

Introduction to Nanomaterials and Nanotechnology

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Unit VI: Introduction to Nanomaterials and Nanotechnology (7 Hours)

Introduction to Nanostructures: Carbon Nanotubes (CNT), Graphenes, Fullerenes

Quantum Dots and Semiconductor Nanoparticles, Metal-based Nanostructures (Iron Oxide Nanoparticles), Nanowires, Nanobiosensors

Science of Self-assembly - From Natural to Artificial Structures Nanoparticles in Biological Labeling and Cellular Imaging.

1 m 1 cm 1 mm 1 micron (1 μm) 1 nm

$$1 \text{ nm} = 10^{-9} \text{ m}$$

Introduction to Nanotechnology

The introduction of 'nano' car by TATA motors has greatly popularised the term 'nano' among the Indian masses. The word *nano* signifying very small objects of the range of 1–100 nm has gained importance in the last two decades. *Nano* literally means dwarf (10^{-9}) and can be used as a prefix to the fundamental properties such as mass, time and length to give important scientific properties such as:

Nanogram 10^{-9} g

Nanosecond 10^{-9} s

Nanometer 10^{-9} m.

The science of small objects has grown rapidly in the past two decades as the behavior of matter at 'nano' level is considerably different from the bulk behavior of the matter. The physical, chemical, electrical, optical and magnetic properties of nanomaterials are significantly different from the properties of the same material of bigger size. For example, a metal with a grain size of 10 nm is seven times harder and tougher than its counterpart with the size of hundreds of nanometers.

Moreover, the nanomaterials have a relatively larger surface area than ordinary materials and this has a significant effect on their physical properties and chemical reactivities. It has been observed that certain substances that are ordinarily unreactive become reactive in their nanoscale form because of their high surface area. The quantum effects of matter at bulk level and nano level varies significantly. (The specific surface area increases three times when the dimensions decrease from micrometer to nanometer.)

Nanoscience and Nanochemistry It is the science of nanoparticles or the particles whose size varies from 1 to 10 nm in at least one dimension. Nanochemistry exploits this size range for various chemical reactions and chemical purposes, which would not be possible otherwise at the bulk level. Nanotechnology utilizes the behavior of particles at the 'nano' level in various production processes.

How much is a nanometer?

One nanometer is equivalent to one billionth (one thousand millionth) of a meter. These particles are not visible to the human eye and can be seen only under a powerful microscope. The size of various objects can help to have a visual perception of a nano-sized objects.

- Human hair is about 100,000 nm wide.
- Red blood cell is about 2000–5000 nm wide.
- Human DNA is 2.5 nm wide.
- Diameter of carbon nanotube is 1.0–1.3 nm.
- Water molecule is about 0.3 nm across.
- An ant is 4 million nm big!

Now you can visualize how small a nanometer is!



DNA
2.5 nanometers
diameter



Bacterium
2.5 micrometers
long



Large Raindrop
2.5 millimeters
diameter



Strand of Hair
100 micrometers
diameter



Ant
4 millimeters
long



Red blood corpuscles
(2–5 micrometers)



Buckyball
(1 nm)

Figure 23.1 *Sizes of various common objects*

Properties of Nanomaterials

The properties of nanomaterials are very different from those of the bulk material. The nanosize increases the surface area and has a marked effect on the electrical, electronic, optical and catalytic properties. They also introduce many new properties in materials such as bucky tubes (carbon nanotubes) are very stiff and have high tensile strength, and CdSe shows fluorescent emission over a broad range. The properties of materials such as melting point and conductivity show a marked change. Melting point depresses by about 50% in nanoscale and the metals change from conductors to semiconductors and also to insulators. For example, bulk gold is golden in color, it is lustrous, ductile, good conductor of heat and electricity, is chemically inert and does not react with most reagents and is unaffected by air. It has a high melting point of 1080 °C. Nanogold on the other hand is never golden; it has a variety of colors depending upon the shape and size of the nanoparticles. It is not a metal but a semiconductor that melts at a relatively low temperature (-940 °C). Moreover, nanogold acts as a good catalyst. Similarly, the electronic, optical, electrical and catalytic properties of nanosilver are very different from those of bulk silver. The other effects on the properties of nanomaterials are as follows.

Optical properties

Nanomaterials have interesting optical properties. Optical properties are markedly affected by the shape, size and surface characteristics, doping characteristics and environmental interactions of the nanoparticles. For example, CdSe nanoparticles show fluorescent emission over a broad range.

Electrical properties At nanoscale, the conductivity changes from metal to semiconductors to insulators, that is, from high to low.

Mechanical properties Nanoparticles generally have good tensile strength, elasticity and fracture resistance. They are therefore used as fillers in polymers to improve their mechanical properties.

Magnetic properties Many substances such as gold and platinum which are non-magnetic in bulk become magnetic at the nanosize. Magnetic nanoparticles of Pd, Pt and Au can be obtained from non-magnetic bulk materials.

Self-assembly

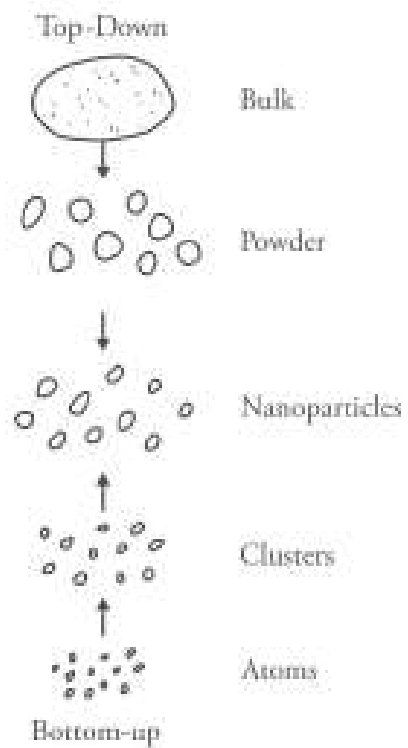


Figure 23.2 *The top-down and bottom-up approaches*

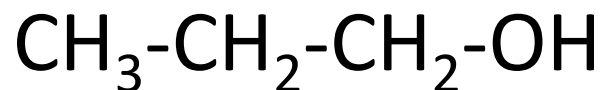
Self-assembly (Bottom-up approach for the Preparation of Nanomaterials)

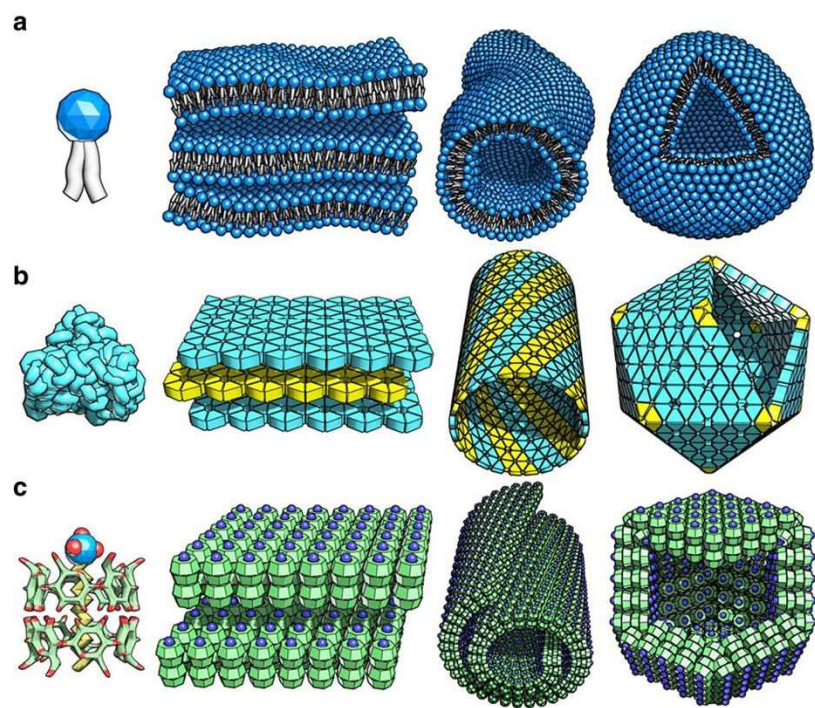
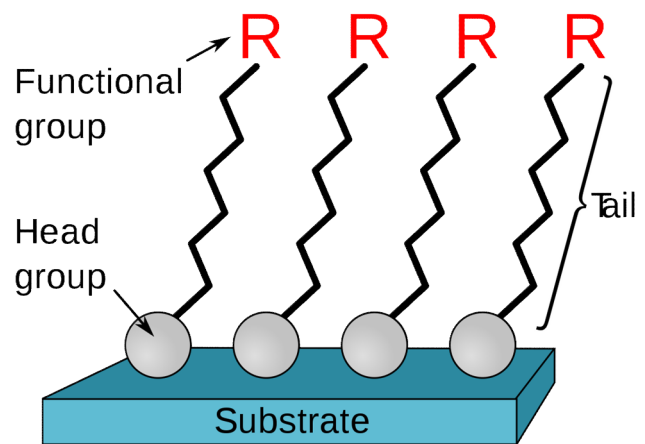
As discussed earlier, nanomaterials are particles having size in the range of 1 to 100 nm at least in one dimension. These materials can be made up of a large number of atoms. Owing to their small sizes, their properties are considerably different from the bulk materials. Nanomaterials can be prepared either by dividing the bulky materials into small particles of the above-mentioned dimension (top-down approach) or by assembling very small particles and binding them to the desired size of 1–100 nm (bottom-up approach). Self-assembly is the basic principle underlying the bottom-up approach that helps to synthesize nanomaterials and enables them to organise into regular patterns with lowest energy configurations. Self-assembly enables very small atoms to be arranged into ordered patterns or arrays to help them perform a particular function. The components assemble or aggregate without the guidance of any external force. For example, alkanethiols form self-assembled

Examples: Self-assembly

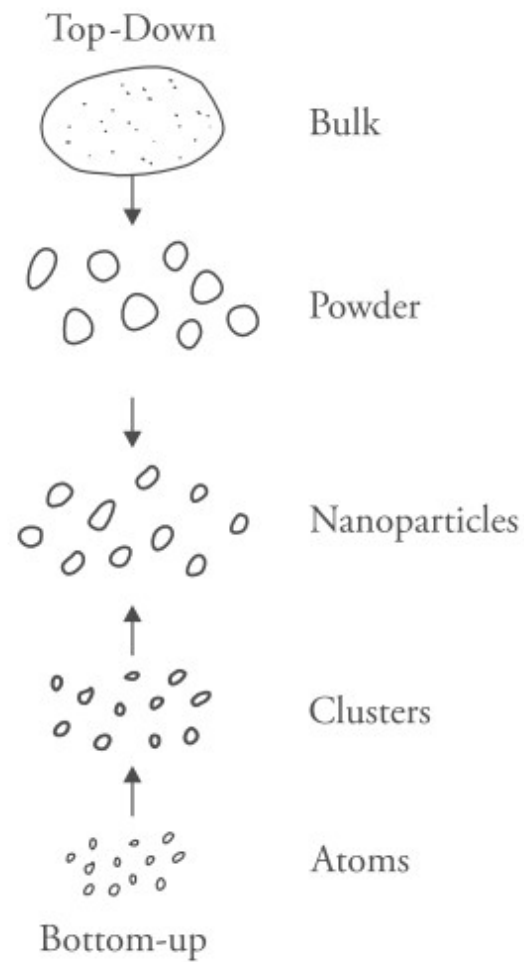
Examples: Alkane thiols form self-assembled

monolayers (SAMs) on gold colloids. CdSe nanoparticles are formed by the self-assembly of atoms into a stable crystalline form (molecular self-assembly). A three-dimensional photonic crystal is formed by the further self-assembly of CdSe nanoparticles (material self-assembly). Other common examples of self-assembly are the formation of surfactants in soap bubbles, crystallisation of water into solid ice, crystallisation of viruses for X-ray determination and alignment of liquid crystals. Biological systems, RNA, proteins and nucleic acids are all self-assembled. Living organisms represent a collection of hierarchically arranged self-assembled structures from molecular to macroscopic level. Nanoscience focuses on self-assembly at a scale of less than 100 nm.





The top-down and bottom-up approaches



Types of Self-assembly

Self-assembly can be static or dynamic. Atomic and molecular crystals, liquid crystals, self-assembled monolayers, colloidal crystals, bubble rafts and liquid bilayers all represent static assemblies. Examples of dynamic self-assemblies are solar system, galaxies, macro- and mesoscopic structures, etc. A few common types of self-assemblies are discussed below

- (i) *Molecular self-assembly* Molecular self-assembly refers to the assembling of molecules without the aid of any external force. The molecules assemble spontaneously into stable and structured aggregates. The driving forces behind molecular self-assembly are reversible non-covalent interactions such as van der Waals forces, hydrogen bonds, metal–ligand bonds, π – π interactions, etc. The reversibility of forces help components of self-assembled aggregates to adjust mutually. Molecular self-assembly can be intermolecular as well as intramolecular. Intramolecular self-assembly generally brings about folding and the term molecular self-assembly actually refers to intramolecular self-assembly.
- (ii) *Material self-assembly* Material self-assembly results from the assembling of various nano-sized blocks. In these lattices, the atoms of conventional solids are replaced by nanomaterials. In material self-assembly, the organic, inorganic and polymeric chemical components with well-defined functions integrate into electronic, photonic, mechanical, analytical and chemical systems for an intended nanotechnological application. Systems capable of performing electronic operations such as switching, gating, rectification and amplification are designed by using materials' self-assembly.

Molecular vs Material Self-assembly

Molecular v/s material self-assembly

In molecular self-assembly, the molecules enter into self-organisation, forming structures with properties different from the individual constituent moieties.

In material self-assembly, the individual blocks make up a useful and thermodynamically stable structure.

Self-assembling materials

- (a) **Ultrathin film** It is a 1-Å-thick film of atom spread on a flat surface. The film is produced by the vaporisation and subsequent deposition of atoms on a solid substrate. This technique that produces one-atom-thick layers is called the atomic layer deposition. Ultrathin films are not very stable and the surface atoms get clustered to form a thick film several atomic layers in thickness.

Molecular vs Material Self-assembly

- (b) **Langmuir–Blodgett (LB) film** A dilute solution of amphiphilic molecules (molecules having both water-loving and water-hating parts) spread on the surface of water. These molecules do not dissolve in water and when the solvent sticking to them evaporates they are left floating at the water–air interface and organise into a one-molecule-thick layer (monolayer), two-molecule-thick layer (bilayer) or several-molecule-thick layer (multilayer) (Fig. 23.3).

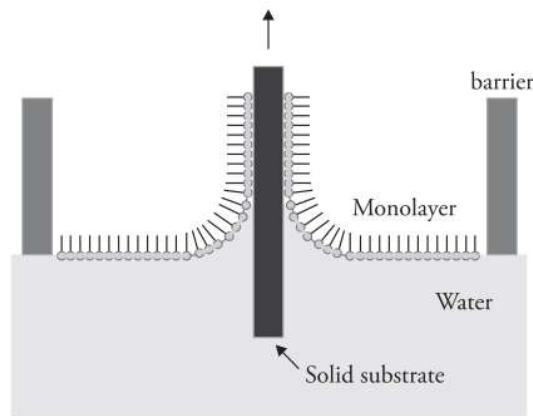


Figure 23.3 *Langmuir–Blodgett film*

The polar part of the molecule attaches itself to water and the non-polar hydrophobic region orients away from the surface. The hydrophobic region of neighboring molecules stick to each other. The surface area is then decreased by compressing the monolayer with a moving barrier while monitoring the surface pressure. This results in the formation of a two-dimensional condensed monomolecular layer at the water–air interface. Such layers are formed by surfactants above the critical micellar concentration.

Molecular vs Material Self-assembly

- (c) **Self-assembled monolayer** A self-assembled monolayer (SAM) is formed by the adsorption of an active surfactant on a solid surface. An SAM film can be deposited by vapor phase deposition. The formation of SAMs does not require the application of external pressure.

Self-assembly helps in the formation of monolayers of organic molecules on noble metals. Monolayers made of long-chain organic molecules with functional groups such as -SH, -CN, -COOH and -NH₂ are deposited on metal surfaces such as Au, Cu, Ag, Pd, Pt and Hg as well as semiconducting surfaces such as Si, GaAs, Indium coated tin oxide (ITO), etc. SAMs find application in the manufacture of monoelectronic devices, sensor arrays, super capacitors, catalysts, rechargeable power sources, etc.

Monolayers on gold Self-assembled monolayers of organic molecules such as thiols or phosphonic acids are deposited on gold surface. The thiol molecules get covalently bonded to gold surface and get arranged in two dimensions over the gold surface. These layers are stable because of bond formation between the gold surface and the organic molecules.

- (d) **Mesoscale self-assembly (MESA)** The size of mesoscale self-assembly (MESA) varies from 10 nm to 10 mm (1cm). The components of MESA are bigger than molecules; hence, apart from the forces employed in molecular self-assembly they can utilise a wide range of other interactions such as capillary, electrostatic, magnetic, optical, gravitational and fluidic

Protein Based Nanostructures: S- layers- structures, self assembly, Recrystallization, Diagnostics, lipids chips ; Engineered Nanopores- potential applications, methods of production, protein engineering, supported Bilayers, Membrane arrays; protein microarrays; Magnetosomes- Nanoscale magnetic iron minerals in bacteria; Bacteriorhodopsin and its potential in technical applications & preparation of Bacteriorhodopsin films.

Molecular vs Material Self-assembly

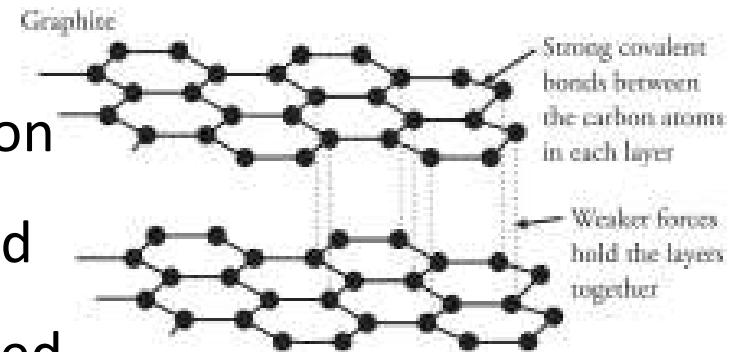
sheer. The self-assembly of objects in a mesoscale can be used to fabricate complex systems that cannot be made otherwise. Mesoscale objects self-assemble to yield colloidal crystals, bubble raft, two-dimensional arrays of nanometer- and micrometer-sized beads, gold colloids assembled by DNA duplex formation, etc.

Introduction to Nanostructures

1. Graphite
2. Graphene
3. Carbon nanotubes (CNTs)

1. Graphite

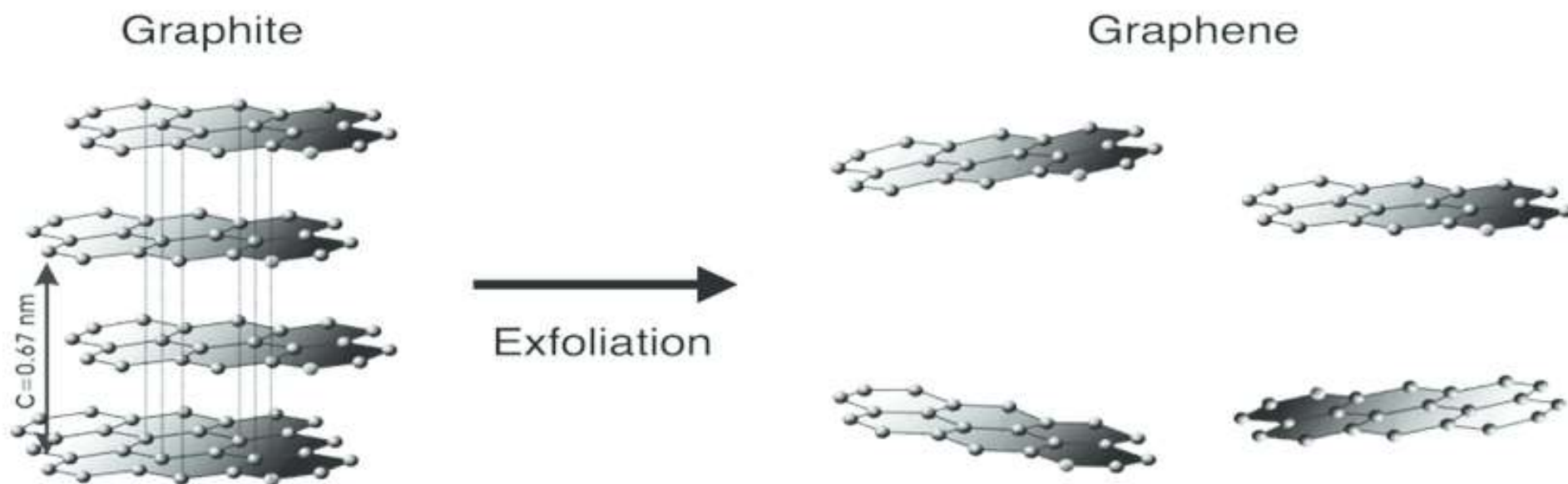
- 2nd allotrope of Carbon
- Carbon atoms arranged in the form of a hexagon
- Carbon atoms in the hexagon are **sp²** hybridized
- Only 3 valence electrons of each C atom involved in forming σ bonds using **sp²** hybrid orbital)
- The 4th electron forms a π bond; the π electrons are mobile, delocalized and responsible for electrical conductivity of graphite
- The layers of graphite are loosely bonded by weak van der Waals forces; Bcoz of these weak bonds between different layers, they slip over each other making graphite soft and slipperv



Uses of Graphite

- Used in pencils for writing
- Used as a lubricant in brake linings
- Bcoz of the high MP, it is used in making crucibles, refractories, and moulds containing molten metals
- Used for making carbon brushes in electrical motors
- High pure graphite is used for producing moderator rods for reactors

Difference between Graphite and Graphene



Carbon nanotubes (CNTs)

What are carbon nanotubes?

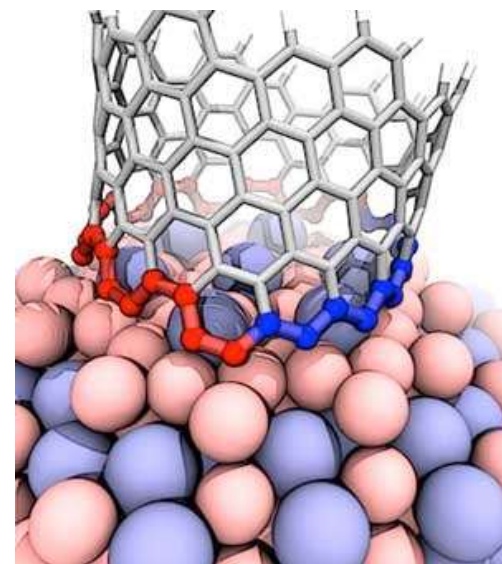
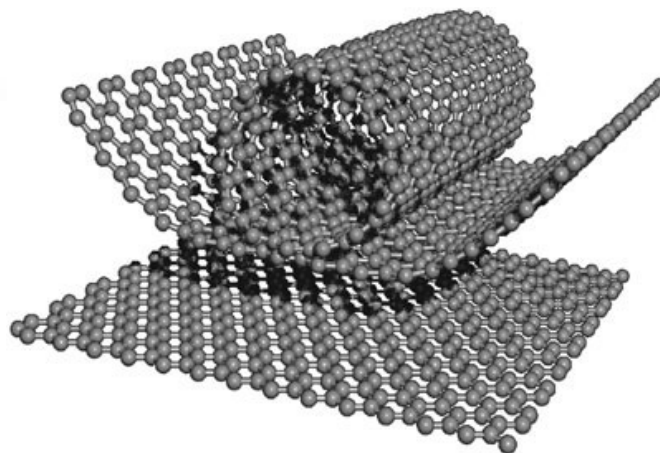
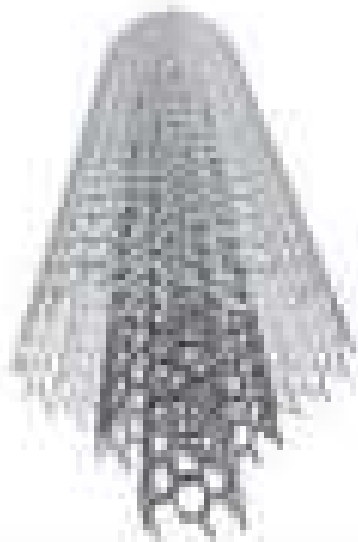
Carbon nanotubes (CNTs) are cylindrical molecules that consist of rolled-up sheets of single-layer carbon atoms (graphene). They can be single-walled (SWCNT) with a diameter of less than 1 nanometer (nm) or multi-walled (MWCNT), consisting of several concentrically interlinked nanotubes, with diameters reaching more than 100 nm. Their length can reach several micrometers or even millimeters.

Structure

SWCNT



MWCNT



Types of CNTs

1. Single-walled CNTs
2. Multi-walled CNTs

Synthesis of CNTs

Refer material / notes

Applications of CNTs

Refer material / notes

Introduction to Nanostructures

4. Fullerenes

C_{20}

C_{24}

C_{28}

C_{32}

C_{36}

C_{50}

C_{60}

C_{70}



Buckminster Fullerene C_{60}
Football or Soccer ball

1985: Robert Curl

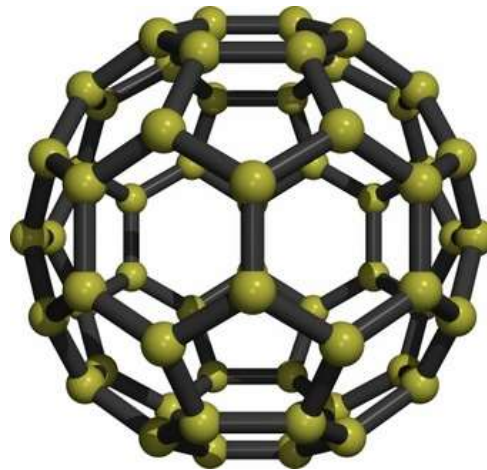
Kroto

Smalley

✓ Discovered 3rd allotrope of Carbon

Structure of Fullerene C₆₀

- ✓ Truncated icosahedron structure
- ✓ 12 pentagons & 20 hexagons



Preparation of Fullerene C₆₀

- 1. Arc vaporization of Graphite:** Resistive vaporization of graphite in He atmosphere
Resistive vaporization is initiated by passing high current through the rods.
The black soot contains C₆₀ and larger fullerenes, extracted using various chromatographic techniques.
- 2. Contact Arc method:** Arc vaporization was modified by maintaining an electric arc between the two graphite electrodes in contact with an atmosphere of He.
Most of the power is dissipated in the arc. Individual fullerenes can be separated by chromatographic techniques using alumina-hexane.
- 3. Other methods:** Combustion of hydrocarbons: Upto 40% fullerene containing soot can be prepared from a benzene-oxygen combustion flame in Ar atmosphere.

Properties of C₆₀

1. Black powder material
2. Gives magenta colored solution in aromatic hydrocarbons
3. Unlike the other two allotropes, C₆₀ exists as discrete molecules
4. Forms a translucent magenta fcc crystal on sublimation
5. It reacts with alkali metals to form fullerides of type M₃C₆₀.
These fullerides are reported to exhibit superconductivity at low temperatures

Applications of C₆₀

1. When mixed with alkali metals, they can be used to produce superconductors
2. It serves as lubricant due to spherical structure and also ball bearing.
3. Used to prepare soft ferromagnets (TDAE C₆₀) (tetrakisdimethylamino ethylene)
4. They can also be used in rechargeable batteries as catalysts, in microelectronic devices, non-linear optical devices etc.

5. Nano Peapods

Carbon peapod: A hybrid nanomaterial consisting of spheroidal [fullerenes](#) encapsulated within a [carbon nanotube](#).

It is named due to their resemblance to the seedpod of the pea plant.

Since the properties of carbon peapods differ from those of nanotubes and fullerenes, the carbon peapod can be recognized as a new type of a self-assembled graphitic structure.

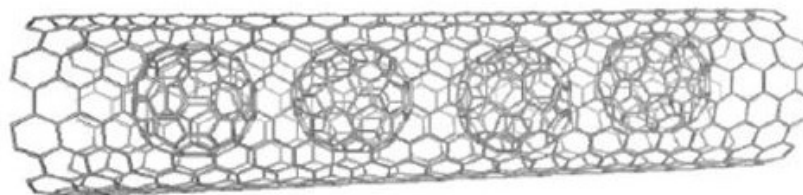
Preparation: Carbon peapods can be naturally produced during carbon nanotube synthesis by **pulsed laser vaporization**.

Applications:

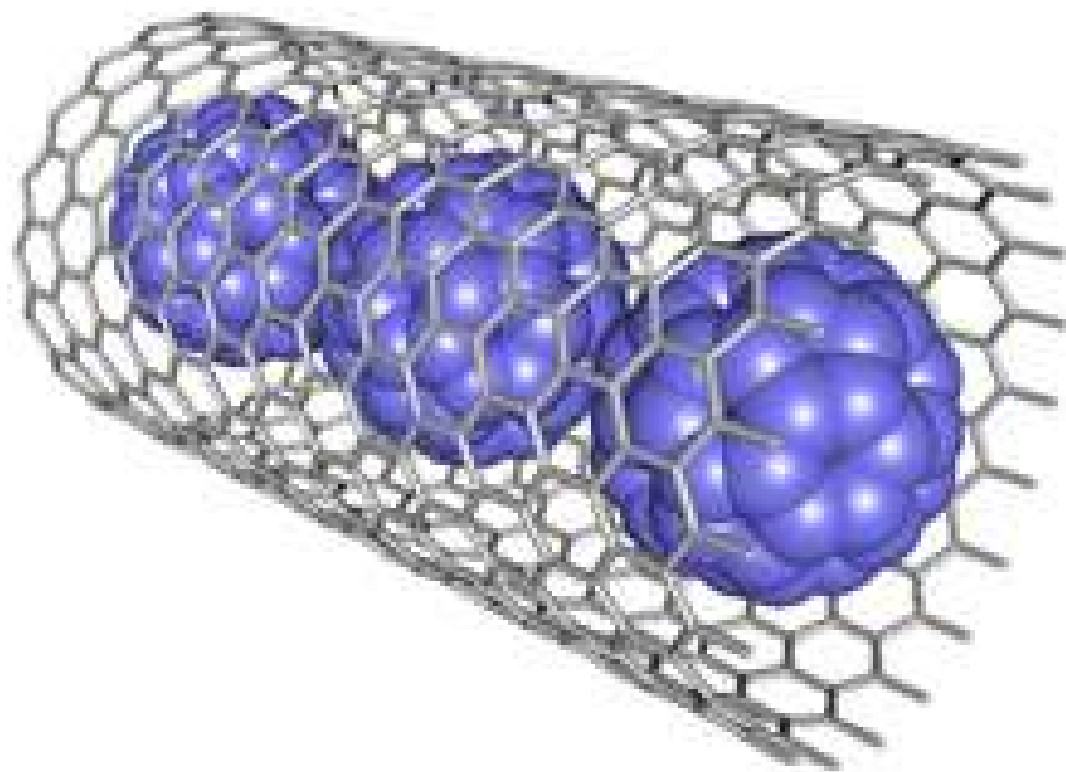
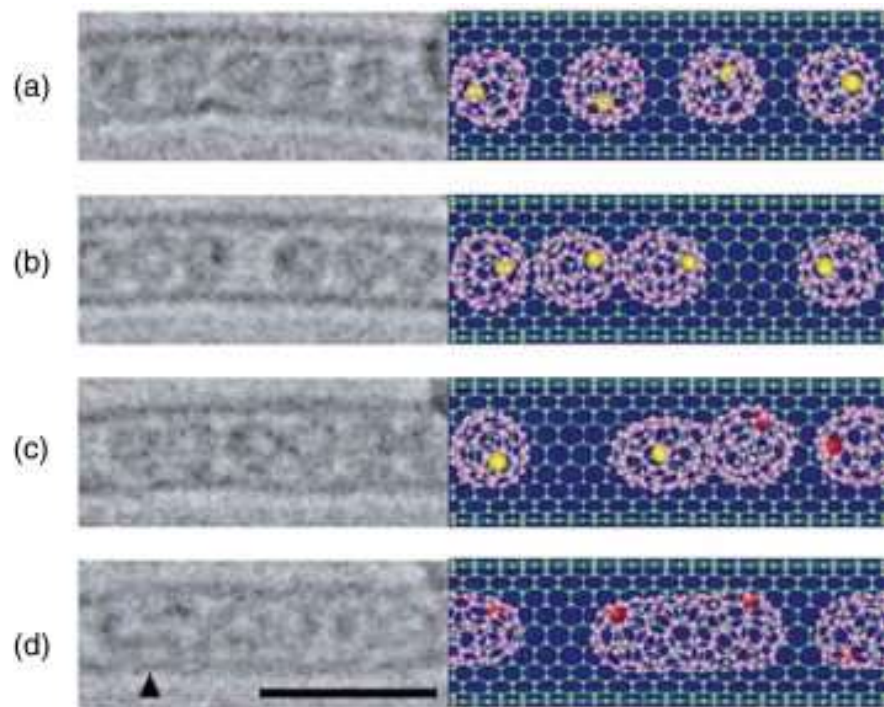
Possible applications of nano-peapods include [nanoscale lasers](#), [single electron transistors](#), spin-qubit arrays for quantum computing, nanopipettes, and data storage devices thanks to the memory effects and superconductivity of nano-peapods.

Nano Peapods

- Single-walled carbon nanotubes (SWNTs) encapsulating C₆₀
- Conventional synthesis of nanopeapods had a lot of challenges. Reactions had to be run under very difficult conditions and were very restricting.
 - Vaporization of thermally stable fullerene molecules
 - At least 350°C in high vacuum
- Theoretical studies showed the activation barrier for this reaction to be only ~0.37eV.
 - The reaction should proceed at room temperature



Khlobystov, Andrei N., David A. Britz, Jiawei Wang, S. Adam O'neil, Martyn Poliakoff, and G. Andrew D. Briggs. "Low Temperature Assembly of Fullerene Arrays in Single-Walled Carbon Nanotubes Using Supercritical Fluids." *Journal of Materials Chemistry* 14 (2004): 2852-2857. Royal Society of Chemistry Archive. University of Rochester. 22 Mar. 2007



6. Quantum Dots (QDs)

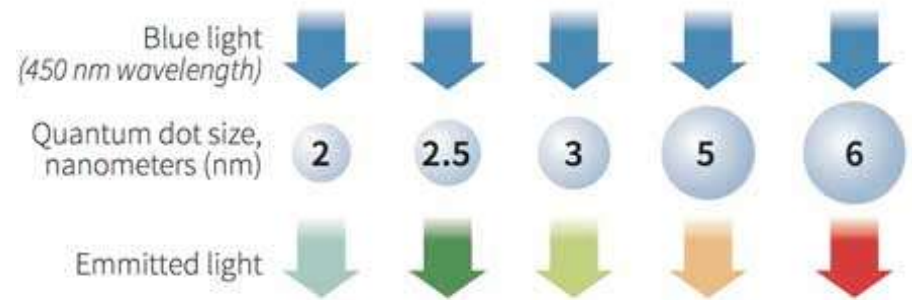
What are Quantum Dots ?

Quantum dots (QDs): Man-made semiconductor **nanocrystals** with size < 10 nm that can transport electrons. When UV light hits these semiconducting nanoparticles, they can emit light of various colors.

➤ **Nanocrystal:** A nanocrystal is an inorganic entity in which the constituent atoms or ions have a crystalline arrangement in at least one dimension and their size is less than 100 nm.

Why QDs are important ?

The atom-like energy states of QDs contribute to special optical properties, such as a particle-size dependent wavelength of fluorescence; an effect which is used in fabricating optical probes for biological and medical imaging.



Quantum dots are nanoscale man-made crystals that have the ability to convert a spectrum of light into different colors. Each dot emits a different color depending on its size

Quantum Dots (QDs)

Quantum dot (QD) Nanoparticles range from 2 to 10 nm in diameter and are made strictly from semiconductor materials such as chalcogenides (selenides and sulphides) of metals such as cadmium or zinc (CdSe or ZnS or InP). The size and structure of the QDs can be carefully controlled.

Synthesis: i) Top-down approach

ii) Bottom-up

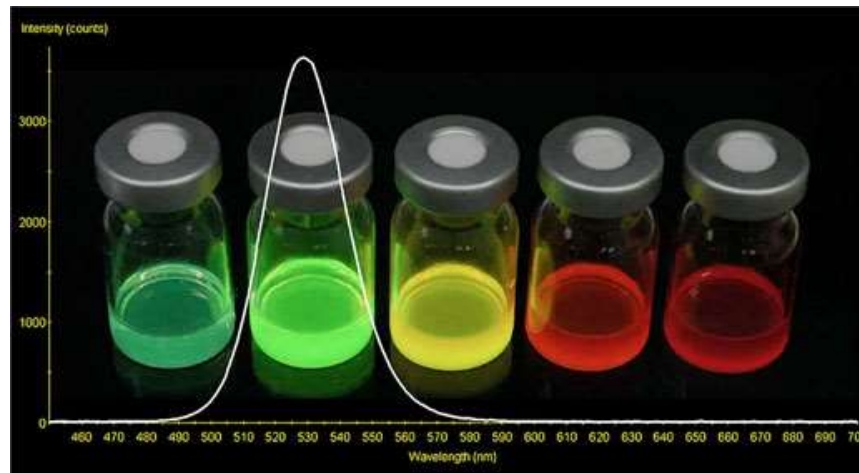
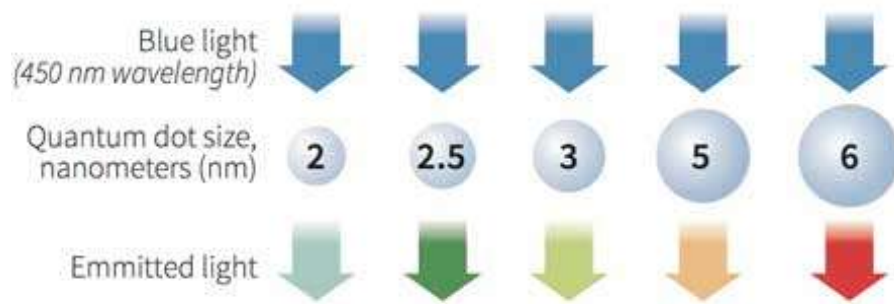
All the general methods used for the preparation of nanomaterials can be applied to the synthesis of QDs.

Synthesis of InP QDs:

Indium oxalate + Indium chloride or Indium fluoride are used as precursors for indium and trimethylsilylphosphine is used as the precursor for phosphorus.

A mixture of trioctylphosphine oxide (TOPO) and trioctylphosphine acts as colloidal stabilisers. The precursors are decomposed at a temperature greater than 200 °C. The nanocrystals are precipitated by adding methanol to the dispersion.

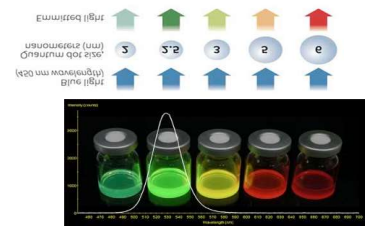
Quantum Dots (QDs)



Vials of quantum dots producing vivid colors. For instance, a cadmium-based quantum dot showing pure, highly specific green color response.

Properties of Quantum Dots

- Optical properties of QDs are affected by
 - i) nature of the surface
 - ii) area of the surface
- Properties change when an electron leaves the surface
- QDs emit photons under excitation and these are visible to the human eye as light
- By controlling their size, it is possible to monitor their wavelength of emission and this in turn determines the color of light perceived by the human eye



Applications of Quantum Dots

- They are used in photolysis reactions and in the manufacture of dye-sensitized solar cells
- Similar to nanocrystals, QDs also find their application as biological labels, bioconjugates and as drug carriers
- In the electronic industry, they are used for the preparation of photovoltaic cells and other electrochemical devices
- They also find use in environmental technologies for the removal of pollutants from the environment (CdS nanocrystals fix atmospheric CO₂)

Applications of Quantum Dots

- As these artificial semiconductor nanoparticles that have found applications in composites, solar cells and fluorescent biological labels.
- Quantum dots are artificial nanostructures that can possess many varied properties, depending on their material and shape. For instance, due to their particular electronic properties they can be used as active materials in single-electron transistors.
- A reliable manufacturing technology that makes use of quantum dots' properties – for a wide-ranging number of applications in such areas as catalysis, electronics, photonics, information storage, imaging, medicine, or sensing – needs to be capable of churning out large quantities of nanocrystals where each batch is produced according to the exactly same parameters.

Applications of QDs in detail

Quantum dots are used in medicine

Quantum dots enable researchers to study cell processes at the level of a single molecule and may significantly improve the diagnosis and treatment of diseases such as cancers. QDs are either used as active sensor elements in high-resolution cellular imaging, where the fluorescence properties of the quantum dots are changed upon reaction with the analyte, or in passive label probes where selective receptor molecules such as antibodies have been conjugated to the surface of the dots.

Quantum dots could revolutionize medicine. Unfortunately, most of them are toxic. Ironically, the existence of heavy metals in QDs such as cadmium, a well-established human toxicant and carcinogen, poses potential dangers especially for future medical application, where qdots are deliberately injected into the body.

As the use of nanomaterials for biomedical applications is increasing, environmental pollution and toxicity have to be addressed, and the development of a non-toxic and biocompatible nanomaterial is becoming an important issue.

Applications of QDs in detail

Quantum dots are used in photovoltaics

The attractiveness of using quantum dots for making solar cells lies in several advantages over other approaches: They can be manufactured in an energy-saving room-temperature process; they can be made from abundant, inexpensive materials that do not require extensive purification, as silicon does; and they can be applied to a variety of inexpensive and even flexible substrate materials, such as lightweight plastics.

Although using quantum dots as the basis for solar cells is not a new idea, attempts to make photovoltaic devices have not yet achieved sufficiently high efficiency in converting sunlight to power.

A promising route for [quantum dot solar cells](#) is a semiconductor ink with the goal of enabling the coating of large areas of solar cell substrates in a single deposition step and thereby eliminating tens of deposition steps necessary with the previous layer-by-layer method.

Applications of QDs in detail

Quantum dot TVs and displays

The most commonly known use of quantum dots nowadays may be TV screens. Samsung and LG launched their QLED TVs in 2015, and a few other companies followed not long after.

Quantum dots, because they are both photo-active (photoluminescent) and electro-active (electroluminescent) and have unique physical properties, will be at the core of [next-generation displays](#). Compared to organic luminescent materials used in organic light emitting diodes (OLEDs), QD-based materials have purer colors, longer lifetime, lower manufacturing cost, and lower power consumption. Another key advantage is that, because QDs can be deposited on virtually any substrate, you can expect printable and flexible – even rollable – [quantum dot displays](#) of all sizes.

Other types of QDs

Graphene quantum dots

Perovskite quantum dots

7. Nanowires

- **Nanowires:** Nanowires have diameter of the order of a nanometer (10^{-9} m) and their length-to-width ratio is greater than 1000. Hence, they are referred to as 1-dimensional materials.

Various types of Nanowires are:

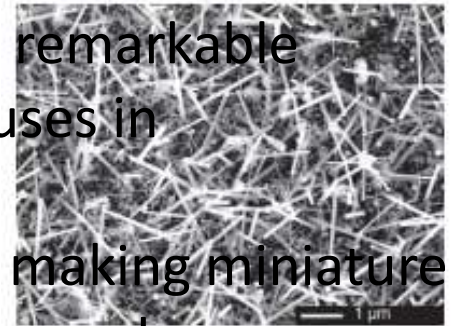
- ✓ Metallic (e.g., Ni, Pt and Au)
- ✓ Semiconducting (e.g., silicon, gallium nitride and indium phosphide)
- ✓ Insulating (e.g., SiO_2 and TiO_2)
- ✓ Molecules that have repeating molecular units.
They can be organic (DNA) or inorganic ($\text{Mo}_6\text{S}_{9-x}\text{I}_x$)

Properties of Nanowires

- Depending upon the material with which the nanowires are made, they can be metallic, semiconductors or insulators.
- Nanowires behave like ballistic conductors.
- In normal conductors, the speed of the conducting electrons reduces because of collision with atoms, whereas in ballistic conductors, electrons travel through the conductor without colliding with the atoms.
- Nanowires can conduct efficiently without heating the conductor wire.

Applications of Nanowires

- Nanowires find extensive applications because of their remarkable optical, electronic and magnetic properties. They find uses in
- Nanowires conduct electricity; hence, they are used in making miniature circuits for transistors and other basic electronic devices such as junction diodes and logic gates.
- Nanowires are also used in quantum computers. Research has shown that InAs nanowires when attached to aluminium electrode make aluminium a superconductor at low temperature because of proximity effect.



Germanium nanowires

Source: <https://www.intechopen.com/books/nanowires-fundamental-research/growth-of-germanium-nanowires-on-a-flexible-organic-substrate>

Applications of Nanowires

- Nanowires generate electricity from kinetic energy (piezoelectric effect).
- Piezoelectric nanowires can be used to provide power to nano-sized systems in future.
- Co-axial nanowires improve the efficiency of solar cells.
- Nano-sized devices such as nano robots are made of nanowires. These nano robots are used to treat diseases such as cancer.
- Used in thermoelectric cooling systems.
- Nanowires are used to link tiny components in externally small circuits.

Preparation of Nanomaterials

Nanomaterials can be synthesised in a number of ways. The various methods generally employed for the synthesis of nanomaterials are as follows.

- (i) **Mechanical grinding** This method of synthesis of nanomaterials follows a top-down approach. In this method, the nanoparticles are not synthesised by assembling small particles but by the structural decomposition of larger particles by the use of mechanical mills. This method is simple and inexpensive but causes environmental pollution.
- (ii) **Wet chemical synthesis** Wet synthesis can follow the top-down approach in which a single crystal is etched into nano-sized particles in aqueous solution. Porous silicon is synthesised by electrochemical etching. It can also follow a bottom-up approach where small particles agglomerate in a controlled manner to form nanosized particles.
- (a) *Sol gel process* It is a very popular method used for the preparation of oxide nanomaterials. The sol-gel process involves hydrolysis followed by condensation. A metal or metalloid employed as a precursor is dispersed in acid or water to form a sol. Gel is obtained from this sol by the removal of water.



Metal alkoxide



The various steps involved are as follows:

- (i) First the solvated solution of the alkoxide or metal is formed.
- (ii) Solvation is followed by polycondensation due to the formation of oxide or alcohol-bridged network. This leads to gelation and increases the viscosity of the solution dramatically.
- (iii) Gradually, the gel solidifies and the smaller particles aggregate to form larger particles, a process called coarsening.
- (iv) This is followed by drying of the gel where water and volatile liquids are removed from the gel network. After this the surface-bound M-OH groups are removed so that the gel is stabilised against rehydration.

The above method of synthesis follows the bottom-up approach, where it is essential to control the growth of the agglomerating particles. The bottom-up method, although slow, leads to the formation of mono-sized nanoparticles.

- (2) **Gas-phase synthesis of nanomaterials** Gas-phase synthesis is gaining importance as they have certain advantages

Advantages

- The size, shape and chemical composition of the nanomaterials can easily be controlled.
- Substances formed are of high purity.
- The reaction mechanism is easily controllable.

The conventional gas phase synthesis is the chemical vapor deposition (CVD) method that can be either homogeneous CVD or heterogeneous CVD. In these synthetic routes, small clusters of nanoparticles are produced because of condensation.

In homogeneous CVD, the particles in the gaseous phase diffuse under the influence of thermophoretic forces and deposit on the cold surface. These deposits are either scrapped off to yield nanopowders or 'particulate films' are formed by depositing them onto the substrate.

Chemical vapor deposition can be achieved in a number of ways

- (a) **Furnace heating** The appropriate material is heated in a furnace upto a temperature of 2000 °C. The material is evaporated in an inert atmosphere (e.g., helium). If a compound is to be formed then the precursor is fed at very low pressure into the furnace in the presence of the substance with which it has to react. The hot particles are then condensed into small clusters. The clusters grow as long as they are in the supersaturated region. The size is controlled by removing them rapidly from the supersaturated region with the help of a carrier gas. This method is simple and the particle size can be controlled by controlling the rate of evaporation, rate of condensation and the rate of removal of cluster with the assistance of carrier gas.
- (b) **Flame-assisted ultrasonic spray pyrolysis** In this method the precursor is nebulised to obtain its vapors. These vapors are then pyrolysed by burning in an acetylene oxygen flame or hydrogen oxygen flame. The high pressure may result in highly agglomerated powders; hence, the low-pressure range is maintained to reduce the aggregation of particles. This method is used to obtain ZrO_2 nanoparticles [precursor $\text{Zr}(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_4$] and silica nanoparticles (silica tetrachloride is heated in an oxyhydrogen flame). It is also widely used to obtain titanium dioxide, fused silica and carbon black. As the flame has an oxidative atmosphere, this method is limited to the formation of oxides (Fig. 23.4).

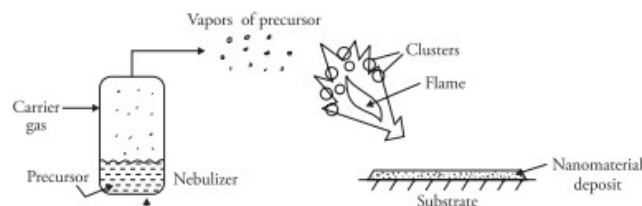


Figure 23.4 Flame assisted ultrasonic spray pyrolysis

- (c) **Gas condensation processing (GPC)** In this method the desired substance is vaporised by thermal evaporation or by sputtering in an inert atmosphere of He, Ne, Ar and Kr or by a laser beam. The particles are then condensed and collected either in a solvent or by deposition on a collection device. This method helps in the synthesis of pure nanocrystalline substances. Generally, refractory metal crucibles of W, Ta or Mo are used for evaporation, and if the substance reacts with crucible then evaporation is accomplished by a laser beam or electron beam.

- (d) **Chemical vapor condensation (CVC)** In chemical vapor condensation, the source of evaporation is replaced by a hot wall reactor. To avoid the formation of thin films and to promote homogeneous nucleation of precursor particles the gas flow rate and residence time of the precursor particles is adjusted.

The vapors of precursor are introduced into the hot wall reactor, where, by adjusting the conditions, nano-sized clusters are formed that are condensed and removed. This method is useful for the synthesis of nanoparticles of nitrides, carbides, BaTiO_3 or other composite structures (Fig. 23.5).

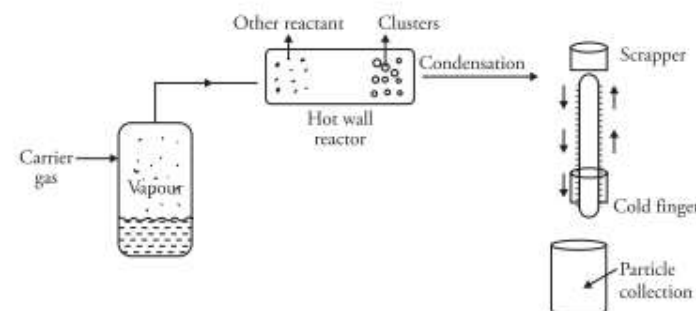


Figure 23.5 Schematic representation of a CVC reactor

- (e) **Sputtered plasma processing** This method is similar to the gas phase condensation method, except that the precursor is sputtered using rare gases and then the particles agglomerate to produce nanomaterials. This method finds use in the synthesis of nanoparticles of various alloys, oxides, carbides, nitrides, etc.
- (f) **Microwave plasma processing** In this technique the precursor is vaporised using plasma instead of high temperature. In this method, the precursor is introduced from the front of the reaction vessel that is made of quartz and is placed in a cavity connected to a microwave generator. The advantage of plasma-assisted pyrolysis is that the precursor can be activated at low temperatures that prevent the excessive agglomeration of the primary particles. The primary precursor can be coated with another phase by introducing the second precursor into the reactor. This method is employed for coating ZrO_2 nanoparticles with Al_2O_3 . The inner ZrO_2 is crystalline, whereas Al_2O_3 is amorphous. By reversing the reaction sequence amorphous Al_2O_3 can be coated with crystalline ZrO_2 . This method can be used to obtain both nanoparticles as well as thin film of nanoparticles.

Iron oxide, Fe_3O_4 (magnetite) nanoparticles

- Magnetic nanoparticles are nanoparticles type which can easily be tracked, manipulated and targeted using external magnetic field.
- When magnetic field is applied to nanoparticle, a dipole is induced, when no field is applied nanoparticles return to original non-magnetic state.
- These are composed of elements iron, cobalt, nickel and their oxides.
- Iron oxide nanoparticles are common magnetic nanoparticles used due to high electrical resistivity, chemical stability, mechanical hardness, magnetic properties in radiofrequency region.
- Magnetic nanoparticles are useful for catalysis, magnetic fluids, data storage, biomedicine, magnetic resonance imaging (MRI), environmental remediation.

Types of magnetic nanoparticles

1. **Metal and metal oxide nanoparticles-** Include transition metals Fe, Co, Ni, show ferromagnetism at low temperature and paramagnetism at high temperature. Oxides of these metals also show magnetic behavior, Iron oxide commonly used.
2. **Ferrites-** Ferrites belong to nonconductive class of ferromagnetic materials derived from metal oxides as $\alpha\text{-Fe}_2\text{O}_3$, magnetite (Fe_3O_4). Ferrites have three different structural symmetries: garnet, hexagonal, and cubic or spinel ferrites which are determined by the size and charge of the metal ions that balance the charge of the oxygen ions and their relative amounts.
3. **Dilute metal semiconductors-** These possess characteristics of both semiconductors as well as magnetic properties. In DMS, a fraction of the cations in the lattice are substituted by magnetic ions, and atomic spin on these magnetic ions interacts with the carriers in the lattice to bring ferromagnetic order in the material. Thus, these materials have unusual magnetic characteristics due to the presence of isolated magnetic ions in semiconducting lattice. The DMS includes simple oxides like SnO_2 , ZnO , TiO_2 , or mixed oxides doped with several transition metals (Fe, Co, Ni, Mn) or rare earth metals (Dy, Eu, Er).

Preparation of Metal oxide, Fe_3O_4 (magnetite) nanoparticles

1. Co-precipitation

- I. Widely used method for synthesis of oxide nanoparticles.
- II. Addition of base (NaOH , NH_4OH) to $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution at room temperature or elevated temperature.
- III. Size and shape can be controlled by
 - Variation of different salts such as chlorides, sulphates and nitrates
 - Variation in $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio
 - Temperature and pH variation (Eg: Precipitation at 60°C produces Fe_2O_3 nps, precipitation at 80°C produces Fe_3O_4 nps)
 - Ionic strength of media

Advantages	Disadvantages
Low reaction temperature	Insufficient size control distribution
Short reaction time	Uncontrolled shape

2. **Microemulsion method** – surfactant used for iron oxide nanoparticle is sodium dioctylfosuccinate (Aerosol OT or AOT)

3. **Solvothermal, hydrothermal method** –

- The process takes place in autoclave and reactor under high temperature and pressure.
- Low reaction temperature, low reaction time and low cost are characteristic of this method.
- Can be used in combination with microwave, sol-gel processes that help in formation of single phased material with higher stability.

4. **Chemical vapor deposition** -

- Synthesis of iron oxide by reaction of FeCl_3 with water at 1000°C
- Low yield, existence of complex phase and difficulty in separating iron oxide nanoparticles from impurities.
- Thermal CVD and MOCVD can also be used for preparation of iron oxide nanoparticles.

Applications of Fe₃O₄ NPs

- Fe₃O₄ or Magnetite nps used in numerous application due to
 - a) Chemical stability
 - b) Biocompatibility
 - c) Low toxicity
 - d) Small size, large surface area
 - e) Superparamagnetic property and easy manipulation under applied field allows nps to be reused or recycled.
 - **Drug delivery** - can be used for targetted drug delivery,
 - **Magnetic resonance tomography (MRT)** –
 - permits non invasive visualization of cross sectional images of human body, where magnetic nanoparticles are used as contrast agents.
 - Magnetite can differentiate between healthy and malignant liver cells.
 - Functionalization with ligands can improve their use.
 - Can also be used for removal of metals Hg, Cu, Co, Cr, Pb from water and also used for hard disk drives.
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