TOP DOWN AND BOTTOM UP APPROACHES

There are plenty of methods to synthesis nano materials. These methods are grouped into two categories namely Top-Down and Bottom-Up techniques. The techniques are classified based on the phase of the starting material. In the Top-down class of techniques, the starting material is in solid state, whereas in Bottom-Up techniques the starting material is either in gaseous state or in liquid state.

Top-down approach refers to a **subtractive** process in which a bulk starting material is divided into smaller ones of nanosize. Bottom-up approach refers to an **additive** process that starts with precursor atoms (or) molecules which combine to form nanosized structure. In bottom-up approach, nanostructures are built atom-by-atom or molecule-by-molecule. Depending on the requirement we have to select an appropriate method for prepration of nano materials.

Few methods are listed here

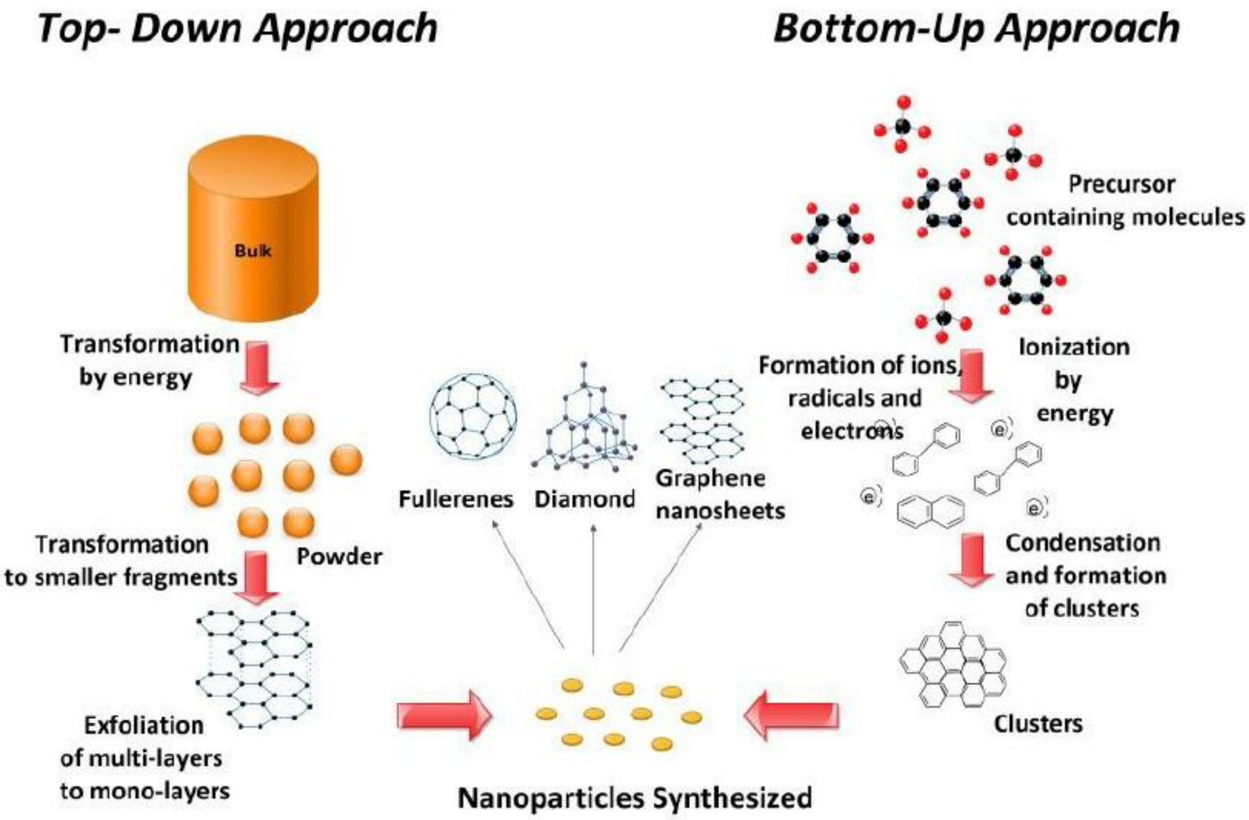
Top-Down techniques	Bottom-Up techniques
1) Mechanical grinding(Ball Milling) 2) Lithography 3) Etching 4) Erosion	1) Sol gel method 2) Chemical Vapour Deposition 3) Physical Vapour Deposition 4) Electrochemical deposition 5) Hydrothermal method 6) Atomic layer deposition

TOP-DOWN TECHNIQUES

Ball milling

Ball milling also known as mechanical grinding is a simple and popular method. Here the materials are grinded into extremely fine powders. It is one of the most important processes used in industries to synthesize nanomaterials. This method has many advantages such as compact design, energy efficient, minimum maintenance, inexpensive and scalable.

It works on the principle of impact. The size reduction is achieved through the impact caused when the balls drop from the top of the chamber in which the source material is placed.



Top-down and bottom-up processes of nanosized material preparation.

Etching

The process of removing a surface layer from a metal or plastic surface through chemical erosion is known as chemical etching. This process involves one or more chemical reactions that consume the original reactants and produce new species.

The chemical used for etching is called an etchant. In this process, the wafer to be etched can be immersed in a bath of etchant. Generally, etchants such as HCl, HNO_3, H_3SO_4 and H_3PO_4 are used for etching semiconductor oxide thin films.

Nanolithography

Lithography is the transfer of a required pattern from a master slide/plate/mask to another medium. Nanolithography is one of widely used top down techniques for the preparation of nanostructured materials and patterns.

Nanolithography techniques is based on depositing, masking, etching or writing the desired patterns with dimensions of the order of nanometers on a solid material surface. Using this technique, a pattern or design can be transferred at once on the surface of a device by exposure with a radiation.

Depending on the exposure radiation sources, like photons, X-rays, electrons and ions, the technique is classified as photolithography, X-ray lithography, electron-beam lithography and ion beam lithography, respectively.

BOTTOM-UP TECHNIQUES

Physical Vapour Deposition (PVD)

Vacuum evaporation is one of the common physical vapor deposition methods. The source material to be deposited is evaporated in a high vacuum, by heating it using one of the following hearing sources: direct resistance, eddy current, electron beam, laser beam or an arc discharge. The vacuum allows vapor particles to travel directly to the substrate, where they condense to form a thin solid film.

Chemical Vapour Deposition (CVD)

The material precursor is heated and evaporated. The atoms and molecules are in gaseous phase. The atoms or molecules react homogenously or heterogeneously and deposits on a solid surface. By CVD we can produce defect free and high purity nano materials.

Sol-Gel Synthesis

Sol-gel is one of the simple wet chemical techniques suitable for the preparation of nanoparticles (mostly oxides) and nanocrytalline thin films. It is a superior method to all available methods since this method is employed for large scale production at low cost.This method is based on inorganic polymerization reaction including hydrolysis, polycondensation, gelation, aging, drying and calcinations or sintering.

Electro-chemical deposition

Electro-chemical deposition is a process in which an electric current is used to reduce dissolved metal cations, so that they form a thin coherent metal coating on an electrode. It is also called electro-plating.

Atomic layer deposition

It is a subclass of chemical vapour deposition used to deposit ultra thin films. In ALD, two chemicals (precursor) react with the surface of a material one at a time in a sequential, self - limiting manner. The reactant molecules react only with a finite number of reactive sites on the surface.

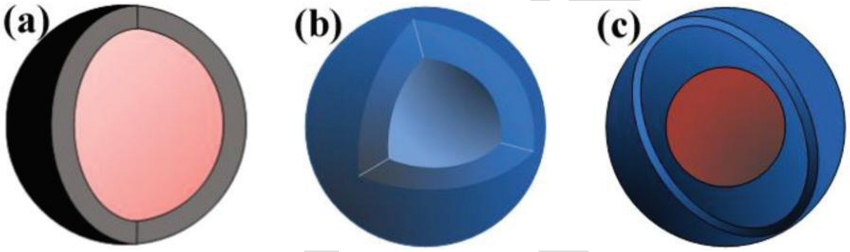
CORE-SHELL NANOSTRUCTURES

Core-shell nanostructures have unique structural features that consist of an inner core and an external shell of different chemical compositions. These structural features allow the possibility of combining distinctive properties of varied materials. Comparatively, core-shell nanostructures have exhibited improved physical and chemical properties relative to their single-component counterparts.

The core–shell structures are composite materials that contain an inner core coated with one or more layers (shells) of different materials. The materials of the core–shell structures can exist in different combinations, such as core and shell materials that are organic or inorganic.

A large number of core-shell nanostructures have been successfully fabricated using approaches ranging from laser ablation, high temperature evaporation to hydrothermal methods.

One method to accomplish these objectives is through the coating of nanoparticles with one or more layers of other materials that have interesting properties. The surrounding layer is called the shell, and the original nanoparticle is named as the core. It has been discovered that the constructed layer, or shell, can change the function and properties of the original core. In other words, the core can exhibit new chemical or catalytic reactivity with shell formation.

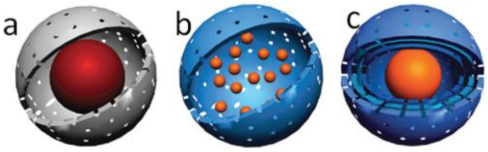


Multifunctional nanomaterials including (a) core–shell, (b) hollow core–shell, and (c) rattle core–shell nanostructures

This **core–shell** concept presents two materials with two functions in one structure, as shown in Fig. 1a. By increasing the number of shells and/or the number of materials, the functions of the newly formed structure can consequently be increased, which then offers unlimited possibilities and extensive applications in many fields.

The suitable design and geometry of the core–shell structure allows the formation of other novel architectures, such as **hollow core–shell structures** (as shown in Fig. 1b) through removal of the core and **rattle core–shell architecture** (Fig. 1c) – creation of one or more cavities between the outer shell and the inner solid core, producing a structure known as the rattle-type or yolk–shell.

In addition to the usual spherical morphology of core–shell nanoparticles, there are many other possible shapes of core/shell nanoarchitectures, depending on the various core morphologies that are available, including nanorods, nanotubes, nanowires, nanorings and nanostars.



Designs to produce the different nanorattle architectures of

(a) core–shell, (b) multiple-core and (c) multiple-shell.

Core–shell Nanomaterials fabrication

Several approaches have been established to construct a protective layer or shell around different types of nanoparticle cores. In all of these methods, the cores are formed first, and then shell formation takes place. The core can be composed of various metals, metal oxides, quantum dots, and polymer materials. The core surfaces provide nucleation sites (seeds) for the shell atoms to nucleate and grow through sol–gel or chemical precipitation approaches. In other word, the core acts as a substrate for shell deposition. Different types of shell materials require different coating or shell formation strategies.

Metal oxide shell. Metal oxide is a class of materials that possess a wide spectrum of properties. SiO_2, Al_2O_3, ZrO_2, TiO_2 are few metal oxide shells. SiO2 is the most common metal oxide used for shell formation. The well-established synthesis route used to prepare nanoparticle@SiO2 core–shell nanostructures is the **sol–gel approach**, which involves hydrolysis and condensation of the silica precursor (tetraethyl orthosilicate). The sol–gel approach has been implemented for the coating of noble metal nanocores with silica shells, such as Au@SiO2,99 Ag@SiO2.

Applications

The improved properties find broader range of applications including electronics, magnetism, optics, and catalysis

1. A magnetic core can be covered with a porous silica shell that can be loaded with drugs and provide biocompatibility, while the core can simultaneously be used for targeted delivery to a specific organ.
2. Quantum dots cores have been used for bio-imaging and diagnostic applications.
3. Iron, nickel, cobalt, manganese, chromium and gadolinium nanocores play important roles in magnetic resonance imaging as well as separation technology.
4. The **hollow structures** have high storage capacity.
5. The large fraction of empty space in the hollow structures has been used as a system for the loading and controlled release of special materials, such as drugs, genes, peptides, and biological molecules.
6. The hollow cavity within the sphere can be used as a nano reactor with catalytically active species loaded for catalytic reactions, or to tune the refractive index, decrease density, improve particle resistance toward continuous volume change.
7. The **rattle structure** possesses the combined properties of the solid cores, such as magnetic, metal, or quantum dot nanoparticles, together with those of the void in-between the core and the shell, which can be used for extra storage. Rattle core–shell multifunctional nanomaterials have shown promising applications as nanoreactors, drug/gene delivery agents and lithium-ion batteries.

SUPERCONDUCTIVITY IN C_{60}

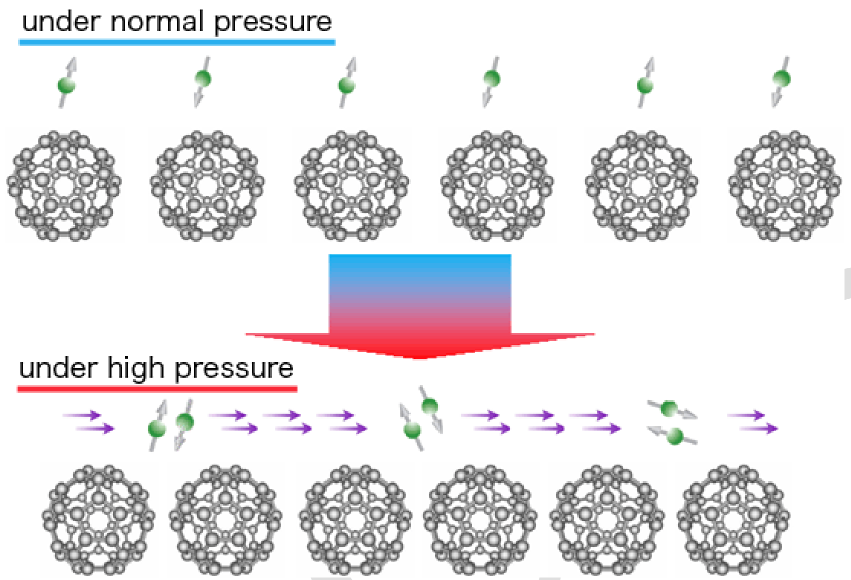
Among the different new materials with high temperature superconductivity, fullerene compounds play a significant part. Fullerenes are hollow-shaped carbon molecular aggregates the simplest and most symmetric of which is the C60 molecule composed of 20 hexagons and 12 pentagons.

Solid C60 forms, a **face – centred cubic (fcc) lattice** with a lattice constant of 14.17 A^0 at room temperature. The molecular structure of this compound gives it significant superconducting properties. The interaction responsible for the electron pairing is located on the buckyball and is caused by the vibration modes of the ball. The intercluster separation is less than interplanar separation in graphite. In addition, there are sizable empty holes, which constitute 26% of the total cell volume, within the fcc C60 lattice.

As fullerene molecule is highly electronegative, it readily forms compounds with electron donating atoms, the most common examples being alkali metals. This reaction leads to production of an interesting class of compounds known as **alkali-doped fullerides**, wherein alkali metal atoms fill in the space between Buckyballs and donate valence electron to the neighbouring C60 molecule. When alkali metals are intercalated into the fcc lattice, they occupy these interstitial sites and forms distinct crystalline structures.

If alkali atoms are potassium or rubidium, the compounds are superconductors, and they conduct electric current without any resistance at temperatures below 20-40 K e.g., K3C 60 , Rb3C60. Pressure applied to reduce the distance between fullerenes enables to increase the metal characteristics and change the *Tc*. When pressure is applied to the fullerene, the intermolecular distance is shortened, the electrons start moving, and the fullerene is transformed into a metal and exhibits superconductivity.

The same effect is observed at ambient pressure if the alkaline is replaced by another alkaline with a smaller ionic radius. For instance, Rb3C60 has a critical temperature Tc of 27 K (-246°C). If a strong pressure is applied to the compound Cs3C60, the Tc can increase to 40 K.



The superconductivity of this fullerene with a high Tc is related to its electrical properties, which enable its transformation from an insulator to a metal. Hole doped fullerenes exhibit higher critical temperature than electron doped fullerenes. A hole-doped C60 superconducting system C60/CHBr3, exhibites very high critical temperature Tc = 117K at ambient pressure. It is the greatest Tc for an organic superconductor with a buckyball doped with holes and intercalated with CHBr3.

ZEOLITE CAGES

Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminium, silicon, and oxygen in their regular framework and metals including Ti, Sn, Zn, and so on; cations and water are located in the pores. Swedish geologist Axel Cronstedt (discoverer of nickel)—coined the name "zeolite" literally means "boiling stone". The silicon and aluminium atoms are **tetrahedrally coordinated** with each other through shared oxygen atoms..zeolites are similar to clay minerals. More specifically, both are alumino-silicates. They differ, however, in their crystalline structure.

Many types of clay have a layered crystalline structure (similar to a deck of cards) and are subject to shrinking and swelling as water is absorbed and removed between the layers. In contrast, zeolites have a rigid, 3-dimensional crystalline structure (similar to a honeycomb) consisting of a network of interconnected tunnels and cages. Water moves freely in and out of these pores but the zeolites framework remains rigid.

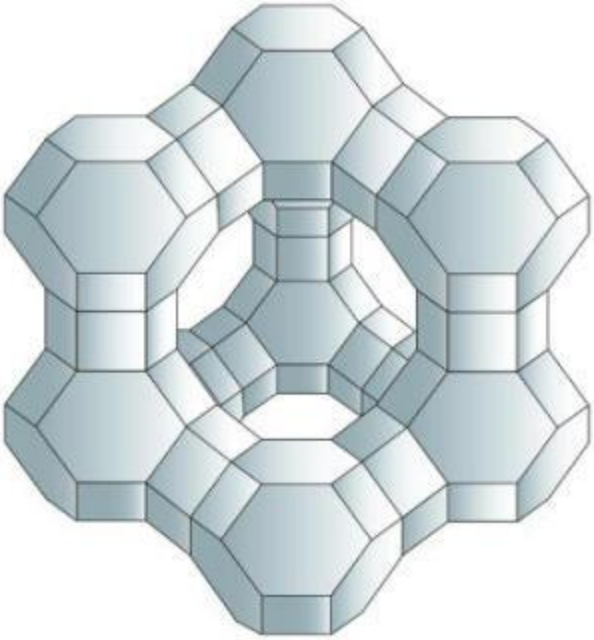
Zeolites are also known as **"molecular sieves**", the term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The **porous zeolite is host to water molecules and ions of potassium and calcium**, as well as a variety of other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the "sieving" property.

Synthesis: Hydrothermal Crystallization

Similar to the conventional micron-sized crystals, the nanosized zeolites are synthesized under hydrothermal conditions in closed vessels. In the synthesis of nanosized zeolites special attention is paid to the preparation of the **initial precursor** system in order to favour **the nucleation process**. The importance of the nucleation is due to the fact that the number of nuclei in the system **determines the ultimate crystal size**; thus an abundant nucleation leads to very small crystals while if the system yields a few viable nuclei the crystals formed are large.

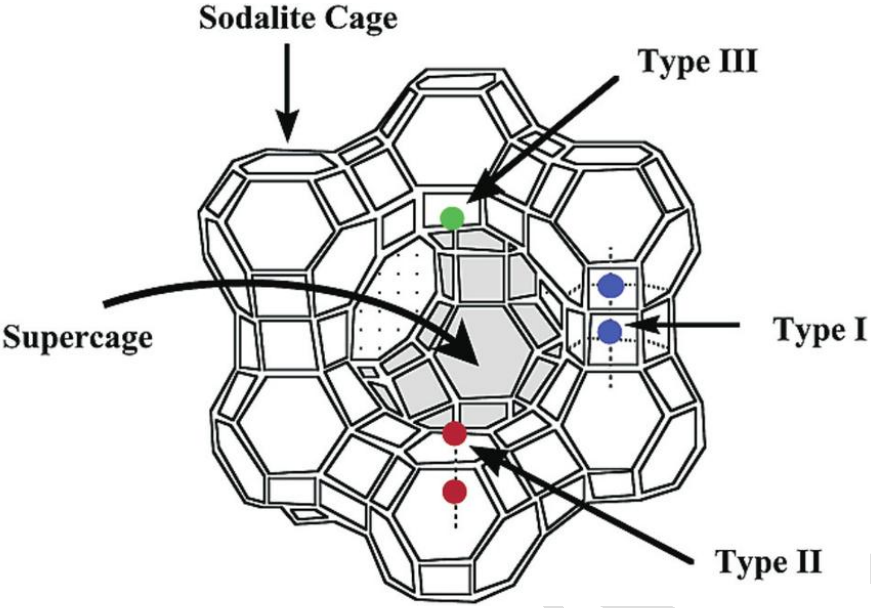
The stabilization of a precursor suspension containing only discrete zeolite precursor particles requires specific conditions in each stage of the preparation. Firstly, the employed **reactants and the temperature of mixing have to be properly selected**.

Furthermore, the **alkali metal content has to be as low as** possible in order to **avoid aggregation** between the particles.



The absence of alkali metal cations is compensated by abundant amounts of tetraalkylammonium **(TAA)** hydroxides that keep the basicity of the system high and act as structure directing agents **(SDAs).**

The homogenisation of the reactants is gentle to avoid the aggregation of precursor particles. Thus a water clear suspension containing particles that are uniform in size is stabilized. Consequently the nanosized particles obtained are uniform in size and the agglomeration of the particles is limited.



Upon heating, the amorphous precursor particles convert into nanosized zeolite crystals. The final appearance of the suspension depends on the size and the concentration of particles, and it varies between turbid and milky white.

Applications/ Uses

1. Zeolites are widely used as **ion-exchange beds** in domestic and commercial water purification, softening, and other applications.
2. In chemistry, zeolites are used to **separate molecules** (only molecules of certain sizes and shapes can pass through), and as traps for molecules so they can be analyzed.
3. Zeolites are also widely used as **catalysts and sorbents**. Their well-defined pore structure and adjustable acidity make them highly active in a large variety of reactions.
4. Zeolites have the potential of providing precise and **specific separation of gases**, including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include noble gases, N_2, O_2, freon and formaldehyde.

5. Zeolites assist silver in naturally emitting light, which could lead to **new lighting technologies**—supplementing or replacing fluorescent lights or LEDs. The fabrication of **optical devices** using zeolite nanoparticles has attracted considerable attention due to their rigid structure, high thermal stability and availability in different morphologies.
6. **On-board oxygen generating systems** (OBOGS) and Oxygen concentrators use zeolites in conjunction with pressure swing adsorption to remove nitrogen from compressed air in order to supply oxygen for aircrews at high altitudes, as well as home and portable oxygen supplies.
7. Emphasis has been placed on the development of zeolite films as low-dielectric constant layers for (i) **future generation computer chips**, (ii) environmentally benign **corrosion-resistant** coatings for aerospace alloys, and (iii) hydrophilic and bacteriological coatings for gravity-independent **water separation in space stations**.
8. The zeolite layers show great mechanical stability and hardness, which make them interesting for membranes for **seawater desalination** and **proton exchange membrane** fuel cells.
9. Another use of nanosized zeolites is based on the encapsulation of organic or inorganic guest molecules in the channels of zeolite nanocrystals for **light harvesting**, and **photovoltaic applications**.