

# CHEMISTRY ASSIGNMENT

Praneesh Sharma

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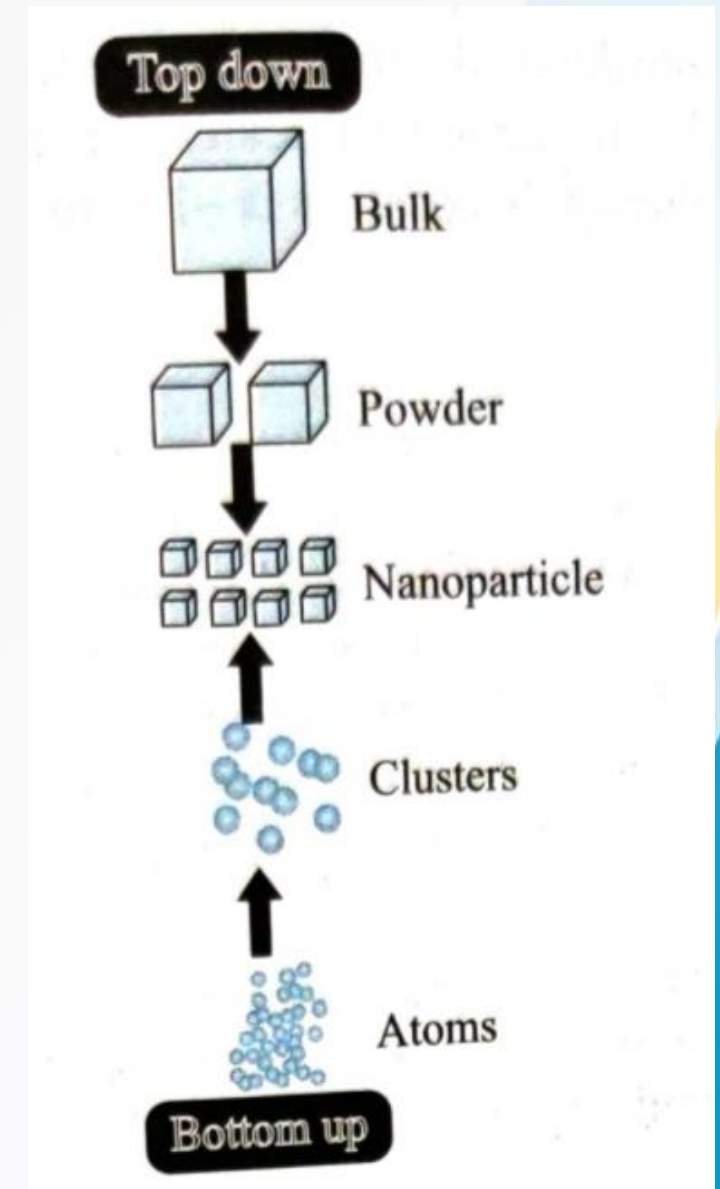
# Nanostructured Materials

Nanostructured materials may be defined as those materials whose structural elements - clusters, crystallites or molecules - have dimensions in the 1 to 100 nm range. The explosion in both academic and industrial interest in these materials over the past decade arises from the remarkable variations in fundamental electrical, optical and magnetic properties that occur as one progresses from an 'infinitely extended' solid to a particle of material consisting of a countable number of atoms.



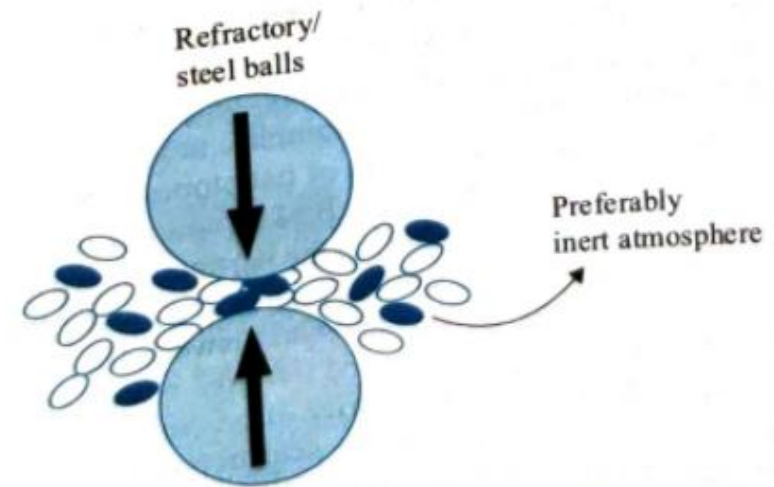
# Preparation Of Nanomaterials

- **Top-Down Approach:** These approaches use large(macroscopic) initial structures, which can be externally controlled in the processing of nanostructures. Typical examples are etching through the mask, ball mining, and application os severe plastic deformation. This method, by nature, is not cheap and quick to manufacture. Rather this method's is slow and not suitable for large scale production.
- **Bottom-up Approach:** These approaches include the miniatureization 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. Typical examples are quantum dot formation during exitaxial growth and formation of nanoparticles from colloidal dispersion. The methods in this approach are of four types: gas-phase method, liquid-phase method, solid-phase method, and biological method.



# High Energy Ball Milling

The primary objective of the milling are to reduce particle size, solid-state alloying, mixing or blending, and particle shape changes. Powders with typical particle diameters of about 50 micrometer are placed together with a number of hardened steel or tungsten carbide(WC) coated balls in a sealed container preferably in an inert atmosphere which is shaken or violently agitated. Since the kinetic energy of the balls is a function of their mass and velocity, dense materials (steel or tungsten carbide) are preferred to ceramic balls. by using high frequencies and small amplitudes or vibration, it is possible to generate high energy milling forces. During the continuous severe plastic deformation associated with mechanical attrition, a continuous refinement of the internal structure of the powder particles to nanometer scales occurs during high energy mechanical attrition . The temperature rise during this process is -100 to 200C.



**Fig. 17.4** Schematic representation of the principle of mechanical milling



# Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a technique used to produce high purity solid materials, typically thin films. In a CVD process, substrates are exposed to one or more precursor materials in the gaseous state. The precursors react or decompose on the substrate surface to yield a coating of the required material. Frequently, volatile byproducts are also produced, which are removed by gas flow through the reaction chamber. The primary step is activating the reaction between the substrate surface and the precursor. The activation is achieved either by thermal means (thermal CVD) or by using plasma (plasma-assisted CVD). Both these techniques are schematically employed widely for various processes throughout the semiconductor industry. CVD is widely employed in micro-fabrication processes to deposit materials in various forms, including monocrystalline, polycrystalline, amorphous, and epitaxial. The materials include silicon, carbon nanofibres, carbon nanotubes, silicon carbide, and various high  $k$ -dielectrics. The term 'high  $K$ -dielectric' refers to a material with a high dielectric constant  $K$ , as compared to silicon dioxide.

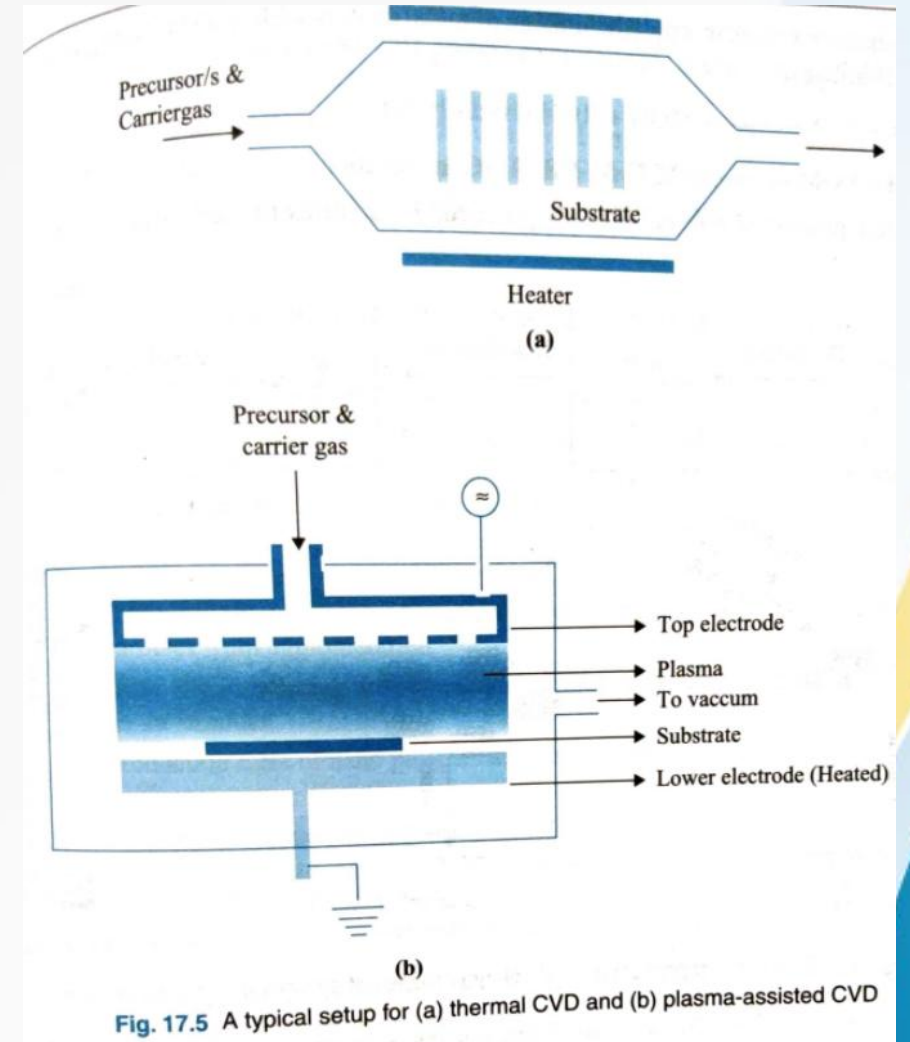


Fig. 17.5 A typical setup for (a) thermal CVD and (b) plasma-assisted CVD

# CVD Method for preparation of carbon nanotubes

Substrate is prepared with a layer of metal catalyst particles (commonly nickel, cobalt, iron, or a combination). Diameters of the nanotubes depend on the size of the metal particles. Two gases are blended into the reactor, viz., a carbon-containing gas (such as acetylene, ethylene, ethanol, or methane) and a carrier gas (such as ammonia, nitrogen, or hydrogen). Substrate is now heated to  $\sim 700^{\circ}\text{C}$  which initiates the growth of nanotubes. Nanotubes grow at the sites of the metal catalyst. The carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. Catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate. Advantages are that the method can be used for large-scale industrial production, has large length of tubes, is simple to perform, and purity of product. One issue in this synthesis route is the removal of the catalyst support via an acid treatment, which sometimes could destroy the original structure of the carbon nanotubes. However, alternative catalyst supports that are soluble in water have proven effective for nanotube growth.

# Wet Chemical Synthesis

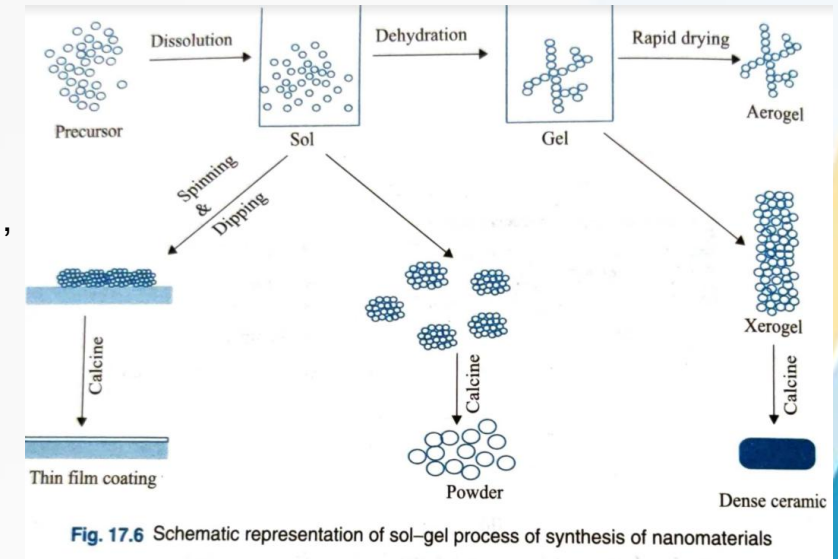
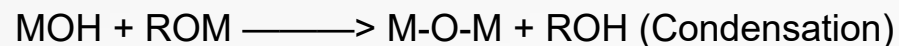
In principle, wet chemical synthesis of nanomaterials can be classified into two broad groups:

top-down method, where single crystals are etched in an aqueous solution: Or producing nanomaterials, e.g., the synthesis of porous silicon by electrochemical etching; bottom up method, which consists of sol-gel method, precipitation, “ — te containing the desired precursors are mixed in a controlled fashion to form a colloidal solution. Let us discuss

the sol-gel process in details. Sol-gel method of synthesizing nanomaterials is widely employed to prepare oxide materials. The sol-gel process involves the fabrication of inorganic networks, mostly metal oxides, through the formation of a colloidal suspension, i.e., sol and its subsequent gelation to

form a network in a continuous liquid phase, i.e., gel. Typical precursors for synthesizing such colloids are metal alkoxides such as  $\text{Si}(\text{OEt})_4$  (tetraethyl orthosilicate or TEOS). The precursor is processed to form a dispersible oxide, i.e., sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol-gel transition acid. Removal and shape. Calcination of the gel produces the oxide. The reactions are the particle size

chemistry based on the hydrolysis and condensation of metal in the sol-gel oxides  $\text{M}(\text{OR})_n$ , is described here. Condensation occurs through the linkage of metal centers with oxo- $(\text{M}-\text{O}-\text{M})$  or hydroxo- $(\text{M}-\text{OH}-\text{M})$  bridges.



# Wet Chemical Synthesis

## Advantages:

- The main advantage is that one can get monosized nanoparticles by any bottom-up approach.
- It is a cheap and low-temperature technique.
- This is widely used for synthesizing nonmetallic inorganic materials such as glasses, glass ceramics, or ceramic materials at very low temperatures as compared to the traditional high temperature processes that require melting glass or firing ceramics.

## Limitations:

- Difficulties in controlling the growth of the particles and stopping the newly formed particles from agglomeration.
- Difficulty in ensuring the completion of reactions so that no unwanted reactant is left on the product.
- Production rates of nano powders are very low in this process.

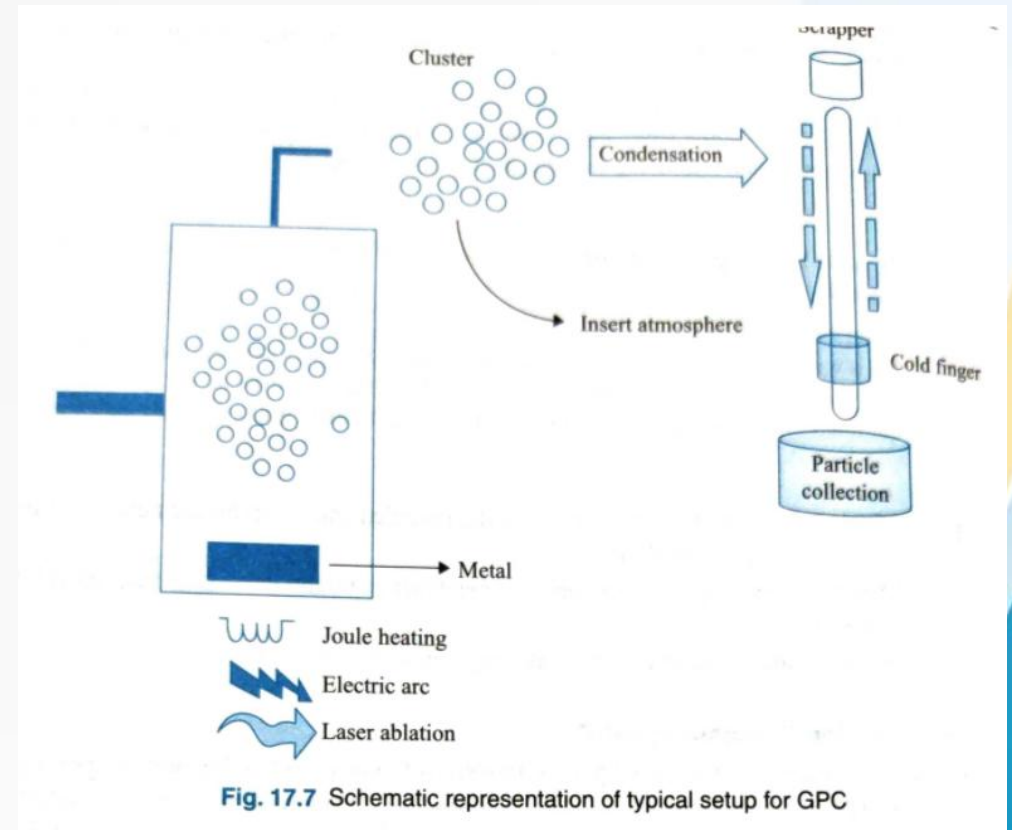


# Gas Condensation Processing (GPC)

The set up for gas condensation processing (GPC) consists of a vacuum chamber with evaporation arrangement and particle collection equipment. In the process, the metallic or inorganic material is vaporized using thermal evaporation sources such as Joule-heated refractory crucibles, electron beam evaporation devices, or sputtering sources in an inert atmosphere. Inert gas is continuously allowed to enter into the chamber and removed by pumps so that a dynamic vacuum is generated. The gas cools the vapor and nanoparticles form in the vicinity of the Source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase. The particle size depends critically on the residence time of the Particles in the growth regime and can be influenced by the gas pressure, kind of inert gas used, He, Ar, or Kr, and on the evaporation rate, i.e., vapor pressure of the evaporating material. The average particle size can be made to increase by increasing gas pressure, vapor pressure, and mass of the inert gas. A rotating cylindrical device cooled with liquid nitrogen (cold finger) is employed for the particle collection. The nanoparticles are extracted from the gas flow by thermophoretic forces and get deposited loosely on the surface of the collection device as a powder. Finally, the nanoparticles are removed from the surface of the cylinder by means of a Taper. The schematic presentation for GPC is shown in Figure.

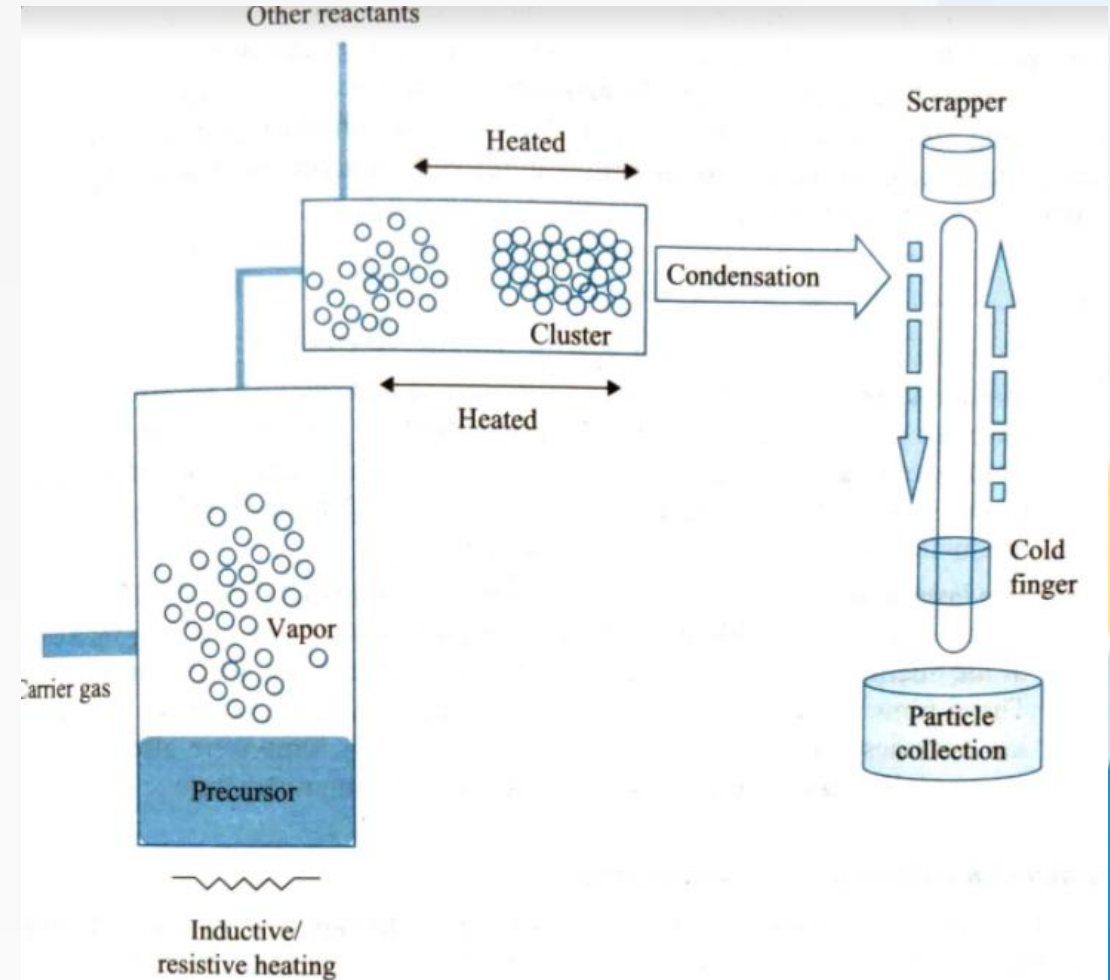
# Gas Condensation Processing (GPC)

- The method is extremely slow and therefore limited to a laboratory scale.
- Control of the composition of the particles has been difficult and reproducibility is poor.
- Evaporation is usually achieved from refractory metal crucibles such as W, Ta, or Mo. However, for metals with high melting points and those that react with the crucibles, sputtering or laser or electron beam evaporation is used.
- Sputtering is a non-thermal process in which surface atoms are physically ejected from the surface by momentum transfer from an energetic bombarding species of atomic or molecular size.
- Synthesis of alloys or inter-metallic compounds by thermal evaporation can only be done in exceptional cases where the vapor pressures of the constituent elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed.
- Composite materials such as Cu<sub>3</sub>Bi or W/ga can be synthesized by simultaneous evaporation from two separate crucibles onto a rotating collection device.



# Chemical Vapor Condensation (CVC)

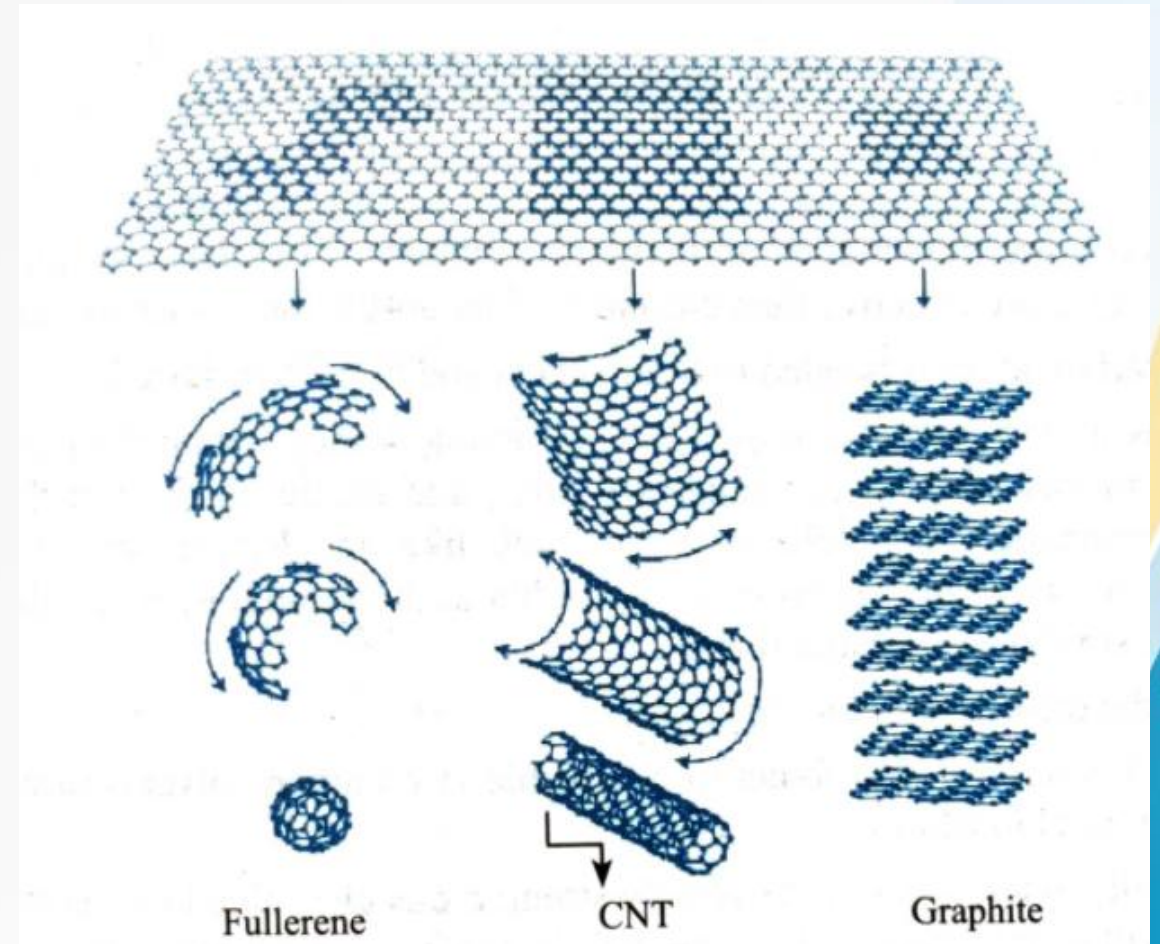
Another process called chemical vapor condensation (CVC) was developed in Germany in 1994. It involves pyrolysis of vapors of metal organic precursors in a reduced pressure atmosphere. Particles of  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$  and nanowhiskers have been produced by CVC method. A metalorganic precursor is introduced in the hot zone of the reactor using mass flow controller. For instance, hexamethyldisilazane  $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$  was used to produce  $\text{SiC}_x\text{NyO}_z$  powder by CVC technique. The reactor allows synthesis of mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of reactor and coated nanoparticles, n- $\text{ZrO}_2$ , coated with n- $\text{Al}_2\text{O}_3$  by supplying a second precursor in a second stage of reactor. The process yields quantities in excess of 20 g/hr. The yield can be further improved by enlarging the diameter of hot wall reactor and mass of fluid through the reactor.



**Fig. 17.8** A schematic of a typical CVC reactor

# Carbon Nanomaterials

Typical examples of carbon nanomaterials are fullerenes and cylindrical nanotubes. The other shapes such as nanowires and nanocones are also found. Graphene is the mother of all carbon nanomaterials. It is a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice. The two-dimensional (2-D) graphene sheet can be wrapped up into zero dimensional (0-D) fullerenes, rolled into one-dimensional (1-D) nanotubes or stacked in 3-D graphite and other structures. Thus, carbon nano-structures are accordingly classified as zero-dimensional, one-dimensional, two-dimensional, and three-dimensional nanostructures.





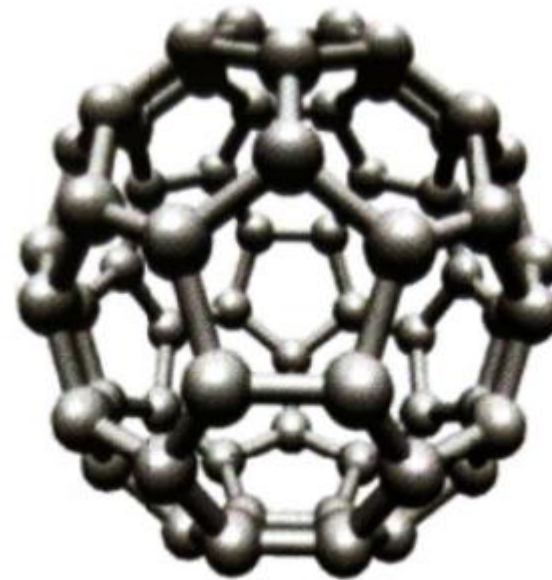
# Fullerenes

A fullerene is an allotrope of carbon whose molecule consists of carbon atoms connected by single and double bonds so as to form a closed or partially closed mesh, with fused rings of five to seven atoms. The molecule may be a hollow sphere, ellipsoid, tube, or many other shapes and sizes. Graphene (isolated atomic layers of graphite), which is a flat mesh of regular hexagonal rings, can be seen as an extreme member of the family.

Fullerenes with a closed mesh topology are informally denoted by their empirical formula  $C_n$ , often written  $C_n$ , where  $n$  is the number of carbon atoms. However, for some values of  $n$  there may be more than one isomer.

## Applications:

- Miniature 'ball bearings' to lubricate surfaces, drug delivery vehicles, and electronic units.
- MRI agents in medical world.
- Fullerenes can be added to polymer structures to create new copolymers with specific physical and mechanical properties.
- Used as proton exchange membranes for fuel cells.
- Fullerenes have the potential ability to transfer hydrogen, and hence are used as catalysts for hydrogenation.



**Fig. 17. 11** Bucky-ball ( $C_{60}$ ) fullerene



# Carbon Nanotubes (CNT)

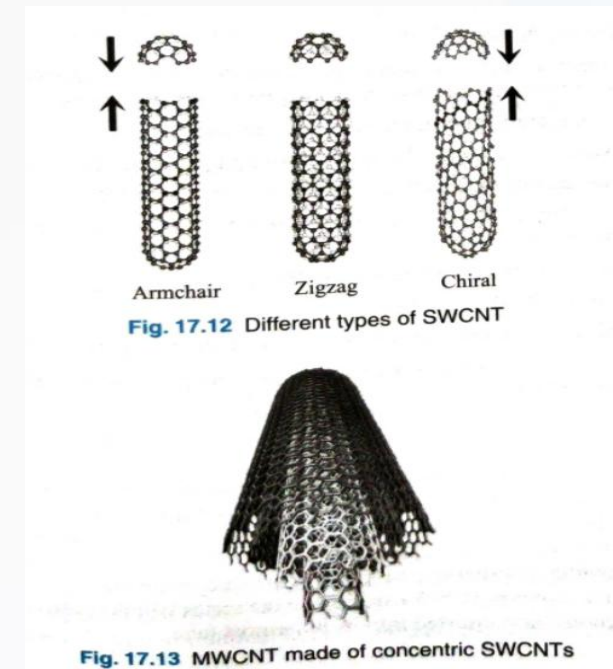
Carbon nanotubes (CNTs) are tubes made of carbon with diameters typically measured in nanometers.

Carbon nanotubes often refer to single-wall carbon nanotubes (SWCNTs) with diameters in the range of a nanometer. Single-wall carbon nanotubes are one of the allotropes of carbon, intermediate between fullerene cages and flat graphene.

Carbon nanotubes also often refer to multi-wall carbon nanotubes (MWCNTs) consisting of nested single-wall carbon nanotubes weakly bound together by van der Waals interactions in a tree ring-like structure. If not identical, these tubes are very similar to Oberlin, Endo, and Koyama's long straight and parallel carbon layers cylindrically arranged around a hollow tube. Multi-wall carbon nanotubes are also sometimes used to refer to double- and triple-wall carbon nanotubes.

## Applications:

- In conducting polymers.
- In electronics such as memory, semiconductor components, and transparent conducting films for touch screens, displays, and solar cells.
- Used for preparation of structural materials such as textiles, body armour, concrete, sports equipment, high tensile strength fibres and bridges.
- To build ultra-capacitors in which energy storage capacity is much higher than the traditional capacitors.



# Nanowires

A nanowire is a nanostructure, with the diameter of the order of a nanometre ( $10^{-9}$  metres). More generally, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length. At these scales, quantum mechanical effects are important—which coined the term "quantum wires". Many different types of nanowires exist, including superconducting (e.g. YBCO[1]), metallic (e.g. Ni, Pt, Au, Ag), semiconducting (e.g. silicon nanowires (SiNWs), InP, GaN) and insulating (e.g. SiO<sub>2</sub>, TiO<sub>2</sub>). Molecular nanowires are composed of repeating molecular units either organic (e.g. DNA) or inorganic (e.g. Mo<sub>6</sub>S<sub>9</sub>-xIx).

## Applications:

- Enhancing mechanical properties of composites.
- Used to prepare active electronic components such as p-n junction and logic gates.
- Semiconductor nanowire crossings are expected to play a very important role in the future of digital computing
- Nanowires have potential applications in high-density data storage, either as magnetic read heads or as patterned storage media.



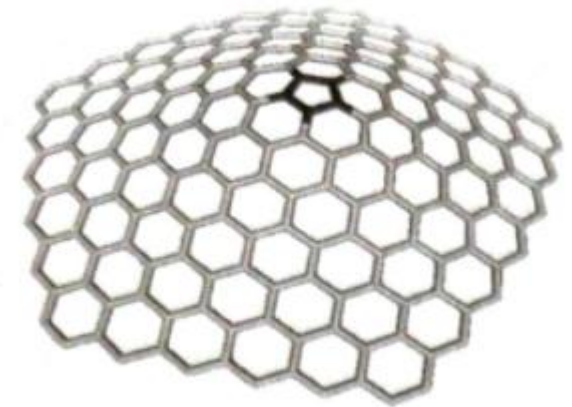
**Fig. 17.14** Carbon nanowire inside an MWCNT

# Nanocones

Carbon nanocones are conical structures which are made predominantly from carbon and which have at least one dimension of the order one micrometer or smaller. Nanocones have height and base diameter of the same order of magnitude; this distinguishes them from tipped nanowires which are much longer than their diameter. Nanocones occur on the surface of natural graphite. Hollow carbon nanocones can also be produced by decomposing hydrocarbons with a plasma torch. Electron microscopy reveals that the opening angle (apex) of the cones is not arbitrary, but has preferred values of approximately  $20^\circ$ ,  $40^\circ$ , and  $60^\circ$ . This observation was explained by a model of the cone wall composed of wrapped graphene sheets, where the geometrical requirement for seamless connection naturally accounted for the semi-discrete character and the absolute values of the cone angle. A related carbon nanoform is the single-walled carbon nanohorn which typically form aggregates 80–100 nm in size.

## Applications:

- **Nanocones can be used as base polymers or in diluted form both in the catalyst and in the cross linker components.**
- **Nanocone surface can be widely used in other fields such as ELISA, bio/chemical sensor, bead-based assays, affinity-based separation, and SPR spectroscopy.**



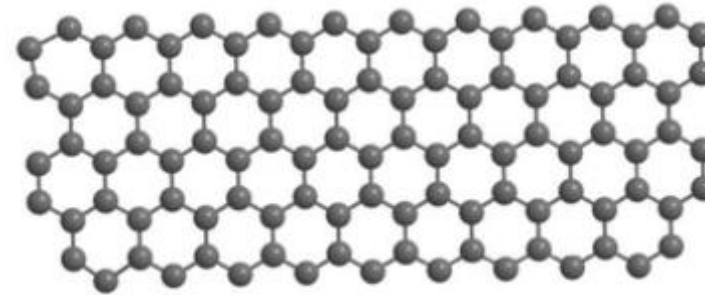
**Fig. 17.15 Nanocone**

# Nanographites

Nanographites are molecular systems, where graphene sheets of dimensions of the order nanometres are stacked. They are also known as exfoliated graphite nanoplatelets, which consist of several graphene sheets stacked together to a total thickness between 1 and 15 nm, where the platelet diameter ranges from the sub-micron to over 100 microns. Exfoliated graphite nanoplatelets were typically produced by acid intercalation into multilayered graphite structure followed by thermal exfoliation and a controlled size reduction. Since graphite is the stiffest material found in nature (Young's Modulus = 1060 GPa), having a modulus several times that of clay, accompanied with excellent electrical and thermal conductivity, the nanoplatelets should have similar properties to carbon-based nanomaterials including carbon nanotubes, nanofibres, and fullerenes, yet the estimated cost is substantially low as compared to other carbon nanomaterials.

## Applications:

- Composite materials made with polymers, such as plastics, nylon, or rubber, can be made electrically or thermally conductive with the addition of small amounts of xGnP.
- These nanoparticles can change the fundamental properties of plastics, enabling them to perform more like metals with metallic properties.



**Nanographite**

THANK YOU