UNIT-IV
NANOMATERIALS - AN INTRODUCTION AND SYNTHETIC METHODS.

Definition of non-dimensional materials

According to the recommendations of commission of European Union, nanomaterial means “A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.” A nanometer is one millionth of a millimetre approximately 100,000 times smaller than the diameter of a human hair. In other words, nanomaterials describe, in principle, materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometres ($10^{-9}$ meter) but is usually 1—100 nm (the usual definition of nanoscale).

Nanomaterials are cornerstones of nanoscience and nanotechnology. Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.

Historical Milestones of Nanomaterials

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. One of the first scientific reports was the synthesis of colloidal gold particles by Michael Faraday as early as 1857. In fact, the history of nanomaterials dates back to 1200 -1300 BC with the discovery of soluble gold in Egypt and China. The Lycurgus cup used during 290 - 325 AD in Alexandria or Rome is another example. First book on colloidal gold by F. Antonii was known since 1618. Book on drinkable gold that contains metallic gold in neutral media written by J. Von Löwenstern-Kunckel from Germany was known as early as 1676.

Nanostructured catalysts have also been investigated for over 70 years. By the early 1940’s, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements. Probably most celebrated historical comment on the advancement of nanomaterials was the public speculation by physicist Richard Feynman in 1959 about the effects of manipulating minuscule bits of condensed matter in his famous talk “There’s plenty of room at the bottom”.

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In the 1960s and 1970s metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert-gas evaporation technique was published by Granqvist and Buhrman. Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its color and its resistance to acids and bio corrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a super lattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the super lattice are present, as has been shown by the fabrication of synthetic samples.

In 1986, a very-high-resolution type of scanning probe microscopy invented, it more than 1000 times better than the optical diffraction limit. The scientists in IBM Almaden Research Center in San Jose, California, of the used a scanning tunneling microscope to position 35 individual xenon atoms on a substrate of chilled crystal of nickel to form the acronym "IBM". They also created chains of xenon atoms similar in form to molecules in 1989. In 1991, after the discovery and verification of the fullerenes, Sumio Iijima of NEC observed multiwall nanotubes formed in a carbon arc discharge, and two years later, he and Donald Bethune at IBM independently observed single-wall nanotubes – bucky tubes. These pure carbon polymers could now be understood in the context of fullerenes, changing the perception of them to molecules, with all that special designation implies. Nanotubes had been fullerenized. Zyvex was founded in 1997, as the first molecular nanotechnology company, with the vision of developing atomically precise manufacturing. President Clinton’s FY 2001 budget request includes a $227 million (84%) increase in the government’s investment in nanotechnology research and development. The Administration is making this major new initiative, called the National Nanotechnology Initiative (NNI), a top priority. This was followed by 21st Century Nanotechnology Research and Development Act, USA in the year 2003. Further, more an action plan on nanosciences and nanotechnologies was devised in Europe in the year 2005.

Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing manipulation of mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled material is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. The nanophase silicon, which differs from normal silicon in physical
and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. Similarly when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

In the year 2016 Nobel Prize for Chemistry has been awarded to a trio of scientists for their pioneering work in developing nano-molecular machines. These gadgets measure just a thousandth of a human hair in width, and they're poised to revolutionize everything from manufacturing and materials to medicine and the functioning of the human body. The winners of this year’s prize are Jean-Pierre Sauvage from the University of Strasbourg, France, Sir J. Fraser Stoddart from Northwestern University in Illinois, and Bernard L. Feringa from the University of Groningen in the Netherlands.

**Unique Properties of Nanomaterials**

Nanomaterials are of interest because of its scale and unique optical, magnetic, electrical, and other properties emerge. They are a link between bulk materials and atomic or molecular structures. While bulk materials have constant physical properties regardless of its size, among nanoparticles the size often dictates the physical and chemical properties. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials, those larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material.

The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours.

**Physical properties of nanoparticles**

Nanoparticles are unique because of their large surface area and this dominates the contributions made by the small bulk of the material. For example, zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions.
Other examples of the physical properties of nanoparticles:

- Coloured nanoparticles of yellow gold and gray silicon are red in color
- Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C)
- Absorption of solar radiation in photovoltaic cells is much higher in nanoparticles than it is in thin films of continuous sheets of bulk material (since the particles are smaller), they absorb greater amount of solar radiation

**Optical properties of nanoparticles are unique.** Nanoparticles also often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. One example of this is that gold nanoparticles appear deep red to black in solution.

**Formation of suspensions.** An important physical property of nanoparticles is their ability to form suspensions. This is possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences. In bulk materials this interactions usually result in a material either sinking or floating in a liquid.

**Magnetization and other properties of nanoparticles.** Other properties unique among nanoparticles are quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super-paramagnetism in magnetic materials. For example, ferroelectric materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage. Thus this property is not always desired in nanoparticles.

**Diffusion properties of nanoparticles.** At elevated temperatures especially, nanoparticles possess the property of diffusion. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. Although this does not affect the density of the final product but there is a chance of agglomeration.

**Hardness of nanoparticles.** Clay nanoparticles, when incorporated into polymer matrices, increase reinforcement, leading to stronger plastics. These nanoparticles are hard, and impart their properties to the polymer (plastic). Nanoparticles have also been attached to textile fibers in order to create smart and functional clothing.

**Semisolid or soft nanoparticles.** Semi-solid and soft nanoparticles have been manufactured. Notable of these is the liposome. Various types of liposome nanoparticles are
currently used clinically as delivery systems for anticancer drugs, antibiotics and antifungal drugs and vaccines.

**Dimensionality.** Nanoparticles are generally classified based on their dimensionality, morphology, composition, uniformity, and agglomeration. They can have 0, 1, 2 and 3 dimension and the details are discussed under the title classification of nanomaterials.

Nanomaterials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. The range of commercial nanomaterials available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nano-coatings and nano-composites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butylrubber/ nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings. Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles. Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

**Quantum dots**

Quantum dots (QDs) are tiny crystals that have special properties due to their size and chemical makeup. Quantum dots are only about $1/10,000^{th}$ the width of a human hair, and contain several hundred to several thousand atoms, depicted as different coloured spheres in the image below. The structure of a quantum dot plays an important role in its properties (Figure 1).
Figure 1 The physical structure of quantum dots

QDs can be optically excited. However, a lot of physics behind those properties still remain unknown. On absorbing photons, electrons in QDs gain energy leading to the creation of excitons. An exciton is a bound state of an electron and a quasi particle called a hole. After relaxation from the excitonic excited state to its lower energy state, the electron and hole recombine (exciton recombination), emitting a photon. The overall process of optical excitation, relaxation of excited state, recombination of electron and hole and fluorescent emission is called photoluminescence (PL). The number of photons emitted can be measured as a function of energy, which gives the PL spectrum.

Fluorescent resonant energy transfer (FRET) is a very common separation dependent phenomenon among many dyes. The unique properties of QDs make them ideal FRET pair. By measuring the separation dependent FRET level between QDs, one can discover the physics behind this phenomenon: whether the interaction is dipole-dipole or dipole-quadrupole dependence, which is an interest physics topic to be explored. If the separation dependence interaction is well controlled, it is highly possible to make QDs as a “calibrated” nano-scale ruler for potential biology application.

The energy gap of excitons in QDs is strongly size dependent. This size dependent phenomenon is due to the effect of confinement: The smaller QDs have stronger confinement making the energy gap larger. Similarly, a larger size gives a smaller energy gap. Hence, QDs with different emission colours can be made from the same material by changing their size. Colloidal QDs, which are synthesized by relatively inexpensive wet chemistry methods, make it possible to have the desired particle size which makes it easy to find QDs with the
energy spectrum we need and high quantum yield (number of photons absorbed over the number of photons emitted), even at room temperature. Currently, CdSe or CdTe QDs with a ZnS shell are commonly used and studied. The Core/Shell structure diminishes chemical damage to the fluorescence core. ZnS is optically transparent to the emission range, therefore there are no photon losses associated to the shell with visible light emission.

Different from many organic dyes, the emission light spectra of QDs are narrower and more symmetric than conventional organic dyes, making the sensitivity of detection higher than for organic dyes. Because of this property, QDs are attractive fluorophores for biological imaging (biological tagging), useful materials in the electronics, medical and other industries. In the display and lighting industries, these properties are harnessed to generate vivid colours with low power consumption for mobile phones, televisions, and general lighting so the consumer benefits from longer battery life, beautiful pictures and video, and a lower electricity bill.

**Classification of Nanomaterials**

Nanomaterials can be categorized based on dimensions, origin and their structural configuration.

**Classification based on the dimensions**

Siegel classified nanomaterials based on the dimensions as zero dimensional, one dimensional, two dimensional and three dimensional nanostructures (Figure 2). Which are characterized by an ultra fine grain size (< 50 nm) or by a dimensionality limited to 50 nm.

![Classification of Nanomaterials](image)

**Figure 2** Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

**a) Zero dimensional (0-D) nanomaterials**: These nanomaterials have nano-dimensions in all the three directions. Metallic nanoparticles including gold and silver nanoparticles and semiconductor such as quantum dots are the perfect example of this kind of nanoparticles. Most of these nanoparticles are spherical in size and the diameter of these particles will be
in the 1-50 nm range. Cubes and polygons shapes are also found for this kind of nanomaterials. Zero dimensional Nanoparticles can be amorphous or crystalline, single crystalline or polycrystalline, composed of single or multi-chemical elements, exhibit various shapes and forms, exist individually or incorporated in a matrix, be metallic, ceramic, or polymeric.

b) One dimensional (1-D): In these nanostructures, one dimension of the nanostructure will be outside the nanometer range. These include nanowires, nanorods, and nanotubes. These materials are long (several micrometer in length), but with diameter of only a few nanometer. Nanowire and nanotubes of metals, oxides and other materials are few examples of this kind of materials. One dimensional nanoparticles can be amorphous or crystalline, single crystalline or polycrystalline, chemically pure or impure, standalone materials or embedded in within another medium, metallic, ceramic, or polymeric.

c) Two dimensional (2-D): In this type of nanomaterials, two dimensions are outside the nanometer range. These include different kind of nano films such as coatings and thin-film-multilayers, nano sheets or nano-walls. The area of the nano films can be large (several square micrometer), but the thickness is always in nano scale range. Two dimensional nanoparticles can be amorphous or crystalline, made up of various chemical compositions, used as a single layer or as multilayer structures, deposited on a substrate, integrated in a surrounding matrix material, metallic, ceramic, or polymeric.

d) Three Dimensional (3-D): All dimensions of a three dimensional material are outside the nano meter range. These include bulk materials composed of the individual blocks which are in the nanometer scale (1-100 nm). Three dimensional nanoparticles can contain dispersions of nanoparticle, bundles of nanowires, and nanotubes as well as multiananolayers.

Classification based on their origin
i) Natural nanomaterials: Nanomaterials which are belonging to resource of nature are defined as natural nanometer. Virus, protein molecules including antibody originated from nature are some natural nano structured materials. In addition following are few examples, mineral such as clays, natural colloids, such as milk and blood (liquid colloids), fog (aerosol type), gelatine (gel type), mineralised natural materials, such as shells, corals and bones, insect wings and opals, spider silk, lotus leaf, Gecko feet, volcanic ash, ocean spray, etc.
ii) Artificial nanomaterial: Artificial nanoparticles are those which are prepared deliberately through a well-defined mechanical and fabrication process. The examples of such materials are carbon nanotubes, semiconductor nanoparticles like quantum dots etc.

**Classification based on structural configuration**

i) Carbon based nano-materials: The nature of this kind of nanomaterials is hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal configured carbon nanomaterials are defined as fullerenes, while cylindrical ones are described as nanotubes.

ii) Metal Based Materials: The main component of these particles is metal. These nanomaterials include nanogold, nanosilver and metal oxides, such as titanium dioxide and closely packed semiconductor like quantum dots.

iii) Dendrimers: Dendrimers are highly branched macromolecules with the dimensions nanometer-scale. The surface of a dendrimer posses numerous chain which can be modified to perform specific chemical functions. PAMAM dendrimer is the best illustration of this kind of materials.

iv) Composites: Nanocomposite can be described as a multiphase solid material where at least one of the phases has one, two or three dimensions in nanoscale. The most common examples of these materials are colloids, gels and copolymers.

**Examples of Nanomaterials**

Nanomaterials (gold, carbon, metals, meta oxides and alloys) with variety of morphologies (shapes) are depicted in Figure 3.
Nanomaterial - Synthesis and Processing

There are many different ways of creating nanostructures. Macromolecules or nanoparticles or bucky balls or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (sometimes also called bio-mimetic processes). Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application.

Hydrothermal synthesis

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.

Uses: A large numbers of compounds belonging to practically all classes have been synthesized under hydrothermal conditions, elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals that have been efficiently grown are emeralds, rubies, quartz, alexandrite and others. The method has proved to be extremely efficient both in the search for new compounds with
specific physical properties and in the systematic physicochemical investigation of intricate multi-component systems at elevated temperatures and pressures.

**Solvothermal synthesis**

Solvothermal synthesis is a method of producing chemical compounds. It is very similar to the hydrothermal route (where the synthesis is conducted in a stainless steel autoclave), the only difference being that the precursor solution is usually not aqueous (however, this is not always the case in all literature uses of the expression (Figure 3). Using the solvothermal route gains one the benefits of both the sol-gel and hydrothermal routes. Thus solvothermal synthesis allows for the precise control over the size, shape distribution, and crystallinity of metaloxide nanoparticles or nanostructures. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type, and precursor type. Solvothermal synthesis has been used in laboratory to make nano structured titanium dioxide, graphene, carbon and other materials.

![Figure 3 Schematic diagram of solvo-thermal synthesis setup. 1. stainless steel autoclave, 2. precursor solution, 3. teflon liner, 4. stainless steel lid.](image)

**Microwave irradiation**

Various TiO$_2$ nanomaterials materials have been synthesised using microwave radiation. Microwave techniques eliminate the use of high temperature calcination for extended periods of time and allow for fast, reproducible synthesis of crystalline TiO$_2$ nanomaterials (Figure 4). High quality rutile rods were developed combining hydrothermal and microwave synthesis, while TiO$_2$ hollow, open ended nanotubes were synthesised through reacting anatase and rutile crystals in NaOH solution.
Figure 4 Drawing of two extremes of microwave-assisted reactions. The vial on the left contains a solution with a large tan (such as water). Upon microwave irradiation, the microwaves minimally penetrate the reaction volume due to efficient absorption by the solvent.

**Sol-gel process**

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands (Figure 5). The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as Si(OEt)$_4$ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR)$_z$ can be described as follows:

\[
\begin{align*}
\text{MOR} + \text{H}_2\text{O} & \rightarrow \text{MOH} + \text{ROH} \quad \text{(hydrolysis)} \\
\text{MOH} + \text{ROM} & \rightarrow \text{M-O-M} + \text{ROH} \quad \text{(condensation)}
\end{align*}
\]

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.
Figure 5 Schematic representation of sol-gel process of synthesis of nanomaterial.

a. Formation of different stable solutions of the alkoxide or solvated metal precursor.
b. Gelation resulting from the formation of an oxide- or alcohol-bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscosity of the solution.
c. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
d. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a xerogel. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an aerogel.
e. Dehydration, during which surface-bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 8000 °C.
f. Densification and decomposition of the gels at high temperatures (T > 8000 °C). The pores of the gel network are collapsed, and remaining organic species are volatilized.
Interest in this synthetic method arises due to the possibility of synthesizing non-metallic inorganic materials like glasses, glass ceramics, or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics. The major difficulties to overcome in developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process. Also, production rates of nano-powders are very low by this process. The main advantage is one can get monosized nano-particles by any bottom-up approach.

**Chemical Vapour Condensation (CVC)**

As shown schematically in figure 6, the evaporative source used in Gas Condensation Processing (GPC) is replaced by a hot wall reactor in the Chemical Vapour Condensation or the CVC process. Depending on the processing parameters, nucleation of nanoparticles is observed during chemical vapour deposition (CVC) of thin films and poses a major problem in obtaining good film qualities. The original idea of the novel CVC process which is schematically shown below where, it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained.

![Figure 6: Schematic representation of chemical vapour deposition](image.png)

Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of...
nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller. Additionally, more complex oxides such as BaTiO₃ or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature. The extension to production of nanoparticles requires the determination of a modified parameter field in order to promote particle formation instead of film formation. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of

1. mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and
2. coated nanoparticles, i.e., n-ZrO₂ coated with n-Al₂O₃ or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor. Figure 6 shows schematic representation of CVC reactor.

Because, CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

**Gas Condensation Processing (GPC)**

In this technique, a metallic or inorganic material, e.g. a suboxide, is vaporised using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr). Cluster 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 (Figure 7). The cluster or particle size depends critically on the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar or Kr, and on the evaporation rate/vapour pressure of the evaporating material. With increasing gas pressure, vapour pressure and mass of the inert gas used the average particle size of the nanoparticles increases. Log normal size distributions have been found experimentally and have been explained theoretically by the growth mechanisms of the particles. Even in more complex processes such as the low pressure combustion flame synthesis where a number of chemical reactions are involved the size distributions are determined to be lognormal.
Figure 7 Schematic representation of typical set-up for gas phase condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.

Originally, a rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no agglomeration. Subsequently, the nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate. In addition to this cold finger device several techniques known from aerosol science have now been implemented for the use in gas condensation systems such as corona discharge, etc. These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders. However, these methods can only be used in a system designed for gas flow, i.e. a dynamic vacuum is generated by means of both continuous pumping and gas inlet via mass flow controller. A major advantage over convectional gas flow is the improved control of the particle sizes. It has been found that the particle size distributions in gas flow systems, which are also lognormal, are shifted towards smaller average values with an appreciable reduction of the standard deviation of the distribution. Depending on the flow rate of the He gas, particle sizes are reduced by 80% and standard deviations by 18%.
The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo). If metals with high melting points or metals which react with the crucibles, are to be prepared, sputtering, i.e. for W and Zr, or laser or electron beam evaporation has to be used. Synthesis of alloys or intermetallic compounds by thermal evaporation can only be done in the exceptional cases that the vapour pressures of the elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed. Composite materials such as Cu/Bi or W/Ga have been synthesised by simultaneous evaporation from two separate crucibles onto a rotating collection device. It has been found that excellent intermixing on the scale of the particle size can be obtained. However, control of the composition of the elements has been difficult and reproducibility is poor. Nanocrystalline oxide powders are formed by controlled post oxidation of primary nanoparticles of a pure metal (e.g. Ti to TiO$_2$) or a suboxide (e.g. ZrO to ZrO$_2$). Although the gas condensation method including the variations have been widely employed to prepared a variety of metallic and ceramic materials, quantities have so far been limited to a laboratory scale. The quantities of metals are below 1 g/day, while quantities of oxides can be as high as 20 g/day for simple oxides such as CeO$_2$ or ZrO$_2$. These quantities are sufficient for materials testing but not for industrial production. However, it should be mentioned that the scale-up of the gas condensation method for industrial production of nanocrystalline oxides by a company called nanophase technologies has been successful.

**Reverse Micelle Synthesis**

The reverse micelles can be used as templates for the synthesis of inorganic nanomaterials by precipitation technique. This technique enables nano-precipitation of the materials such as metal, semiconductor, metal oxide and insoluble salt nanoparticles. When the precipitation is carried out in an aqueous medium, the rate of precipitation is too rapid to allow fine control of the particle size. Further, the distribution of particle size is quite wide. The particles generated by the conventional precipitation techniques are generally isotropic in properties as there is no control of particle shape. Therefore, there is a need for a technique which will enable precise control of particle size, its distribution and shape. Reverse miceller colloidal precipitation fulfils this need.

Amphiphilic surfactant molecules when present in an organic solvent form reverse micelles hence the surfactant concentration exceeds a certain critical value known as the critical micelle concentration (CMC). Reverse micelles are self assembled nanostructures with hydrophilic heads of surfactant molecules oriented inwards and hydrophobic tails
outwards in the organic solvent matrix (Figure 8). These micelles can be spherical, cylindrical or lamellar depending upon the type and amount of the surfactant. These reverse micelles permit formation of ‘water-in-oil’ emulsion wherein small water droplets are embedded inside the reverse micelle. The size of the droplet can be controlled by the amount of water present (Droplet size control).

These water droplets undergo Brownian motion which results into their collision accompanied by the mixing and exchange of water among the droplets. The droplets of original size are reformed. (Water exchange process). When two different colloidal solutions, each with an individual reactant in their reverse micelles, are mixed, the precipitation reaction occurs in the micelle. The nanoparticles thus get formed. The size of the particle is confined by the size of the micelle which is of the order of few nanometers.

![Figure 8](image)

*Figure 8* A drawing of (a) a reverse micelle and (b) a more realistic model of reverse micelle.

Thus, the reverse micelle formation, droplet size control and water exchange are the three key processes in nanoparticle formation by the reverse miceller technique. This technique can be employed for the following type of reactions:
1. Precipitation by double decomposition: Synthesis of silver halide nano particles from silver nitrate and sodium halide reverse micelles
2. Reduction: Metal nanoparticles like iron, silver, copper, zinc can be made starting with their divalent surfactants \([\text{M(AOT)}_2]\) and a reductant like hydrazine.
3. Hydrolysis followed by condensation: Metal oxides like vanadium pentoxide can be synthesized starting with alkoxides dissolved in organic phase and hydrolysis taking place in aqueous micelle.

**Polymer Mediated Synthesis**

Polymer mediated nanoparticles represent one of most the important nanomaterials in current nanotechnology. Polymer self-assembly of nanoparticles yields stabilized metal and semiconductor nanocomposites as well as provides access to structured nanoscale materials.
The properties of these materials can be tuned by varying the size and shape of the metal cluster as well as by altering the composition of the monolayer that covers the particles. Furthermore, the functionality and structure of the polymer can be modified, which lends an additional element of control to the entire assembly process. This “bottom-up” approach provides a methodology that is complementary to “top-down” lithographic methods, providing access to structures smaller and with greater 3-dimensional (3-D) control than is possible through sophisticated lithographic techniques such as electron-beam lithography.

Monodisperse polymer-mediated platinum (Pt) nanoparticles could be synthesized by photoreduction in the presence of polyethylenimine (PEI), a hyperbranched polymer. The photoreduction of Pt complexes is an attractive method because,

- large number of platinum nuclei are homogeneously and instantaneously produced, so the reduction reaction arises uniformly performed in the solution, thus the size of final nanoparticles is very uniform.
- Controlled reduction of metal ions can be carried out without using excess reducing agent, and no adsorbing contamination on the product occurs in the preparation process.
- The photochemical method can be cost-effective and convenient.

It involves reduction of platinum ions into nanoparticles in protective media to prevent the metal nanoparticles from aggregating. Water soluble polymers such as poly(vinyl alcohol) (PVA) and poly(N-vinyl-2-pyrrolidone) (PVP) have been widely used as protective media for colloidal dispersions. Stabilizers play an important role in controlling the formation of nanoparticles as well as their dispersion stability. On the other hand the presence of too strong capping agents on the nanoparticles surfaces can produce a detrimental impact on the particle’s catalytic properties. For example, PVP capped Pt nanoparticles do not show any electrocatalytic activity toward oxygen reduction or methanol oxidation because of too strong affinity of PVP to Pt.

Polyethylenimine (PEI) is a hydrophilic polymer with primary, secondary and tertiary amino groups and overall positive charge in neutral aqueous solution. Because of abundant positive charge, it is a widely used stabilizer to coat nanoparticles to achieve surface functionalization. The positively charged amine groups stabilized the nanoparticles in solution and can also be used to form self-assembled mono layers on common electrodes.
S. Laschi and coworkers developed glassy carbon electrodes modified with a dispersion of multi-wall carbon nano tubes in PEI. It exhibits excellent electro catalytic activity towards the analyte. PEI contains one of the highest densities of amine groups among all polymers, this is the reason for the highly efficient dispersion of nanoparticles in PEI as well as for the high electro activity of the PEI/CNT immobilized on the electrode surface. Polyelectrolyte-capped Pt nanoparticles can be synthesized in aqueous solution, and their assembly on electrodes can allow control of size distribution, shape, and surface density. Thus, assembling charged Pt nanoparticles on an electrode may increase efficiency and utilization.

Pan and co-workers demonstrated that self-assembled Pt nanoparticles electrode and membrane-electrode assembly of polymer electrolyte fuel cells can be prepared by using charged Pt nanoparticles with an ultra low Pt loading. Zaki and coworkers showed that nanostructured Pt electrodes were assembled from solution-prepared polyacrylate-capped Pt nanoparticles by virtue of electrostatic and hydrophobic interactions with a cationic polyelectrolyte poly(diallyldimethylammonium) (PDDA). Electrochemical characterization of polyelectrolyte-stabilized Pt nanoparticles showed that these surfaces are catalytically active for many reactions such as oxygen reduction, methanol oxidation, and hydrogen oxidation.

**Protein microtubule mediated synthesis of nanomaterials**

The synthesis of increasingly miniaturized structures using alternative techniques is strongly motivated by future applications in areas such as nanoelectronics. Microtubules, highly oriented protein assemblies with defined surface functionalities, can serve as bioorganic templates for the bottom-up synthesis of metal nanostructures (Figure 9).

![Figure 9](image)

*Figure 9* Protein microtubule mediated synthesis of silver nanostructures
Depending on the kind of reducing agent and the pH value used, small silver particles could be nucleated and densely bound to the tubular structure of the bio-template. These particles could be enlarged to grain sizes of 10-30 nm by applying hydroquinone and silver ions. g/protein structures with different morphologies are produced, from microtubules densely covered with small Ag nanoparticles to continuous Ag nanowires. Even completely continuous nanowires could be achieved by using a similar method.

The first step in the synthesis involves microtubule protein purification from porcine brain by an in vitro assembly-disassembly process. The final protein concentration was about 1 mg mL\(^{-1}\). The microtubules were assembled in vitro in a buffer solution of 20 mM PIPES (pH 6.8), 80 mM NaNO\(_3\), 0.5 mM Mg(NO\(_3\))\(_2\), and 1 mM EGTA by adding 0.25 M GTP and, after 20 min, 10 mM taxol (from Taxus brevifolia) and warming the sample to 37 °C. The microtubule formation was followed by turbidity measurements at λ = 360 nm and controlled by electron microscopy. The assembled microtubules were chemically fixed in 0.1% glutaric dialdehyde. The samples were finally dialyzed against PIPES buffer (diluted 10-fold with H\(_2\)O) to eliminate excess glutaric dialdehyde.

Synthesis of Silver Nanoparticles with NaBH\(_4\) involves addition of a 600- µL portion of an aqueous AgNO\(_3\) solution (1 mM) to 60 µL of microtubule suspension and reduced by rapidly adding 180 µL of an aqueous NaBH\(_4\) solution (2.5 mM) at 0 °C. The resulting microtubule-bound silver nanoparticles was further developed with 240 µL of hydroquinone solution (0.05 M in water) and 360 µL of AgNO\(_3\) solution (5 mM in water).

Similarly, synthesis of silver nanowires involves addition of a 60-µL sample of assembled microtubules (fixed with glutaric dialdehyde, see above) to 630 µL with PIPES buffer. The protein assemblies were then incubated with 30 µL of an aqueous AgNO\(_3\) solution (0.1 M) for 2 h at room temperature in the dark. In a second step, 240 µL of a reduction bath containing hydroquinone (0.05 M in water) was added. The reaction was typically stopped by adding an excess of Na\(_2\)S\(_2\)O\(_3\) (120 µL of a 0.25 M solution in water) after 1, 2.5, or 7 min or by adsorption of the sample on a TEM grid. When the diluted microtubules were incubated with only 10 µL of the aqueous AgNO\(_3\) solution, large silver aggregates were attached to the microtubules, and no continuous silver coating was observed.

One problem, however, concerned the stability of these structures in solution, as they tend to agglomerate into extended networks. There remains a great potential to apply these metallization techniques to other protein assemblies to produce silver/protein composites with interesting material properties. Highly ordered protein assemblies of tubular structure and high geometric aspect ratio are used as bioorganic templates.
Synthesis of nanoparticles using microorganism

The study of biosynthesis of nanomaterials offers a valuable contribution into materials chemistry. The ability of some microorganisms such as bacteria and fungi to control the synthesis of metallic nanoparticles should be employed in the search for new materials. Biosynthetic methods have been investigated as an alternative to chemical and physical ones. These methods can be divided into two categories depending on the place where the nanoparticles or nanostructures are created as many microorganisms can provide inorganic materials either intra- or extra-cellularly. For example, bacteria *Pseudomonas strutzeri* isolated from silver mine materials is able to reduce Ag+ ions and accumulates silver nanoparticles, the size of such nanoparticles being in the range 16–40 nm, with the average diameter of 27 nm. The examples also include magnetotactic bacteria which produce magnetite (Fe₃O₄) or greigite (Fe₃S₄) and diatoms which produce siliceous material. The intracellular methods need a special ion transportation system into the microbial cell. Formation of magnetite particles proceeds through a sequence of events: reduction of Fe(III) to Fe(II), precipitation of amorphous oxide and subsequent transformation to magnetite.

Gold nanoparticles have also been synthesized in human cells, both in cancer and non-cancer ones; the scanning microscopic images confirmed that their morphologies differed significantly. This behaviour can have an implication to cancer diagnostics. In contrast, extracellular synthesis of nanoparticles occurs in alkalothermophilic actinomycete, *Thermomonospora sp.*, which reduces gold ions. The metabolic activity of microorganisms can lead to precipitation of nanoparticles in external environment of a cell, the fungi being extremely good candidates for such processes. The extracellular synthesis of silver and gold nanoparticles by the fungus *Colletotrichum* sp. or *Aspergillus fumigatus* has been reported. A novel biological method for synthesis of silver nanoparticles using *Vericillum* was proposed by Mukherjee et. al; a two-step mechanism was suggested. The first step involves trapping of Ag+ ions at the surface of the fungal cells. In the second step, enzymes present in the cell reduce silver ions. The extracellular production of metal nanoparticles by several strains of the fungus *Fusarium oxysporum* has been described by Duran et al. The presence of hydrogenase in the *F. oxysporium* broth was demonstrated. This extracellular enzyme shows excellent redox properties and it can act as an electron shuttle in metal reduction.

It was evident that electron shuttles or other reducing agents (e.g., hydroquinones) released by microorganisms are capable of reducing ions to nanoparticles. The neem (*Azadirachta indica*) leaf broth and aqueous solution of silver nitrate or chloroauric acid were
used for the extracellular synthesis of pure metallic silver and gold particles. The time required for Ag+ and Au\(^{3+}\) ions to reduce was 4 h and 2 h, respectively, being extremely short compared to both bacteria and fungi (24 h and 120 h). Surface active constituents of the leaf broth stabilize nanoparticle suspensions – an aqueous suspension showed stability even after 4 weeks. Our aim in the present contribution was to synthesize and characterize silver nanoparticles obtained by use of *Penicillium* fungi isolated from the soil.

**Sonochemical synthesis**

There are two types of effects mediated by ultrasound: chemical and physical. When the quantity of bubbles is low - using standard laboratory equipment - it is mainly physical rate acceleration that plays a role. For example, a specific effect is the asymmetric collapse near a solid surface, which forms microjets (Figure 10). This effect is the reason why ultrasound is very effective in cleaning, and is also responsible for rate acceleration in multiphasic reactions, since surface cleaning and erosion lead to improved mass transport.

![Microjet formed in a sonochemical method](Microjet.png)

**Figure 10** Microjets formed in a sonochemical method

For example, when ultrasound is applied to an Ullmann reaction that normally requires a 10-fold excess of copper and 48 h of reaction time, this can be reduced to a 4-fold excess of copper and a reaction time of 10 h. The particle size of the copper shrinks from 87 to 25 μm, but the increase in the surface area cannot fully explain the increase in reactivity. It was suggested that sonication also assists in the breakdown of intermediates and desorption of the products from the surface (Scheme 1).

![Ullmann reaction under sonochemical condition](UllmannReaction.png)

**Scheme 1** Ullmann reaction under sonochemical condition

Typically, ionic reactions are accelerated by physical effects - better mass transport - which is also called "False Sonochemistry". If the extreme conditions within the bubble lead
to totally new reaction pathways, for example via radicals generated in the vapor phase that would only have a transient existence in the bulk liquid, we speak about "sonochemical switching". Such a switch has been observed for example in the following Kornblum-Russel reaction (Scheme 2) where sonication favors an SET pathway:

\[
\begin{align*}
\text{Br} & \quad \text{NO}_2 \\
\rightarrow & \quad \text{LiCl} \\
\rightarrow & \quad \text{NO}_2
\end{align*}
\]

Scheme 2 Kornblum-Russel reaction under sonochemical condition

Applications for sonochemistry can be found in many areas, but sonochemical processes are most widely developed for heterogeneous reactions. Currently, sonochemistry is a multidisciplinary field in which chemists, physicists, chemical engineers and mathematicians must cooperate to develop a better understanding of the processes that take place within the collapsing bubbles to develop totally new applications. However, the potential for making improvements in many types of reaction suggests that every chemical laboratory should be equipped with at least one cleaning bath for simple trials.

**Hydrodynamic Cavitation**

Cavitation is the process in which formation and collapse of micro bubbles. This process can be carried out by using venturi meter, orifice meter or valve. According to the Bernoulli’s principle, if liquid is flowing through the orifice plate than velocity is increased. If we are providing throttling valve before the caviting device than the throttling is possible. Due to throttling, the pressure at vena contract point becomes decreases and its decreases below the entering pressure i.e. vapor pressure. Due to the above condition millions of cavities are generated. After the vena contract the pressure recovery of liquid is started at the downstream side. In the downstream side process of cavity collapse occurs. In this process some amount of energy is lost so that permanent pressure drop occurs. The intensity of cavity collapse depends upon the amount of pressure drop. The value of pressure drop depends on the size of the caviting device as well as flow rate of the liquid. If these two parameters are maintained than we are getting the desired result. During the collapse of bubble the temperature is increases very rapidly.
Inorganic Nanomaterials

Inorganic nanoparticles are extremely important in modern technologies. They can be synthesized easily and cheaply and can also be more readily integrated into devices. They find application in variety of fields such as magnetic storage media, as metal oxide nanoparticles to improve performance of oxide thin films as conducting media in commercial gas and vapor sensors, as semiconductors for light-emitting devices and other areas related to the energy sector, such as solar energy and energy storage devices (fuel cells, rechargeable batteries, etc.), expanding the role of nanosized particles in the field of catalysis, art conservation, and biomedicine.

Titanium Dioxide (TiO$_2$)

Titanium dioxide (TiO$_2$) has attracted great attention in the field of environmental purification and can be used as a kind of solar energy cell. When irradiated with UV light, TiO$_2$ nano sized powder shows strong oxidizability and reducibility. It is well known fact that TiO$_2$ has three crystalline forms of anatase, rutile and brookite. Among these three crystalline forms, rutile phase is the most thermodynamically stable, whereas brookite and anatase are meta stable and transformed to rutile on heating. Different synthetic methods such as sol-gel micro emulsion or reverse micelles, and hydrothermal synthesis have been used to derive the nanoparticles of titanium dioxide. Compared to other methods, sol-gel process is regarded as a good method to synthesis ultra-fine metallic oxide and has been widely employed for preparing titanium dioxide nanoparticles.

Crystal Structure of TiO$_2$ Nanoparticles

The unit cell structures of the rutile and anatase TiO$_2$ (Figure 11). These two structures can be described in terms of chains of TiO$_6$ octahedra, where each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2-}$ ions. The two crystal structures differ in the distortion of each octahedron and by the assembly pattern of the octahedra chains. In rutile, the octahedron shows a slight orthorhombic distortion; in anatase, the octahedron is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are larger, whereas the Ti-O distances are shorter than those in rutile. In the rutile structure, each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while, in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These
differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO$_2$.

Figure 11 Crystal Structure Of TiO$_2$ Nanoparticles

**Synthesis of TiO$_2$ by Sol-gel method**

The sol-gel method is a versatile process used in making various ceramic materials. In a typical sol-gel process, a colloidal suspension, or a sol, is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. A wet gel will form when the sol is cast into a mold, and the wet gel is converted into a dense ceramic with further drying and heat treatment. A highly porous and extremely low-density material called an aerogel is obtained if the solvent in a wet gel is removed under a supercritical condition. Ceramic fibers can be drawn from the sol when the viscosity of a sol is adjusted into a proper viscosity range. Ultrafine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques. Under proper conditions, nanomaterials can be obtained.

A 20 ml of solution Titanium tetra iso propoxide was added drop by drop into the 22 ml of solution containing 10 ml of iso-propanol and 12 ml deionised water under constant stirring at 80º C into the round bottom beaker. After 1 h, concentrated HNO$_3$ (8 ml) mixed with deionised water was added into the TTIP solution and keep it under constant stirring at 60 ºC for 6 h highly viscous sol gel was obtained. The prepared sol-gel was heated at 300 ºC for 2 h in the open atmosphere. After annealing, the TiO$_2$ nano crystalline 2 g powder was obtained. Further preparation of TiO$_2$ film, the prepared powder was added in the ratio of
1:10 of the solution of iso-propanol. The TiO₂ nanoparticles deposited on titanium substrate (0.5 cm²) using the dip coating method.

Applications of TiO₂

In is used in the paper industry for improving the opacity of paper as a catalyst in synthesis of biscoumarins (Scheme 3).

![Scheme 3](image)

Scheme 3 Nano TiO₂ catalysed synthesis of biscoumarins

Titanium oxide exhibits good photo catalytic properties, hence finds application in antiseptic and antibacterial compositions, degrading organic contaminants and germs, UV-resistant material, manufacture of printing ink, self-cleaning ceramics and glass, coating, etc., making of cosmetic products such as sunscreen creams, whitening creams, morning and night creams, skin milks, etc.

Zinc oxide (ZnO)

Nanostructured ZnO materials have received broad attention due to their distinguished performance in electronics, optics and photonics. From the 1960s, synthesis of ZnO thin films has been an active field because of their applications as sensors, transducers and catalysts. ZnO is a key technological material. The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in disordered nanoparticles and thin films. ZnO is transparent to visible light and can be made highly conductive by doping. ZnO is a versatile functional material that has a diverse group of growth morphologies, such as nanocombs, nanorings, nanohelices/nanosprings, nanobelts, nanowires and nanocages.
Crystal and surface structure of ZnO

Wurtzite zinc oxide has a hexagonal structure (space group C\textit{6}\textit{mc}) with lattice parameters $a = 0.3296$ and $c = 0.52065$ nm. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O\textsuperscript{2−} and Zn\textsuperscript{2+} ions, stacked alternately along the $c$-axis (Figure 12).

![Figure 12](image)

**Figure 12** The wurtzite structure model of ZnO. The tetrahedral coordination of Zn–O

The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently piezoelectricity and pyroelectricity. Another important characteristic of ZnO is polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(000−1) surfaces, resulting in a normal dipole moment and spontaneous polarization along the $c$-axis as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO \textsuperscript{−}(0001) are exceptions they are atomically flat, stable and without reconstruction. Efforts to understand the superior stability of the ZnO \textsuperscript{±}(0001) polar surfaces are at the forefront of research in today’s surface physics. The other two most commonly observed facets for ZnO are \{2−1−1\} and \{01−10\}, which are non-polar surfaces and have lower energy than the \{0001\} facets.

Zinc oxide finds application in various areas. It is used in the manufacture of rubber and cigarettes (used as a filter). Popularly known calamine lotion is made out of zinc oxide powder. It is also used in a host of other creams and ointments that are used to treat skin diseases. Ceramic industry has a number of uses for zinc oxide powder. It is also used as an additive in food products such as breakfast cereals. Various paints use zinc oxide as a coating agent and as an additive in the manufacture of concrete.
Nano cadmium oxide (CdO)

Cadmium oxide has gained tremendous attention due to its interesting properties like direct band gap of 2.3 eV. It is widely used in the applications like the preparation of cadmium coated baths and manufacture of paint pigments. Nanostructure CdO was synthesized by sol–gel method using metal precursor cadmium acetate. Cadmium acetate was added slowly in 500 ml clear solution of starch and distilled water and the solution was stirred. While stirring, equimolar ammonia in aqueous solution was added drop by drop. Then stirring was carried for another two hours and the solution was kept overnight. Next day the solution was filtered and precipitate of CdO was obtained which was heated overnight at 80ºC. Next day crystalline form of CdO was sintered up to 600ºC. At 80ºC the colour of CdO was light red and at 600ºC, it was reddish brown.

Polyaniline-CdO nanocomposite was obtained by in-situ polymerization. Initially polymerization of monomer aniline was initiated by drop wise addition of ammonium peroxidisulphate in acidic medium in which specific quantity of synthesized CdO powder was added. The stirring was continued for 2 hours and then solution was kept overnight. Next day, the mixture was filtered, washed with distilled water and the methanol and then dried at 80ºC for overnight. By changing the weight percentage of CdO with aniline monomer (5%, 10%, 20%) a series of Polyaniline-CdO nano composites was obtained.

Applications of CdO

Cadmium oxide was used in applications such as photodiodes, photovoltaic cells, solar cells, transparent electrodes, liquid crystal displays, IR detectors, gas sensors and antireflection coat. Major uses for cadmium oxide are as an ingredient for electroplating baths, and in pigments.

Nano Cadmium sulphide (CdS)

Cadmium sulfide is yellow in color and is a semiconductor of electricity. It exists as two different polymorphs, hexagonal greenockite and cubic hawleyite. CdS in bulk has band gap energy of 2.42eV at 300K with absorption maxima at 515 nm. It can attain three types of crystal structures namely wurtzite, zinc blend and high pressure rock-salt phase (Figure 13). Among these, wurtzite is the most stable of the three phases and can be easily synthesized. Wurtzite phase have been observed in both the bulk and nanocrystalline CdS while cubic and rock-salt phases are observed only in nanocrystalline CdS.
The wurtzite form comprises of hexagonal close packing (hcp) in which the stacking sequence of the atoms is ABABAB…, while, the zinc blende and rock salt structure have the stacking sequence of the atoms as ABCABCA…, i.e., called cubic close packing (ccp) (Figure 14) In hexagonal wurtzite and cubic zinc blend, each atom is coordinated to four other atoms in tetrahedral fashion such that each atom has four neighboring atoms of the opposite type, whereas in rock-salt each atom is coordinated to six other atoms in octahedral fashion such that each atom has six neighboring atoms of the opposite kind.

The CdS nanoparticles were synthesized by chemical precipitation method using Cadmium acetate and sodium sulfide as the starting materials. 0.1 M solution of Cd(CH$_3$COO)$_2$ and Na$_2$S reactants was prepared using millipore water. 50 ml of 0.1M cadmium acetate solution was taken in 250 ml Round bottom flask and stirred for 30 minutes.
using magnetic stirrer. After 20 mins. 0.01M tetrabutylammonium bromide (TBAB) dissolved in water was added to it and continued stirring for 30 mins to get homogeneous solution and then 0.1M solution of sodium sulfide was added dropwise to the solution of cadmium acetate under continuous stirring until the formation of yellow precipitate and stirring was continued for 2h to complete the reaction. The pH was maintained at 9-10 by adding ammonia solution in basic medium. The chemical reaction is,

$$\text{Cd(CH}_3\text{COO)}_2 + \text{Na}_2\text{S} \rightarrow \text{CdS} + 2\text{CH}_3\text{COONa}$$

The solution was allowed to settle down for 2h, and the particles were precipitated into ethanol. The solid yellow product was washed by suspending them in ethanol. The reaction product was repeatedly washed with ethanol to clear the surfactant impurities from the CdS nanoparticles and centrifuged for 20 mins for three times with ethanol at high rpm level. And then the product was dried at 150°C for 3h under reduced pressure at ambient temperature.

Synthetic cadmium pigments based on cadmium sulfide are valued for their good thermal stability, light and weather fastness, chemical resistance and high opacity. As a pigment, CdS is known as cadmium yellow. Cadmium sulfide is also used in the production of solar cells where it is used as a buffer layer in the manufacture of CIGS (Copper-Indium-Gallium-Selenide) solar cells.

**Reaction in Nanospace**

A wide array of self-assembled molecular capsules based on various building blocks and noncovalent interactions has been developed in the last decade. The nanospace within these supramolecular capsules is generally in the range of 300–500 Å which is sufficient for the selective encapsulation of one large or a number of smaller molecules. The structure of the different capsules varies significantly, and as a result guest shielding and guest exchange rates strongly depend on the capsule applied. A diversity of chemical processes has been carried out within molecular capsules and the effects observed so far are, although academic, very interesting. Reactions can be accelerated and the selectivity of a chemical process can be changed completely. These observations can be explained by stabilization of the reaction transition state by the capsule (based on enthalpic and entropic contributions) or by concentration effects in the case of bimolecular reactions, such as Diels–Alder reactions. More important are the unique reaction selectivities induced by the novel finite microenvironment within the capsule. The size and shape of the nanoreactor’s cavity and that of the nanoreactor’s gates can control the substrate selectivity by controlling the access to the
cavity. In a same manner it can protect an active-site located in the cavity that otherwise would be poisoned by chemicals present in solution.

The regio and chemo selectivities can be changed by the capsule by changing the ratio of reaction rates of competing pathways. This was for example observed for encapsulated rhodium complexes that were used as hydroformylation catalysts. In addition to these effects, reaction intermediates have been observed in nanoreactors that otherwise have too short lifetimes for identification. In these occasions the reaction rate of the subsequent step after the formation of the intermediate is slowed down by the nanocapsule. Product inhibition, which is a frequently encountered problem in bimolecular coupling reactions carried out within enclosed cavities, is fundamentally related to the former. The coupling product might have a higher affinity for the capsule than the substrates, and consequently product release from the nanoreactor becomes the slowest step in the reaction. Product inhibition can prohibit the utility of nanoreactors as true catalysts.

Self-assembled capsules also have guest exchange mechanisms via partial disassembly of the capsule, whereas exchange for the covalent analogues is restricted to portal slippage. It is this unique property that enables the combination of complete encapsulation with sufficiently fast in–out exchange, which might prove to be the advantage in the catalysis application. Although the research field is still in its infancy, several examples of reactions carried out within self-assembled nanoreactors appeared and demonstrate the power of the concept. Detailed studies are still needed to fully understand the mechanisms behind the effects observed when carrying out reactions in nanoreactors. However, molecular capsules have also been used to control reactions that take place outside the capsule for example by controlling the release of reagents, making the nanoreactor applications virtually unlimited.

**Nanoconfinement**

Nanoconfinement is receiving increasing interest in the field of energy storage and has been applied to different metal hydride systems in order to improve their properties for hydrogen storage. Modified hydrogen sorption kinetics and thermodynamics of metal hydrides have been achieved by nano size effects. Recent advancements in nanoscience and nanotechnology, increasing numbers of chemical reactions are conducted in confined or nearly confined nanospaces. Thus, reactions between a few organic molecules and between bio-molecules, or the fabrication of inorganic and metallic nanoclusters is confined to a
nanospace, exhibit distinct properties compared to the same processes involving macroscopic systems. Beyond these cases, the stabilization of labile intermediates by an open-ended self-folding cavitand, of reaction products in mesoporous silica and of nucleotide dimers (duplexes) formed via hydrogen-bonding inside self-assembled coordination cages (potentially pertinent to molecular information processing in DNA-based computing) was recently observed. Finally, this effect is expected to be important in the growing nanotechnological utilization of chemical reactions conducted within confined nanospaces, as well as in theoretical physical chemistry in general, due to the fundamental deviations from classical thermodynamics of macroscopic systems.

Nanocapsules

A nanocapsule is a nanoscale shell made from a nontoxic polymer. They are vesicular systems made of a polymeric membrane which encapsulates an inner liquid core at the nanoscale. Nanocapsules have many uses, including promising medical applications for drug delivery, food enhancement, nutraceuticals, and for self-healing materials. The benefits of encapsulation methods are for protection of these substances against adverse environment, for controlled release, and for precision targeting. Nanocapsules can potentially be used as MRI-guided nanorobots or nanobots, although challenges remain.

The nano-sized structure of nanocapsules allows permeating through cell membranes, which makes them effective carriers of medicine in biological systems. The specific processing of nanocapsules gives them unique properties in how they release drugs in certain situations. Generally, there are three physico-chemical release mechanisms that are used to release the drug or medicine from the polymeric shell of the nanocapsule.

The delivery of nanocapsules could happen through different mechanism on such process is hydration and diffusion. In this release mechanism the nanocapsule will swell due to the effects of hydration. Once the nanocapsule is has swollen to a point where it stretches, the polymeric membrane it will allow for diffusion of the drug through the polymeric membrane and into the biological system.

Another type of mechanism for the delivery of nanocapsules is enzymatic reaction. The polymer shell must be first selected to coordinate with the enzymes produced by the human body to produce and enzymatic reaction. This reaction will cause a rupture in the polymeric membrane which allows the drug to be dispersed into the system. After the rupture the drug dissociates from the swelled nanocapsule and diffuses out into the rest of the cell.
Cavitands

Inspired by the exquisite specificity of biomolecules such as antibodies for target antigens, attempts were made through supra molecular chemistry approach to do the same for small molecule targets through the use of synthetic receptors called cavitands. These molecules have the potential to be selective, because of their unique biomimetic nanostructures. Cavitands derive their name from the shape of their cavities (Figure 15). These molecules are designed to bind target molecules to form guest-host complexes. By tuning the cavity depth, shape, and chemical functionality that controls the synergistic interactions with analyte molecules, cavitands for a range of molecular targets may be designed and synthesized. This strategy for selectivity-enhancement is fundamentally different from that used in other chemically selective coatings (for example, polymers) that rely on the solubility of the targets with the coating layer.

![Figure 15](image)

**Figure 15** Three cavitands: (a) MeCav (methylen-bridged), (b) PzCav (pyrazine-bridged), and (c) QxCav (quinoxalines-bridged) with varying depths and therefore complexing ability with target molecule.

Although target molecules may bind selectively to such tailored cavitand molecules, it is equally important to transduce the binding event by using an appropriate technique that has high sensitivity. A real-time, label-free, optical technique called surface plasmon resonance (SPR), refractive index changes induced by analyte-cavitand interactions provide selective signals for sensitive chemical vapor detection.

Three cavitands named MeCav (for methylene-bridged), PzCav (pyrazine-bridged), and QxCav (quinoxalines-bridged) shows selectivity toward aromatic vapors (Figure 15). The presence of alkyl tails (R) at the bottom of the cavity is to make them soluble in common solvents such as chloroform. Cavitand solutions (0.38 mM) in chloroform were spin coated onto surface plasmon resonance substrates (50-nm thick gold-coated cover glass). Spin
coating was performed at 4000 rpm for 60 s at room temperature. The spin coating parameters gave a film thickness (confirmed using spectroscopic ellipsometry) of nearly 4 nm. For targets, a variety of analyte vapors belonging to different chemical classes were studied. QxCav with the deepest cavity was designed to form guest-host complexes with aromatic vapors, whereas cavitands with shallower cavities (such as MeCav and PzCav) were not expected to be as selective toward such guest molecules. Cavitands finds application as a platform for the study of protein structure and detect sarcosine in water and urine solutions.

**Cucurbiturils**

Cucurbiturils are macrocyclic molecules consisting of glycoluril repeat units. These compounds are particularly interesting to chemists because they are molecular containers that are capable of binding other molecules within their cavity (Figure 16).

![Figure 16 Structure of various cucurbiturils](image)

The name is actually derived from the resemblance of this molecule with a pumpkin of the family of Cucurbitaceae. The cavity of cucurbit[6]uril has nanoscale dimensions with an approximate height of 9.1 Å, outer diameter 5.8 Å and inner diameter 3.9 Å. Cucurbiturils are commonly written as cucurbit[n]uril, where n is the number of glycoluril units. Two common abbreviations are CB[n], or simply CBn.

![Figure 17 Synthesis of CBn homologues by condensation of glycoluril (1) and formaldehyde](image)
The synthesis of cucurbiturils was first reported in 1905 by Behrend. Cucurbiturils can be synthesized by the acid-catalyzed condensation of glycoluril and formaldehyde (Figure 17).

Cucurbiturils are efficient host molecules in molecular recognition and have a particularly high affinity for positively charged or cationic compounds. High association constants with positively charged molecules are attributed to the carbonyl groups that line each end of the cavity and can interact with cations in a similar fashion to crown ethers. The affinity of cucurbiturils can be very high.

Host guest interactions also significantly influence solubility behavior of cucurbiturils. Cucurbit[6]uril dissolves poorly in just about any solvent but solubility is greatly improved in a solution of potassium hydroxide or in an acidic solution. The cavitand forms a positively charged inclusion compound with a potassium ion or a hydronium ion respectively which have much greater solubility that the uncomplexed neutral molecule.

Cucurbiturils host-guest properties have been explored for drug delivery vehicles. The potential of this application has been explored with cucurbit[7]uril that forms an inclusion compound with the important cancer fighting drug oxaliplatin. Encapsulation of fluorescent in cucurbiturils can leads to numerous applications. Benefits of encapsulation are solubilazation, deaggregation, photostabilization. Cucurbiturils forms stable complexes with various guests, including drug molecules, amino acids and peptides, saccharides, dyes, hydrocarbons, perfluorinated hydrocarbons, and even high molecular weight guests such as proteins (e.g., human insulin).

**Zeolites**

Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO$_4$) and silica (SiO$_4$). In simpler words, they're solids with a relatively open, three-dimensional crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them (Figure 18). Zeolites form with many different crystalline structures, which have large open pores (sometimes referred to as cavities) in a very regular arrangement and roughly the same size as small molecules. There are about 40 naturally occurring zeolites, forming in both volcanic and sedimentary rocks; according to the US Geological Survey, the most commonly mined forms include chabazite, clinoptilolite, and mordenite.
Dozens more artificial, synthetic zeolites (around 150) have been designed for specific purposes, the best known of which are zeolite A (commonly used as a laundry detergent), zeolites X and Y (two different types of faujasites, used for catalytic cracking), and the petroleum catalyst ZSM-5 (a branded name for pentasil-zeolite). Although all zeolites are aluminosilicates, some contain more alumina, while others contain more silica. Alumina-rich zeolites are attracted to polar molecules such as water, while silica-rich zeolites work better with nonpolar molecules.

Properties: Zeolites are very stable solids that resist the kinds of environmental conditions that challenge many other materials. High temperatures don't bother them because they have relatively high melting points (over 1000°C), and they don't burn. They also resist high pressures, don't dissolve in water or other inorganic solvents, and don't oxidize in the air. The counter-cations in zeolites are mobile, and may easily be exchanged. This results in ion exchange capability utilized e.g. in detergents and in waste water purification.

One of the major uses of zeolites is as heterogeneous catalysts. The cage-like structure of zeolites makes them useful in all sorts of ways. One of the biggest everyday uses for zeolites is in water softeners and water filters. In ion-exchange water softeners, for example, hard water (rich in calcium and magnesium ions) is piped through a column filled with sodium-containing zeolites. The zeolites trap the calcium and magnesium ions and release sodium ions in their place, so the water becomes softer but richer in sodium. Many everyday laundry and dishwasher detergents contain zeolites to remove calcium and magnesium and soften water so they work more effectively.
Two other very common, everyday uses of zeolites are in odor control and pet litter; in both, the porous crystalline structure of the zeolites helps by trapping unwanted liquids and odor molecules. This simple idea, so effective in our homes, has much more important uses outside them: zeolites have proved extremely effective at removing radioactive particles from nuclear waste and cleaning up soils contaminated with toxic heavy metals. (Following the Fukushima nuclear disaster in Japan in 2011, rice farmers spread zeolites on their fields in an attempt to trap any lingering radioactive contaminants.) The many other uses for zeolites includes concrete production, soil-conditioners, and animal food.

An important use for zeolites is as catalysts in drug (pharmaceutical) production and in the petrochemical industry, where they're used in catalytic crackers to break large hydrocarbon molecules into gasoline, diesel, kerosene, waxes and all kinds of other byproducts of petroleum. Again, it's the porous structure of zeolites that proves important. The many pores in a zeolite's open structure are like millions of tiny test tubes where atoms and molecules become trapped and chemical reactions readily take place. Since the pores in a particular zeolite are of a fixed size and shape, zeolite catalysts can work selectively on certain molecules, which is why they're sometimes referred to as shape-selective catalysts (they can select the molecules they work on in other ways beside shape and size, however). Like all catalysts, zeolites are reusable over and over again.

**Metal-organic framework**

Metal–Organic Frameworks (MOFs) or porous coordination networks are a class of advanced materials designed by employing various metal ions and organic linkers. MOFs have emerged as an extensive class of crystalline materials with high porosity in nature. Unlike other porous materials like zeolites, activated carbon, and metal-complex hydrides etc., MOFs are branch of materials having many virtues such as thermal stability, discrete ordered structure, ultra-low densities (i.e. 1.00 to 0.09 g cm$^{-3}$), large internal surface area extending beyond 6000 m$^2$/g, ease of synthesis and with broad-spectrum of properties suited for physical and chemical applications. These striking features led to incessant research for the development of many new porous materials. On an elemental level, MOFs epitomize the elegance of chemical structures and the relevance of combination of inorganic and organic components.

In contrast to the nomenclature, MOF materials can be developed by connecting together both metal ions or metal oxides and polytopic organic struts or linkers. Organic
linkers with different functionality, i.e. bidentate to polydentate aromatic carboxylates (Figure 19) have been used to develop the new MOFs.

Figure 19 Potential polytopic organic acids as linkers in MOFs. (i) oxalic acid, (ii) terephthalic acid, (iii) trimesic acid, (iv) adamantane-1,3,5,7-tetracarboxylic acid, (v) fumaric acid, (vi) 4,5-imidazoledicarboxylic acid, (vii) 1,4-butanedicarboxylic acid, (viii) 4,6-dihydroxy benzene-1,2,5-trisulfonic acid, (ix) biphenyl-4,40-dicarboxylic acid, (x) 2,5-dihydroxyterephthalic acid, (xi) 6,60-dichloro-4,40-di(pyridin-4-yl)-1,10 -binaphthyl-2,20 -diol, (xii) 2,6-naphthalenedicarboxylic acid and (xiii) 1,3,5-benzenetribenzoic acid.

Novel Metal–Organic Framework materials can be achieved, when several influencing factors are taken into consideration. While preserving the structural framework building units is the most important, significant attention has been paid to the synthesis of new organic ligands for linkers and optimal conditions for development of metal–organic ligand bond. The characteristics of ligand such as length of ligand, bulkiness, bond angles, chirality, etc., and the geometries attained by the metal ions expressively influence the structure of MOFs.

In recent years, the advantages of hydrothermal technique in the crystal engineering have been more explored. In the case of MOFs, hydrothermal synthesis is adorable due to two reasons. Firstly, the solubility problem of heavy organic molecules under the experimental conditions can be minimized. Secondly, nucleation process can be initiated rapidly for the formation of rare complexes under the same experimental conditions. As the viscosity of water is reduced under these conditions, the activity of mobilization of precursors is favored. Under these conditions thermodynamically meta stable phases of coordination networks or MOFs can be isolated. The crystal growth can be enhanced in steel autoclaves placed in programmable hot air ovens at running temperatures below 300 °C with certain retention time. Different temperatures are maintained at the opposite ends of the vessel, hotter end dissolves the nutrients whereas growth of seeds begins at cooler side of the vessel.
MOF can be employed for separation of small gases such as hydrogen, methane, acetylene, oxygen, carbon dioxide, and nitrogen is very important for industrial processes because these small gases can be utilized as energy sources and raw materials for the production of a range of chemical product compounds. Similarly MOFs can be used for CO₂ capture, methane storage, C₂H₂ / C₂H₄ separation, synthesis of luminescent materials and in heterogeneous catalysis.

**Porous silicon**

Porous silicon was discovered in 1956 by Uhlir while performing electropolishing experiments on silicon wafers using an electrolyte containing hydrofluoric acid (HF). He found that under the appropriate conditions of applied current and solution composition, the silicon did not dissolve uniformly but instead fine holes were produced, which propagated primarily in the direction in the wafer. Therefore, porous silicon formation was obtained by electrochemical dissolution of silicon wafers in aqueous or ethanoic HF solutions.

Porous silicon is a very promising material due to its excellent mechanical and thermal properties, its obvious compatibility with silicon-based microelectronics and its low cost. Its large surface area within a small volume, its controllable pore sizes, its convenient surface chemistry, and the ability to modulate its refractive index as a function of depth makes porous silicon a suitable dielectric material for the formation of multilayers.

In the 1990s Leigh Canham published his results on red-luminescence from porous silicon, that was explained in terms of quantum confinement of carriers in nano-crystals of silicon which are present in the pore walls. Since that time, the interest of researchers and technologists to this material (and other porous semiconductors as well) is constantly growing and the number of publications dedicated to this class of materials increases every year. With the discovery of efficient visible light emission from porous silicon came an explosion of work focused on creating silicon-based optoelectronic switches, displays, and lasers. During the last twenty years, the optical properties of porous silicon have become a very intense area of research.

All these features also leads, on one hand, to interesting optical properties by mixing silicon with air in the effective medium approximation. On the other hand the pores allow the penetration of chemical and biological substances, liquids, cells, molecules to change i.e. the optical behavior of the original system. These effects inspired research into different applications like optical sensing applications and biomedical applications.
Electrochemical etching of porous silicon

One of the most important advantages of porous silicon is its simple and easy preparation. Since the first studies of Uhlir and Turner, and lately Cahnam, porous silicon has been mainly obtained by electrochemical dissolution of silicon wafers in solutions based on hydrofluoric acid (HF). A schematic of the porous silicon formation process can be seen in figure 20. The surface of a silicon wafer, contacted on the back, is in contact with a solution containing hydrofluoric acid (HF). After applying a voltage (in the right direction) between the wafer backside contact and an electrode in the HF solution, a pore growth by silicon dissolution starts, provided certain key parameters are set correctly.

![Figure 20 Schematic diagram of the porous silicon anodization circuit.](image)

Anodization parameters

The porous silicon formation process with electrochemical anodization has been widely developed by many authors. The parameters that influence on this formation process are the substrate doping, the current density, the HF concentration: the higher the concentration, the lower the pore size and the porosity. HF concentration determines the upper limit to current density values. With a fixed and low HF concentration the range over which the current density can be varied is short, and it becomes wider by increasing the HF concentration. The solvent where the HF is diluted is an important factor. Since porous silicon is organophilic and hydrophobic, the use of ethanol guarantees a higher homogeneity, due to a better wettability of the surface than deionized water.

Etching time is an important factor. Longer etching times lead to thicker layers, but for long times an anisotropy in depth in the layer due to the chemical action of the electrolyte is introduced. The illumination during the etch is essential for n-type substrates. The porosity, thickness, pore diameter and microstructure of porous silicon depend on the anodization conditions.
Porous silicon finds application in different areas as shown in the table given below

<table>
<thead>
<tr>
<th>Application area</th>
<th>Role of porous silicon</th>
<th>Key property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optoelectronics</td>
<td>LED, Waveguide, Field emitter, Optical memory</td>
<td>Efficient electroluminescence, Tunability of refractive index, Hot carrier emission Non-linear properties</td>
</tr>
<tr>
<td>Micro-optics</td>
<td>Fabry-perot Filters Photonic bandgap structures, all optical switching</td>
<td>Refractive index modulation Regular macropore array Highly non-linear properties</td>
</tr>
<tr>
<td>Energy conversion</td>
<td>Antireflection coatings Photo-electrochemical cells</td>
<td>Low refractive index Photocorrosion cells</td>
</tr>
<tr>
<td>Environmental monitoring</td>
<td>Gas sensing</td>
<td>Ambient sensitive properties</td>
</tr>
<tr>
<td>Microelectronics</td>
<td>Micro-capacitor Insulator layer Low-K material</td>
<td>High specific surface area High resistance Electrical properties</td>
</tr>
<tr>
<td>Wafer technology</td>
<td>Buffer layer in heteroepitaxy SOI wafers</td>
<td>Variable lattice parameter High etching selectivity</td>
</tr>
<tr>
<td>Micromachining</td>
<td>Thick sacrificial layer</td>
<td>Highly controllable etching</td>
</tr>
<tr>
<td>Biotechnology</td>
<td>Tissue bonding Biosensor</td>
<td>Tunable chemical reactivity Enzyme immobilization</td>
</tr>
</tbody>
</table>

**Nanocatalysis**

Catalysis is one of the longest-established uses for nanoparticles. Aluminium, iron, titanium dioxide, clays, and silica have all been used as catalysts in nanoparticle form for many years. The properties of these particles which make them useful as catalysts has not been fully understood. Nanoparticle catalysts have a very large surface area, which has a straightforward positive effect on reaction rate. However, there are structure- and shape-based properties at the nanoscale, which can also effect the catalytic activity of a material.
Homogeneous nano catalysts (Figure 21) are used in the same medium as the reactants for nanoparticles. This typically means a solution or suspension of nanoparticles in a solvent. The most important issue to consider when designing a nanocatalyst for use in a solution is to prevent aggregation, nanoparticles are naturally attracted towards one another in these conditions, and will clump together to form larger particles if not prevented from doing so, removing their large surface area and other benefits.

Figure 21 Nanoparticle catalysts can be much more active and selective than the same materials in bulk or larger particle form - partly due to the increased surface area, but also due to additional size effects.

The most effective way to stabilize nanoparticles in solution is to attach long chain molecules to the surface. These make it impossible for the nanoparticles to get so close that they stick together. However, they can also reduce the access to the nanoparticle surface for the reacting molecules, decreasing overall catalytic activity. The other main concern with homogeneous nanocatalysts is recovery. Nanoparticles are notoriously difficult to remove from a solution, and the extra steps needed to do so could completely negate the process simplification due to using the catalyst in the first place. If the nanoparticles cannot be recovered, they pose an environmental risk, as well as threatening the profitability of the process. Most nanoparticles cannot be destroyed by incineration, and the effects of nanoparticle accumulation in ecosystems are largely unknown.

Heterogeneous Nanocatalysts

Heterogeneous catalysis is often considered to be more environmentally friendly. This involves a catalyst which is in a different phase to the reactants. The catalyst is usually solid,
or immobilized on a solid inert matrix (Figure 22). This gets around the issue of waste and recoverability, as the solid catalyst can in most cases simply be filtered out.

![Image](image_url)

**Figure 22** Heterogeneous catalysts are much easier to remove from the reaction mixture, and are also more adaptable to continuous flow processes.

A great deal of research has been done to investigate the catalytic potential of various nanoparticle-support systems. Recent examples include palladium, iron, gold, nickel and platinum nanoparticles. Supports used range from silica or aluminum to carbon fibres. Another area of heterogeneous nanocatalysts which has been explored is nanostructured solids. Nanoporous materials can be manufactured by growing the solid material around a molecular template. Nanoscale features can also be etched into the surface of a catalyst using standard lithography techniques - this can allow a degree of control over reactant flow on the catalyst surface, as well as increasing surface area.