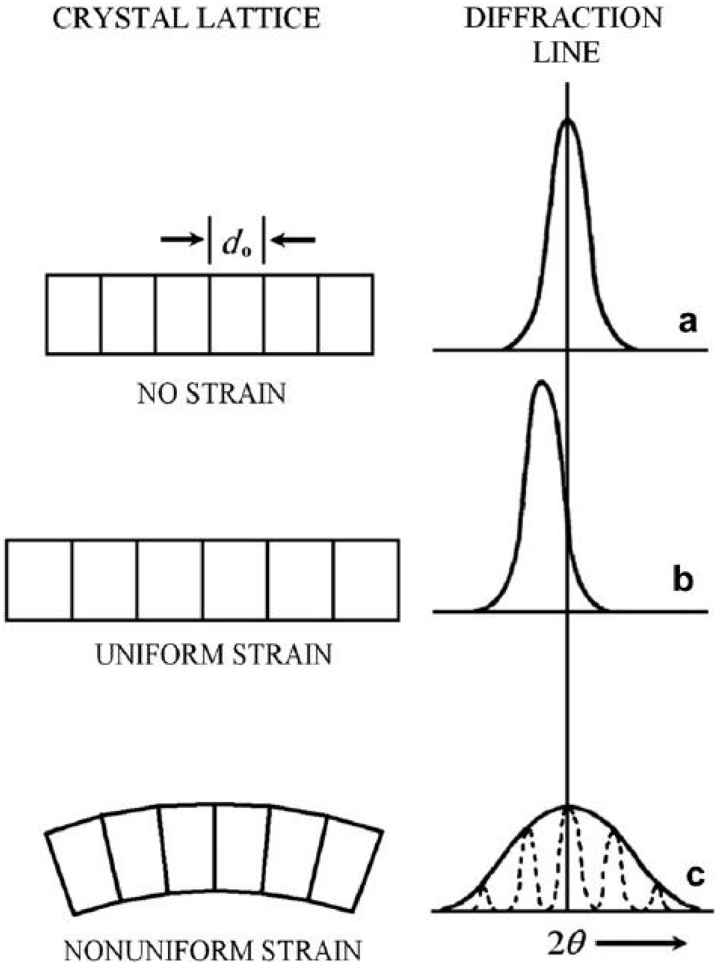


Figure 4: The effect of lattice strain on the position and width of the diffraction line.

Part of a strain-free grain and a set of intersecting reflection planes, all present at the equilibrium distance (d0), is shown on the left side of part (a) of Figure 4. The diffraction line from these planes appears on the right side of part (a) of Figure 4. If a uniform tensile strain is applied along the angles perpendicular to the reflection planes, their distance becomes greater than d0, and the corresponding diffraction line shifts to smaller angles (part (b) of Figure 4). If the grain bends and the strain is non-uniform—meaning tensile strain (greater than d0) at the upper sections and compressive strain (less than or equal to d0) at the lower sections—the diffraction line will appear as shown in part (c). The relationship between the broadening of the diffraction line and non-uniform strain can be obtained by integrating Bragg's law which is beyond the scope of this article.

## 3. Conclusion

X-ray diffraction is a very effective and non-destructive method for characterizing crystalline materials, providing valuable information. This article introduced and reviewed X-ray diffraction and also explained the types of information that can be derived from the X-ray diffraction patterns of single-crystal and polycrystalline materials. It was discussed that much of human knowledge related to polycrystalline materials has been gained through studies on single crystals, as such studies allow for the measurement of properties of each individual component of a composite material. It was emphasized that a single-crystal sample in a Bragg diffractometer can only generate one family of peaks in the diffraction pattern. It was noted that an X-ray diffraction photograph can contain quantitative information about grain size in polycrystalline materials. The effect of grain size on the diffraction image was discussed in detail. It was mentioned that when the size of individual crystals is smaller than 0.1 micrometers, the term particle size is typically used. Two main and widely used methods for determining particle size in polycrystalline materials—Scherrer's method and Williamson-Hall method—were thoroughly studied. It was noted that the main advantage of the Williamson-Hall method over the Scherrer method is that it includes the effect of lattice strain in addition to particle size in the calculations for measuring particle size. In general, peak broadening is indicative of a decrease in particle or crystallite size.

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## Applications of Nanotechnology

- Methods of Wastewater Treatment (1 and 2)
- Targeted Drug Delivery

# Methods of Wastewater Treatment (1)

## Abstract

Today, the lack of sufficient clean water has become one of the most important challenges for human societies. On the other hand, population growth and the expansion of industries have disrupted the natural water purification cycles. Therefore, the use of unnatural methods to treat wastewater is essential to protect human health and the environment. There are various methods for wastewater treatment, ranging from traditional methods and treatment plants to modern purification techniques. The old wastewater treatment methods have many limitations, which is why new methods have gained special attention. Nanotechnology, using the unique properties of nanostructures, offers efficient solutions in this area. This article examines different types of wastewater, old treatment methods, and the use of photocatalytic nanomaterials for wastewater treatment.

Keywords: wastewater treatment, treatment plants, photocatalysts, organic pollutants, inorganic pollutants, heavy metals

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## Introduction

About two-thirds of the Earth's surface is covered with water. However, for many years, humanity has been facing the problem of a lack of clean water. Nature automatically purifies water and provides clean water to humans; however, the continuous growth of the population and the expansion of industries have disrupted the natural water purification cycle, leading to a shortage of clean water. Approximately 90% of diseases in developing countries are caused by polluted water. Therefore, wastewater treatment is a very important issue for preserving the environment and human health. Traditional wastewater treatment methods require significant investment, a large amount of energy, and extensive infrastructure. For this reason, finding low-cost, high-efficiency technologies is of great importance. Nanotechnology offers effective solutions to address these challenges. This technology involves using materials at the nanoscale to solve problems. Nanomaterials have high surface energy, large specific surface area, and surface-dependent properties. This article will examine different types of wastewater, traditional wastewater treatment methods, and wastewater treatment using photocatalysts.

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## 2. Wastewater and Treatment Methods

## 2.1. Types of Wastewater and Their Components

Wastewater can be divided into two categories: domestic wastewater and industrial wastewater. Domestic wastewater, also known as municipal sewage, is more diluted than industrial wastewater and is made up of more than 99% water. The remaining portion consists of suspended solids, biodegradable organic compounds, inorganic solids, nutrients, metals, and pathogenic microorganisms. Biodegradable organic compounds are carbon-based materials like proteins, carbohydrates, and fats that can be converted into carbon dioxide. Municipal sewage also contains nutrients such as nitrogen and phosphorus, which need to be treated to prevent environmental toxicity.

Industrial wastewater comes from factories, agricultural farms, and public activities (hospitals, stores, restaurants, etc.). The composition of industrial wastewater depends on its source. For example, wastewater from textile industries primarily contains organic dyes, while wastewater from restaurants mainly consists of fats. Additionally, wastewater generated by various industries and agricultural land contains large amounts of harmful chemicals and organic pollutants. Heavy metal ions are another component found in industrial wastewater that are toxic to living organisms.

## 2.2. Wastewater Treatment

Wastewater treatment is a process in which pollutants are removed from the water phase before they are released into the environment, using physical or chemical processes. There are many methods for treating domestic and industrial wastewater. The most common method is municipal treatment plants, which, when used efficiently, can remove a significant portion of the pollutants from the water. This treatment method consists of three stages: preliminary, primary, and secondary treatment.

The preliminary stage involves the removal of large or heavy particles from the wastewater. This includes screening and removing gravel and sand. In the screening process, large floating pieces such as stones, paper, and plastic are separated using filters. The materials removed by the filters are usually either buried or burned. The next step, after screening, is the removal of sand and gravel, which is done through sedimentation.

After passing through the preliminary stage, the remaining wastewater enters the primary stage. This stage involves removing a large portion of suspended solids from the wastewater through sedimentation. The wastewater enters sedimentation tanks, where there is enough time for solids (sludge) to settle. The wastewater stays in the tank for several hours, allowing the sludge to settle and a scum layer to form on the surface. The scum overflows from the top, and the sludge is separated from the bottom, after which the wastewater moves to the secondary stage. During the primary treatment stage, up to 40% of the Biological Oxygen Demand (BOD) is reduced. (BOD refers to the amount of oxygen required for microorganisms to oxidize the organic matter in the wastewater. Reducing this value means less oxygen is needed for treatment, thus removing some organic pollutants.) Additionally, 80% to 90% of the suspended solids are removed from the wastewater in this stage. Although primary treatment removes a significant portion of the pollutants in the wastewater, it does not provide enough assurance for the complete removal of all harmful pollutants.

The remaining wastewater from the primary stage contains a significant amount of organic pollutants and a small amount of suspended solids. To remove these remaining pollutants, the wastewater enters the secondary treatment stage. This stage involves biological processes that reduce the BOD level of the wastewater and also remove a small amount of suspended metals. In this stage, the wastewater undergoes intense aeration to promote the growth of aerobic bacteria and other microorganisms that break down organic pollutants into water and carbon dioxide. In addition to removing organic pollutants, some nutrients, such as nitrogen and phosphorus, are also removed during this stage. Figure 1 shows an overview of the complete treatment process, which includes all three stages.

After the wastewater treatment stages are completed, it is important to ensure that the remaining water is sufficiently clean before being released into the environment. Additionally, the sludge generated during the treatment process contains many harmful pollutants, so managing the leftover sludge is of great importance. Typically, before discharging the wastewater into the environment, processes like chlorination or disinfection using ultraviolet (UV) radiation are carried out. The sludge undergoes an anaerobic process, where anaerobic bacteria grow in the sludge. These bacteria break down the organic solids in the sludge into water-soluble byproducts or gases (mostly methane and carbon dioxide), reducing the amount of organic solids in the sludge. The methane gas produced during this process can be used as fuel in other parts of the treatment plant. The remaining sludge is then used for landfilling.

After these conventional stages, some treatment plants add a third stage of wastewater treatment, which involves disinfection. In this stage, remaining organic and inorganic pollutants, as well as microorganisms left over from the secondary stage, are removed using physical and chemical methods. After passing through the third treatment stage, the wastewater meets the required standards for drinking water. However, this stage is very costly and is rarely used by industries.

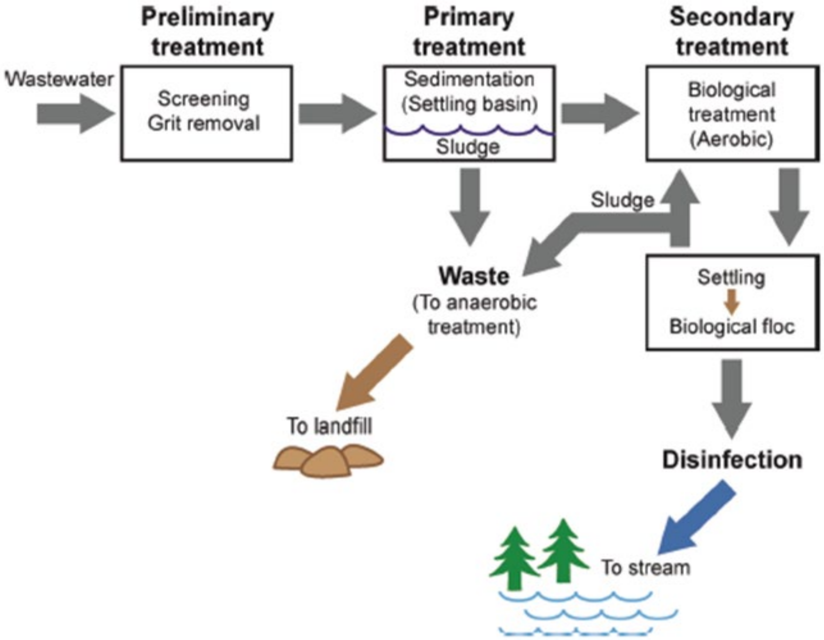

Figure 1 – Overview of the wastewater treatment process in a treatment plant[٢]

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3. The Use of Nanotechnology for Wastewater Treatment

Nanoscience and nanotechnology focus on the study of materials at the nanoscale. At these dimensions, materials exhibit unique and remarkable properties. The reason behind these properties is the small size of the particles. Nanotechnology involves manipulating, controlling, and combining atoms and molecules to create materials, compounds, and structures at the nanoscale. In recent years, the development of tools and methods based on nanotechnology has significantly contributed to solving problems related to wastewater treatment. The importance of these methods lies in the small size of nanoparticles, their high reactivity, and the ability to produce them using environmentally friendly methods. The most effective methods for wastewater treatment are as follows:

Photocatalytic processes

Nano adsorbent-based technologies

Nanofiltration processes

4. Photocatalytic Processes

Nanoscience and Nanotechnology study materials at very small scales, specifically at the nanoscale (1 to 100 nanometers). At this size, materials show unique and interesting properties. Nanotechnology uses these properties to solve various problems, including wastewater treatment. One effective method for wastewater treatment is the use of nanoparticles and photocatalysts. This method removes pollutants from water by using light to activate the particles.

In a photocatalytic process, semiconductor nanoparticles are used. When light shines on them, they can break down pollutants in wastewater. This process involves several steps, where reactants are absorbed onto the surface of the catalyst, chemical reactions take place, and non-toxic products are eventually produced. This method is especially effective for removing both organic and inorganic pollutants.

Photocatalyst nanoparticles must have certain qualities, such as the ability to absorb light, stability under light, and low cost. Some of the most common photocatalysts include titanium dioxide and zinc oxide. To improve the performance of these photocatalysts, methods like doping (adding other materials to the nanoparticle structure) and using visible light instead of ultraviolet light have been suggested.

These methods have become a popular choice in water treatment because they are highly effective and use natural resources, like sunlight, to treat wastewater. A complete explanation of the reactions involved in photocatalytic processes is beyond the scope of this article. A summary of these reactions is shown in Figure 2.

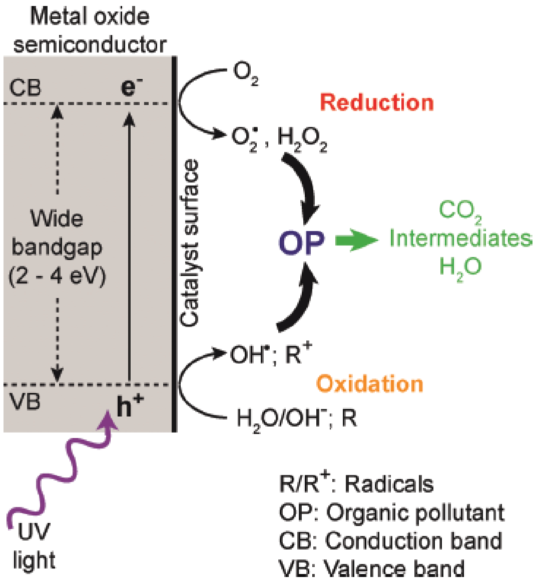

Figure 2. Photocatalytic treatment process [8]

4.1 Removal of Organic Pollutants

The photocatalytic process is widely used for the treatment of harmful organic pollutants, converting them into harmless substances such as carbon dioxide and water. This technique is effective in removing a wide variety of organic compounds, including alcohols, carboxylic acids, phenolic derivatives, and chlorinated aromatic compounds. The discharge of organic dyes from textile industries into rivers has become one of the major concerns in developing countries. To treat these pollutants, semiconductor nanoparticles like titanium dioxide ($TiO_2$) and zinc oxide (ZnO) are commonly used.

### 4.2 Removal of Inorganic Pollutants

Photocatalytic reactions can effectively remove inorganic pollutants, including halide ions, cyanide, thiocyanate, ammonia, nitrates, and nitrides, from water. Studies have shown that titanium dioxide nanoparticles have successfully removed silver nitrate and mercury (II) chloride from water through the photocatalytic process. Additionally, zinc oxide nanoparticles, when activated by visible light, have been able to treat pollutants such as potassium cyanide and hexavalent chromium. Research using a cadmium sulfide/titanate nanocomposite has demonstrated the photocatalytic oxidation of ammonia in water.

### 4.3 Heavy Metal Removal

The removal of heavy metals from wastewater is another significant challenge in wastewater treatment plants, as their concentration can vary depending on the type of wastewater. Removing these pollutants is crucial for protecting human health and improving water quality. However, due to the rarity and high value of some of these metals, their recovery is often preferred over their removal. The photocatalytic process has proven to be effective in recovering a variety of heavy metals.

For example, the recovery of trivalent gold, quadrivalent platinum, and trivalent rhodium using titanium dioxide nanoparticles has been demonstrated. In one study, 90% of gold was recovered under visible light irradiation at a pH of zero. In another study, titanium dioxide nanoparticles were used to remove cadmium from wastewater. Using light with a wavelength of 253.7 nm, over 90% of the cadmium in the wastewater was removed, and it was adsorbed onto the surface of the titanium dioxide nanoparticles.

To recover mercury from wastewater containing mercury ions, a group of researchers used activated carbon and titanium dioxide nanoparticles. By combining these materials and irradiating them with light, 70% of the mercury in the wastewater was recovered on the activated carbon and titanium dioxide nanoparticles.

### 4.4 Microbe Removal

Most photocatalysts also exhibit antimicrobial properties and are effective in preventing the growth of microorganisms. The process of removing microbes essentially involves the destruction of their cell walls using active radicals produced during photocatalytic reactions. These radicals ultimately lead to the breakdown of the microbes. Various bacteria, such as Escherichia coli (gram-negative) and Staphylococcus aureus (gram-positive), can be removed from wastewater using the photocatalytic process.

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## 5- Summary and Conclusion

Wastewater treatment is a process in which pollutants are removed from water using physical or chemical processes. Urban wastewater mainly consists of water, while industrial wastewater, depending on its source, may be rich in organic dyes, fats, metals, and other pollutants. Typically, treatment plants purify wastewater in three stages. However, these stages are not always capable of removing all pollutants, such as organic dyes and heavy metals. Additionally, the overall cost of such treatment methods is high due to the need for extensive infrastructure.

Nanoparticles, due to their large surface area and high reactivity, can be used in wastewater treatment processes. Photocatalysts are a category of nanoparticles that, when exposed to light (with energy equal to or greater than their bandgap), produce electron-hole pairs (excitons). These excitons can generate hydroxyl radicals in a moist environment, which can oxidize and remove pollutants from wastewater. By using photocatalysts, it is possible to remove organic and inorganic pollutants, heavy metals, and microbes from wastewater.

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# Methods of Wastewater Treatment (2)

## Abstract

In recent decades, access to clean water and preventing environmental pollution caused by industrial wastewater have become significant challenges for humanity. Traditional water and wastewater treatment methods lack the ability to remove some pollutants and are also expensive. Nanotechnology, by leveraging the unique properties of nanostructures, offers novel methods for wastewater treatment that are both effective and cost-efficient. This article examines two common nanotechnology-based methods for wastewater treatment: nanoadsorbents and nanofiltration.

Keywords: Nanoadsorbent – Nanofiltration – Wastewater treatment

## 1. Introduction

Traditional wastewater treatment methods are unable to remove certain organic, inorganic pollutants, and heavy metals. Additionally, these methods require large spaces and incur high costs. Nanostructures, due to their high surface area resulting from their small size, possess significant capacity to adsorb pollutants. Moreover, filters made with nanoscale pores can effectively block even the smallest pollutants. In a previous article, the method of wastewater treatment using photocatalysts was discussed. In this article, we focus on nanoadsorbents and nanofiltration methods.

## 2. Nanoadsorbents

Adsorption is a process where a substance is attracted and bound to another material, known as the adsorbent, through physical or chemical interactions. Adsorbents are commonly used in water treatment and purification to remove organic and inorganic pollutants from wastewater. In general, the process of pollutant adsorption on the adsorbent surface occurs in three stages:

- Transfer of the pollutant from wastewater to the adsorbent surface
- Adsorption onto the adsorbent surface
- Transfer of the pollutant into the adsorbent

Nanoparticles have two important properties that make them effective adsorbents. Nanomaterials have a much higher surface area compared to bulk materials, and they can be functionalized with various functional groups to selectively adsorb desired pollutants. Moreover, nanoadsorbents have nanoscale porosity, which significantly aids in the adsorption process. Furthermore, pollutants can be removed from the nanoadsorbents, allowing them to be reused, i.e., recovered. For instance, self-assembled iron oxide nanostructures have shown the ability to adsorb heavy metal ions and organic dyes from wastewater. Since nanoparticles can have magnetic properties, they can be easily separated from water using magnetic separation techniques, and the magnetic adsorbent can be recovered through catalytic combustion at 300°C. Catalytic combustion is a process in which a catalyst oxidizes a substance when sufficient heat is provided.

The following are some commonly used adsorbents.

### 2.1 Carbon-Based Nanoadsorbents

Carbon nanomaterials have been widely used for adsorbing both organic and inorganic pollutants in wastewater. In addition to these nanomaterials, activated carbon is the most well-known material for pollutant adsorption due to its high adsorption capacity, high thermal stability, resistance to abrasive wear, and low cost. Granular activated carbon has been used to remove a variety of organic pollutants and foul substances from water. A study has shown that activated carbon effectively adsorbs benzene and toluene from industrial wastewater, with adsorption capacities of 450 mg of benzene per gram of water and 700 mg of toluene per gram of water. It has also been observed that activated carbon can adsorb heavy metal ions such as mercury, nickel, cobalt, cadmium, copper, lead, and chromium in both +3 and +4 oxidation states.

Carbon nanotubes (CNTs) are another group of carbon-based nanoadsorbents. Due to their large surface area, high chemical and thermal stability, and specifically their ability to functionalize the surface, carbon nanotubes are considered some of the strongest adsorbents. A study investigated the adsorption of 2-dichlorobenzene along with lead and cadmium from water. The adsorption of these pollutants depends on the morphology and surface condition of the carbon nanotubes. Defects and surface roughness on carbon nanotubes are essential for better adsorption of pollutants. Figure 1 shows the effect of various treatments and functionalization on the adsorption capacity of nanotubes. When polar surface agents are applied to the nanotubes, polar organic pollutants are adsorbed more efficiently. However, when non-functionalized nanotubes are used, the adsorption efficiency for polar pollutants is lower, while the adsorption of nonpolar pollutants increases.

Both carbon nanotubes and activated carbon exhibit high adsorption rates and capacities, along with high chemical and thermal stability, making them suitable for wastewater treatment. However, their complete separation from water is difficult due to their small size. To address this issue, magnetic nanoparticles can be combined with carbon nanotubes or activated carbon, allowing easy separation from water through magnetic fields.

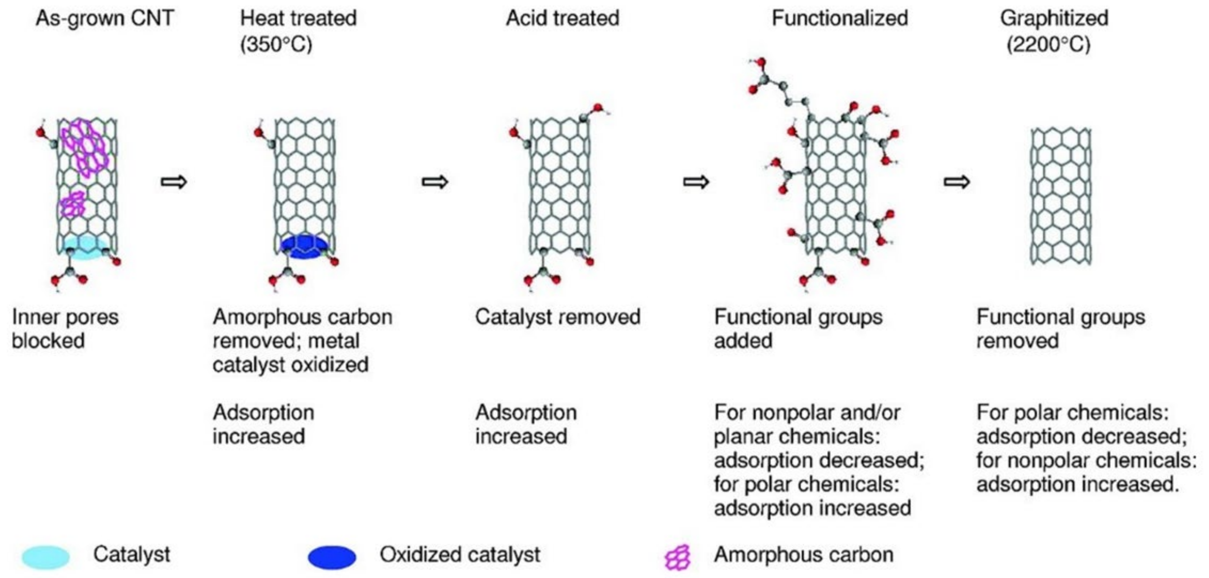

Figure1: The effect of various treatments and functionalization of nanotubes on their absorption

## 2.2 Biological Adsorbents

In some wastewaters, organic pollutants at low concentrations (in the pico- or nanogram per liter range) cannot be completely removed. Biological adsorbents, derived from biological materials, can effectively remove such pollutants. Biological adsorbents have beneficial properties, including low cost, high efficiency, no need for nutrient addition, and reusability. A study used a DNA-based material for the selective removal of dioxin derivatives. DNA recovery is simple and can be achieved by washing with hexane. Numerous studies have been conducted on biosorbents containing trioline for the removal of organic pollutants. The advantage of using trioline-containing adsorbents lies in their high adsorption capacity, as well as their low solubility and permeability due to their high molecular weight.

Biological adsorbents are also used to remove heavy metal ions. Chitosan-based adsorbents have shown high efficiency in adsorbing heavy metals. Metal ion adsorption in chitosan occurs through chelation reactions on the amino acid groups of chitosan. Chelation is a reaction where molecules bind to metal ions, forming multiple coordinate bonds with a ligand. These ligands are known as chelating agents.

## 2.3 Metal Oxide Nanoadsorbents

Common metal oxides used as adsorbents include iron, manganese, silicon, titanium, and tungsten oxides. Like other adsorbents, these oxides are cost-effective and can be functionalized for targeted adsorption. Iron oxide-based nanoadsorbents can be used to remove multiple organic pollutants from wastewater. Due to the magnetic properties of iron oxide nanoparticles, these nanoadsorbents can be easily separated from the liquid phase using magnetic fields.

Layered nanoadsorbents (e.g., aluminum-zinc hydroxide) can be used to remove organic pollutants from wastewater, especially those containing organic dyes from textile industries. The adsorption efficiency of lead ions depends not only on the electrostatic behavior of the nanoadsorbents but also on chemical interactions. As a result, manganese oxides exhibit higher lead adsorption efficiency compared to iron oxides. Furthermore, regarding the adsorption of europium by aluminum oxide nanoparticles, it was found that adsorption is strongly dependent on pH but independent of ionic strength.

### 2.4 Zeolites

Zeolites have high surface area and ion-exchange capacity, making them strong adsorbents for water treatment. Most zeolites are natural, but they can also be commercially produced. A study used hexadecyltrimethylammonium-modified zeolite to adsorb phenolic derivatives in water. The HDTMA molecules form a micellar bilayer on the surface of the zeolite, increasing its adsorption capacity. Another study used zeolite modified with a mixture of bacteria to degrade pyridine and quinoline. The biodegradation of these substances leads to the production of ammonium ions, which are then adsorbed by the zeolite. Thus, the simultaneous degradation of pyridine and quinoline, along with ammonium adsorption, occurs in zeolites modified with bacteria.

Zeolites are also used to adsorb heavy metal ions. In a study, the adsorption of lead and cadmium using two natural zeolites, kabazit and clinoptilolite, was investigated. These zeolites, pre-treated with sodium hydroxide, removed up to 99% of lead and cadmium from wastewater. The high porosity of zeolites increases their adsorption capacity, and their photocatalytic properties help reduce the high toxicity of heavy metals.

### 2.5 Zero-Valent Iron Nanoparticles

Zero-valent iron nanoparticles are materials used to remove various organic and inorganic pollutants from water. Due to their high surface energy, these nanoparticles are highly reactive and unstable. Therefore, various methods have been studied to enhance their stability, such as surface modification, creating emulsions for better miscibility, forming intermetallic compounds for improved reactivity, and loading them onto carbon substrates for uniform distribution in liquids.

Zero-valent iron nanoparticles can reduce heavy metal ions such as copper and silver, and they are capable of adsorbing metals like zinc and cadmium directly, eliminating their mobility. Additionally, the magnetic properties of these nanoparticles aid in their easy separation from the fluid. Zero-valent iron nanoparticles are highly efficient in adsorbing and precipitating arsenic ions (both +3 and +5 oxidation states). Adsorption of these ions occurs through weak electrostatic interactions between the ions and the binding sites on the nanoparticle. A study used zero-valent iron nanoparticles encapsulated in chitosan for arsenic removal from wastewater and found that, across a wide pH range (from 2 to 9), anions such as sulfate, phosphate, and silicate had no impact on arsenic adsorption, and arsenic was nearly completely removed from the wastewater.

Beyond arsenic, zero-valent iron nanoparticles are also used to remove various metal ions from wastewater, including chromium, copper, lead, barium, and cobalt. These nanoparticles are also effective in removing or recovering dissolved metal ions from wastewater, such as hexavalent chromium or hexavalent uranium, and are also effective against other organic and inorganic pollutants.

## 2.6 Hydrogels

Hydrogels are very strong adsorbents for removing heavy metals from wastewater. Their high adsorption capacity is due to their three-dimensional network and the ability to accommodate various functional groups on them. Hydrogels have the ability to absorb large amounts of water due to their inherent properties, including cross-linking between network chains, flexibility of chains, and high free volume. However, the main problem in the practical use of hydrogels is the low mechanical strength of these materials. To solve this problem, the addition of hydrophobic compounds to the hydrogel structure can be used.

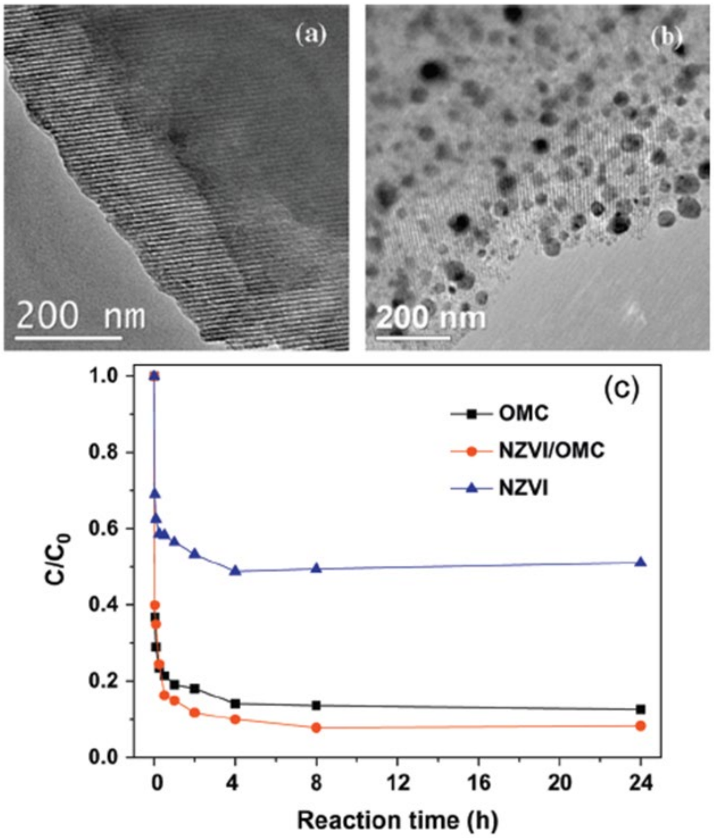

Figure 2. a) Transmission electron microscope image of mesoporous carbon and b) composite of mesoporous carbon and zero-capacity iron nanoparticles c) ratio of pollutant concentration to initial concentration over time for each of the adsorbents

Polymeric nanocomposites in the form of hydrogels can be used to remove heavy metal ions from wastewater. These nanocomposites have the ability to swell in an aqueous environment, thus exhibiting high adsorption capacity. Hydrogels made from acrylic, vinyl, and other monomeric groups such as acrylic acid, acrylamide, hydroxyethyl methacrylamide, vinyl pyridine, etc., have shown high efficiency in adsorbing heavy metals and some other soluble species. In one study, an amphoteric hydrogel superadsorbent (NIPAAm/DAPB/AA) was synthesized using the reverse microemulsion process and was able to remove divalent lead and mercury ions from water. The hydrogel nanoparticles used had a size of 30 to 40 nanometers, and it was observed that the adsorption efficiency for lead ions was higher than that for mercury ions for this type of hydrogel.

## 3. Nanofiltration

Filtration is one of the most common and important steps in water and wastewater treatment, which separates solid components from liquid using a filter or membrane. Nanofiltration is a membrane separation technique that is driven by pressure. This method is expanding for water and wastewater treatment due to its ability to reject substances based on electric charge and its high permeability rate. Since nanofiltration requires lower pressure (7 to 30 atmospheres) compared to reverse osmosis (20 to 100 atmospheres), it has been welcomed due to its energy efficiency [29].

The properties of membranes used in nanofiltration fall between the non-porous reverse osmosis membranes and the porous ultrafiltration membranes. Additionally, the passage of materials through the membrane in the nanofiltration process occurs via solution diffusion. Moreover, some nanofiltration membranes have a fixed surface charge, leading to selective filtration of compounds, in addition to physical filtration. The process of water hardness reduction using nanofiltration is schematically shown in Figure 3. The pore size of nanofiltration membranes is very small (usually between 1 to 5 nanometers), and most solutes are effectively separated by the membrane. However, the membrane's surface charge allows monovalent ions in hard water to pass through the filter, while multivalent ions remain. For neutral species, the size exclusion mechanism is dominant, and particles can pass through the membrane based on their size. However, for charged species, both size exclusion and electrostatic interactions mechanisms are present. Today, nanofiltration is used in wastewater treatment in various industries, such as textiles, pharmaceuticals, dairy, petrochemical, and others. Due to its unique mechanism and the availability of various membranes, nanofiltration can be used to remove most organic and inorganic pollutants. Typically, polymers are used to make nanofiltration membranes because their manufacturing process is easy, they have high flexibility, and they are cost-effective. However, polymeric membranes have low chemical stability and short lifespans. On the other hand, ceramic membranes, made from inorganic materials, offer higher chemical and thermal stability, resulting in a longer lifespan, but their production costs are high, and they lack flexibility. Nanomaterials can play a significant role in the production of nanofiltration membranes, reducing production costs and increasing flexibility. Below, the application of some nanostructures in the nanofiltration process is described.

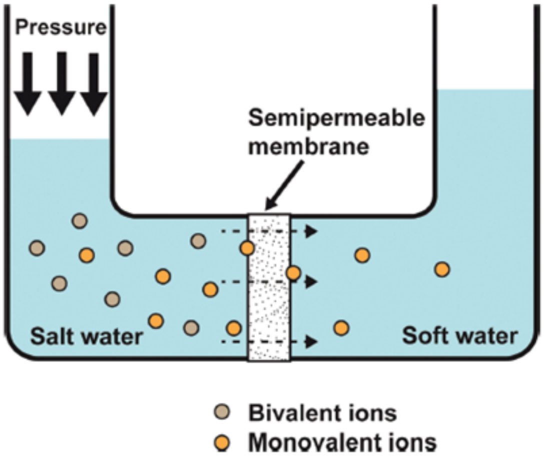

Figure3: The process of water hardness reduction using nanofiltration

### 3.1 Carbon Nanostructures

Carbon nanostructures have been widely used in many membranes due to their simplicity of production, high mechanical stability, and excellent ability to prevent the passage of contaminants. Membranes based on carbon nanotubes exhibit high permeability and also a high rate of preventing the passage of contaminants. The small pore size of carbon nanotubes (between 1 and 10 nanometers) allows only water to pass through, preventing the passage of other chemical and biological contaminants. The most important advantage of nanotube-based membranes is that they are strong like ceramics and flexible like polymers. Furthermore, water permeability through carbon nanotubes is very high. In a study using carbon nanotubes, a membrane with a pore size of 1 nanometer was produced. Compared to other commercially available membranes, this membrane exhibited three times greater resistance to the passage of organic dyes. Additionally, nanotube-based membranes are capable of filtering bacteria such as Escherichia coli. Apart from the ability to filter materials based on their size, nanotubes also have a high capacity to adsorb diverse chemical and biological contaminants. In one study, a nanotube/ceramic composite was used for filtration, leading to the removal of 98% of fungi and nearly 100% of heavy metal ions. Figure 4 shows a scanning electron microscope image of fungi cells trapped in a nanotube/ceramic composite.

Two-dimensional graphene sheets with a single atomic thickness can also be used as nanofiltration membranes. The production of graphene is cheaper compared to carbon nanotubes, and it has similar chemical and thermal stability, while exhibiting more flexibility than nanotubes. Graphene-based membranes are capable of filtering organic dyes and other nanoparticles. Graphene-based membranes can also be used for water purification. A membrane made of graphene with a thickness of 22 to 53 nanometers was used, and it filtered a high percentage of organic dyes from the water, although its ability to filter multivalent ionic substances was not as high. In another study, graphene oxide was used to create a micrometer-thick membrane, and it was observed that this membrane could block the passage of any liquid, vapor, or gas except water.

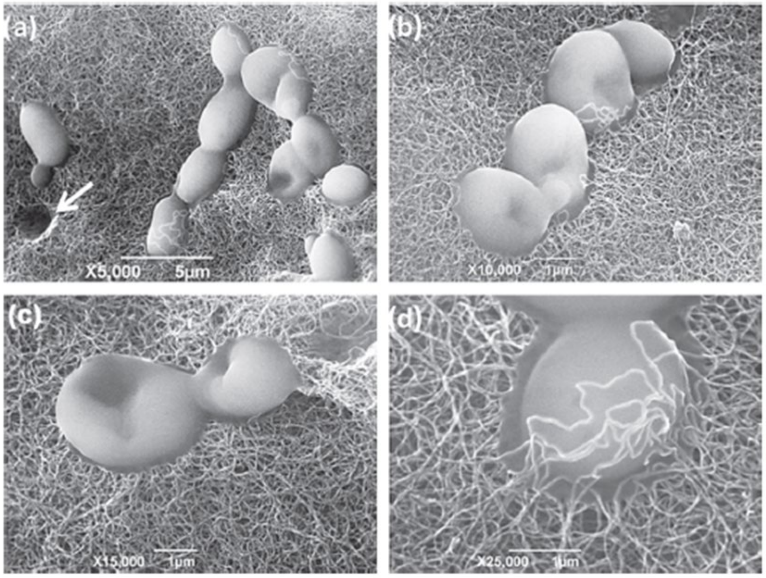

Figure 4. Scanning electron microscope image of nanotube/ceramic composite filter

### 3.2 Metal Oxides

Metal oxides are another category of cost-effective materials for producing nanofilters. Additionally, most of them exhibit photocatalytic properties under irradiation, which allows the membranes made from them to remove various organic and inorganic pollutants, as well as microbes from wastewater. Instead of being merely a physical barrier, the membrane actively contributes to the removal of pollutants. In a study, titanium dioxide nanowires were used to make membranes, and the removal of humic acid and organic materials was investigated. By combining the filtration and photocatalytic properties of these nanoparticles, about 100% of humic acids and over 90% of organic materials were removed under ultraviolet irradiation [40].

To increase rejection rates, these nanoparticles can be combined with gamma alumina nanoparticles. To enhance the corrosion resistance of membranes based on titanium dioxide nanoparticles, zirconium dioxide nanoparticles can be added. By adding these nanoparticles, the membrane becomes stable over a wide pH range (1 to 13). In another study, after adding zinc oxide nanoparticles to a polyphenylsulfone-based membrane, the water flux increased from 76 to 107 liters per square meter per hour. The main reason for the increased flux was the improved hydrophilicity of the membrane due to the presence of zinc oxide nanoparticles, though these nanoparticles did not affect the filtration process.

### 3.3 Zeolites

Zeolites are aluminum silicate crystals classified as microporous materials, with pore diameters ranging from subnanometer to nanometer scale. Due to their aluminum silicate structure, zeolites have high thermal and chemical stability. As a result, these materials exhibit high efficiency in reverse osmosis and nanofiltration applications. Poly(dimethylsiloxane) nanofiltration membranes filled with zeolites are effective membranes capable of separating various chemical pollutants, with high chemical stability and reduced polymer network swelling. Zeolite-containing membranes are also used for the separation of metal compounds and saturated and unsaturated hydrocarbons.

## 4. Conclusion

Nanotechnology offers promising solutions for wastewater treatment, and its methods, including nanoadsorbents and nanofiltration, are proving to be effective in removing various pollutants. These methods have advantages over traditional techniques, such as lower cost, higher efficiency, and the ability to remove a broader range of pollutants. However, challenges like membrane fouling and scalability must be addressed for their widespread adoption. Despite these challenges, nanotechnology-based wastewater treatment systems hold great potential for addressing water pollution and ensuring a sustainable future for water resources.

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# Targeted Drug Delivery (1): Principles and Fundamentals

## Abstract

Drug delivery systems are systems that have the ability to deliver drugs to the desired tissues, organs, cells, and intracellular sites using various carriers. Drug delivery systems are an effective solution for drug administration, allowing for control over the dosage, timing, and location of drug release. The use of targeted systems, which release an adequate concentration of drug at the damaged site, enhances the effectiveness of treatment and prevents side effects on other parts of the body. Additionally, the drug remains in the bloodstream for a longer period of time. The most important application of targeted drug delivery is in the treatment of cancers, as this method reduces the side effects of toxic anticancer drugs. In recent years, the development of various mechanisms to improve drug release in the treatment of various diseases has gained significant attention. This article provides a brief introduction to the process of targeted drug delivery and discusses controlled drug release. Drug delivery systems using physical forces, such as external forces like magnetic fields, ultrasound, light, heat, and electric fields, will be studied in detail.

## Introduction

Common drug delivery methods include oral delivery (such as tablets, capsules, and syrups) and non-oral delivery (such as injections, eye drops, and topical creams). In these methods, the drug is released at specific time intervals after consumption. The release and absorption of the drug into the bloodstream during traditional drug delivery requires the drug to travel through the body. This means the drug is exposed to the acidic environment of the stomach, passes through the tight junctions of intestinal cells, and ultimately enters the hepatic cycle. Currently, most drugs reach their target site using traditional methods like oral and injectable delivery. However, these methods lead to significant loss of the drug as it passes through the digestive system, bloodstream, and intermediate tissues. Therefore, to ensure that the required concentration of the drug reaches the target site, much higher doses must be loaded, which results in increased costs, waste of pharmaceutical materials, and damage to other healthy tissues in the body. Simply put, traditional drug delivery systems operate on the assumption that if enough of the drug enters the bloodstream, some of it will eventually reach the target area. However, much of the released drug along the way causes side effects in healthy tissues.

Targeted drug delivery systems are used to transfer drugs with a specific concentration to damaged tissues in order to achieve an optimal therapeutic effect. The main goals of designing drug delivery systems include: (1) increasing the solubility in water and chemical stability of active pharmaceutical ingredients, (2) improving drug efficacy, and (3) reducing side effects. Modern drug delivery systems have been continuously evolving since the early 1950s, coinciding with the introduction of the first dexedrine release formulation. The targeted drug delivery process helps maintain appropriate drug concentrations over extended periods and significantly reduces many common treatment limitations, such as the number of doses, the initial drug concentration, and side effects caused by the irregular release of the drug in the body.

Each targeted drug delivery system consists of the drug, carrier, and ligand. In such a system, the drug's release, metabolism, and cellular absorption are determined based on the physical and chemical properties of the drug, as well as the biological behavior of the carrier and ligand. Therefore, by optimally designing the carrier and ligand, it is possible to increase the drug's effectiveness in the affected tissue while reducing its toxicity in other healthy tissues. Figure 1 illustrates the components of both targeted and non-targeted drug delivery systems.

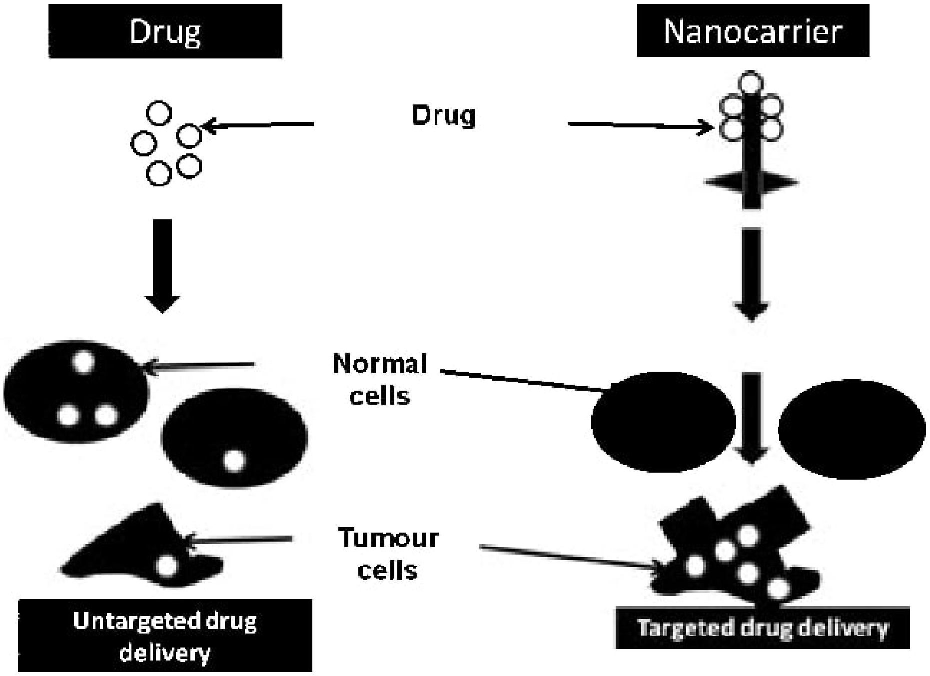

Figure 1 - Schematic representation of the components of targeted and non-targeted drug delivery systems. The enhanced efficiency of targeted drug delivery systems in delivering drugs to cancer cells while avoiding side effects on normal cells is clearly demonstrated. [1].

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## 2- Prerequisites

Before diving into the fundamentals and types of targeted drug delivery systems, it is essential to become familiar with some key concepts, which are discussed below.

Osmotic Pumps: These pumps consist of a central core containing the drug and osmogen, which is covered by a semipermeable membrane. When water is absorbed by the core, the volume of the core increases, which causes the drug-containing solution to be expelled through exits on the membrane. The osmogen itself is made up of salts and carbohydrates. A schematic representation of the drug release mechanism using simple osmotic pumps is shown in Figure 2.

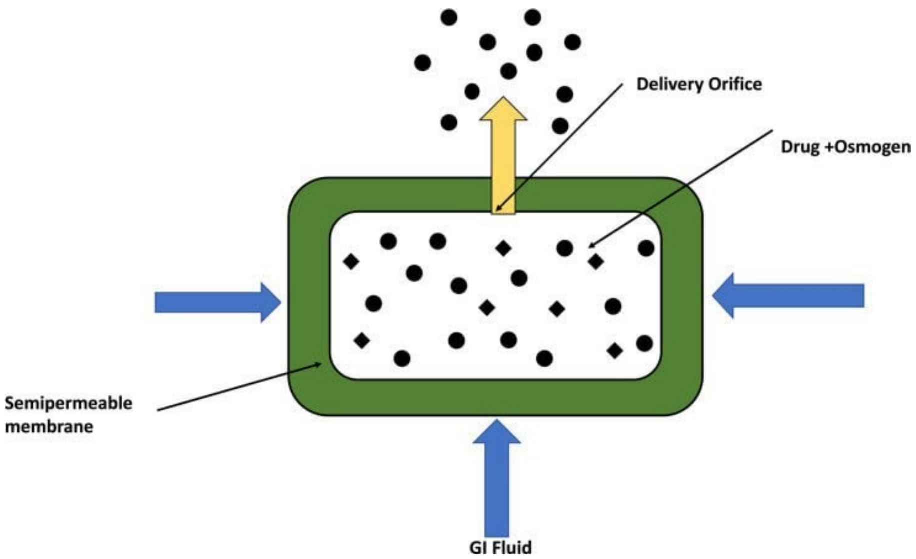

Figure 2 - Schematic of the drug release mechanism using simple osmotic pumps [2].

Half-life in drug delivery is the period during which the amount of a drug in the body reduces to half of its initial value. Generally, the half-life depends on how the body processes and eliminates the drug and can range from a few hours to several weeks.

Micelles are colloidal particles formed by the aggregation of amphiphilic molecules. Amphiphilic molecules have both hydrophilic (polar) and hydrophobic (nonpolar) regions.

Infrared spectrum is divided into three regions: near, mid, and far infrared. The near infrared region is within the wavelength range of 4000-4300 $cm^{-1}$.

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## 3- Drug Release Profile

The drug release profile refers to the amount of drug released into the bloodstream over time. These profiles are particularly important as they help determine the best method for administering a specific drug. An example of a drug release profile with different carriers is shown in Figure 3.

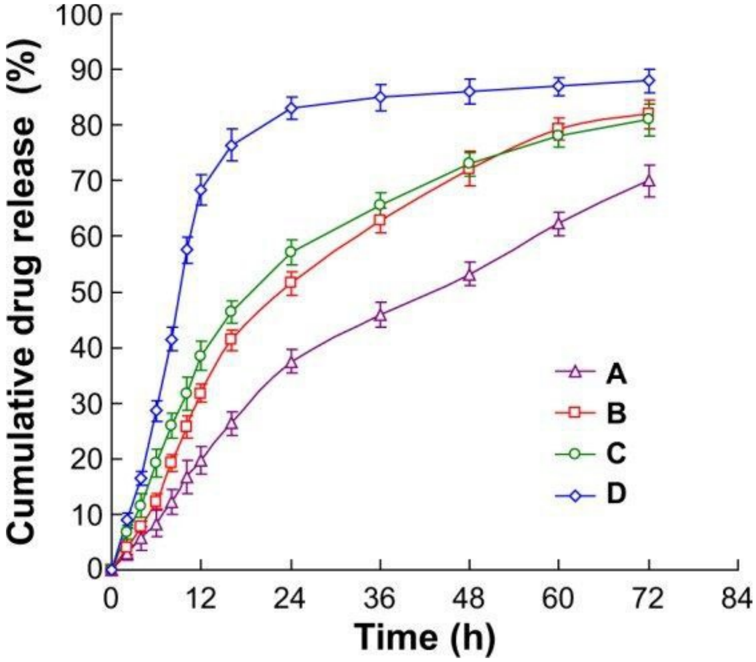

Figure 3 - An example of a drug release profile with different carriers.

In Figure 3, the curves shown in different colors represent different carriers used for drug delivery. The fastest drug release rate happens with the carrier shown in blue, where around 80% of the drug loaded is released in the first 24 hours. Therefore, to improve the effectiveness of targeted drug delivery, it is better to first carefully study the drug release profile. Depending on the needs of the damaged tissue and the required drug concentration over a certain period of time, the appropriate carrier for drug delivery should be chosen.

In general, the amount of drug release depends on one or more specific mechanisms within the body. The main factors that affect the drug release rate in the body include:

The release of the drug attached to the surface.

The release from the carrier matrix (the material that holds the drug).

The release from the walls of microcapsules and microparticles.

The erosion and breakdown of the carrier matrix.

A combination of the erosion and release processes.

Figure 4 shows a diagram of the most important mechanisms of drug release from polymer drug delivery systems.

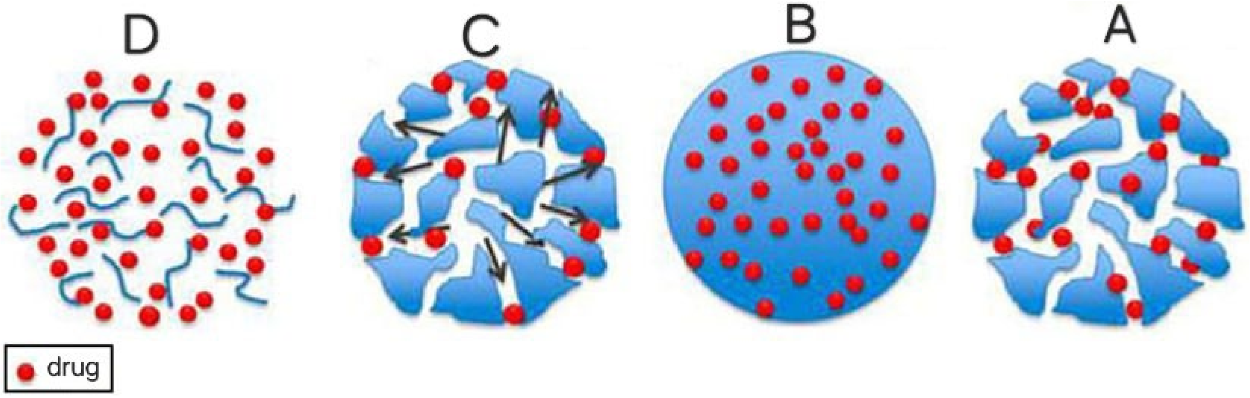

Figure 4 - A diagram of the most important mechanisms of drug release from polymer drug delivery systems: (a) drug release from aqueous pores, (b) release from the polymeric matrix wall, (c) osmotic pump, and (d) erosion.

Figure 4-a shows the drug release mechanism without using a carrier. The main advantage of this mechanism is that it uses conventional formulations, and the production cost is lower. However, when using this mechanism, it's important to keep in mind that for most drugs, the higher the drug plasma concentration, the greater the degradation and elimination of the drug from the blood. Right after intravenous injection or shortly after oral absorption of the drug into the bloodstream, the drug concentration reaches its peak. Therefore, during this time frame, the drug degradation rate is high, and as time passes, the plasma concentration of the drug decreases, and the elimination rate also lowers.

In Figure 4-b, drug release with zero-order systems is shown. In zero-order systems, the rate of drug degradation in the blood plasma is constant, and its half-life can range from a few hours to several months. In zero-order release, the drug is released from the carrier at a constant rate, so the concentration-time profile remains stable. Unlike first-order release, using this drug delivery system eliminates the issue of rapid drug release, making it ideal for long-term treatments. Zero-order release is an ideal solution for improving therapeutic effects and avoiding side effects of the drug.

In the drug release mechanism with the erosion mechanism shown in Figure 4-c, the drug is released after a predetermined delay. Simply put, the drug is placed inside an insoluble capsule that is sealed with an erosion-prone tablet. After some time, as the tablet erodes, the drug begins to be released in the body. The erosion rate of the tablet determines the timing of drug release. Figure 5 shows the drug release profile using various drug delivery systems.

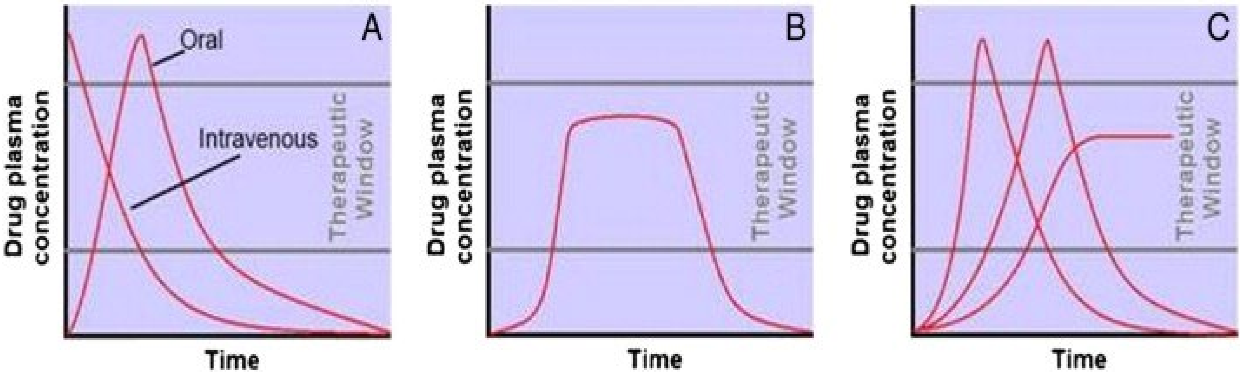

Figure 5 - Drug release profile using different targeted drug delivery systems: (a) Drug release without a carrier, (b) Zero-order drug release, and (c) Drug release with erosion [5].

4. Drug Release Control

As mentioned earlier, traditional drug delivery systems do not allow for control over the time, location, and rate of drug release. Additionally, the amount of drug released in the target tissue must be sufficient to meet the patient's treatment needs until the next dose is given. This is important because, with intermittent doses, fluctuations in drug concentration may go beyond the desired range and cause more side effects.

On the other hand, many drugs are unstable and toxic, and their effectiveness lasts only for a short period of time. Also, some drugs do not dissolve well in water. Nanometric drug delivery systems, which have excellent features such as encapsulating many drugs to protect them during the transfer process and controlled release to the target tissue, are a unique solution to overcome the challenges mentioned above.

A key point about drug delivery systems is their unique chemical, physical, and morphological characteristics. These systems interact with drugs in various ways, such as through covalent and hydrogen bonds (chemical interactions) or electrostatic and van der Waals interactions (physical interactions). This allows them to connect with both polar and non-polar drugs and release them in a controlled manner, at a specified concentration, in the target area.

The chemical composition and shape of nanoparticles, when used as nanocarriers in targeted drug delivery, significantly affect the profile of controlled drug release. In general, drug release from nanometric drug delivery systems occurs through various mechanisms such as diffusion, dissolution, chemical reactions, or release triggered by a specific stimulus.

5. Physical Targeting

One of the methods of programmed drug release during targeted drug delivery is the use of stimulus-responsive drug delivery systems. These systems release their drug load at the desired location in response to changes in structure, solubility, shape, size, or surface charge. The stimuli can be classified based on their origin into two categories: internal and external, or based on the type of signal, into two categories: chemical and physical.

Figure 6 shows several targeted drug delivery systems that respond to external forces like magnetic fields, ultrasound, light, heat, and electric fields for drug release. Among these external factors, the use of magnetic fields, electric fields (electroporation), light, and ultrasound waves have gained significant attention.

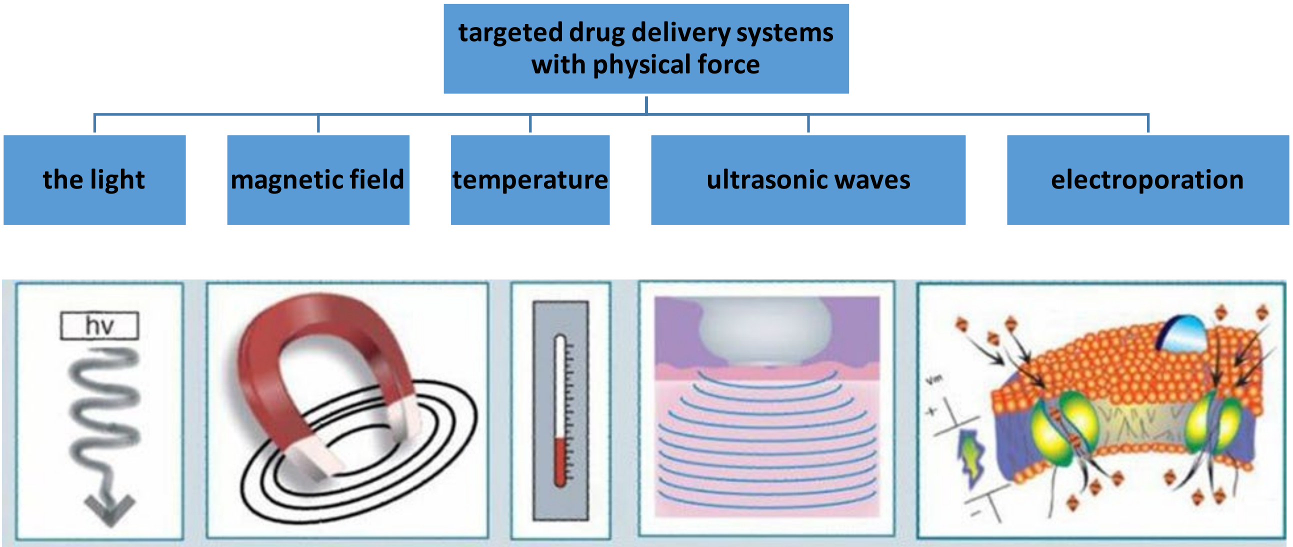

Figure 6 - A number of drug delivery systems with physical forces [6]

## 1-5- Magnetic Nanoparticles and Magnetic Field

In recent years, the use of magnetic nanoparticles in various fields of biomedical engineering, such as magnetic separation of cells and biological components, drug delivery, tumor hyperthermia treatment with radio waves, and MRI imaging, has significantly increased due to their unique properties. Some of these characteristics are listed below:

Interaction of magnetic dipoles due to an external magnetic field. This interaction causes the nanoparticles to accumulate in the target tissue.

The ability to optimize the surface by functionalizing the nanoparticles to increase biocompatibility.

The basic principle behind the use of magnetic nanoparticles in drug delivery is based on the effect of external magnetic fields on polymer-coated magnetic nanoparticles. These nanoparticles serve as carriers. The magnetic field can direct the particles towards the desired therapeutic targets and collect them there. Additionally, the nanometric size of these particles allows them to interact with the cell nucleus. The design of magnetic nanoparticles used in drug delivery systems is very sensitive and complex, and important principles such as the ability to carry and retain the desired drug payload, the capability of carrying multiple drugs and chemicals to enhance therapeutic efficacy, as well as the mechanism and rate of drug release, must be considered.

One of the applications of magnetic nanoparticles in targeted drug delivery is drug delivery to the brain. Drug treatment for the brain, via direct drug injection, requires sedating the patient, opening the skull, and implanting a tube into the brain (which is an invasive method). Recent research has confirmed the possibility of drug delivery to the brain with the highest precision and minimal invasiveness using magnetic nanoparticles.

As seen in Figure 7, in the new drug delivery system, magnetic nanoparticles are packaged with the drug in lipid spheres. When the drug carrier system is exposed to a high-frequency alternating magnetic field, the nanoparticles heat up by about 5°C, and the lipid spheres become porous, releasing the drug materials into the targeted brain area without releasing the magnetic nanoparticles. When the magnetic field is turned off, the lipid spheres are sealed again, and drug release is halted. The use of a magnetic field drug release system is applicable to a wide range of drugs.

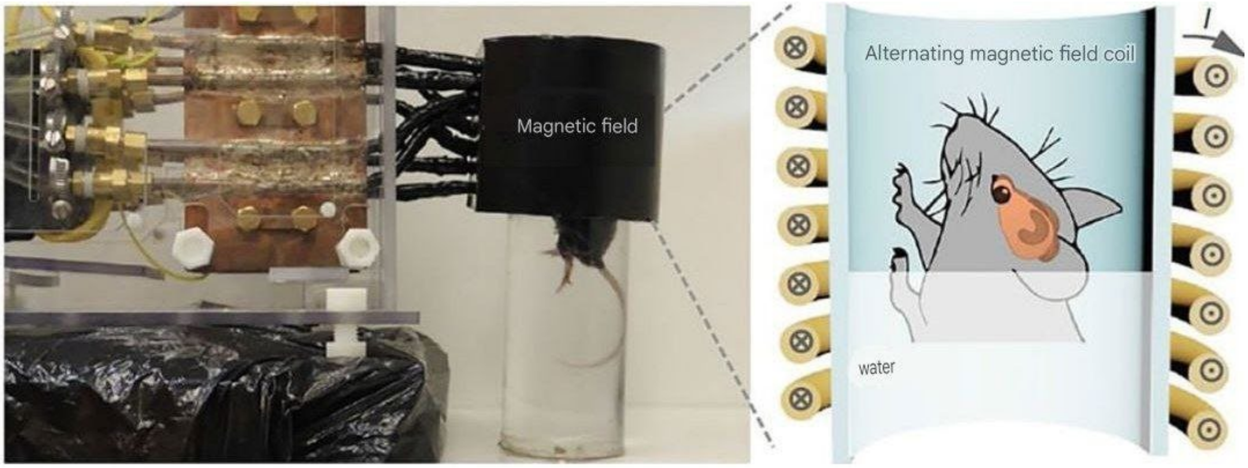

Figure 7 – Laboratory image of the drug delivery system using magnetic nanoparticles under a magnetic field and a diagram of a laboratory mouse placed in a coil of alternating magnetic field [7]

۲-۵- Ultrasound Waves

The application of ultrasound waves to improve drug delivery to target tissues in the body has been studied since the early 1950s. The frequency and intensity of ultrasound waves have various effects on the cells and tissues that are exposed to this energy. Therefore, by adjusting the frequency and intensity of the ultrasound waves, different therapeutic purposes can be achieved.

One of the effects that ultrasound waves have on cells and tissues is sonoporation. In the process of sonoporation, the mechanical force of ultrasound waves increases the size of pores in the plasma membrane. Ultrasound waves, by disrupting the integrity of the plasma membrane and creating pores, make it possible for nanoparticles and drug carriers to enter the cells passively. Figure 8 shows a diagram of the effect of ultrasound waves on the diffusion of drug-carrying nanoparticles and the drug release process.

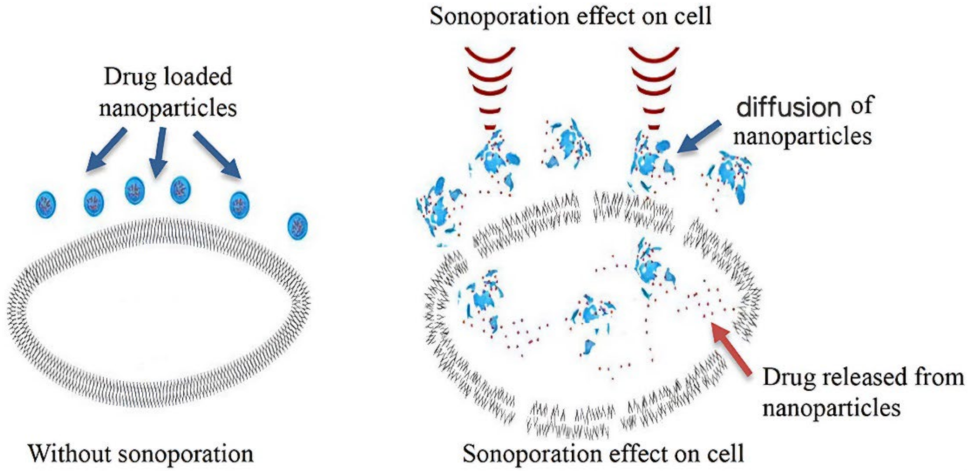

Figure 8 – Diagram of the effect of ultrasound waves on the diffusion of drug-carrying nanoparticles and the drug release process.[^]

One of the drug delivery methods using ultrasound waves involves the production of microbubbles containing drug compounds. Microbubbles have a bilayer structure, consisting of a gas core (perfluorocarbon) and a polymeric membrane, such as polymeric or lipid micelles. Upon the application of ultrasound waves, tiny bubbles are generated within the membrane of these particles, a phenomenon known as cavitation. Over time, the number of small bubbles increases, and the pores in the membrane grow larger. As long as the drug carrier system can withstand the rising internal pressure, the drug is gradually released from the carrier into the target tissue. Figure 9 illustrates the targeted drug delivery using ultrasound waves for drug release in cancerous tissue.

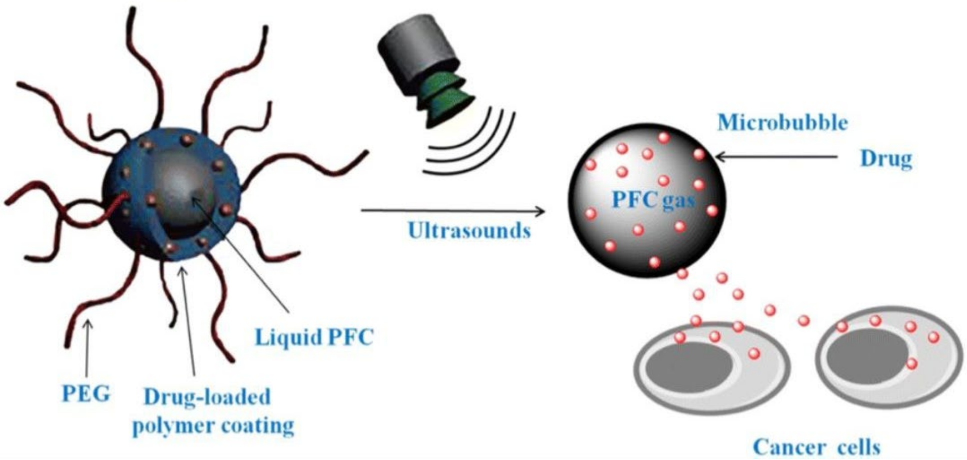

Figure 9 – A diagram of targeted drug delivery using ultrasound waves for drug release in cancerous tissue [11].

Educational Box

Clinical trials are the most important medical studies on humans to examine the effects of drugs and new therapeutic methods. In the first stage, the best way to apply the therapeutic method and the effective dose of the new drug formulation are determined. The second stage involves testing the anti-cancer effects of the drug. In the third stage, the results of the treatment on individuals using the new therapy are compared with the outcomes of conventional and traditional methods. The fourth stage of the study focuses on the side effects of the drugs that have been approved for use and are available in the market.

### 3-5- Temperature

Sonoporation and cavitation are known as the non-thermal effects of ultrasound waves. Using ultrasound waves on living tissue causes the biological molecules to rotate or vibrate. These mechanical movements and compression pressure lead to the generation of localized (unnatural) heat in the target tissue. The use of heat from these waves in medicine is another effect of ultrasound waves, which is referred to as hyperthermia. So far, only a few temperature-sensitive liposomal systems have entered the second or third phase of clinical trials. For example, ThermoDox, a doxorubicin drug for breast and liver cancer treatment, is in phase III, and Allovectin, a gene therapy for melanoma skin cancer, is in phase II of clinical trials. Most drug delivery systems using ultrasound, where the loaded drug is released by temperature increase, are made from lipids with a phase transition temperature around 40°C, as this temperature can be reached by controlling the frequency of radio waves or using high-intensity ultrasound waves. Figure 10 illustrates the heating and physical effects of ultrasound waves used in drug delivery systems.

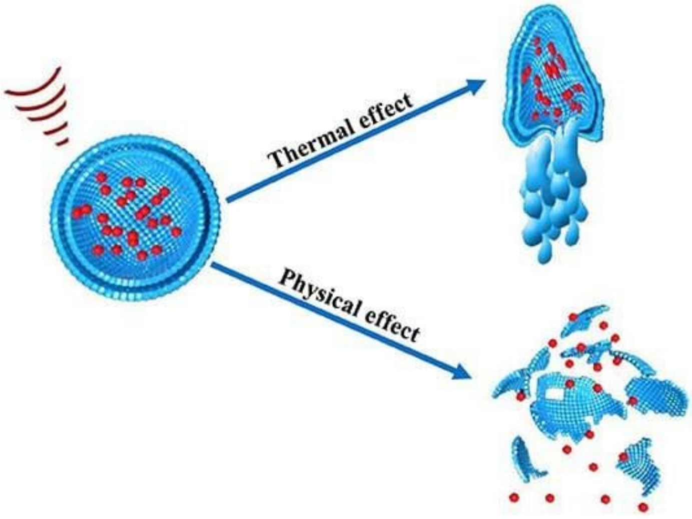

Figure 10 - A schematic of the thermal and physical effects of ultrasound waves in drug delivery systems[12].

### 5-4- Light

The use of light radiation in medical applications has been of interest for many years. In recent decades, light-based treatment methods have significantly developed. The reason for using light radiation in controlled drug release is the ability to control and adjust the physical properties of light, such as intensity and wavelength, using filters, photomasks, and lasers. Various studies have been conducted on single-step or multi-step drug release using light-sensitive systems. The main challenge in successfully using light-based drug release systems is the limited depth of light penetration into the body. However, in some cases, using materials sensitive to higher wavelengths or employing two-photon technologies and near-infrared lasers can overcome this challenge. Specific wavelengths from ultraviolet, visible, and near-infrared spectra are used in targeted drug delivery. The near-infrared region has higher tissue penetration, which reduces light scattering and the likelihood of tissue damage. Therefore, using near-infrared spectra in medical applications and clinical trials is highly effective.

For example, when the anticancer drug doxorubicin, loaded in hollow gold nanoparticles, is exposed to radiation with a wavelength of 808 nm, its anticancer activity increases while drug toxicity decreases. As shown in Figure 11, the conversion of near-infrared radiation into heat increases the rate of drug release

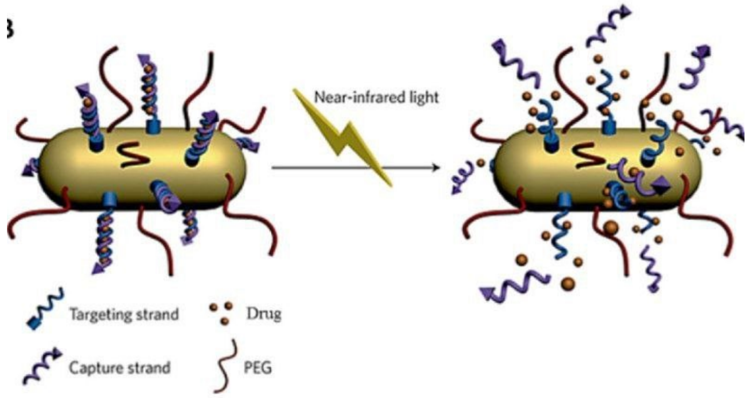

Figure 11 - Diagram showing the effect of near-infrared radiation on the release rate of anticancer drug[11].

### ۵-۵. Electric Field:

The use of electric fields to control and improve the quality of drug delivery was proposed in the 1980s. In this mechanism, high-voltage electric impulses increase the permeability of the cell membrane. In other words, the formation of nanopores in the plasma membrane enables the transfer of drug carriers and molecules, including proteins, antibodies, and oligonucleotides.

## ۶. Conclusion

Drug delivery systems are systems that have the ability to deliver drugs to target tissues, organs, cells, and intracellular organelles using various carriers. These systems offer an appropriate method for drug delivery, providing control over the drug dose, as well as the time and location of drug release. This paper introduced drug delivery systems and their basic principles. It was mentioned that to enhance the effectiveness of targeted drug delivery, the drug release profile should first be examined precisely, and based on the specific needs of the affected tissue for drug concentration over a defined period, the appropriate carrier should be selected. The main factors influencing the drug release rate in the body were identified. It was also pointed out that many drugs are unstable and toxic, with a short therapeutic window. Furthermore, some drugs have poor solubility in water. Nanometric drug carriers, with excellent features such as encapsulating many drugs for protection during the transfer process, controlled release, and targeted delivery to tissues, provide a unique solution to these challenges. It was emphasized that one of the methods for programmed drug release during targeted drug delivery is using stimulus-responsive delivery systems. These systems release their drug payload at the desired location in response to changes in structure, solubility, shape, size, or surface charge when exposed to one or more stimuli. The fundamentals and challenges of drug delivery systems using external physical forces such as magnetic fields, ultrasound, light, heat, and electric fields, as well as the advantages and applications of these systems, were discussed and examined.

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# Safety of nanomaterials

- **Toxicity of Nanomaterials (1): Principles and Basics**
- **Toxicity of Nanomaterials (2): Effective Parameters**

# Toxicity of Nanomaterials (1): Principles and Basics

Abstract

The issue of nanomaterial toxicity became a major concern after the development of nanomaterials in various industries. Many substances that do not show toxic properties in bulk can become toxic when reduced to the nanoscale, potentially causing problems for humans, animals, or plants. Some of the reported toxic effects of nanomaterials include gene mutations, cancer, heart and respiratory diseases, and liver damage. In many cases, these risks can be mitigated through simple measures, such as proper coating. However, awareness of these risks is crucial and necessary. This paper reviews the toxic properties of nanomaterials and the potential health, environmental, fire, and explosion hazards associated with exposure to nanomaterials.

Keywords: Toxicity, Nanomaterials, Nanotoxicology, Gene Mutation, Cell Death

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## ١- Introduction

If we examine the exposure of the environment to nanoparticles, we find that nanoparticles can easily be transported through the air and easily adhere to external surfaces, but detecting them in the environment is very difficult. Nanoparticles may enter our food chain through the environment, impact the biosphere, and cause structural changes in liquids such as water (biogenic nanoparticles).

Nanomaterials have unique properties due to quantum size effects and the large surface area to volume ratio, which affect their toxicity. Recent research shows that materials that are harmless in bulk form can become more reactive at the nanoscale and can have toxic, dangerous, and harmful effects. This issue is the main subject of a branch of science called nanotoxicology.

In most cases, nanoparticles are unsafe for biological systems. Based on research on nanoparticle toxicity, many of these materials may enter the human body and cause toxicity at the cellular level in tissues and organs. Interestingly, the materials that make up these nanoparticles may not themselves be carcinogenic or allergenic, but the resulting nanoparticles, even if chemically neutral, can absorb some toxic species or lead to the formation of toxic products through reactions with bodily fluids, causing subsequent harmful effects. Some nanoparticles also have high catalytic properties and can react strongly with oxygen. These reactions can lead to tissue damage, including inflammation and other toxic effects. Nanoparticles that float in the air can also cause asthma and atherosclerosis (heart vessel blockage). For example, fullerenes, which have a high ability to absorb electrons, generate harmful free radicals and cause environmental hazards. These effects have also been reported for carbon nanotubes and quantum dots. However, it should be noted that ultrafine particles with low solubility are more toxic than larger particles based on mass. This paper aims to explore the toxic effects of nanomaterials.

## 2- Hazards of Nanomaterials

When nanoparticles enter the body, they can freely circulate through the bloodstream and reach organs such as the liver or brain. For example, nanoparticles can penetrate into the deeper layers of the lungs and, through the bloodstream, pass through the blood-brain barrier. The danger of exposure to nanoparticles largely depends on the nature of the materials. Nanomaterials within a solid matrix, if not cut or broken down, pose fewer potential risks. When working with nanoparticles in a solution, the formation of nanoparticle aerosols through stirring, mixing, or sonication poses a risk. The greatest danger of exposure to nanoparticles arises when using dry nanoparticle powders. As a general rule, nanoparticles smaller than 10 nanometers behave more like gases and can pass through the skin and lung tissue and penetrate the cell membrane. Once inside the cell, they may cause toxicity or disrupt the cell’s natural chemistry. For example, carbon nanotubes are structurally similar to asbestos fibers, and if inhaled in large quantities over long periods, they can cause pulmonary fibrosis.

The harmful effects of nanoparticle interactions with the body depend on their size, chemical composition, surface structure, solubility, shape, and how the individual nanoparticles are assembled. Due to their small size and high surface area, nanoparticles can easily bind to toxic pollutants, and if inhaled, they can lead to various lung diseases in mammals. About 80% of nanoparticles that enter the body through inhalation and settle as particles can move through the bloodstream.

The distribution of nanoparticles in the bodies of living organisms may depend on their size and surface properties, such as hydrophilicity, polarity, and catalytic activity. For example, as particle size decreases, the surface area per unit mass increases, thus nanoparticles exhibit more chemical and biological activity in the body. As a general rule, smaller nanoparticles may be more toxic than their larger counterparts and are absorbed by body cells more quickly than larger particles.

Table 1 lists the most important nanoparticles widely used in engineering applications, and their toxicity on human and animal species has been studied.

| Type of Nanomaterial | Main Uses | Related Properties | Toxicity Properties |
|---|---|---|---|
| Iron Oxide | Hyperthermia, drug delivery, biomedical and diagnostic applications | - These nanoparticles accumulate in the liver and other phagocytic organs like the spleen, lungs, and brain after inhalation.<br>- When iron oxide nanoparticles enter cells, they remain in cell | - The presence of iron oxide nanoparticles in the body can cause inflammation, cell lysis (cell breakdown), disruption of the blood clotting system, and reduced cell survival. |

| | | | |
|---|---|---|---|
| | | organelles for a long time and are released into the cytoplasm after breaking down. | |
| Zinc Oxide | Personal care products, sunscreens, paints, UV detectors, gas sensors, and wave filters | - These nanoparticles accumulate in the liver and other phagocytic organs like the spleen, lungs, and brain after inhalation. | - In bacteria and mammalian cells, zinc oxide nanoparticles cause toxicity through mechanisms like cell membrane damage and oxidative stress.<br>- Accumulation of zinc oxide nanoparticles in the human body leads to changes in cell survival, DNA damage, and altered mitochondrial activity in human liver and kidney cells. |
| Titanium Dioxide | Cosmetics, sunscreens, food additives, paints, wastewater treatment, sterilization of implants, and photocatalysts | - Titanium dioxide nanoparticles have low solubility in water and can be used as photocatalysts. | - These nanoparticles have toxic effects and can cause DNA damage, genetic toxicity, and lung inflammation.<br>- When these nanoparticles are exposed to brain cells, they cause cell toxicity in glial cells (neuroglia) and promote brain damage and neurological diseases. |
| Copper Oxide | Antimicrobial agents, semiconductors, heat transfer fluids, solar cells, electronic chips, and gas sensors | - These nanoparticles accumulate in the lungs after inhalation. | - These nanoparticles alter the function of several genes involved in cell cycle progression and genetic damage in human lung cells.<br>- They can cause cell toxicity and genetic toxicity through the production of reactive oxygen species (ROS) and oxidative stress in human lung cells. |

## 2-1- Health Threats

Although determining the exact toxicity parameters of nanoparticles is challenging, studies have shown that high aspect ratio nanomaterials (HARNs) with low water solubility have negative effects on human health. Table 2 provides a summary of the toxicity parameters of some nanomaterials.

| Risk Level | Nanoparticle Characteristics | Example |
|---|---|---|
| High | Insoluble / Low solubility (solubility < 100 mg) | Some carbon nanotubes |
| Medium - High | Insoluble / Low solubility, HARNs with specific toxicity | Silver nanoparticles, gold nanoparticles, zinc oxide nanoparticles |
| Medium - Low | Insoluble or low solubility nanoparticles without specific toxicity | Titanium dioxide nanoparticles |
| Low | Soluble | Sodium dichloride nanoparticles, lipid nanoparticles, fluorine nanoparticles, silica nanoparticles |

Some international organizations, such as the National Institute for Occupational Safety and Health (NIOSH), have developed a comprehensive and intelligent program for the safe use of nanomaterials in the workplace. This program aims to answer the following questions: (1) How might workers be potentially exposed to nanomaterials, and what harmful health effects do these materials have on them? (2) What operational guidelines, personal protective equipment (PPE), and engineering controls can be implemented to minimize the harmful effects of these materials? Some results obtained from studies conducted to develop this program are as follows:

1. During the manufacturing and handling processes of nanomaterials, workers and consumers may be exposed to the release of nanoparticles. This exposure can occur through inhalation, skin contact, and ingestion.

2. Unfortunately, there is limited information available regarding the risks of working with nanoparticles. Therefore, it is necessary for workers to adopt strict control procedures and engineering safety features to minimize exposure to nanoparticles. For example, eating or drinking in the laboratory should be prohibited when working with nanomaterials.

3. When workers handle nanomaterials, they should follow laboratory safety guidelines, including the use of personal protective equipment (PPE) such as gloves, lab coats, safety glasses, face shields, closed-toe shoes, etc., to minimize skin contact with nanoparticles or suspensions containing them. If working with nanoparticle powders, standard laboratory fume hoods should be

used. These hoods are especially important for venting fumes from tube furnaces or reaction vessel tanks (reactors).

4. Laboratory personnel should receive regular training on potential hazards in the laboratory or workplace, safety data sheets (SDS), labeling, signs, etc.

5. Since the disposal and release of nanoparticles into the environment can have a detrimental impact on its safety, standard protocols for the disposal of hazardous chemical waste must be developed and followed.

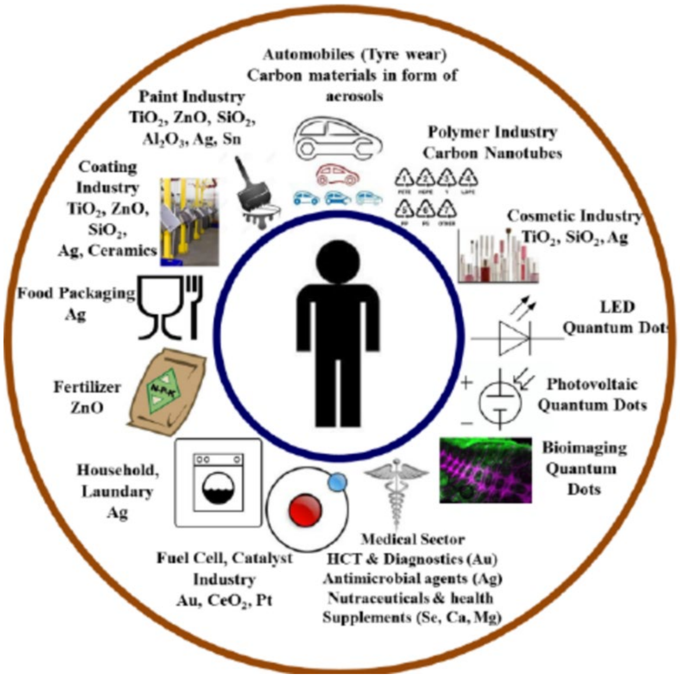

Figure 1 - Examples of potential sources of engineered nanomaterial-containing products and methods of exposure to the human body.

In general, exposure to nanomaterials occurs in three ways. Occupational exposure refers to individuals working with nanomaterials in factories or research laboratories. Consumer exposure involves individuals using products made with nanotechnology, such as cosmetics, healthcare products, and more. Environmental exposure refers to nanoparticles as contaminants in water, air, and soil. To prevent the risks associated with nanoparticle exposure, it is important to know that there are three main pathways through which nanoparticles can enter the human body: inhalation, skin contact, and gastrointestinal ingestion. These three routes are potential ways of exposure to nanoparticles. What determines the toxicity of nanoparticles on biological species is the size, shape, surface area, and surface chemistry of the nanoparticles. The dose of nanoparticles in nanotechnology products is also one of the most important parameters that increase or decrease the toxicity of the products for consumers. An increase in dosage may lead to the unintended release of particles from polymeric, ceramic, and metallic matrices, creating significant environmental hazards. Figure 1 shows the direct and indirect sources of engineered nanomaterials that can enter the human body and living organisms through inhalation, skin contact, and ingestion. Figure 2 illustrates the types of diseases and dysfunctions that may occur in various organs of the body following exposure to nanoparticles.

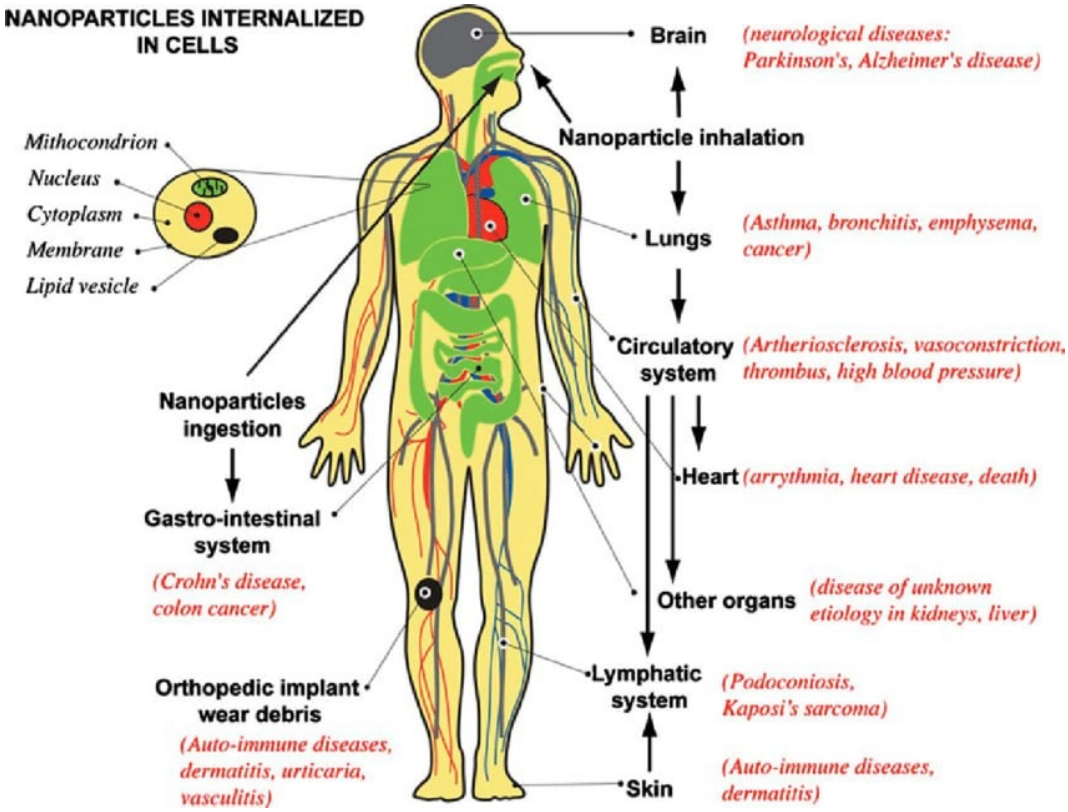

Figure 2 - Pathways of nanoparticle entry into the human body and associated diseases.

### 2-1-1- Inhalation

In general, nanoparticles present in the air, whether in aerosol form or as particles suspended from dry powders, can easily travel long distances due to their small size. The most common route of nanoparticle entry into the human body is through inhalation in the workplace environment.

Nanoparticles, depending on their geometric size, can settle at various points in the respiratory system. The penetration and deposition of inhaled particles in the lungs may occur through one of the following mechanisms: sedimentation, inertial impaction, diffusion, and electrostatic attraction. However, it should be noted that the geometric shape, branching of airways, breathing rate, and the type of breathing (mouth or nasal) affect the mechanism type. Results from recent studies indicate that:

- Inhaled nanoparticles, depending on their size, are primarily found in the upper airways (nose, mouth, throat, larynx, and trachea), but they can also reach deeper sections of the lungs and deposit in the alveoli. Generally, coughing and mucociliary clearance quickly expel particles from most areas of the upper airways, while alveolar macrophages gradually clean the particles around the lungs. It is estimated that about 10% of insoluble particles remain in the human lungs due to very slow clearance.

- Particles with a diameter less than or equal to one micrometer can reach the alveolar sacs and, along with gas exchange, be transported to other parts of the body. In contrast, nanoparticles smaller than 20 nanometers are primarily deposited in the throat and nasal regions through the diffusion mechanism. It is estimated that 90% of 1-nanometer nanoparticles deposit in the throat and nasal area, while the remaining 10% settle in the tracheobronchial tree. Generally, inhaled nanoparticles, in the form of aggregates or agglomerates with a size of one micrometer or larger, settle in areas near the lung alveolar sacs.

- The clearance of nanoparticles from lung tissue is primarily carried out by lung macrophages and pulmonary surfactant protein A (SP-A). This protein binds to the surface of nanoparticles, enhancing their phagocytosis efficiency. In other words, the fate of nanoparticles in different parts of the body depends on their surface interaction with the surrounding biochemical environment.

- The thickness of the capillary walls and alveolar walls is approximately 0.5 micrometers, allowing airborne particles, both micro and nano in size, to easily enter the bloodstream. Observations show that nanoparticles with an average diameter of 35-37 nanometers, once deposited in the nose, can travel through the olfactory nerve and trigeminal nerve to reach the brain.

-Inhalation of nanoparticles can lead to the following problems and diseases in humans: (1) Increased susceptibility to lung cancer; (2) Impaired vasodilation in coronary arteries; and (3) Rapid inflammatory response similar to asthma symptoms.

### 2-1-2- Skin

The skin accounts for more than 10% of the human body's weight and acts as a strong barrier against the entry of nanoparticles from the external environment, helping to maintain body homeostasis and the cells within. The overall structure of the skin consists of three main layers: the epidermis, dermis, and hypodermis. The topic of nanoparticle penetration into the epidermal layer of the skin has been extensively studied in recent years, especially since the cosmetic and personal care industries now use titanium oxide and zinc oxide nanoparticles in sunscreen products. Due to the unique absorptive properties of these nanoparticles, the creams produced can provide high levels of protection against ultraviolet radiation, while remaining transparent to visible light.

Studies conducted on laboratory-reconstructed skin have shown that in order to maintain healthy skin, nanoparticles should not penetrate the dermal layer. Nanoparticles cause cell death by increasing oxidative stress and generating inflammatory cytokines.

In general, nanoparticles can penetrate the epidermal stratum corneum, hair follicles, and sweat glands, as well as areas of burns, wounds, and cuts. Nanoparticles may remain on the surface of the epidermis or the stratum corneum but are unable to penetrate or pass through the living layers of the epidermis, even if they can accumulate in hair follicles. Figure 3 illustrates various methods by which nanoparticles can enter the skin structure.

It is important to note that if the integrity of the skin barrier is compromised for any reason, the absorption of nanoparticles through the skin will increase. The most significant causes of skin barrier degradation include various skin diseases, allergic contact dermatitis (ACD), atopic eczema, psoriasis, mechanical damage, and the use of irritating cleansers and chemical products.

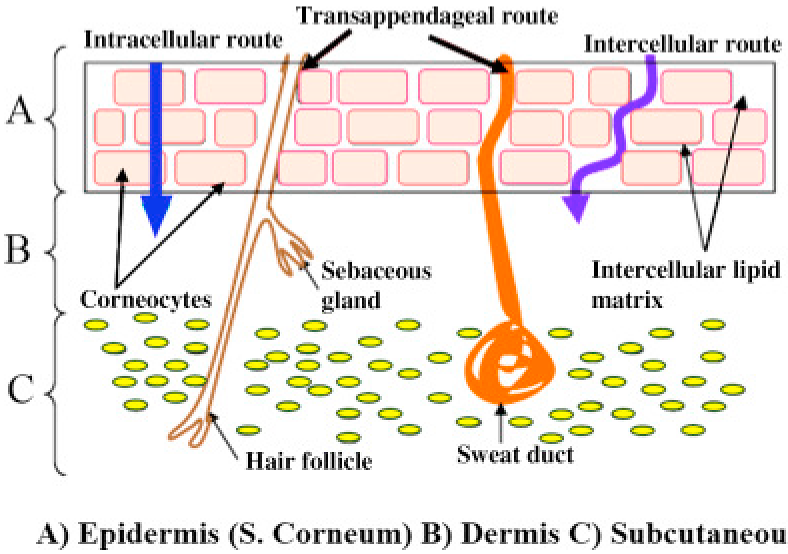

Figure 3 - Pathways of Nanomaterial Penetration through the Skin

Factors such as size, shape, solubility in water, and surface coating significantly affect the potential of nanoparticles to penetrate the skin. However, on average, particles larger than 20 nanometers cannot pass through the live epidermal layer of the skin. Table 3 lists the penetration potential of nanoparticles with different geometric sizes

| Size | Skin Penetration |
|---|---|
| > 45 nm | Low chance of penetrating the skin. |
| 21 – 45 nm | Penetrates through damaged skin (e.g., wounds, burns). |
| 4 – 20 nm | Likely to penetrate, mostly through hair follicles. |
| < 4 nm | Skin penetration has been reported. |

### 2-1-3- Swallowing and Digestion

Swallowing and the entry of nanoparticles through the digestive system is considered to be the least dangerous risk in a laboratory setting. It usually happens accidentally, like when hands touch the mouth. Therefore, by following good hygiene and safety practices in the workplace, wearing gloves and proper work clothing, and thoroughly washing hands after working, the risks of nanoparticles entering the digestive system can be greatly reduced.

Nanoparticles can also enter the body through the consumption of processed food products. For example, to increase the shelf life of some supplements or food ingredients, capsule technology is used. This technology can be based on liposomes. Since liposomes are made of biological molecules, they do not cause any harm to human health. On the other hand, nanoparticles of clay and silver might be used in food packaging to prevent food spoilage and oxidation. Similarly, nanoparticles of silica may be used to improve the fluidity of salt, sugar, and flour. Because of these uses, we need to add all stages of the food chain to the list of ways nanoparticles can enter the human body through the digestive system.

The entire digestive tract is lined with cells that absorb food, so nanoparticles that enter the digestive system are easily and significantly absorbed into the bloodstream, more easily than through the skin or respiratory system. After entering the blood through the lungs, skin, or digestive system, these nanoparticles are absorbed by cells and can settle in organs such as the heart, brain, spleen, kidneys, bone marrow, and liver.

When nanoparticles interact with the mouth, they quickly interact with the mucosal layer of the mouth, penetrate the mouth's epithelium, and disturb the normal balance of the cells in the mouth (the cells under the tongue and in the cheeks). Similarly, these nanoparticles can have unwanted interactions with the digestive system as well. In fact, depending on their nature or if they are unstable, swallowed nanoparticles may either be quickly eliminated or, due to physical or chemical changes, they may accumulate and block the digestive system, possibly leading to death. Studies on the toxic effects of nanoscale food additives, such as TiO2 and SiO2, nanoparticles used in food packaging like ZnO and MgO, and carbon black, on human gut cells show that these materials cause DNA damage in the cells under all conditions.

### 2-2- Fire and Explosion Hazards

One of the main challenges in storing and using nanoparticles is the high risk of fire. When particles are reduced to the nanoscale, some of the surface properties of materials change significantly. For example, the surface area of the particles increases, which leads to more interaction with the surrounding environment and greater chemical activity. The increased reactivity of nanoparticles and their enhanced catalytic properties are other reasons why these materials are more likely to catch fire or explode.

As a real-life example, silver metal doesn’t explode when exposed to mechanical forces or static electricity, and if a fire occurs, it can be put out using water spray or foam. However, silver nanoparticles burn easily in the air. Metal nanoparticles tend to cause more intense explosions compared to carbon-based nanomaterials, and their chemical reactions are different as well. Studies on aluminum and titanium nanoparticles show that these materials are explosive. When they burn, toxic metal oxide gases are released into the air, and to put out the fire, dry powder should be used.

Table 4 lists the structural differences and safety features of silver metal and silver nanoparticles.

| Row | Silver | Silver Nanoparticles |
|---|---|---|
| 1 | Solid, shiny, and metallic white | Gray powder with no smell |
| 2 | Does not explode from static electricity | Explodes from static electricity |
| 3 | Does not burn in open air | Burns easily in open air |
| 4 | No risk of explosion from strong impact on container | Can explode if the container is hit hard |
| 5 | Water spray and foam can be used to put out fire | Water and foam should never be used; dry powder should be used |
| 6 | Can be stored in a regular warehouse, away from direct sunlight | Must be stored in a dry, cool, dark place with proper ventilation and spark-proof conditions |

## 2-3- Environmental Pollution

So far, only a few methods have been developed to measure the concentration of nanoparticles in natural systems. Thus, there is not much information about the amount, distribution, and effects of engineered nanoparticles on animals and plants in the environment. Weather conditions such as humidity, temperature, wind speed, geographical height, and the nature of light can affect the characteristics of nanoparticles that cause their toxicity. At higher temperatures and faster wind speeds, the spread of nanoparticles in the environment and their absorption in plant and animal tissues increases.

Nanoparticles, by creating toxicity for different living species, have destructive effects on the food chain. For example, when nanoparticles come into contact with microorganisms in soil and groundwater, they cause toxic effects on them. Later, fish, insects, or mammals that consume these affected microorganisms are at risk.

### 2-3-1- Aquatic Environment

The use of nanomaterials in products like cosmetics and sunscreen leads to the release of nanoparticles into aquatic environments. These nanoparticles enter aquatic animals through their gills, digestive system, or skin, and depending on the type, size, and shape of the nanoparticles, they cause different toxic effects in various species of aquatic life.

In a study conducted on zebrafish to evaluate the toxicity of silver, copper, nickel, and aluminum nanoparticles, the harmful effects of silver nanoparticles were confirmed. Other studies have also reported the toxic effects of silver colloid nanoparticles on rainbow trout, Daphnia magna (water fleas), and Gambusia fish. Silver nanoparticles, due to their reproductive stress effects, lead to the expulsion of juvenile fish and immature eggs from female fish. The respiratory problems in fish caused by the reaction of nanoparticles with the gill layers lead to suffocation. Therefore, the intentional or accidental release of silver nanoparticles into aquatic ecosystems should be prevented.

### 2-3-2- Soil Environment

The release of nanoparticles may occur from sources such as production facilities, landfills, or sewage treatment plants, either intentionally or accidentally. Soil contains a large number of microorganisms, and exposure to high concentrations of silver nanoparticles for extended periods can reduce microbial population growth to zero. These particles also affect the immune system of earthworms. Zinc oxide (ZnO) nanoparticles have adverse effects on the fertility of earthworms. Cesium nanoparticles, depending on their size and concentration, can disrupt the denitrification process of soil bacteria.

Another way nanoparticles enter the soil is through their use in the formulation of natural or chemical fertilizers and agricultural hydrogels. For example, polymeric hydrogels are used for the long-term irrigation of plant species. These materials can absorb large amounts of rainwater and release it when needed by the plant tissue. In the formulation of hydrogels, silica nanoparticles are often used to improve the mechanical properties and increase the water absorption capacity. Over time, these nanoparticles accumulate in the soil and disrupt the natural bacteria processes within the soil.

## 3- Summary and Conclusion

Today, the use of nanotechnology in scientific and industrial fields has expanded significantly. The application of nanomaterials for therapeutic, diagnostic, agricultural, textile, and other purposes has increased the release of nanoparticles into the human body and the environment. The health and safety risks of nanomaterials include the potential toxicity of various nanoparticles and hazards related to fire and explosion from dust. Various environmental factors can play a role in the toxicity of nanoparticles.

When people are exposed to nanoparticles, they enter important organs such as the lungs, skin, and digestive system through three main routes: inhalation, skin contact, and ingestion. From these pathways, nanoparticles can enter the bloodstream through vascular beds and spread throughout the body. Eventually, after cellular absorption, they may accumulate in the heart, brain, spleen, kidneys, bone marrow, and liver. Additionally, some of these nanoparticles can damage DNA molecules through oxidative stress, leading to potential cancer development.

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# Toxicity of Nanomaterials (2): Effective Parameters

## Abstract

The unique properties of nanoparticles, such as their high surface characteristics and reactivity, are key factors contributing to their increasing application in various industrial and medical fields, with diverse sizes, shapes, and compositions. Nanometric particles interact with living cells, altering their behavior and function. The cellular responses that the body exhibits when exposed to nanoparticles depend on properties such as size, shape, and surface characteristics of the nanoparticles. The intensity of toxicity also depends on the type of cell exposed to the nanoparticles. Currently, nanotoxicology studies are focused on describing the potential effects of nanomaterials when interacting with living cells and assessing their toxicity. However, there are still many uncertainties regarding the mechanisms of toxicity and the different types of toxic nanomaterials. Understanding the various features and toxic properties before using nanoparticles is crucial for their safe application. This article examines the factors influencing the toxicity of nanomaterials, including physical and chemical characteristics such as size, shape, chemical composition, coating, and surface charge of nanoparticles.

Keywords: Nanomaterials, Toxicity, Physical and Chemical Properties, Reactivity

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## 1- Introduction

In today's world, with the continuous development of nanotechnology and the creation of related products, exposure to nanoparticles in environmental pollutants such as water, soil, air, and even in workplaces and laboratories is inevitable for humans. Nanoparticles are solid particles that, like liquids and gases, have the ability to move, spread, and accumulate in various plant and animal tissues. Nanoparticles, by altering their physical-chemical surface properties, actively interact with body cells. Components of cells exposed to nanoparticles undergo damage, deformation, and dysfunction, disrupting the biological functions of the cells. Identical cells respond differently to various types of nanomaterials depending on their size, shape, and surface charge. Similarly, nanomaterials can generate different cellular responses in different cell types. The toxicity of nanomaterials is largely related to factors such as size and surface-area-to-volume ratio (which increases reactivity), chemical composition (the main factor for reactivity), and surface charge (the factor responsible for electrostatic interactions). In addition, there are various structural parameters that also influence the toxicity of nanomaterials, which will be discussed in detail in this article. Currently, studies on the toxicity of nanomaterials are expanding, and a wide range of acute and chronic effects of nanoparticles on the growth and metabolism of living organisms have been reported. Many researchers believe that the toxicity of nanomaterials should be evaluated before their application. This article briefly discusses the factors and physical and chemical parameters that affect the reactivity and toxicity of nanoparticles.

## 2. Effective Features in Nanomaterial Toxicity

The toxicity of nanoparticles arises from the physiological interactions of nanometric particles with the body's cells. Some nanomaterials exhibit cytotoxicity due to their constituent materials, while others are toxic to the body because of the physical-chemical characteristics that emerge at the nanoscale. As a general rule, nanoparticles with smaller sizes of a specific material tend to be more toxic than larger particles of the same material. In addition to the size of nanoparticles, their distribution and accumulation in specific parts and organs of the body is another determining factor in the toxicity of nanomaterials. The accumulation and distribution of nanoparticles in the body directly correlate with the size and surface properties of the particles. Another important parameter influencing the toxicity of nanomaterials in the body is the ability to excrete the particles properly or the unwanted deposition of particles in organs. When nanoparticles accumulate in the body without proper elimination, they can cause more prolonged toxicity. In most nanoparticles, the liver and spleen are the organs where the highest accumulation of particles occurs, although other organs can also exhibit similar potential.

When nanoparticles are ingested, inhaled, or absorbed through the skin, they can produce reactive oxygen species (ROS), including free radicals. These active species induce oxidative stress, inflammation, and ultimately damage biological materials in cells, such as proteins and DNA. The amount of ROS formed depends directly on factors such as particle size, morphology, aggregation and deposition in tissues, chemical composition, surface chemistry (functional chemical groups), surface charge, and solubility. For instance, due to their small size, nanoparticles can pass through tissue junctions and even cellular membranes, causing severe structural damage to mitochondrial organelles or attacking the cell nucleus, leading to mutations in DNA molecules and cell death.

To summarize, the above factors can be condensed into five key features: particle size, surface area of the particles, surface electrostatic status, particle morphology, and the accumulation of particles in organs and tissues.

Extensive studies have been conducted to minimize unwanted interactions between nanomaterials and biological tissues. One suggested approach to reduce these interactions is to apply coatings on the external surface of particles and introduce specific functional groups. However, a challenge that remains is that surface coatings only protect nanoparticles for a short period. After one to four hours, environmental interactions, such as exposure to air or ultraviolet radiation, cause the coating to degrade and disappear. Studies show that this surface instability can be minimized by modifying and engineering certain physical-chemical properties. This article discusses the most important physical-chemical parameters that affect the toxicity of nanomaterials and explores ways to reduce their toxicity. Figure 1 summarizes the discussed parameters.

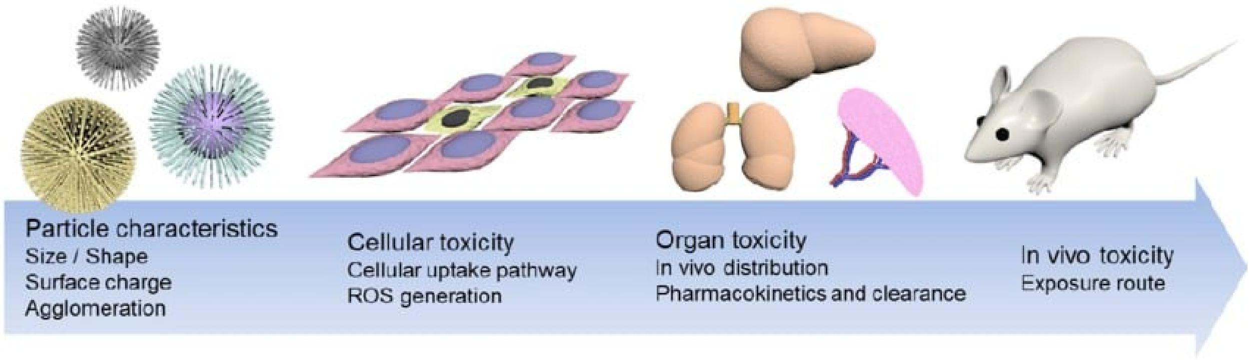

Figure 1 – Diagram of Cellular Toxicity Caused by Nanoparticles

The intrinsic properties of nanoparticles, such as size, surface charge, and aggregation or accumulation patterns, can significantly influence cellular toxicity. The resulting cellular toxicity can impact not only individual cells but also organs and even entire physiological systems.

## 2-1- Particle Size

Because nanoparticles are so small, they have a very high surface-to-volume ratio. This makes them more reactive in biochemical reactions, enhances their catalytic properties, and increases their toxicity. Additionally, nanoparticles have a higher ability to move into human and plant tissues compared to regular, larger particles. As the average size of nanoparticles decreases, their surface area increases significantly, making them more likely to participate in oxidation reactions and cause damage to DNA molecules in animal and plant cells.

The size and surface area of nanoparticles are two of the most important factors that determine how they interact with living systems. Nanoparticles' large surface area increases their reactivity and catalytic activity when they come into contact with cells in the body. This becomes especially important because the size of nanoparticles (1 to 100 nanometers) is comparable to the size of protein molecules (2 to 10 nanometers), the spiral shape of DNA molecules (2 nanometers), and the thickness of cell membranes (10 nanometers). Because of their tiny size, nanoparticles can easily enter cells and cell organelles. As a general rule, smaller nanoparticles are more likely to enter cells (through endocytosis) and are more toxic than larger ones. For example, the following results are from studies examining how the size of nanoparticles affects their interaction with human and animal cells:

- Nanoparticles with a size of 35 nanometers or smaller can pass through the blood-brain barrier. Particles smaller than 40 nanometers or larger have the potential to enter the cell nucleus. Similarly, particles about 100 nanometers in size can pass through the cell membrane.

- Gold nanoparticles larger than 6 nanometers can enter the cell nucleus, while larger nanoparticles (10 or 16 nanometers) can only pass through the cell membrane and stay in the cytoplasm. This means that nanoparticles a few nanometers in size are more toxic than nanoparticles that are 10 nanometers or larger, which cannot enter the nucleus. On the other hand, nanoparticles that are 1.4 nanometers cause cell necrosis, while 1.2-nanometer particles mostly cause apoptosis (a type of programmed cell death).

- Nanoparticles not only can enter the cell nucleus, but if their size is similar to the size of DNA molecules, they can interact with the DNA backbone and its sugar-phosphate groups, disrupting transcription (the process of making RNA from DNA).

- The size of nanoparticles can also affect how they enter cells and how they are distributed throughout the body. Nanoparticles can enter cells through different mechanisms like phagocytosis, micropinocytosis, or specific and nonspecific transport systems. For example, nanoparticles smaller than 5 nanometers usually enter cells non-specifically through movement across the membrane, while nanoparticles around 25 nanometers use pinocytosis to enter the cell's cytoplasm. Also, nanoparticles smaller than 10 nanometers, after being injected into the bloodstream, quickly spread throughout the body, whereas larger nanoparticles (50-250 nanometers) tend to stay in the liver, spleen, and blood. This shows that the immune system recognizes larger nanoparticles and captures them with phagocytic cells to prevent them from spreading to other tissues.

- The main reason nanoparticles are toxic is their ability to enter cell structures, create oxidative stress, damage DNA molecules (both nuclear and mitochondrial), and induce apoptosis. For example, silver nanoparticles release a significant amount of silver ions in the cell environment, causing high toxicity to human lung cells. The size of silver nanoparticles that causes toxicity in lung cells is about 10 nanometers.

- Nanoparticles can adsorb proteins like immunoglobulins, albumin, and others, causing them to cluster and form masses. Depending on the size of the masses, these nanoparticles then enter cells through different endocytosis and pinocytosis pathways after binding to cell membrane receptors.

As a conclusion, reducing the size of particles to the nanoscale affects their interaction with body tissues and their ability to cause cell toxicity in several ways:

1. As the size of the particles decreases, more surface area becomes available for reactive groups. These surface groups can be hydrophilic, hydrophobic, or have catalytic properties. Having more reactive surface groups and a large surface area can help nanoparticles be absorbed by cells.

2. The size of the particles plays a key role in how nanoparticles interact with the circulatory and immune systems. This interaction also determines how particles are distributed and accumulate in different organs. For example, nanoparticles around 25 nanometers enter cells through pinocytosis, while particles smaller than 10 nanometers spread quickly throughout all organs and tissues after being injected into a vein. Larger nanoparticles (50-250 nanometers) are recognized by the immune system and are prevented from entering other tissues.

3. When more atoms and molecules are located on the surface of a nanoparticle, it increases the particle's surface energy, which makes the particle more reactive. In cells, this can lead to changes,

genetic mutations, and disruptions in biochemical reactions, eventually causing cell death. The immune system will then remove these damaged cells.

## 2-2- Particle Shape

Nanoparticles can be made in various shapes and forms, such as spheres, rods, fibers, plates, and complex shapes like pyramids, cubes, and hexagons. The way these particles interact with cells and how toxic they are depends a lot on their shape and structure. For example, spherical nanoparticles are more likely to be taken up by cells (a process called endocytosis) compared to carbon nanotubes or nanofibers. Single-walled carbon nanotubes are also more effective than spherical fullerenes at blocking calcium channels in cell membranes and disrupting the cell's metabolic activity. Recent studies show that carbon nanotubes are more toxic than other types of carbon black or silica particles. As a result, many workers who are exposed to single-walled carbon nanotubes (SWCNTs) beyond the safe limit end up with lung damage. These particles cause kidney cell death by inhibiting cell growth. Similar effects have been reported for zinc oxide (ZnO) nanoparticles. According to these studies, ZnO nanoparticles with a rod-like shape are more toxic to human lung epithelial cells (A549) than spherical ZnO nanoparticles.

Scientific sources agree that spherical nanoparticles are much less toxic than rod-shaped nanoparticles, and rod-shaped particles are less toxic than plate-shaped particles (such as graphene). There are a few key reasons for this:

1. The physical damage caused by spherical nanoparticles to the cell membrane and other parts of the cell is much less than that caused by needle-like, fibrous, triangular, and angular particles (see Figure 2). For example, needle-like uric acid nanocrystals easily cause cell damage and severe tissue inflammation. Similarly, graphene oxide nanoplatelets cause toxicity in living cells by damaging the cell membrane.

2. Spherical nanoparticles have the highest surface-to-volume ratio among all other shapes, which allows them to pass through the cell membrane and enter the cell more easily and quickly. Because of this, plate-like, cylindrical, and non-spherical particles are naturally less likely to be absorbed by immune cells and stay in the bloodstream for longer periods of time.

3. The crystalline structure of nanoparticles can also affect their shape and toxicity. For example, when titanium dioxide (TiO2) nanoparticles crystallize in the rutile phase, they take on a prismatic shape and cause oxidative damage to DNA molecules, disrupt mitosis (the process of cell division), and cause lipid peroxidation (damage to cell membranes). However, when TiO2 nanoparticles crystallize in the anatase phase, they take on an octahedral shape and show less toxicity compared to rutile.

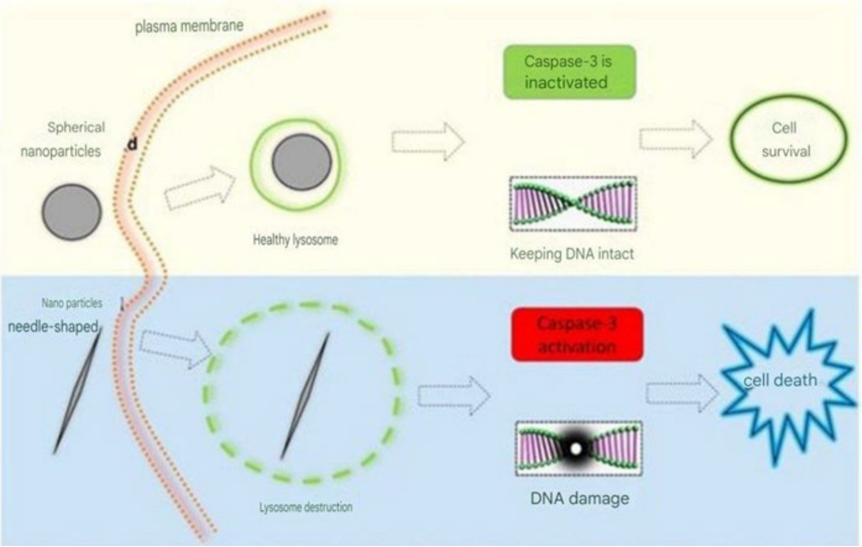

Figure 2 – Cellular toxicity of different nanoparticle shapes

## 2-3- Agglomeration and Particle Accumulation Intensity

Another important factor affecting the toxicity of nanoparticles is their tendency to agglomerate and accumulate in the tissues and organs of the human body and other biological species. Some nanoparticles tend to selectively accumulate in the liver and spleen, while others prefer to remain in the bloodstream and move through bodily fluids. Therefore, the toxicity of each nanoparticle should be assessed based on where it accumulates in the body. For example, a specific nanoparticle might be toxic to liver cells but may have no negative effect on eye cells. Another important parameter is the agglomeration of nanoparticles in the presence of bodily fluids. The tendency of particles to stick together and form submicron clusters can create a suitable environment for the accumulation of proteins, carbohydrates, and lipids, leading to the formation of unwanted biological masses in the body. For example, regardless of the physical-chemical properties of the nanoparticles, such as their chemical composition, agglomeration can be a strong trigger for inflammatory lung damage in humans, leading to fibrosis and cancer.

## 2-4- Stability of Nanoparticles

The stability of nanoparticles in biological systems is primarily dependent on their nature, size, and concentration. Along with these characteristics, the environment within biological systems, such as the human body, also affects nanoparticle stability. For example, most organic and inorganic nanoparticles are soluble at the pH levels commonly found in the human body. Metals and metal oxide nanoparticles can also dissolve well in the body, increasing the concentration of metal ions in cells. This increase in ion concentration within the cytoplasm can stress the cell significantly and disturb its homeostasis. However, in the case of nanoparticles that are insoluble in bodily fluids, such as ceria, zirconia, and titania, only the cell's activity and the number of DNA molecules decrease.

## 2-5- Chemical Composition

Although the toxicity of nanoparticles is largely dependent on their size and shape, their chemical composition is another important and influential factor in their toxicity. For example, zinc oxide nanoparticles with a particle size of 20 nanometers exhibit toxicity through oxidative stress mechanisms, while silicon dioxide nanoparticles with the same particle size alter DNA structure. In Table 1, nanoparticles of various natures and their biological characteristics describing their toxic effects are outlined.

One of the primary reasons for nanoparticle toxicity is the release of metal ions. For example, the release of metal ions from the core of Ag and Cd nanoparticles causes toxicity and cell damage. However, other metal ions, like iron and zinc, are not only not harmful to cells but can even be beneficial; still, at high concentrations, they can become toxic. To reduce or prevent the toxicity of metallic nanoparticles, relatively thick coatings of polymeric compounds, silica layers, gold shells, or non-toxic biocompatible compounds such as chitosan and albumin can be applied to the nanoparticles. Additionally, alloying the nanoparticle core can minimize the release kinetics of metal ions.

Another important point regarding the impact of the chemical composition of nanoparticles on their cellular toxicity is the ability of the particles to absorb protein structures. Some nanoparticles can absorb and alter the structure of proteins, thus changing their nature.

Table 1 - Effect of the chemical nature of nanoparticles on toxicity

| Nanoparticle | Size (Nanometers) | Factors Affecting Toxicity | Examples of Toxicity |
|---|---|---|---|
| Silver | 13-15 | Dependent on surface properties of nanoparticles, Ag+ ion release, and presence of coating on silver nanoparticles | Cell membrane damage, disruption in DNA replication, oxidative attack |
| Gold | 4-5 | Dependent on binding with ligands | Effects on reproduction of daphnia, mammals, algae, and fish; accumulation in liver and oxidative stress |
| TiO2 (Titanium Dioxide) | 40-100 | Dependent on surface chemistry, stability, and placement location | Negative effects on wheat growth and soil enzyme activity; photo-toxicity and DNA fragmentation |

| | | | |
|---|---|---|---|
| Carbon Nanotubes | 20-200 | Dependent on particle size, shape, surface charge, and biodegradability | Human lungs, epithelial cells, embryo toxicity, disruption of cell proliferation, brain, liver, brain, and gut damage; respiratory toxicity, photo-toxicity; effects on seed germination |
| Aminopolystyrene | 20-60 | Dependent on the presence of surface functional groups (cationic form is more toxic) | Toxic to macrophages, liver tumors, epithelial cells, endothelial cells, mitochondrial uptake, and cell death |
| Quantum Dots | Less than 515 | Dependent on surface changes, bioactivity, size, concentration, stability, and environmental factors | Oxidative stress in plants, endothelial toxicity via mitochondrial activation |

### 2-4- Surface Charge

The plasma membrane of living cells is made up of two layers of phospholipids, with cholesterol molecules and proteins potentially embedded between them. Each phospholipid molecule has a hydrophilic head (phosphate group and glycerol) and a hydrophobic tail (long carbon chain). Proteins located on the outer surface of the membrane can attach to sugar molecules or branched carbohydrates, forming compounds known as glycoproteins (see Figure 3). Glycoproteins and the anionic phosphate groups in the phospholipids of the membrane carry a negative charge, which makes them highly attractive to nanoparticles with a positive surface charge through electrostatic interactions.

Because of this, nanoparticles with a positive surface charge are easily absorbed by the cell membrane and are more successful in the endocytosis process compared to particles with a negative surface charge. The positive charge of nanoparticles not only directly influences cellular uptake but can also affect the degradation of DNA molecules and other cell organelles. For example, positively charged polystyrene nanoparticles are more easily absorbed by cells compared to when they have a neutral or negative charge. These nanoparticles can bind to DNA strands (which contain negatively charged phosphate groups) and cause damage, leading to the prolongation of the G1 and G0 phases of the cell cycle. Nanoparticles with a negative charge have no effect on the cell cycle.

As another example, positively charged gold nanoparticles enter blood cells faster and in higher quantities, and are more easily absorbed by lysosomes. Therefore, positively charged gold nanoparticles show more toxicity than negatively charged gold nanoparticles.

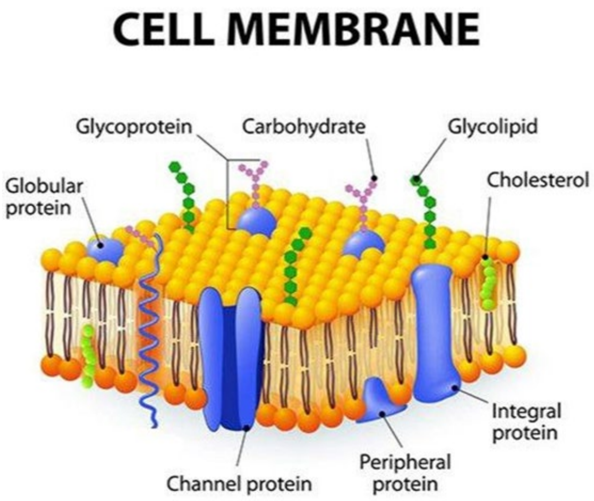

Figure 3 – Cell Membrane: Presence of macromolecular proteins across the membrane along with glycoprotein compounds (sugar + protein) on the outer surface of the membrane.

The higher the surface charge of a nanoparticle, the greater its toxicity. Cationic nanoparticles can stimulate and activate the body's immune system because their positive surface charge causes them to be attracted to the surface of immune cells, such as macrophages, which contain negatively charged sialic acid groups. In contrast, anionic nanoparticles tend to accumulate more in tumor tissues. Therefore, by altering the surface charge of nanoparticles, their release and toxicity can be controlled within the body, making them useful in systems for targeted chemotherapy drug delivery to cancerous tumors.

Nanoparticles with a positive surface charge have a higher potential for opsonization, meaning they can easily absorb proteins, such as antibodies, which facilitate the process of phagocytosis from the blood and biological fluids and hold them on their surface. Opsonization can affect the surface properties of nanoparticles by altering the surface charge, aggregation status, and hydrodynamic diameter of the nanoparticles. On the other hand, the absorption of proteins onto the nanoparticle surface can lead to structural changes in the nanoparticles and may disrupt or completely inhibit the functional activities of the absorbed proteins (such as enzymatic and biological activities). This phenomenon could lead to the development of various diseases, such as amyloidosis.

### 2-5- Surface Coating

The surface charge properties of nanoparticles and their toxicity depend largely on the presence or absence of functional groups in the surface coatings applied. Most common nanomaterials are hydrophobic and insoluble, meaning they tend to cluster together and form deposits in biological systems. If these nanoparticles are chemically unstable, they can release metal ions or free radicals, which can lead to toxicity. Special coatings on nanoparticles, such as surfactants, polymers, and various functional groups, can increase the stability and solubility of the particles in biological liquids. This can help reduce the toxicity of the nanoparticles and allow them to interact more effectively with specific cells. For example, studies on how hydrophilic and hydrophobic particles are distributed in the bodies of animal species showed that hydrophobic particles spread throughout the animal's body and caused death in less than 24 hours. On the other hand, hydrophilic particles had no noticeable effect on the health of the animals.

Different types of biocompatible surface coatings improve the biological properties of nanoparticle-based systems used for targeted drug delivery. For instance, iron oxide nanoparticles are widely used in magnetic resonance imaging (MRI) due to their ability to be controlled by an external magnetic field. Iron oxide nanoparticles coated with branched glycerol polymers, which have many functional groups, can deliver drugs more efficiently and specifically. In cytotoxicity tests, studies on the biocompatibility of iron oxide nanoparticles showed that uncoated samples were toxic to cells at concentrations of 200 µg/ml or higher, while the coated samples did not show this toxicity. Table 2 illustrates how the patterns of accumulation and distribution of drug nanoparticles in the body change with different types of surface coatings.

Table 2 - Effect of Surface Coating of Drug Nanoparticles on Their Fate, Application, and Distribution in the Body

| Coating | Effect | Application |
|---|---|---|
| Without coating | Phagocytosis by macrophages | MRI |
| IgG | Uptake by immune cells | Immune cell tracking |
| PEG | Improved circulation time | Drug delivery |
| Folate | Targeted delivery to tumor tissue | Drug delivery |

## Summary and Conclusion

Nanoparticles, alongside their various industrial and medical applications, exhibit certain toxicological properties due to their interactions with living cells. Natural and human activities have led to the release of significant amounts of different types of nanoparticles into the environment, raising considerable concerns in the fields of health and environmental safety. Toxicological studies at the nanoscale focus on the relationship between the physicochemical properties, such as chemical composition, size, and surface topography, and the degree of interaction between nanoparticles and living cells. The salts present in serum influence the electrostatic properties of nanoparticles, affecting the stability and fate of their interactions with cells. Therefore, the characterization of nanoparticles is important not only in dry environments but also in physiological environments such as serum and bodily fluids (colloidal stability, surface potential, and hydrodynamic diameter).

Individual studies in toxicology require the standardization of tests and laboratory conditions. Considering concentration as an important parameter in toxicity and examining the long-term effects of nanoparticles on homeostasis and cell viability, along with the accumulation and stability of nanoparticles inside cells over several days and weeks, presents a significant challenge. Nevertheless, despite the difficulties in assessing toxicity and measuring nanoparticle concentrations, toxicological studies are expanding. Suitable methods have been published in safety guidelines and regulations to prevent exposure to the risks of nanomaterials, reduce environmental impacts, and ensure the health and safety of workers.

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