

## Historical development of Nanomaterials

The development of nanomaterials has evolved over several decades, with significant contributions from a variety of scientific disciplines, including chemistry, physics, biology, and materials science. The history of nanomaterials can be traced back to both theoretical discoveries and practical innovations. Here's an outline of key milestones in the historical development of nanomaterials:

### *Ancient and Pre-Modern Era (Before 20th Century)*

- **Historical Uses of Nanomaterials:** Although the term "nanomaterials" did not exist, there are historical examples of materials that exhibited nanoscale properties. For instance:
  - **Ancient Roman and Byzantine Glass:** Some historical artifacts, like the Lycurgus Cup (4th century AD), show that ancient civilizations unknowingly used nanomaterials. The cup exhibits a color-changing property when viewed in different lights, a phenomenon caused by nanoscale gold and silver particles embedded in the glass.
  - **Alchemical and Metallurgical Practices:** Early alchemists, as well as ancient metallurgists, unknowingly worked with materials at the nanoscale when they created pigments, dyes, and alloys with special properties.

### *20th Century Foundations*

#### **1920s - 1940s: Early Theoretical Foundations**

- **Quantum Mechanics and Atomic Theory:** The theoretical groundwork for understanding materials at the atomic and molecular scale was laid by early pioneers in quantum mechanics, such as Niels Bohr, Werner Heisenberg, and Erwin Schrödinger. This provided the theoretical basis for understanding phenomena at the nanometer scale, although the tools to directly manipulate materials at that scale did not yet exist.
- **Richard Zsigmondy (1900s):** Zsigmondy, an Austrian scientist, invented the ultramicroscope, a tool that allowed the visualization of nanoparticles such as colloids (particles in the size range of nanometers). This was an important step in understanding the behavior of materials at small scales.

## **1950s - 1960s: Early Concepts of Nanoscience**

- **Nanoscale Engineering:** In the 1950s, the concept of manipulating materials on a very small scale began to gain attention. Scientists started to explore how materials behave at the atomic and molecular level, though practical applications were limited.
- **Fullerenes and Carbon Nanostructures:** In the late 1950s, the notion of "buckyballs" (C<sub>60</sub>) was conceptualized by scientists like R. B. Curl and Harold Kroto in the 1980s, but its theoretical foundation was earlier anticipated by scientists working with carbon structures.

## **1974 - 1980s: Emergence of the Term "Nanotechnology"**

- **Nanotechnology Coined by Norio Taniguchi (1974):** The term "nanotechnology" was coined by Japanese researcher Norio Taniguchi in a paper published in 1974. Taniguchi defined nanotechnology as the "precision synthesis and processing of materials" at the atomic, molecular, or macromolecular level, typically between 1 and 100 nanometers. This marked the formal birth of nanoscience as a distinct field of research.
- **Scanning Tunneling Microscope (STM):** In 1981, the invention of the scanning tunneling microscope (STM) by Gerd Binnig and Heinrich Rohrer at IBM Zurich was a breakthrough, allowing scientists to visualize and manipulate individual atoms and molecules on surfaces. This marked the beginning of hands-on research at the nanoscale.
  - **Binnig and Rohrer** received the Nobel Prize in Physics in 1986 for their invention.

## ***1990s - 2000s: Rapid Advancements and Technological Progress***

### **Self-Assembly and Molecular Nanotechnology**

- **Self-Assembly:** The 1990s saw significant progress in understanding how molecules could be designed to self-assemble into nanostructures. This concept, which has since become a core idea in nanotechnology, holds that molecules can spontaneously organize themselves into functional nanoscale devices.
- **Eric Drexler and Molecular Nanotechnology (1980s-1990s):** Eric Drexler's 1986 book *Engines of Creation* popularized the idea of molecular assemblers—tiny

machines capable of assembling materials atom by atom. Though some of Drexler's ideas were speculative, they helped fuel interest in molecular nanotechnology.

## **Nanomaterials**

Nanomaterials are defined as particles in the form of crystals, rods, or spheres having size between 1 nm and 100 nm at least in one dimension.

A nanometre is one billionth of a meter, or  $10^{-9}$  m. Materials in this range of size exhibit some remarkable specific properties. For example, crystals in the nanometre scale have a low melting point and reduced lattice constants.

Nano systems display electronic, photochemical, electrochemical, optical, magnetic, mechanical or catalytic properties that differ significantly not only from those of molecular units, but also from those of macroscopic systems.

### **Physical properties that make nanomaterials different from bulk (macroscale) materials**

1. Due to smallness of nanomaterials, their mass is extremely small and gravitational forces become negligible, instead electromagnetic forces are dominant in determining the behaviour of atoms and molecules.
2. For objects of very small mass, such as electrons, (wave – particle duality of matter) wave like nature has more pronounced effect. The position of electrons are represented by wave function. Quantum mechanics is used to describe motion and energy instead of classical mechanics.
3. The consequence of this is the tunnelling. It is the penetration of an electron into an energy region that is classically forbidden. For a particle having less energy than the energy required to overcome a potential barrier, there is no probability of finding the particle on the other side of the barrier according to classical theory. But quantum mechanically, there is a finite probability of the particle tunnelling through the barrier. The condition for this to happen is that the thickness (energy potential) of the barrier must be comparable to the wavelength of the particle. This is observed at nanometre scale.
4. Quantum confinement – In a nanomaterial, such as a metal, electrons are confined in space rather than free to move in the bulk of the material.
5. Quantisation of energy – Electrons in a nanomaterial can exist at discrete energy levels.

6. At nanoscale, the random motions are of same scale as the size of the material. This has an influence on how particle behave.

7. Increased surface to volume ratio – One of the distinguishing properties of nanomaterials is that they have increased surface area. This leads to unique properties of materials at nanoscale.

### Synthesis of nanomaterials

There are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures. They are

(1) top-down method of miniaturizing materials,

(2) bottom-up method of building molecular structures atom by atom or molecule by molecule.

The top-down approach has been advanced by Richard Feynman in 1959 lecture stating that “there is plenty of room at the bottom” and it is ideal for obtaining structures with long-range order and for making connections with macroscopic world.

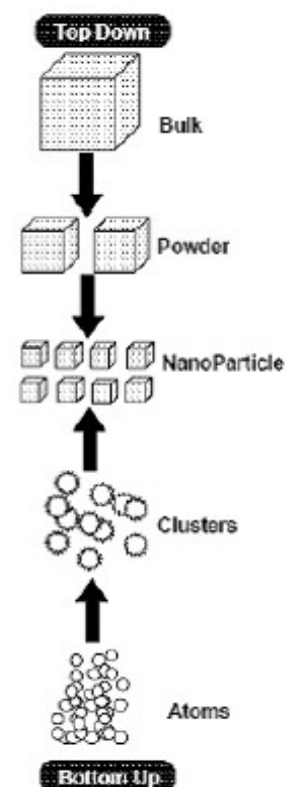
The bottom-up approach was pioneered by Jean-Marie Lehn (revealing that “there is plenty of room at the top”) and it is best suited for assembly and establishing short-range order at the nanoscale.

#### Top-down approach

This approach uses larger (macroscopic) initial structures, which can be externally controlled in the processing of nanostructures.

Typical examples are photolithography, etching through the mask, ball milling and application of severe plastic deformation.

Top-Down: lithography - The most used top-down approach is photolithography. It has been used to manufacture computer chips and produce structures smaller than 100 nm. Typically, an oxidized silicon (Si) wafer is coated with a 1 $\mu$ m thick photoresist layer. After exposure to ultraviolet (UV) light, the



photoresist undergoes a photochemical reaction, which breaks down the polymer by rupturing the polymer chains. Subsequently, when the wafer is rinsed in a developing solution, the exposed areas are removed leading to nanosize material. The other methods are electron-beam lithography and X – ray lithography.

In a ball milling process a powder mixture placed in the ball mill (a cylinder with steel balls which are rotating at high speeds) is subjected to high-energy collision from the balls. At the initial stage of ball milling, the powder particles are flattened by the compressive forces due to the collision of the balls. Micro-forging leads to changes in the shapes of individual particles, or cluster of particles being impacted repeatedly by the milling balls with high kinetic energy. At the intermediate stage of the mechanical alloying process, the intimate mixture of the powder constituents decreases the diffusion distance to the micrometre range. Fracturing and cold welding are the dominant milling processes at this stage. At the final stage of the mechanical alloying process, considerable refinement and reduction in particle size is achieved.

### **Bottom-up approach**

This approach include the miniaturization of materials components (up to atomic level) with further self assembly process leading to the formation of nanostructures. During self-assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structures.

Examples- 1. sol-gel processing, 2. chemical vapour deposition (CVD), 3. plasma or flame spraying synthesis, 4. laser pyrolysis, 5. atomic or molecular condensation – Inert gas condensation.

1. The sol-gel technique for synthesis of nanomaterials is a wet- chemical technique. Such techniques are used for the fabrication of materials starting from a chemical solution (sol, short for solution) which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Precursors in the form of acetates or carbonates or nitrates are taken and then dissolved in deionized water. This starting material is used to produce a colloidal suspension known as gel. After that a gelling agent for example, polyvinyl alcohol is added and this will produce a gel. A thin film coating is made on a substrate for example, Ni or Ti sheets and glass. At last the film is annealed at suitable temperature and then characterized.

2. In a chemical vapour deposition process, vapour is formed in a reaction chamber by pyrolysis reduction, oxidation or nitridation, and then deposited on the surface. Areas of growth are controlled by patterning processes like photolithography or photomasking (deposition patterns are etched on to the surface layers of the wafers).

3. The inert gas condensation (IGC) process is one of the most known and simplest technique for production of nanoparticles (in particular, Me nanopowders). An inorganic material is vaporized inside a vacuum chamber into which an inert gas (typically argon or helium) is periodically admitted. Once the atoms boil off, they quickly lose their energy by colliding with the inert gas. The vapour cools rapidly and supersaturates to form nanoparticles with sizes in the range 2–100 nm that collect on a finger cooled by liquid nitrogen.

4. The production route for 1-D rod-like nanomaterials by liquid phase methods is similar to that for the production of nanoparticles. CVD methods have been adapted to make 1-D nanotubes and nanowires. Catalyst nanoparticles are used to promote nucleation. Nanowires of other materials such as silicon (Si) or germanium (Ge) are grown by vapour-liquid-solid (VLS) methods.

## Classification of Nanomaterials

Nanomaterials are materials that have dimensions in the nano-range (roughly up to 100 nm or size at which there is a drastic change in the properties of the materials).

Nanomaterials can be classified into 3 categories based on the dimension

1. Zero-Dimensional Nanomaterials – If the size of the materials is restricted to  $\leq 100$  nm in all 3 dimensions e.g. Quantum dots (Figure 1 (left)).
2. One-Dimensional Nanomaterials- If the size of the materials is restricted to  $\leq 100$  nm in any 2 dimensions e.g. Quantum wire, rods (Figure 1 (center)).
3. Two-Dimensional Nanomaterials- If the size of the materials is restricted to  $\leq 100$  nm in any 1 dimension e.g. Quantum sheets (Figure 1 (right)).

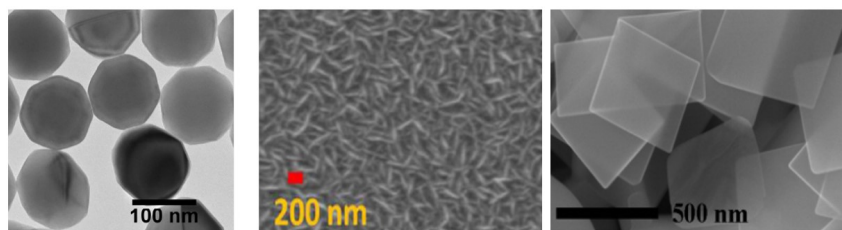


Fig. Left (Quantum dots), center (Quantum rods), and right (quantum sheets)

## Properties of the Nanomaterials

Nanomaterials as compared to their bulk counterparts showed very different properties due to the following reasons

1. High Surface-to-volume ratio- Nanomaterials have a very high surface area as compared to their bulk counterpart. In the bulk, a very small fraction of the constituents appeared at the surface for any reaction, and the rest remained unreacted (or inert), these have a surrounding of themselves. While nanomaterials have most fractions of constituents at the surface and are readily available for any reaction.
2. Quantum Size Effect- When particle size drops to a certain value, the electron energy level near the Fermi level changes from a quasi-continuous energy level to a discrete energy level, that is, energy level splitting or energy gap widening. This effect arises when the size of the particle is comparable to the wavelength of the electrons.

Due to these two reasons, nanoparticles show different properties than their bulk counterpart.

### Chemical properties –

Based on the surface area to volume effect, nanoscale materials have increased total surface area and hence the number of atoms on the surface available for reaction. So, nanomaterial enhances the catalytic properties, reactivity, and efficiency of the reaction (as can be seen in Figure 2, where the reaction rate depends on the size of nanoparticles).

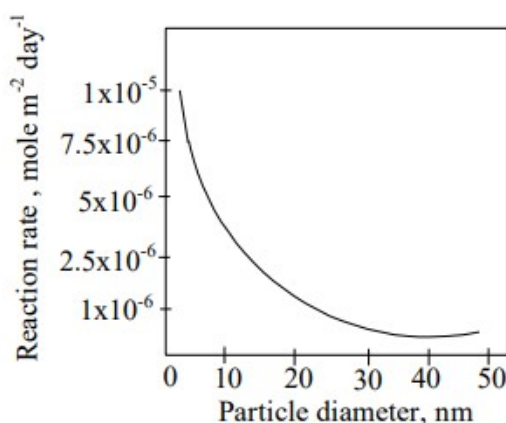


Fig. Effect of size of nanomaterials on the reaction rate

## Electronic Properties-

As in bulk materials energy bands are nearly continuous due to the very small spacing among energy levels. This spacing is directly related to the total number of atoms taking place in the formation of materials. In nanomaterials participating atoms are fewer as compared to the bulk. So, this spacing becomes measurable and now levels can be called discrete levels. Many materials which are conductor in bulk form, become semiconductors or insulators at nano-size. Thus, the change in band gap can be related to the optical properties of the nanomaterials e.g. Gold at room temperature has a yellowish color, while it looks red at nanosized.

## Thermal Properties-

The melting point of a material directly correlates with the bond strength. For nanomaterials, the melting temperature is size dependent and it decreases with the decrease in particle size diameters (as shown in figure 3). Because for nanoscale materials, surface atoms are not bonded in a direction normal to the surface plane, and hence the surface atoms will have more freedom to move.

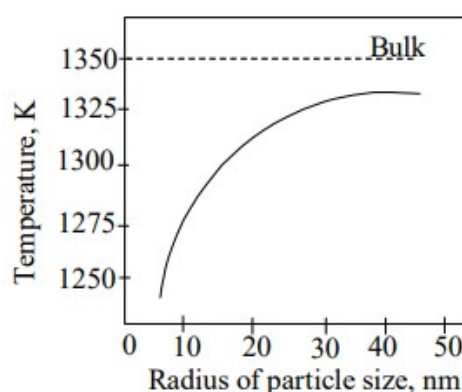


Fig. Effect of size on melting point of materials.

## Magnetic Properties-

The size of magnetic nanoparticles also influences the value of magnetization. The figure 4 illustrates the effect of particle size on the saturation magnetization of zinc ferrite. The magnetization increases significantly below a grain size of 20 nm. Hence, by decreasing the particle size of a granular magnetic material it is possible to improve the quality of magnets fabricated from it.



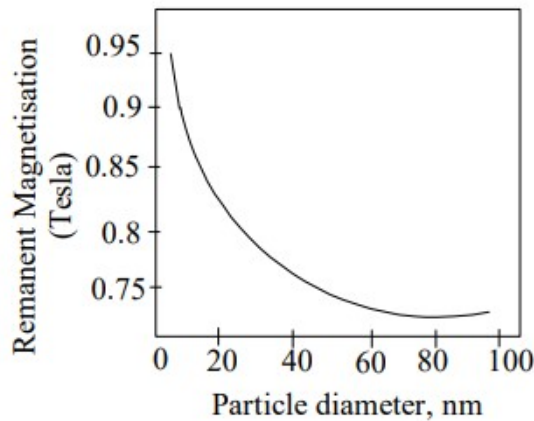


Fig. Effect of Particle Size on the Saturation Magnetization

### Density of States (DOS):

It is defined as the number of different states at a given energy level that electrons are allowed to occupy. The DOS is a measure of how close together the energy levels are to each other. In 3-D structure it is equal to the number of electron states per unit volume per unit energy interval. It is represented by  $g(E)$ . If  $dN$  be the number of available electron states per unit volume at energy  $E$  in the interval  $E$  to  $E+dE$ , then density of state is defined as

$$g(E) = \frac{dN(E)}{d(E)}$$

#### 1. Density of States in Zero-dimension system (Quantum dot)

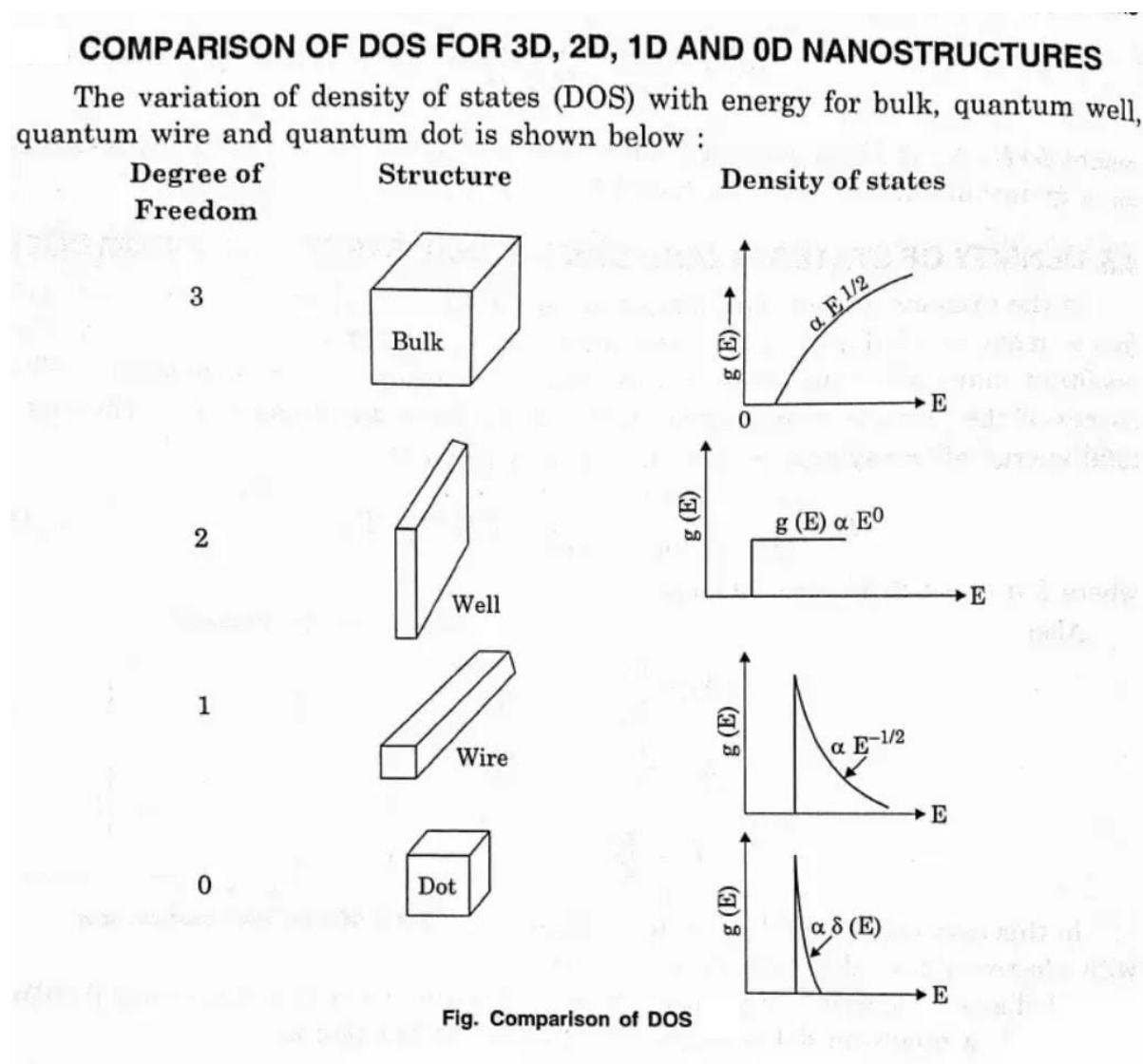
In the extreme case of confinement along all the three directions, particle is not free to move at all. Its motion is confined along all three-direction  $x$ ,  $y$  and  $z$ . The resultant material or nanostructure is called quantum dot or nanoparticles. the energy of the particle is quantized along all the three directions. Therefore, total energy of the system is quantized.

#### 2. Density of States in One-dimension system (Quantum wire)

In a One dimension material such as quantum wire, motion is confined along two directions (say  $y$  and  $z$ ) and free along one direction (say  $x$ ). Thus there is only one degree of freedom. Particle energy is quantized for motion along  $y$  and  $z$  directions. Total energy of the system can be written as sum of the energy along the quantized directions ( $y$  &  $z$ ) and the energy the free direction ( $x$ ).

### 3. Density of States in two-dimension system (Quantum well)

In two-dimensional material such as quantum well, electron motion is confined along one direction (say  $z$ ) and they are free to move along rest of two directions ( $x, y$ ). Thus electron energy is quantized in one dimension. The total energy of the material is sum of the energy along quantized direction and the energy along other two (free) directions.



## **Carbon nanotubes**

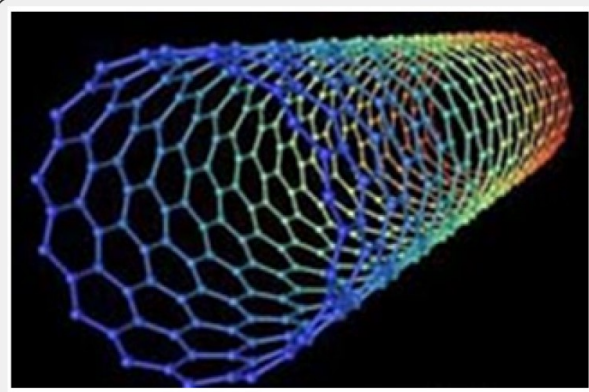
Carbon nanotubes (CNTs) are cylindrical nanostructures made entirely of carbon atoms arranged in a hexagonal lattice. They are a unique form of carbon with extraordinary mechanical, electrical, and thermal properties. CNTs are essentially rolled-up sheets of graphene, and their properties depend on their structure and chirality.

CNTs are fundamental to the field of nanotechnology, representing a revolutionary advancement driven by the unique properties of carbon, an element with an atomic number of 6 that plays a crucial role in this domain. Their discovery by Iijima was unexpected, occurring during an investigation of the surface of a graphite electrode in an electric arc discharge experiment. This chance observation marked the inception of a groundbreaking area of research, catalysing extensive exploration into carbon-based nanostructures and significantly expanding the scope of carbon science.

A carbon nanotube is essentially a cylindrical nanostructure formed by rolling a hexagonal lattice of carbon atoms into a long, thin, hollow tube. Renowned for their nanoscale dimensions, distinctive shapes, and extraordinary physical properties, CNTs have become a focal point in advanced materials research. They exhibit remarkable versatility, as their chemical and physical properties can be finely tuned to meet the demands of various applications. These range from material science and electronics to energy storage, biomedical innovations, and beyond, cementing CNTs as a cornerstone of modern nanotechnology.

### **Types of Carbon Nanotubes**

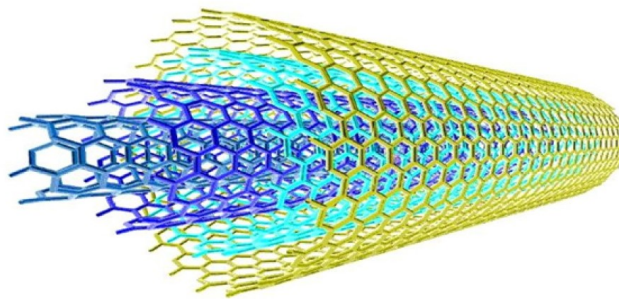
1. Single-Walled Carbon Nanotubes (SWCNTs):
  - Composed of a single layer of graphene rolled into a cylinder.
  - Diameter typically ranges from 0.4 to 3 nm.
  - Exhibit high flexibility and distinct electronic properties (metallic or semiconducting, depending on chirality).



**Figure 1:** Structure of single walled nanotube (SWNT).

## 2. Multi-Walled Carbon Nanotubes (MWCNTs):

- Consist of multiple layers of graphene cylinders nested within one another.
- Outer diameters can range from 2 to 100 nm.
- Less flexible than SWCNTs but stronger and more durable.



**Figure 2:** Structure of multiwalled nanotube.

## Properties of Carbon Nanotubes

### 1. Mechanical Properties

- **High Strength:** CNTs are among the strongest known materials, with tensile strength up to 100 GPa (100 times stronger than steel by weight).
- **Elasticity:** Extremely flexible and can be bent without breaking.
- **Young's Modulus:** Around 1 TPa, making them highly stiff and resistant to deformation.

### 2. Electrical Properties

- **Metallic or Semiconducting:** Their conductivity depends on the chirality (the way graphene sheets are rolled) and diameter.
- **High Current-Carrying Capacity:** CNTs can carry a current density up to  $10^9$  A/cm<sup>2</sup>, much higher than copper.
- **Low Resistance:** Perfectly conductive when metallic, making them excellent materials for nanoelectronics.

### 3. Thermal Properties

- **Exceptional Thermal Conductivity:** CNTs can conduct heat efficiently along their length, with thermal conductivity values over 3000 W/m·K.
- **Thermal Stability:** Can withstand high temperatures (up to 2800°C in vacuum) without degradation.

### 4. Chemical Properties

- **Inertness:** CNTs are chemically stable due to the strong carbon-carbon bonds.
- **Functionalizability:** Surface modification allows attachment of various chemical groups, improving their compatibility with different environments.

### 5. Optical Properties

- CNTs exhibit unique optical absorption and emission properties, which depend on their structure.
- They are used in applications like photodetectors and fluorescent imaging.

## **Applications of Carbon Nanotubes**

1. **Electronics:** Used in transistors, conductive films, and nanoscale circuits.
2. **Energy Storage:** Utilized in batteries, supercapacitors, and fuel cells for high efficiency and energy density.
3. **Composites:** Reinforce polymers and metals to create lightweight, high-strength materials.
4. **Medicine:** Drug delivery systems and biosensors.

5. Environmental Applications: Water purification and air filtration systems due to their adsorptive properties.

## Graphene

Graphene was first isolated by A.K. Geim and K.S. Novoselov at the University of Manchester in 2004. They got Nobel Prize in 2010 for their pioneering work. Graphene is a crystalline allotrope of carbon with two-dimensional, atomic scale, hexagonal pattern. Here each carbon atom forms four bonds, three  $s$  bonds ( $sp^2$  hybridized) with its three neighbours and one  $p$  bond oriented out of plane.

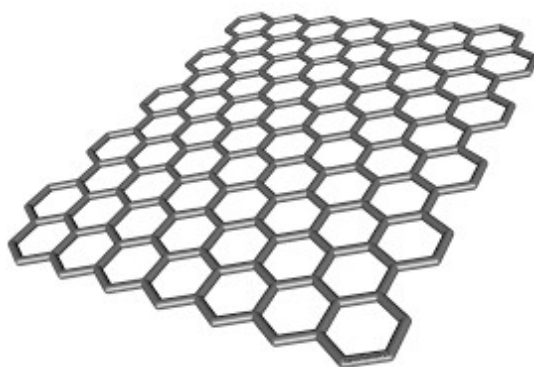
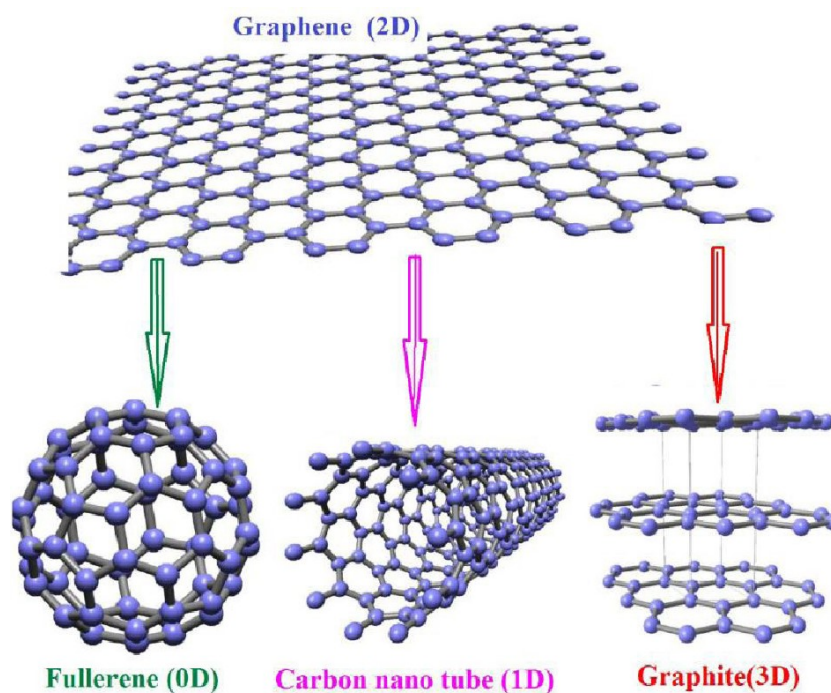


Fig. Graphene sheet

Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes and fullerenes.



**Properties:**

- (i) It is transparent, light weight and flexible.
- (ii) It is 200 times stronger than steel by weight due to its tightly packed carbon atoms.
- (iii) It has ability to conduct heat and electricity with great efficiency.
- (iv) It is biocompatible and non toxic for cells.

**Applications:**

It is used in computer displays and flat panel TVs, ATM touch screens, solar cells, semiconductors, batteries, composite industries, and many more.

**Characterization Techniques (basic ideas):**

There are many methods available to image nanostructured materials (e.g. a nanostructured surface) and to characterize their physical and chemical properties. In general, two fundamental types of characterization methods exist: imaging by microscopy and analysis by spectroscopy.

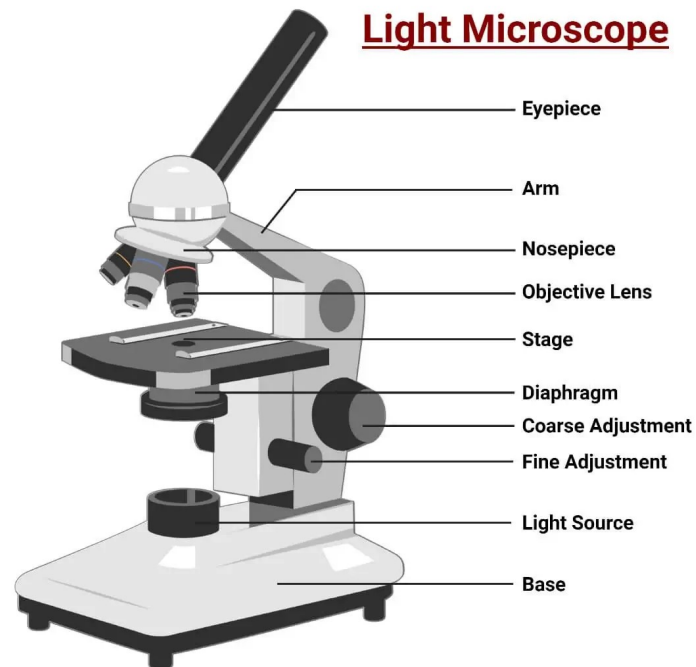
**Optical Microscope**

Optical Microscopy (Light Microscopy) is the microscopy technique that uses transmitted visible light, either natural or artificial, for developing the image of an object. It is the most common type of microscopy. It is further classified into several groups.

An optical microscope uses visible light (i.e. electromagnetic radiation) and a system of lenses to magnify images of small samples. For this reason, it is also called a light microscope. Optical microscopes are the oldest and simplest of the microscopes. The resolution limit of an optical microscope is governed by the wavelength of visible light (As a general rule of thumb, the resolution is about half the wavelength used in the measurement). Visible light is the part of the electromagnetic spectrum with wavelengths between 400 and 700 nm and the resolving power of an optical microscope is around 0.2  $\mu\text{m}$  or 200 nm: thus, for two objects to be distinguishable, they need to be separated by at least 200 nm. Single

objects smaller than this limit are not distinguishable: they are seen as “fuzzy objects”. This is known as the “diffraction limit” of visible light.

Optical microscopes can be used to observe living cells and microorganisms.





## **Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)**

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are the two most common types of electron microscopy. TEM and SEM differ in how they work and what types of images they are able to capture.

### **SEM**

SEM can stand for either Scanning Electron Microscopy or Scanning Electron Microscope. An SEM is a kind of electron microscope that uses a fine beam of focused electrons to scan a sample's surface. The microscope records information about the interaction between the electrons and the sample, creating a magnified image. SEM has the potential to magnify an image up to 2 million times.

SEM images give insight into a sample's topography and elemental composition. SEM is able to capture 3-D black-and-white images of thin or thick samples. The sample's size is limited only by the size of the electron microscope chamber.

To obtain a high-resolution image, an electron source (also known as an electron gun) emits a stream of high-energy electrons towards a sample. The electron beam is focused using electromagnetic lenses. Once the focused stream reaches the sample, it scans its surface in a rectangular raster.

The interaction between the electron beam and the sample creates secondary electrons, backscattered electrons, and X-rays. These interactions are captured to create a magnified image.

### **TEM**

TEM can stand for Transmission Electron Microscopy or Transmission Electron Microscope (TEM). A TEM is a type of electron microscope that uses a broad beam of electrons to create an image of a sample's internal structure. A beam of electrons is transmitted through a sample, creating an image that details a sample's morphology, composition, and crystal structure.

Samples must be incredibly thin, often less than 150 nm thick, to allow electrons to pass through them. After the transmission of the electrons through the sample, they arrive at a detector below and a 2-D image is created.

TEMs have an incredible magnification potential of 10-50 million times. The details provided are at the atomic level, the highest resolution of any electron microscope. TEMs are often used to examine molecular and cellular structures.

An electron source sends a beam of electrons through an ultrathin sample. When the electrons penetrate the sample, they pass through lenses below. This data is used to create images directly on a fluorescent screen or onto a computer screen using a charge-coupled device (CCD) camera.

### SEM Vs TEM

	<b>Scanning Electron Microscopes (SEM)</b>	<b>Transmission Electron Microscopes (TEM)</b>
Electron stream	Fine, focused beam	Broad beam
Image taken	Topographical/surface	Internal structure
Resolution	Lower resolution	Higher resolution
Magnification	Up to 2,000,000 times	Up to 50,000,000 times
Image dimension	3-D	2-D
Sample thickness	Thin and thick samples okay	Ultrathin samples only
Penetrates sample	No	Yes
Sample restriction	Less restrictive	More restrictive
Sample preparation	Less preparation required	More preparation required
Cost	Less expensive	More expensive
Speed	Faster	Slower
Operation	Easy to use	More complicated; requires training