# Unit- 5: Nano-Materials

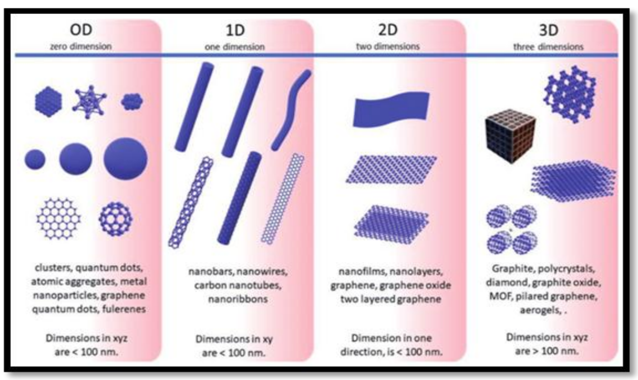
## Introduction and Properties of Nano-Materials

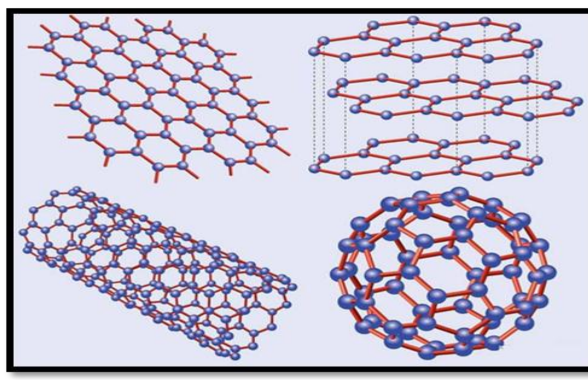
The ideas and concepts behind nanoscience and nanotechnology are given by physicist Prof. Richard Feynman on December 29, 1959. Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, Professor Norio Taniguchi coined the term nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms that modern nanotechnology began.

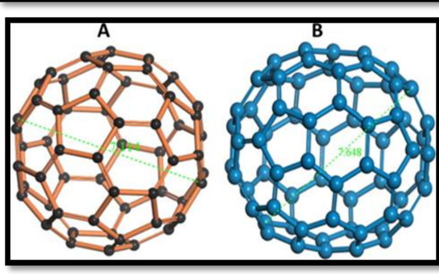
Nanomaterials are any type of material of nanosized thickness **1-100nm**. There are various types, many of which exhibit different properties than bulk materials. One common factor of nanomaterials is that this thickness range is also known as the quantum regime, where quantum effects play a major role in defining the properties. Because of this, nanomaterials often fall into different dimensional categories are it 2D, 1D or 0D.

Nanomaterials can occur naturally, be created as the by-products of combustion reactions, or be produced purposefully through engineering to perform a specialised function. These materials can have different physical and chemical properties to their bulk-form counterparts.

Nanomaterials exist in different dimensions, not only because they can be one atomic layer thick, but by how their electrons can be confined to flow in a certain number of dimensions. For example 2D materials have their electrons confined in one direction, so the electrons then move in two directions, hence the name. The same principle applies for 1D and 0D materials which have their electrons confined in 2 and 3 dimensions respectively; and their electrons can move in 1 and 0 directions respectively.



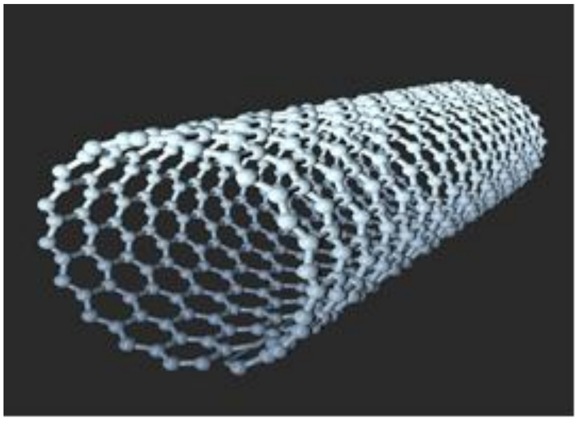



**Different form of Fullerenes/buck balls (A) C and (B) C70.**

## 1D Nano-Materials

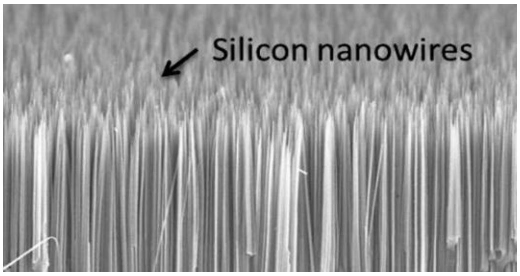
### Nanotubes

Nanotubes, be it a carbon nanotube or inorganic nanotube, are materials which are elongated in one dimension, with a length-to-diameter ratio of up to 132,000,000:1. Nanotubes direct electrons along the elongated axis and come in many forms, including single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT), chiral nanotubes, armchair nanotubes and zigzag nanotubes.



### Nanowires

Nanowires, otherwise known as quantum wires, are another well-known 1D material. Again, nanowires are elongated in one direction, albeit with a much lower width to length ratio of 1:1000. The most common nanowires are silver nanowires, which are also known to be highly electrically conductive. Nanowires are known for exhibiting many different quantum effects, which alongside their unidirectional electron movement have made them ideal materials for various electronic applications.




## 0D Materials

### Quantum Dots

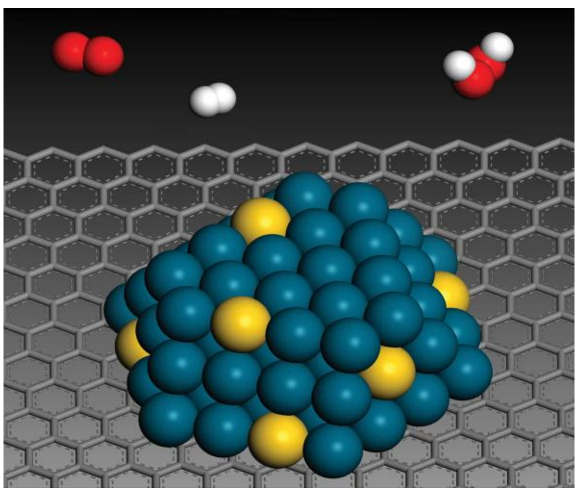
Quantum dots are a very common and useful type of nanoparticle, where the electrons are confined in all 3-dimensions. Quantum dots are small semiconducting particles that have been greatly used in displays and solar cells. Quantum dots emit a certain wavelength of light when they encounter either light or electricity and many quantum dots can be easily tuned. Quantum dots composed of cadmium, such as cadmium selenide (CdSe), are the widest class of quantum dots that have been studied.

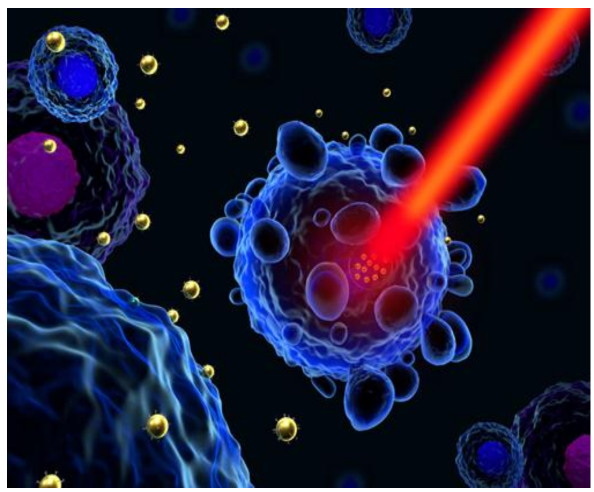
**Fullerenes**

Fullerenes come in two forms - pure carbon and has most common is $C_{60}$ as it is the most energetically and structurally stable form. Fullerenes composed of boron have also been predicted. Carbon fullerenes are composed of both single and double bonds, which are arranged into pentagons and hexagons. It is the pentagons which give the fullerenes their curvature. All fullerenes contain 12 pentagons, with a differing number of hexagons.

**Nanoparticles**

Overall, nanoparticles come in many forms. There are too many to individually discuss, but some of the most common are: single element nanoparticles, such as silver and gold nanoparticles which are used in medical imaging; metal oxide nanoparticles, including titanium dioxide nanoparticles used in white paint formulations.

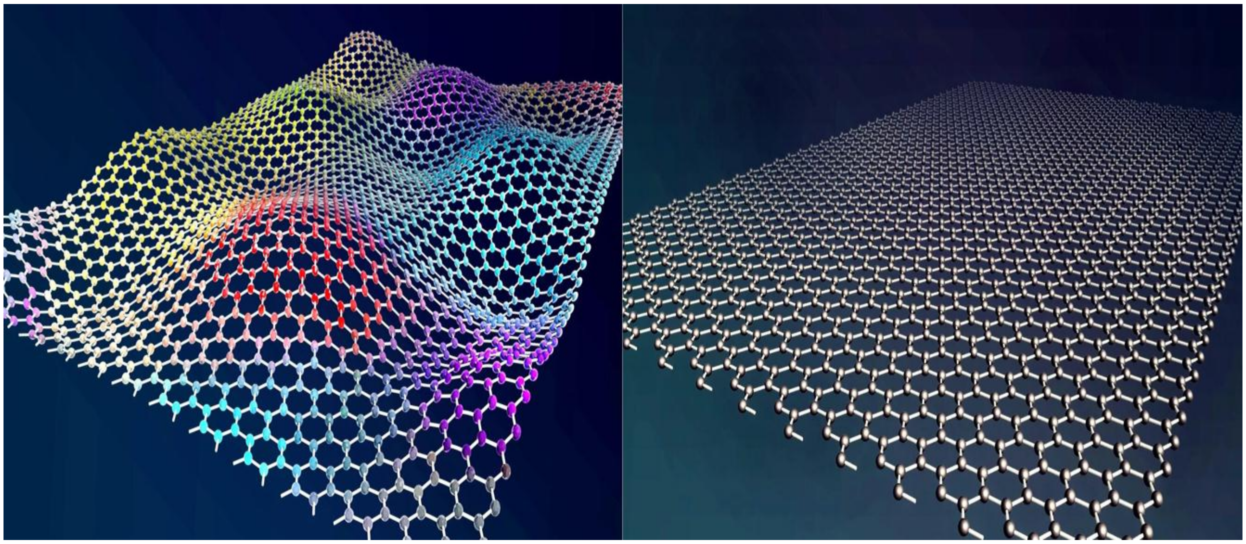




## 2D Materials

There are many types of 2D materials, such as phosphorene (phosphorous) and, of course, graphene (carbon). Graphene is by far the most useful and the closest material to commercialization within this list, especially as some of these are still theoretical materials. However, graphene and the various other 2D atomic materials possess an excellent array of optical, physical and electrical properties that make them useful for a wide range of applications.

Once graphene has been successfully used across many applications at a commercial level, it is expected that many of the other 2D materials will follow suit, although it could take a while.



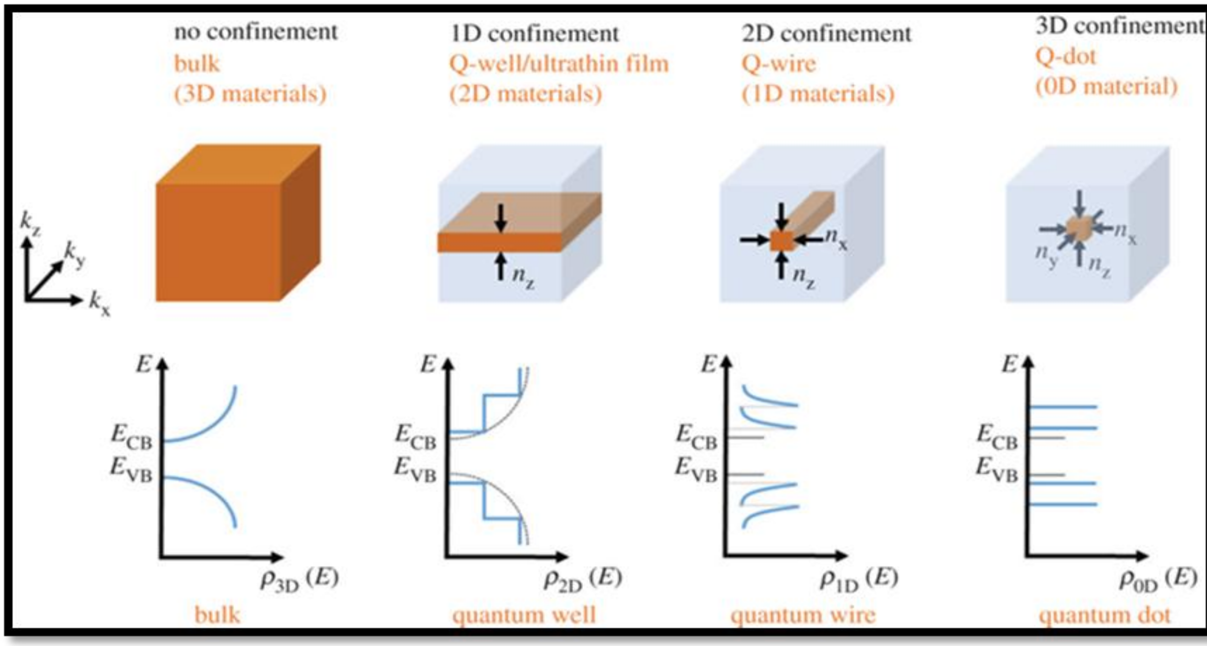
## Basics Concept of Quantum Dots, Quantum Wires and Quantum Well

**Bulk Material:** It is a three dimensional structure in which there is no confinement along any direction. All of its dimensions are larger than the exciton Bohr radius. The particle is free to move throughout the volume of the material. No quantization of the particle motion occurs i.e., particle have a continuous range of energies between a minimum and maximum. Low dimensional structures are classified on the basis of number of reduced dimensions they possess. Dimensionality refers to the number of degrees of freedom possessed by the particle. The low dimensional structures, on the basin of dimensionality, are of the following types:

**Quantum Well**: It is a two-dimensional nanostructure in which there in confinement along one direction and particle is free to move in other two directional (i.e., in a plane). Particle possesses discrete (or quantized) energies associated with the confinement dimension. Particle energies are continuous along the other two (unconfined) dimensions.

**Quantum Wire**: It is a one dimensional nanostructure in which there is confinement along two directions and particle is free to move in the third direction. Particle has discrete energies associated with these two directions of confinement and continuous along the third (unconfined) direction.

**Quantum Dot**: The extreme case in which confinement of the particle occurs in all the three directions, results in a zero-dimensional nanostructure, called quantum dot. In this case, the number of degrees of freedom of the particle is zero. Particle has discrete energies associated with its motion along all the three directions. Examples of zero dimensional objects are-nanoparticles, clusters, colloids, nanocrystals, and fullerenes. Quantum dots are composed of several to a few thousand atoms.



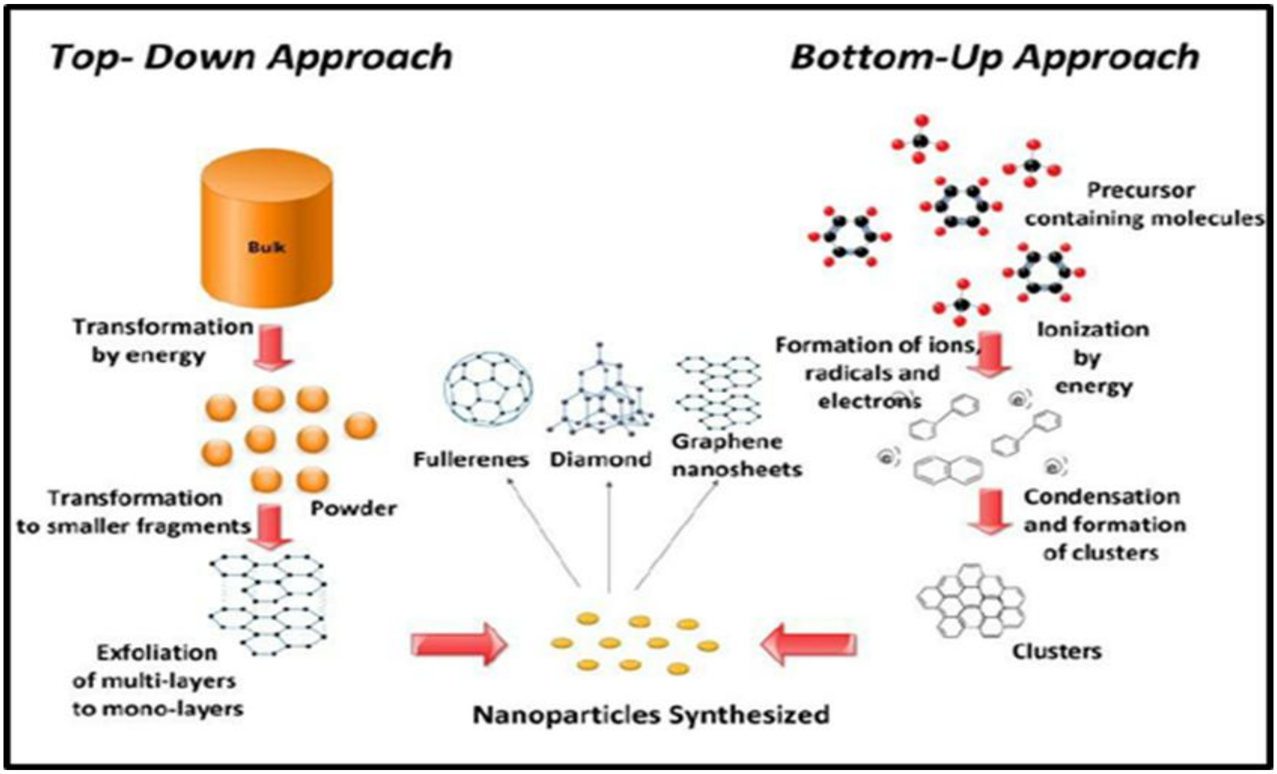

## Fabrication of Nano-Materials

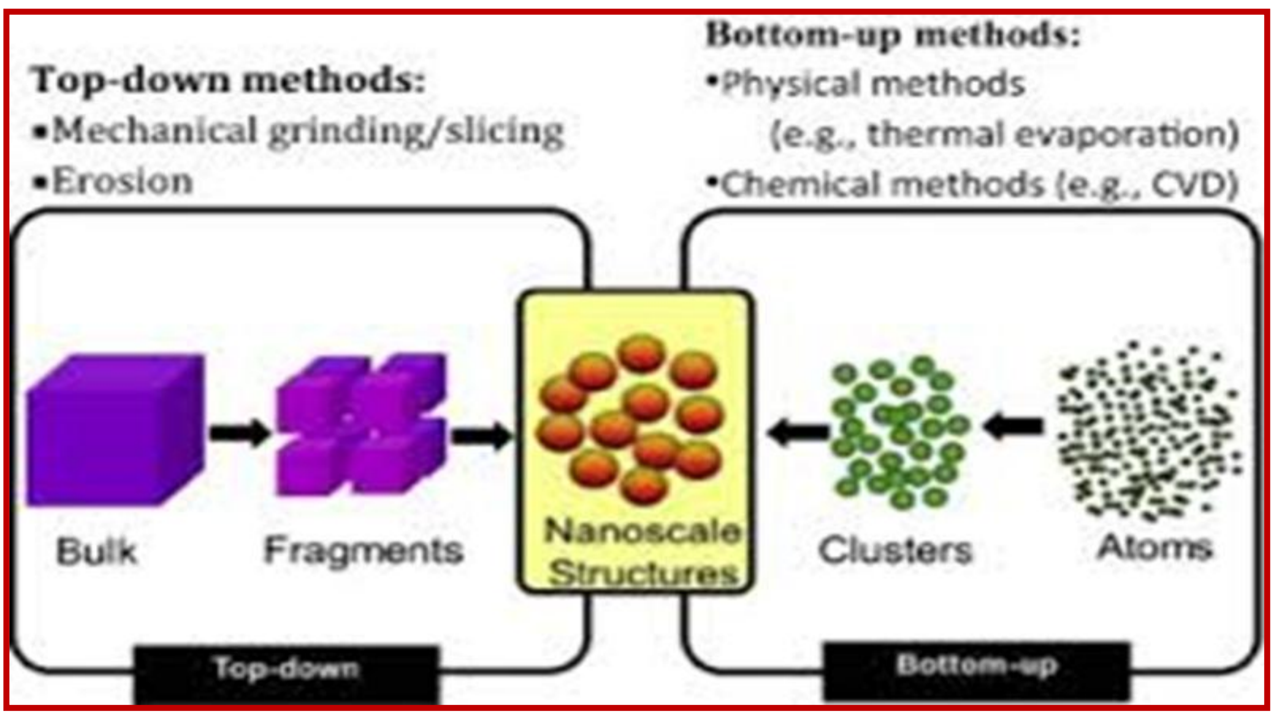
Nanofabrication has been a critical area of research in the last two decades and has found wide-ranging applications for improving material properties, sensitive clinical diagnostics, and detection, improving the efficiency of electron transport processes within materials, generating high energy densities leading to pulse power, novel therapeutic mechanisms, environmental remediation and control**. Nanostructures, nanomaterials, and nanocomposites can be fabricated using two different techniques, (1) top-down and (2) bottom-up.**

**The top-down method** is used for patterning of bulk materials by either subtractive or additive methods to realize nano-sized structures. Several methods are used to fabricate nanostructures using the top-down approach such as photolithography, scanning lithography, laser machining, soft lithography, nanocontact printing, nanosphere lithography, colloidal lithography, scanning probe lithography, ion implantation, diffusion, deposition. It has several limitations such as development of imperfections in processed materials, high cost (lithographic processes), requirement of high surface finished materials, longer etching times.

**In the bottom-up approach,** nanostructures are fabricated by building upon single atoms or molecules. In this method, controlled segregation of atoms or molecules occurs as they are assembled into desired nanostructures **(2-10 nm size range).** In general, there are two basic methods utilizing the bottom-up approach, i.e., gas-phase synthesis and liquid-phase formation.

Some of the methods used in bottom-up approach include plasma arcing, **chemical vapor deposition process**, metal organic decomposition, laser pyrolysis, molecular beam epitaxy.


Top- Down Approach
Bottom-Up Approach
Bulk
Transformation by energy
Powder
Transformation to smaller fragments
Exfoliation of multi-layers to mono-layers
Fullerenes
Diamond
Graphene nanosheets
Nanoparticles Synthesized
Precursor containing molecules
Formation of ions, radicals and electrons
Ionization by energy
Condensation and formation of clusters
Clusters

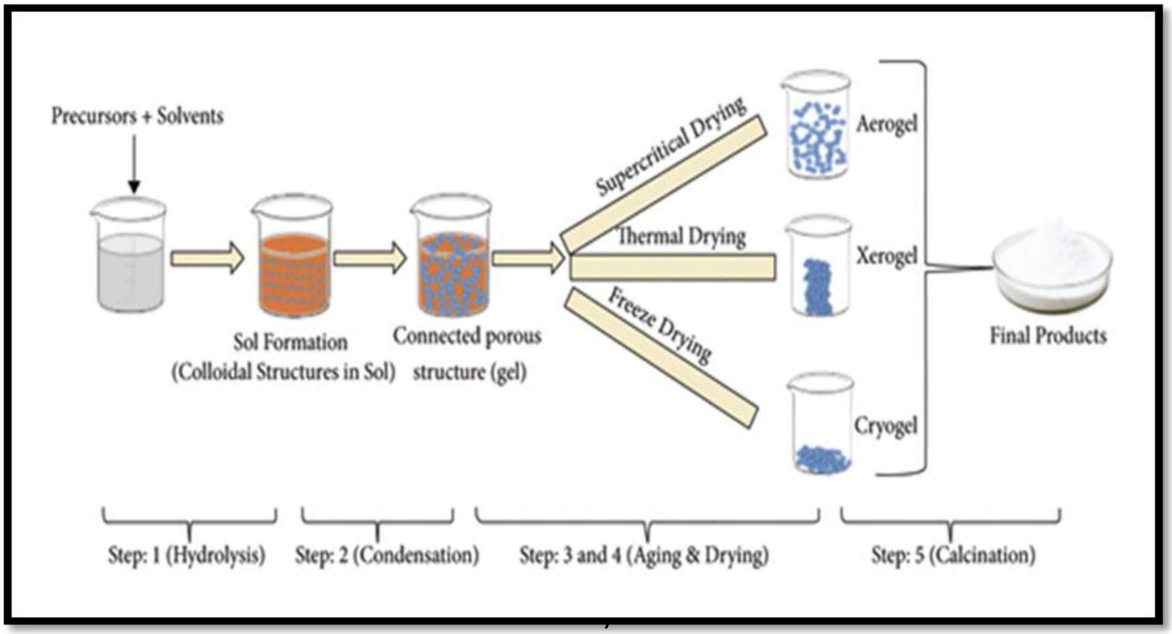

Top-down methods:
•Mechanical grinding/slicing
•Erosion
Bottom-up methods:
•Physical methods
(e.g., thermal evaporation)
•Chemical methods (e.g., CVD)
Bulk
Fragments
Nanoscale Structures
Clusters
Atoms
Top-down
Bottom-up

**Nanomaterial by Sol-Gel Method:**

The sol-gel process is performed at low temperatures (usually less than 100°C) and in the liquid state. Of course, the final product is solid, and these solids are formed as a result of the polymerization process, which involves the establishment of M-OH-M or M-O-M (where M represents the metal atom) between the metal atoms in the raw materials. The sol-gel process is a more chemical method (wet chemical method) for the synthesis of various nanostructures, especially metal oxide nanoparticles. This process is able to control the composition and microstructure at the molecular level with the ability to form material in bulk, powder, fiber, and thin film. In addition, various types of materials can be synthesized by sol-gel method including inorganic, organic, and hybrid materials

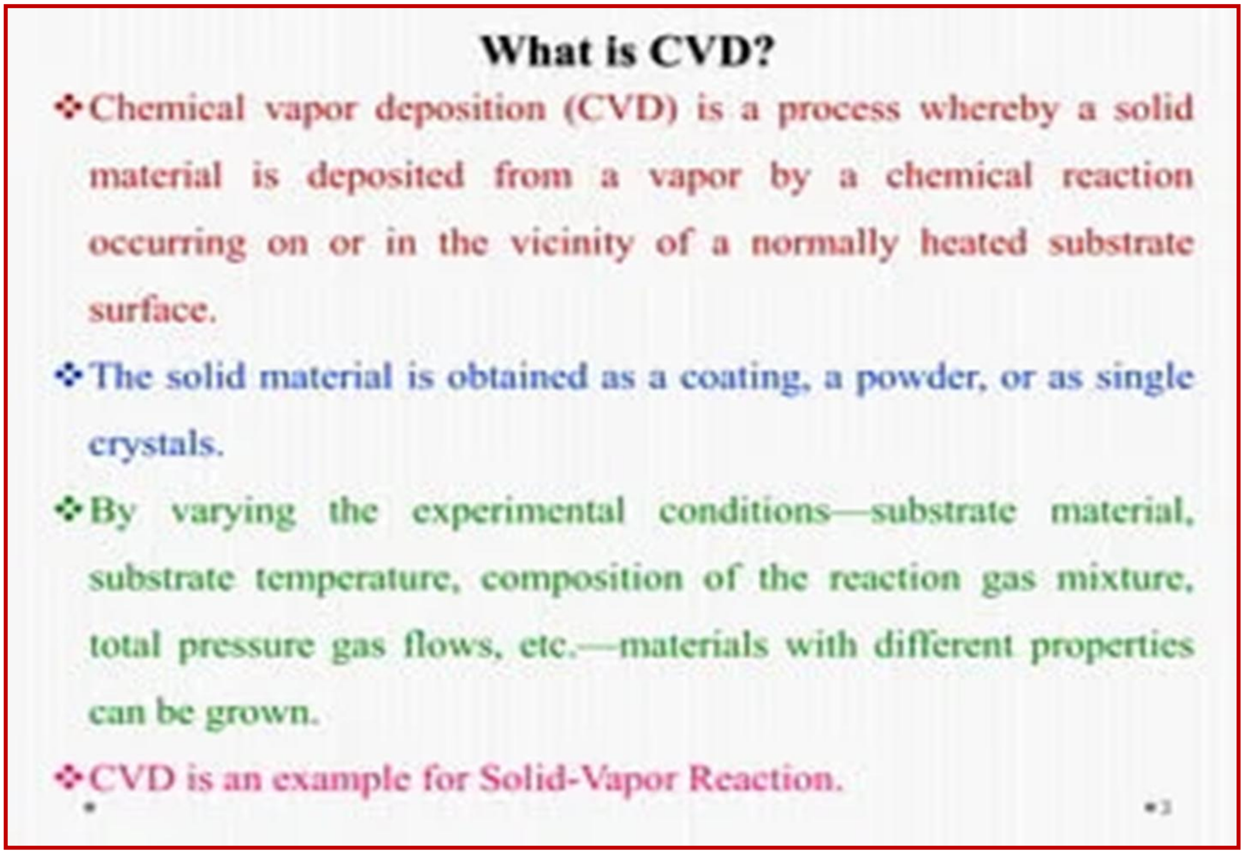
In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis. The sol-gel method is a cost-effective method and due to the low reaction temperature there is good control over the chemical composition of the products. The sol-gel method can be used in the process of making ceramics as a molding material and can be used as an intermediate between thin films of metal oxides in various applications. The materials obtained from the sol-gel method are used in various optical, electronic, energy, surface engineering, biosensors, and pharmaceutical and separation technologies (such as chromatography). The sol-gel method is a conventional and industrial method for the synthesis of nanoparticles with different chemical composition.

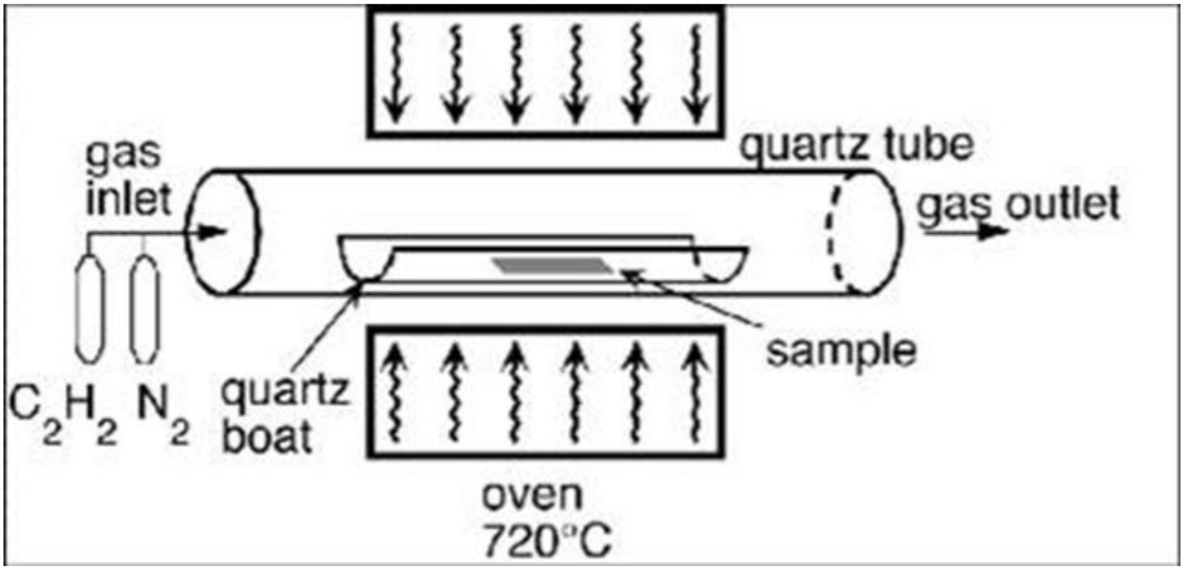
**Generally, there are three approaches that have been employed to fabricate solgel film: (i) gelation of a solution of solid colloidal particles, (ii) hydrolysis and polycondensation of alkoxides followed by hypercritical drying of gels, and (iii) hydrolysis and polycondensation of alkoxide followed by aging and drying under ambient conditions.**



**Chemical Vapor Deposition (CVD)**

Chemical vapor deposition (CVD) is the technique in which substances that are in vapor phase are condensed to generate solid phase material. This method changes optical, electrical, and mechanical attributes as well as corrosion resistance of different substances. Chemical vapor deposition process is mostly used in the semiconductor industry for depositing thin films of various materials. The process involves exposure of the substrate to one or more volatile precursors. These precursors decompose the substrate and react with it to produce the desired deposit. In the process, vaporized precursors are first adsorbed onto a substrate at a high temperature, which then react with one another or decompose and produce crystals. There are three main steps involved in the process: (i) reactants are transported onto the growth surface by a boundary layer, (ii) chemical reactions take place on the growth surface, and (iii) by-products formed by the gas-phase reaction are removed from the growth surface. Homogeneous nucleation takes place in gas phase, whereas heterogeneous nucleation takes place in the substrate.






Chemical vapor deposition (CVD) technique was first reported to produce Multi Wall Nanotubes (MWNTs) and Single Wall Nanotubes (SWNTs). CVD technique can be achieved by taking a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. The CVD process uses hydrocarbons as the carbon sources including methane, carbon monoxide and acetylene. The hydrocarbons flow through the quartz tube being in an oven at a high temperature (~ 720 $^0$C). Schematic diagram of the chemical vapor deposition apparatus is shown in Fig.  At high temperature, the hydrocarbons are broken to be the hydrogen carbon bond, producing pure carbon molecules. Then, the carbon will diffuse toward the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. **The advantages of the CVD process were low power input, lower temperature range, relatively high purity and, most importantly, possibility to scale up the process. This method can produce both MWNTs and SWNTs depending on the temperature, in which production of SWNTs will occur at a higher temperature than MWNTs.**

**Applications of Nanomaterials**

- Some of the commercial nanomaterials available in the market are cosmetics, strain resistant textiles, electronics, sunscreens, paints, etc…Nanocoatings and nanocomposites are being used in various consumer products such as sports equipment, windows, automobiles, etc..To protect the damage caused to beverages from sunlight, glass bottles are being coated with nanocoating which blocks the UV rays. Using nano-clay composites longer-lasting tennis balls are being manufactured. Nanoscale silica is used as a filler in dental fillings.

- The optical properties of the nanomaterials are used to form optical detectors, sensors, lasers, displays, solar cells. This property is also used in biomedicine and photo electrochemistry. In microbial fuel cells, the electrodes are made up of carbon nanotubes. Nano crystalline zinc selenide is used in the display screens to increase the resolution of the pixels forming High Definition TV sets and personal computers. In the microelectronic industry, miniaturizing of circuits such as transistors, diodes, resistors, and capacitors is emphasized.

- Nanowires are being used in forming junction less transistors. Nanomaterials are also used as catalysts in automobile catalytic converters and power generation systems, to react with toxic gases such as carbon monoxide and nitrogen oxide, thereby preventing the environmental pollution caused by them. To increase the sun protection factor (SPF) in the sunscreens nano-TiO2 is used. To provide a highly active surface to the sensors, engineered nanolayers are used.

- Fullerenes are used in cancer to treat cancer cells such as melanoma. These have also found use as light-activated antimicrobial agents. Due to their optical and electrical properties, quantum dots, nanowires, and nanorods have highly opted for Optoelectronics. Nanomaterials are being tested for applications in tissue engineering, drug delivery, and biosensors. Nanozymes are the artificial enzymes used for biosensing, bioimaging, tumor detection.

**Properties of Nanomaterials**

- As we go towards the nanoscale level from the molecular level, the electronic properties of materials get modified due to the quantum size effect. Change in the mechanical, thermal and catalytic properties of the materials can be seen with the increase in surface area to volume ratio at the nanoscale level.

- Many of the insulator materials start behaving as conductors at their nanoscale dimensions. Similarly, as we reach the nanoscale dimensions many interesting quantum and surface phenomena can be observed.

- Particle size, shape, chemical composition, crystal structure, physicochemical stability, surface area, and surface energy, etc…attributes to the physicochemical properties of the nanomaterials. As the surface area to volume ratio of the nanomaterials increases, their surface becomes more reactive on itself and other systems. The size of the nanomaterials plays a significant role in their pharmacological behavior. When nanomaterials interact with water or other dispersion media they can rearrange their crystal structure. The size, composition and surface charge of the nanomaterials affect their aggregation states. The magnetic, physicochemical and psychokinetic properties of these materials get affected by surface coating. These materials produce ROS when their surface reacts with oxygen, ozone, and transition materials.

- At the nanoscale level, the interaction between particles is either due to the van der Waal forces or strong polar or covalent bonds. The surface properties of the nanomaterials and their interactions with other elements and environments can be modified with the use of polyelectrolytes.