

Unit-I Synthetic Methods (Nanomaterials)

Nanomaterials describe, in principle, materials of which a single unit small sized (in at least one dimension) between 1 and 1000 nanometers (10^{-9} meter) but usually is 1 to 100 nm (the usual definition of nanoscale measured in kelvin).

Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. Nanomaterials are slowly becoming commercialized and beginning to emerge as commodities.

Sources

Engineered

Engineered nanomaterials have been deliberately engineered and manufactured by humans to have certain required properties. Legacy nanomaterials are those that were in commercial production prior to the development of nanotechnology as incremental advancements over other colloidal or particulate materials. They include carbon black and titanium dioxide nanoparticles.

Incidental

Nanomaterials may be incidentally produced as a byproduct of mechanical or industrial processes. Sources of incidental nanoparticles include vehicle engine exhausts, welding fumes, combustion processes from domestic solid fuel heating and cooking. For instance, the class of nanomaterials called fullerenes are generated by burning gas, biomass, and candle. It can also be a byproduct of wear and corrosion products. Incidental atmospheric nanoparticles are often referred to as ultrafine particles, which are unintentionally produced during an intentional operation, and could contribute to air pollution.

Natural

Biological systems often feature natural, functional nanomaterials. The structure of foraminifera (mainly chalk) and viruses (protein, capsid), the wax crystals covering a lotus or nasturtium leaf, spider and spider-mite silk, the blue hue of tarantulas, the "spatulae" on the bottom of gecko feet, some butterfly wing scales, natural colloids (milk, blood), horny materials (skin, claws, beaks, feathers, horns, hair), paper, cotton, nacre, corals, and even our own bone matrix are all natural organic nanomaterials.

Natural inorganic nanomaterials occur through crystal growth in the diverse chemical conditions of the Earth's crust. For example, clays display complex nanostructures due to anisotropy of their underlying crystal structure, and volcanic activity can give rise to opals, which are an instance of a naturally occurring photonic crystals due to their nanoscale structure. Fires represent particularly complex reactions and can produce pigments, cement, fumed silica etc. Natural sources of nanoparticles include combustion products forest fires, volcanic ash, ocean spray, and the radioactive decay of radon gas. Natural nanomaterials can also be formed through weathering processes of metal- or anion-containing rocks, as well as at acid mine drainage sites.

Types

Nano-objects are often categorized as to how many of their dimensions fall in the nanoscale. A nanoparticle is defined a nano-object with all three external dimensions in the nanoscale, whose longest and the shortest axes do not differ significantly. A nanofiber has two external dimensions in the nanoscale, with nanotubes being hollow nanofibers and nanorods being solid nanofibers. A nanoplate has one external dimension in the nanoscale, and if the two larger dimensions are significantly different it is called a nanoribbon. For nanofibers and nanoplates, the other dimensions may or may not be in the nanoscale, but must be significantly larger. A significant different in all cases is noted to be typically at least a factor of 3.

Nanostructured materials are often categorized by what phases of matter they contain. A nanocomposite is a solid containing at least one physically or chemically distinct region, or collection of regions, having at least one dimension in the nanoscale.. A nanofoam has a liquid or solid matrix, filled with a gaseous phase, where one of the two phases has dimensions on the nanoscale. A nanoporous material is a solid material containing nanopores, cavities with dimensions on the nanoscale. A nanocrystalline material has a significant fraction of crystal grains in the nanoscale.

In other sources, nanoporous materials and nanofoam are sometimes considered nanostructures but not nanomaterials because only the voids and not the materials themselves are nanoscale. Although the ISO definition only considers round nano-objects to be nanoparticles, other sources use the term nanoparticle for all shapes.

Nanoparticles

Nanoparticles have all three dimensions on the nanoscale. Nanoparticles can also be embedded in a bulk solid to form a nanocomposite.

Fullerenes

The fullerenes are a class of allotropes of carbon which conceptually are graphene sheets rolled into tubes or spheres. These include the carbon nanotubes (or silicon nanotubes) which are of interest both because of their mechanical strength and also because of their electrical properties. The first fullerene molecule to be discovered, and the family's namesake, buckminsterfullerene (C₆₀), was prepared in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University. The name was a homage to Buckminster Fuller, whose geodesic domes it resembles. Fullerenes have since been found to occur in nature. More recently, fullerenes have been detected in outer space.

For the past decade, the chemical and physical properties of fullerenes have been a hot topic in the field of research and development, and are likely to continue to be for a long time. In April 2003, fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure of resistant bacteria and even target certain types of cancer cells such as melanoma. The October 2005 issue of Chemistry and Biology contains an article describing the use of fullerenes as light-activated antimicrobial agents. In the field of nanotechnology, heat resistance and superconductivity are among the properties attracting intense research.

A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated. There are many calculations that have been done using ab-initio Quantum Methods applied to fullerenes. By DFT and TDDFT methods one can obtain IR, Raman and UV spectra. Results of such calculations can be compared with experimental results.

Metal-based nanoparticles

Inorganic nanomaterials, (e.g. quantum dots, nanowires and nanorods) because of their interesting optical and electrical properties, could be used in optoelectronics. Furthermore, the optical and electronic properties of nanomaterials which depend on their size and shape can be tuned via synthetic techniques. There are the possibilities to use those materials in organic material based optoelectronic devices such as Organic solar cells, OLEDs etc. The operating principles of such devices are governed by photoinduced processes like electron transfer and energy transfer. The performance of the devices depends on the efficiency of the photoinduced process responsible for their functioning. Therefore, better understanding of those photoinduced processes in organic/inorganic nanomaterial composite systems is necessary in order to use them in optoelectronic devices.

Nanoparticles or nanocrystals made of metals, semiconductors, or oxides are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other properties. Nanoparticles have been used as quantum dots and as chemical catalysts such as nanomaterial-based catalysts. Recently, a range of nanoparticles are extensively investigated for biomedical applications including tissue engineering, drug delivery, biosensor. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials.

Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The change in properties is not always desirable. Ferroelectric materials smaller than 10 nm can switch their polarization direction using room temperature thermal energy, thus making them useless for memory storage. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. For example, gold nanoparticles appear deep red to black in solution.

The often very high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering is possible at lower temperatures and over shorter durations than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles

to agglomerate do complicate matters. The surface effects of nanoparticles also reduces the incipient melting temperature.

One-dimensional nanostructures

The smallest possible crystalline wires with cross-section as small as a single atom can be engineered in cylindrical confinement. Carbon nanotubes, a natural semi-1D nanostructure, can be used as a template for synthesis. Confinement provides mechanical stabilization and prevents linear atomic chains from disintegration; other structures of 1D nanowires are predicted to be mechanically stable even upon isolation from the templates.

Two-dimensional nanostructures

2D materials are crystalline materials consisting of a two-dimensional single layer of atoms. The most important representative graphene was discovered in 2004. Thin films with nanoscale thicknesses are considered nanostructures, but are sometimes not considered nanomaterials because they do not exist separately from the substrate.

Bulk nanostructured materials

Some bulk materials contain features on the nanoscale, including nanocomposites, nanocrystalline materials, nanostructured films, and nanotextured surfaces. Box-shaped graphene (BSG) nanostructure is an example of 3D nanomaterial. BSG nanostructure has appeared after mechanical cleavage of pyrolytic graphite. This nanostructure is a multilayer system of parallel hollow nanochannels located along the surface and having quadrangular cross-section. The thickness of the channel walls is approximately equal to 1 nm. The typical width of channel facets makes about 25 nm.

Applications

Nano materials are used in a variety of, manufacturing processes, products and healthcare including paints, filters, insulation and lubricant additives. In healthcare Nanozymes are nanomaterials with enzyme-like characteristics. They are an emerging type of artificial enzyme, which have been used for wide applications in such as biosensing, bioimaging, tumor diagnosis, antibiofouling and more. In paints nanomaterials are used to improve UV protection and improve ease of cleaning. High quality filters may be produced using nanostructures, these filters are capable of removing particulate as small as a virus as seen in a water filter created by Seldon Technologies. In the air purification field, nano technology was used to combat the spread of MERS in Saudi Arabian hospitals in 2012.

Nanomaterials are being used in modern and human-safe insulation technologies, in the past they were found in Asbestos-based insulation. As a lubricant additive, nano materials have the ability to reduce friction in moving parts. Worn and corroded parts can also be repaired with self-assembling anisotropic nanoparticles called TriboTEX. Nanomaterials can also be used in three-way-catalyst (TWC) applications. TWC converters have the advantage of controlling the emission of nitrogen oxides (NO_x), which are precursors to acid rain and smog. In core-shell structure, nanomaterials form shell as the catalyst support to protect the noble metals such as palladium and rhodium. The primary function is that the supports can be used for carrying catalysts active components, making them highly dispersed, reducing the use of noble metals, enhancing catalysts activity, and improving the mechanical strength.

Historical Milestones of Nanomaterials

The history of nanotechnology traces the development of the concepts and experimental work falling under the broad category of nanotechnology. Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time. The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985, with the elucidation and popularization of a conceptual framework for the goals of nanotechnology beginning with the 1986 publication of the book *Engines of Creation*. The field was subject to growing public awareness and controversy in the early 2000s, with prominent debates about both its potential implications as well as the feasibility of the applications envisioned by advocates of molecular nanotechnology, and with governments moving to promote and fund research into nanotechnology. The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nanomaterials rather than the transformative applications envisioned by the field.

Early uses of nanomaterials

The earliest evidence of the use and applications of nanotechnology can be traced back to carbon nanotubes, cementite nanowires found in the microstructure of wootz steel manufactured in ancient India from the time period of 600 BC and exported globally. Although nanoparticles are associated with modern science, they were used by artisans as far back as the ninth century in Mesopotamia for creating a glittering effect on the surface of pots.

In modern times, pottery from the Middle Ages and Renaissance often retains a distinct gold- or copper-colored metallic glitter. This luster is caused by a metallic film that was applied to the transparent surface of a glazing, which contains silver and copper nanoparticles dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles are created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre, and clay on the surface of previously-glazed pottery. The technique originated in the Muslim world. As Muslims were not allowed to use gold in artistic representations, they sought a way to create a similar effect without using real gold. The solution they found was using luster.

Conceptual origins

Richard Feynman

The American physicist Richard Feynman lectured, "There's Plenty of Room at the Bottom," at an American Physical Society meeting at Caltech on December 29, 1959, which is often held to have provided inspiration for the field of nanotechnology. Feynman had described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Van der Waals attraction would become more important.

After Feynman's death, a scholar studying the historical development of nanotechnology has concluded that his actual role in catalyzing nanotechnology research was limited, based on recollections from many of the people active in the nascent field in the 1980s and 1990s. Chris

Toumey, a cultural anthropologist at the University of South Carolina, found that the published versions of Feynman's talk had a negligible influence in the twenty years after it was first published, as measured by citations in the scientific literature, and not much more influence in the decade after the Scanning Tunneling Microscope was invented in 1981. Subsequently, interest in "Plenty of Room" in the scientific literature greatly increased in the early 1990s. This is probably because the term "nanotechnology" gained serious attention just before that time, following its use by K. Eric Drexler in his 1986 book, *Engines of Creation: The Coming Era of Nanotechnology*, which took the Feynman concept of a billion tiny factories and added the idea that they could make more copies of themselves via computer control instead of control by a human operator; and in a cover article headlined "Nanotechnology", published later that year in a mass-circulation science-oriented magazine, *Omni*. Toumey's analysis also includes comments from distinguished scientists in nanotechnology who say that "Plenty of Room" did not influence their early work, and in fact most of them had not read it until a later date.

These and other developments hint that the retroactive rediscovery of Feynman's "Plenty of Room" gave nanotechnology a packaged history that provided an early date of December 1959, plus a connection to the charisma and genius of Richard Feynman. Feynman's stature as a Nobel laureate and as an iconic figure in 20th century science surely helped advocates of nanotechnology and provided a valuable intellectual link to the past.

Norio Taniguchi

The Japanese scientist called Norio Taniguchi of Tokyo University of Science was first to use the term "nano-technology" in a 1974 conference, to describe semiconductor processes such as thin film deposition and ion beam milling exhibiting characteristic control on the order of a nanometer. His definition was, "'Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule." However, the term was not used again until 1981 when Eric Drexler, who was unaware of Taniguchi's prior use of the term, published his first paper on nanotechnology in 1981.

K. Eric Drexler

In the 1980s the idea of nanotechnology as a deterministic, rather than stochastic, handling of individual atoms and molecules was conceptually explored in depth by K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and two influential books.

In 1980, Drexler encountered Feynman's provocative 1959 talk "There's Plenty of Room at the Bottom" while preparing his initial scientific paper on the subject, "Molecular Engineering: An approach to the development of general capabilities for molecular manipulation," published in the *Proceedings of the National Academy of Sciences* in 1981. The term "nanotechnology" (which paralleled Taniguchi's "nano-technology") was independently applied by Drexler in his 1986 book *Engines of Creation: The Coming Era of Nanotechnology*, which proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity. He also first published the term "grey goo" to describe what might happen if a hypothetical self-replicating machine, capable of independent operation, were constructed and released. Drexler's vision of nanotechnology is often called "Molecular Nanotechnology" (MNT) or "molecular manufacturing."

His 1991 Ph.D. work at the MIT Media Lab was the first doctoral degree on the topic of molecular nanotechnology and (after some editing) his thesis, "Molecular Machinery and Manufacturing with Applications to Computation," was published as Nanosystems: Molecular Machinery, Manufacturing, and Computation, which received the Association of American Publishers award for Best Computer Science Book of 1992. Drexler founded the Foresight Institute in 1986 with the mission of "Preparing for nanotechnology." Drexler is no longer a member of the Foresight Institute.

Unique Properties of Nanomaterials

The main parameters of interest with respect to nanoparticle safety are:

Physical properties

- Size, shape, specific surface area, aspect ratio
- Agglomeration/aggregation state
- Size distribution
- Surface morphology/topography
- Structure, including crystallinity and defect structure
- Solubility

Chemical properties

- Structural formula/molecular structure
- Composition of nanomaterial (including degree of purity, known impurities or additives)
- Phase identity
- Surface chemistry (composition, charge, tension, reactive sites, physical structure, photocatalytic properties, zeta potential)
- Hydrophilicity/lipophilicity

Nanosize

Nanoparticle, n—in nanotechnology, a sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers) and which may or may not exhibit a size-related intensive property.

Quantum dots

Quantum dots (QDs) are tiny semiconductor particles a few nanometres in size, having optical and electronic properties that differ from larger particles due to quantum mechanics. They are a central topic in nanotechnology. When the quantum dots are illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conductance band. The excited electron can drop back into the valence band releasing its energy by the emission of light. This light emission (photoluminescence) is illustrated in the figure on the right. The color of that light depends on the energy difference between the conductance band and the valence band.

Inorganic Nanomaterials

Using theoretical structure search methods (e.g. global optimisation, data mining) and classical and quantum mechanical calculations we determine the structure and properties of technologically important inorganic materials (e.g. ZnO, TiO₂, CdS, CeO₂) when one or more of their dimensions is reduced to the nanoscale. Our studies range from nanoclusters and nanoparticles to nanofilms and nanoporous materials. We are particularly interested in the non-bulk-like properties of inorganic nanoclusters and how they can provide inspiration for novel nanostructured materials (e.g. low density polymorphs) for technological applications.

Inorganic nanomaterials are stable, robust, resistant, highly functional, and are quite easily cleared from the body. Furthermore, inorganic materials exhibit truly exciting mechanical, optical, physical and electrical phenomena at the nanoscale which can be tailored through changes in material, phase, shape, size and surface characteristics. Oftentimes, it is necessary to add a biocompatible surface to inorganic nanoparticles to avoid toxicity, especially for heavy metals.

Semiconductor Nanomaterials

Quantum dots are the most well-known semiconductor nanoemitter. These are typically very small in size ~5nm, which is smaller or equal to the exciton Bohr radius giving quantum confinement. Electrons are subatomic particles with a negative elementary electric charge, electron holes is an empty position in an atom or lattice that an electron could occupy. An exciton is a bound state where an electron and electron hole are electrostatically attracted to each other through Coulombic forces. An exciton Bohr radius is the separation distance between the hole and electron. Due to 3 dimensional confinement effects, quantised energy levels are produced in the filled low energy valence band and in the empty conduction band of the quantum dots which is very unlike bulk semiconductors. The energy gap between the conduction and valence band varies with the size of the quantum dot which explains the tunable emissions (colour) when excited. Additionally, alloyed quantum dots can be further tuned because the bandgap is approximately equal to the weighted average of the composite semiconductor material. Quantum dots excited in the near-infrared are expected to be revolutionary in biomedical imaging. There has been concerns about the stability and toxicity, as many quantum dots lose luminescence intensity when exposed to light/air/oxygen/water and they are generally composed of heavy metal materials.

Synthesis

The goal of any synthetic method for nanomaterials is to yield a material that exhibits properties that are a result of their characteristic length scale being in the nanometer range (1 – 100 nm). Accordingly, the synthetic method should exhibit control of size in this range so that one property or another can be attained. Often the methods are divided into two main types, "bottom up" and "top down".

Bottom up methods

Bottom up methods involve the assembly of atoms or molecules into nanostructured arrays. In these methods the raw material sources can be in the form of gases, liquids or solids. The latter require some sort of disassembly prior to their incorporation onto a nanostructure. Bottom up methods generally fall into two categories: chaotic and controlled.

Chaotic processes involve elevating the constituent atoms or molecules to a chaotic state and then suddenly changing the conditions so as to make that state unstable. Through the clever manipulation of any number of parameters, products form largely as a result of the insuring kinetics. The collapse from the chaotic state can be difficult or impossible to control and so ensemble statistics often govern the resulting size distribution and average size. Accordingly, nanoparticle formation is controlled through manipulation of the end state of the products. Examples of chaotic processes are laser ablation, exploding wire, arc, flame pyrolysis, combustion, and precipitation synthesis techniques.

Controlled processes involve the controlled delivery of the constituent atoms or molecules to the site(s) of nanoparticle formation such that the nanoparticle can grow to a prescribed sizes in a controlled manner. Generally the state of the constituent atoms or molecules are never far from that needed for nanoparticle formation. Accordingly, nanoparticle formation is controlled through the control of the state of the reactants. Examples of controlled processes are self-limiting growth solution, self-limited chemical vapor deposition, shaped pulse femtosecond laser techniques, and molecular beam epitaxy.

Top down methods

Top down methods adopt some 'force' (e. g. mechanical force, laser) to break bulk materials into nanoparticles. A popular method involves mechanical break apart bulk materials into nanomaterials is 'ball milling'. Besides, nanoparticles can also be made by laser ablation which apply short pulse lasers (e. g. femtosecond laser) to ablate a target (solid).

Characterization

Novel effects can occur in materials when structures are formed with sizes comparable to any one of many possible length scales, such as the de Broglie wavelength of electrons, or the optical wavelengths of high energy photons. In these cases quantum mechanical effects can dominate material properties. One example is quantum confinement where the electronic properties of solids are altered with great reductions in particle size. The optical properties of nanoparticles, e.g. fluorescence, also become a function of the particle diameter. This effect does not come into play by going from macrosocopic to micrometer dimensions, but becomes pronounced when the nanometer scale is reached.

In addition to optical and electronic properties, the novel mechanical properties of many nanomaterials is the subject of nanomechanics research. When added to a bulk material, nanoparticles can strongly influence the mechanical properties of the material, such as the stiffness or elasticity. For example, traditional polymers can be reinforced by nanoparticles (such as carbon nanotubes) resulting in novel materials which can be used as lightweight replacements for metals. Such composite materials may enable a weight reduction accompanied by an increase in stability and improved functionality. Finally, nanostructured materials with small particle size such as zeolites, and asbestos, are used as catalysts in a wide range of critical industrial chemical reactions. The further development of such catalysts can form the basis of more efficient, environmentally friendly chemical processes.

The first observations and size measurements of nano-particles were made during the first decade of the 20th century. Zsigmondy made detailed studies of gold sols and other nanomaterials with sizes down to 10 nm and less. He published a book in 1914. He used an ultramicroscope that employs a dark field method for seeing particles with sizes much less than light wavelength. There are traditional techniques developed during the 20th century in interface and colloid science for characterizing nanomaterials. These are widely used for first generation passive nanomaterials specified in the next section.

These methods include several different techniques for characterizing particle size distribution. This characterization is imperative because many materials that are expected to be nano-sized are actually aggregated in solutions. Some of methods are based on light scattering. Others apply ultrasound, such as ultrasound attenuation spectroscopy for testing concentrated nano-dispersions and microemulsions. There is also a group of traditional techniques for characterizing surface charge or zeta potential of nano-particles in solutions. This information is required for proper system stabilization, preventing its aggregation or flocculation. These methods include microelectrophoresis, electrophoretic light scattering and electroacoustics. The last one, for instance colloid vibration current method is suitable for characterizing concentrated systems.

Uniformity

The chemical processing and synthesis of high performance technological components for the private, industrial and military sectors requires the use of high purity ceramics, polymers, glass-ceramics and material composites. In condensed bodies formed from fine powders, the irregular sizes and shapes of nanoparticles in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact. Uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to in microstructural inhomogeneities. Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved.

In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

It would therefore appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions which will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over particle-particle interactions. A number of dispersants such as ammonium citrate (aqueous) and imidazoline or oleyl alcohol (nonaqueous) are promising solutions as possible

additives for enhanced dispersion and deagglomeration. Monodisperse nanoparticles and colloids provide this potential.

Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid which results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established. Such defective polycrystalline colloidal structures would appear to be the basic elements of sub-micrometer colloidal materials science, and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in microstructural evolution in high performance materials and components

Hydrothermal Synthesis

Hydrothermal synthesis is typically carried out in a pressurised vessel called an autoclave with the reaction in aqueous solution. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation. Hydrothermal synthesis is widely used for the preparation of TiO₂ nanoparticles which can easily be obtained through hydrothermal treatment of peptised precipitates of a titanium precursor with water [9]. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase and surface chemistry through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time [10].

Solvothermal Method

The Solvothermal method is identical to the hydrothermal method except that a variety of solvents other than water can be used for this process. This method has been found to be a versatile route for the synthesis of a wide variety of nanoparticles with narrow size distributions, particularly when organic solvents with high boiling points are chosen. The solvothermal method normally has better control of the size and shape distributions and the crystallinity than the hydrothermal method, and has been employed to synthesize TiO₂ nanoparticles and nanorods with/without the aid of surfactants.

Chemical Vapor Deposition (CVD)

This process is often used in the semiconductor industry to produce high-purity, high-performance thin films. In a typical CVD process, the substrate is exposed to volatile precursors, which react and/or decompose on the substrate surface to produce the desired film. Frequently, volatile by products that are produced are removed by gas flow through the reaction chamber. The quality of the deposited materials strongly depends on the reaction temperature, the reaction rate, and the concentration of the precursors [11]. Cao et al. prepared Sn⁴⁺-doped TiO₂ nanoparticles films by the CVD method and found that more surface defects were present on the surface due to doping with Sn [12]. Gracia et al. synthesized M (Cr, V, Fe, Co)-doped TiO₂ by CVD and found that TiO₂ crystallized into the anatase or rutile structures depending on the type and amount of cation present in the synthesis process. Moreover, upon annealing, partial segregation of the cations in the form of M₂O_n was observed [13]. The advantages of this method include the uniform coating of the nanoparticles or nano film. However, this process has limitations including the higher temperatures required, and it is difficult to scaleup [14].

Combustion

Combustion synthesis leads to highly crystalline particles with large surface areas [21, 22]. The process involves a rapid heating of a solution containing redox groups. During combustion, the temperature reaches approximately 650°C for one or two minutes making the material crystalline. Since the time is so short, the transition from anatase to rutile is inhibited.

Gas Phase Methods

Gas phase methods are ideal for the production of thin films. Gas phase can be carried out chemically or physically. Chemical Vapour Deposition (CVD) is a widely used industrial technique that can coat large areas in a short space of time. During the procedure, titanium dioxide is formed from a chemical reaction or decomposition of a precursor in the gas phase [23, 24]. Physical vapour deposition (PVD) is another thin film deposition technique. Films are formed from the gas phase but without a chemical transition from precursor to product. For TiO₂ thin films, a focused beam of electrons heats the titanium dioxide material. The electrons are produced from a tungsten wire heated by a current. This is known as Electron beam (E-beam) evaporation. Titanium dioxide films deposited with E-beam evaporation have superior characteristics over CVD grown films such as, smoothness, conductivity, presence of contaminations and crystallinity. Reduced TiO₂ powder (heated at 900°C in a hydrogen atmosphere) is necessary for the required conductance needed to focus an electron beam on the TiO₂ [25].

Microwave Synthesis

Various TiO₂ 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 TiO₂ nanomaterials. Corradi et al prepared colloidal TiO₂ nanoparticle suspensions within 5 minutes using microwave radiation [26]. High quality rutile rods were developed combining hydrothermal and microwave synthesis, while TiO₂ hollow, open ended nanotubes were synthesised through reacting anatase and rutile crystals in NaOH solution [27, 28].

Sol-Gel Method

The sol-gel method is a versatile process used for synthesizing various oxide materials [29]. This synthetic method generally allows control of the texture, the chemical, and the morphological properties of the solid. This method also has several advantages over other methods, such as allowing impregnation or coprecipitation, which can be used to introduce dopants. The major advantages of the sol-gel technique includes molecular scale mixing, high purity of the precursors, and homogeneity of the sol-gel products with a high purity of physical, morphological, and chemical properties [30]. 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 [31].

Any factor that affects either or both of these reactions is likely to impact the properties of the gel. These factors, generally referred to as sol-gel parameters, includes type of precursor, type of solvent, water content, acid or base content, precursor concentration, and temperature. These parameters affect the structure of the initial gel and, in turn, the properties of the material at all subsequent processing steps. After gelation, the wet gel can be optionally aged in its mother

liquor, or in another solvent, and washed. The time between the formation of a gel and its drying, known as aging, is also an important parameter. A gel is not static during aging but can continue to undergo hydrolysis and condensation [32].

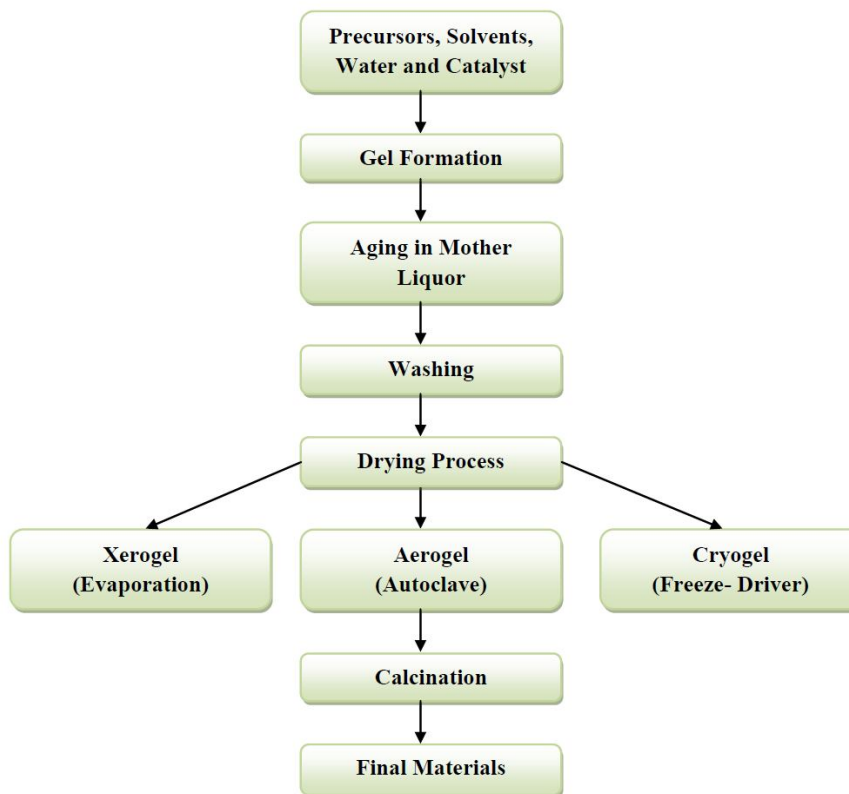
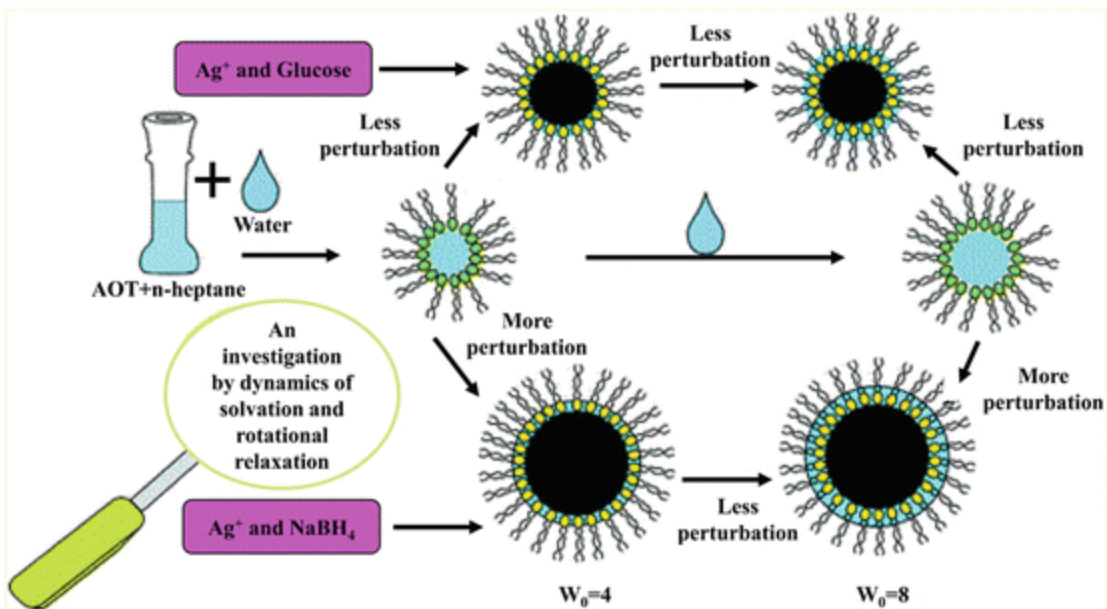


Figure: Sol-Gel and Drying Flowchart

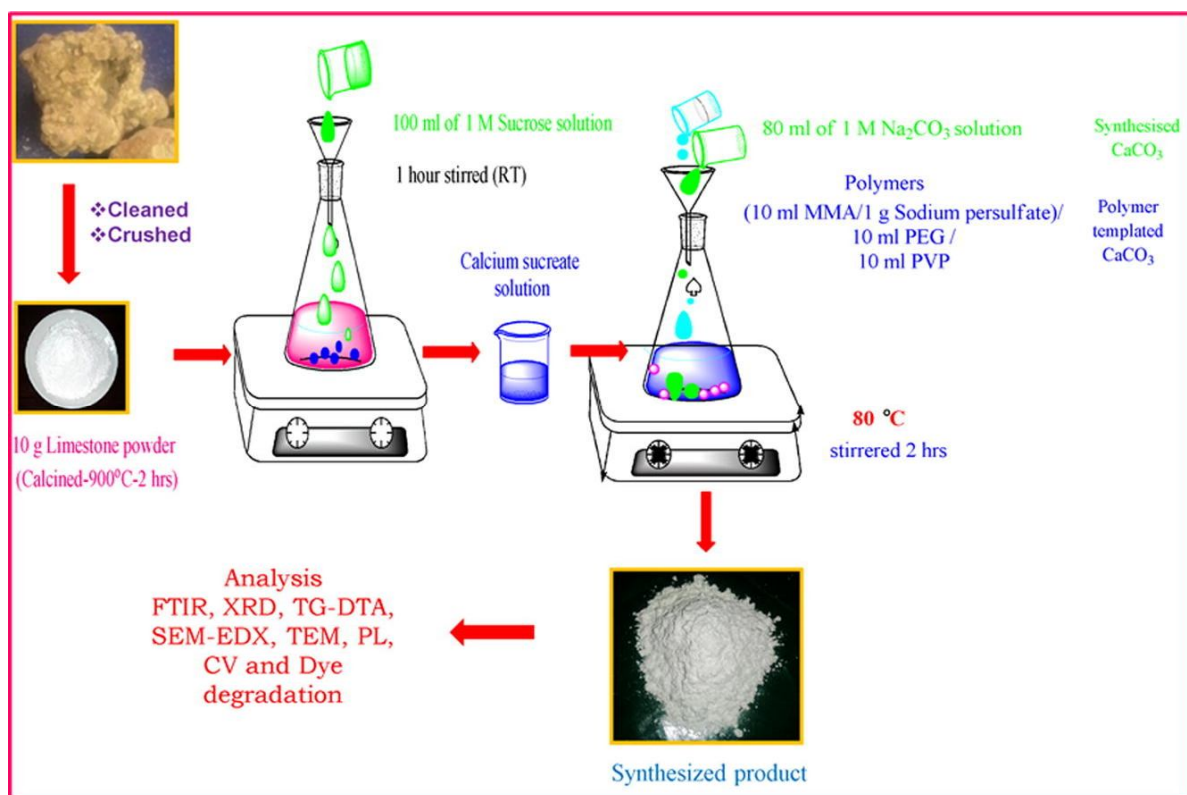
Reverse Micelles Synthesis

Reverse Micelles for Nanoparticle Synthesis and Biomolecule Separation. Reverse micelles are used for the selective separation and purification of biomolecules, and for the synthesis of nanoparticles. Reverse micelles are nanometer-size droplets of aqueous phase, stabilized by surfactants in an organic phase.



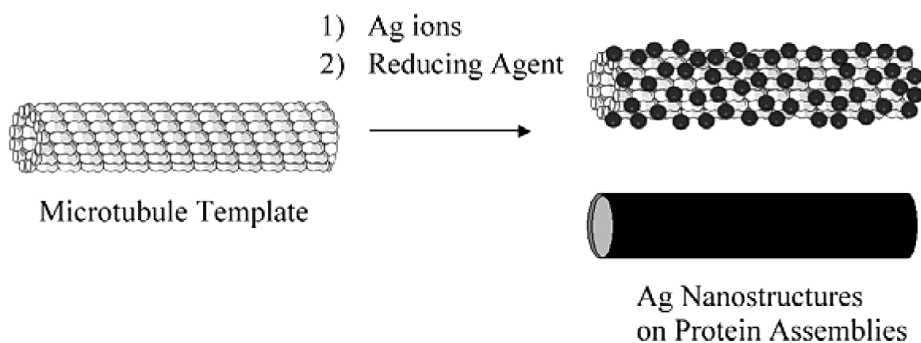
Polymer-mediated synthesis

A new method was developed to prepare highly dispersed Pt nanoparticles on carbon black to use as proton exchange membrane (PEM) fuel cell catalysts. This method involves using a polymer, poly(vinylpyrrolidone) (PVP), to prevent particle aggregation and thereby reduce nanoparticle sizes to achieve high dispersion. It was found that Pt nanoparticles mediated by PVP are smaller than those obtained without PVP and have a narrower size distribution. Well-dispersed Pt nanoparticles with metal loadings from 5 to 35 wt % were obtained on carbon black (Vulcan XC-72R). It was found that well-dispersed Pt nanoparticles on carbon black could be synthesized at a PVP monomers-to-Pt atoms ratio of 0.1 under our experimental conditions. Larger amounts of PVP did not produce smaller nanoparticles, but rather reduced the Pt mass loading on carbon black.



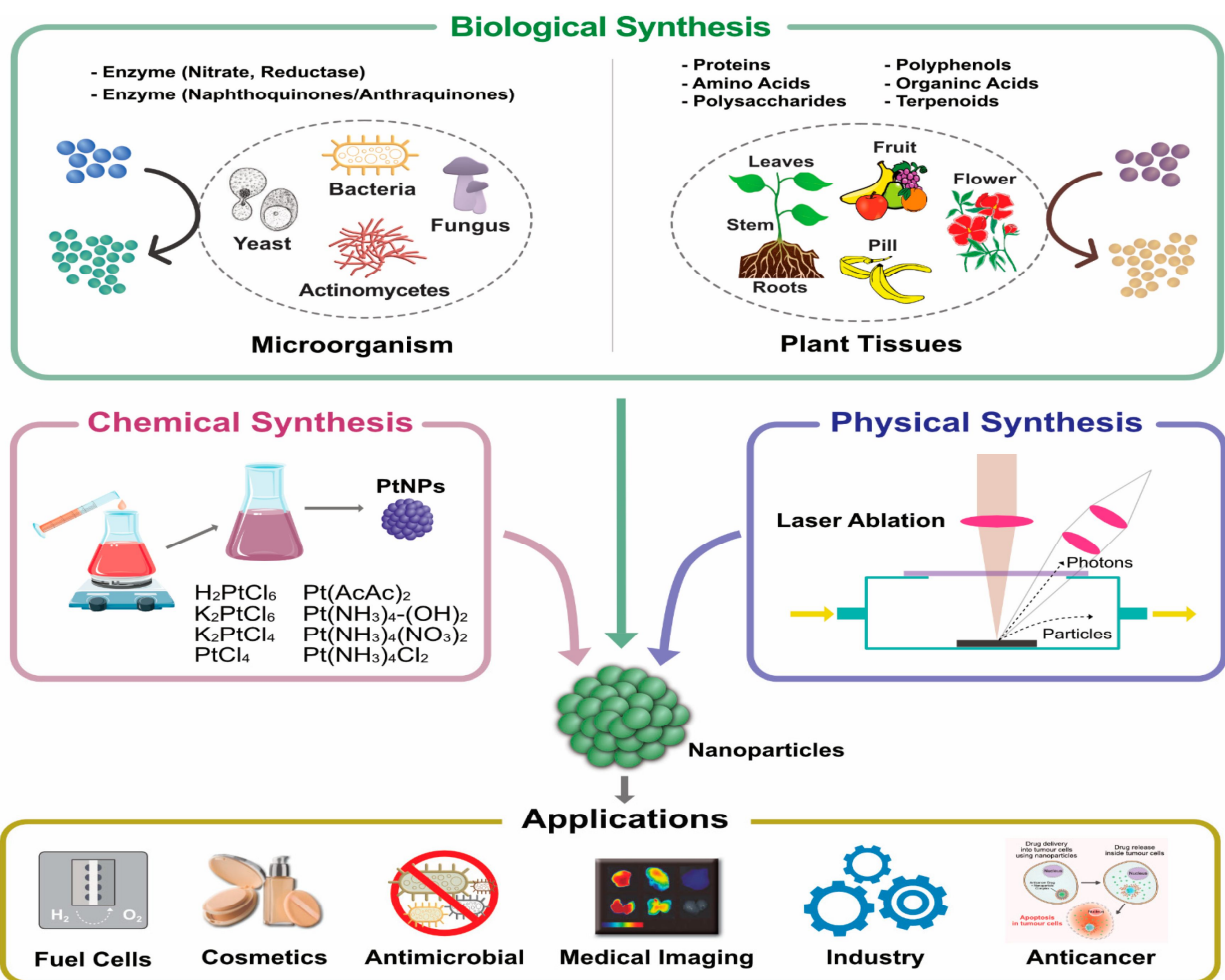
Protein-mediated synthesis

Casein, a milk protein, is used to produce biotolerable and highly stable silver nanoparticles with a fair control over their size without using any additional reducing agent. These silver nanoparticles undergo reversible agglomeration to form protein-silver nanoparticle composite agglomerates as pH approaches to the isoelectric point of casein protein (pI=4.6). These agglomerates can then easily be re-dispersed in alkaline aqueous media with no obvious change in their optical properties. The nanoparticles can withstand high salt concentration (~0.5M), and can also be freeze-dried, stored as dry powder and then dispersed in aqueous media whenever required. More interestingly, by controlling the concentration of casein protein and pH, it was also possible to control the self-assembly of silver nanoparticles to produce fairly uniform spherical agglomerates.



Synthesis of Nanoparticles by Microorganisms

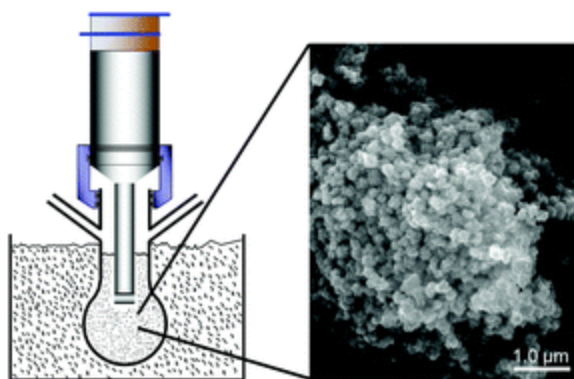
The development of eco-friendly technologies in material synthesis is of considerable importance to expand their biological applications. Nowadays, a variety of inorganic nanoparticles with well-defined chemical composition, size, and morphology have been synthesized by using different microorganisms, and their applications in many cutting-edge technological areas have been explored. This paper highlights the recent developments of the biosynthesis of inorganic nanoparticles including metallic nanoparticles, oxide nanoparticles, sulfide nanoparticles, and other typical nanoparticles. The applications of these biosynthesized nanoparticles in a wide spectrum of potential areas are presented including targeted drug delivery, cancer treatment, gene therapy and DNA analysis, antibacterial agents, biosensors, enhancing reaction rates, separation science, and magnetic resonance imaging (MRI).



Sonochemical synthesis of nanomaterials

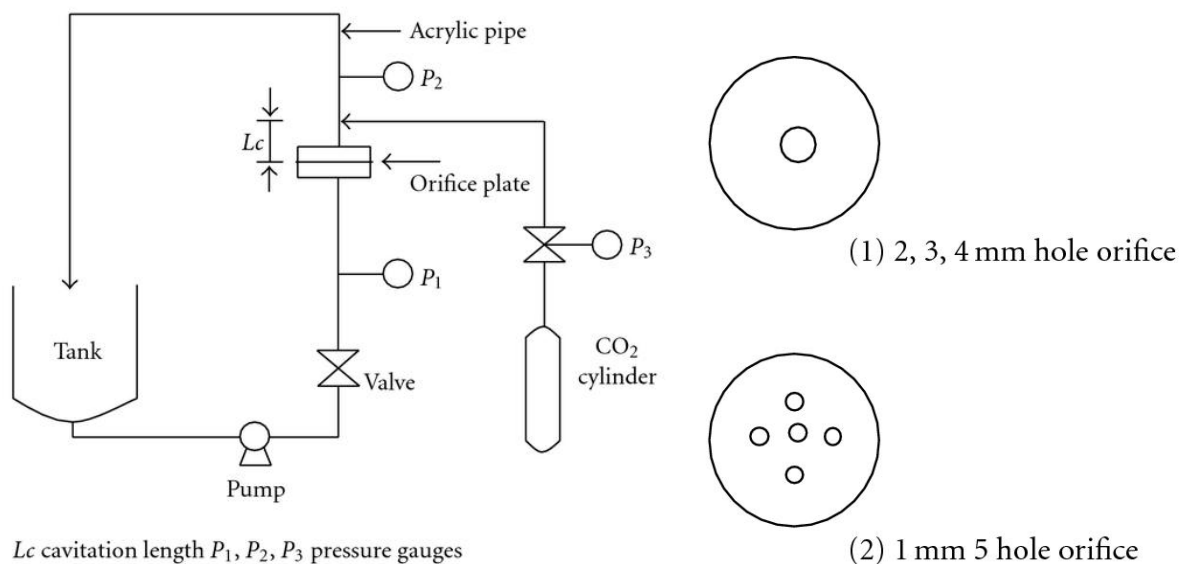
High intensity ultrasound can be used for the production of novel materials and provides an unusual route to known materials without bulk high temperatures, high pressures, or long reaction times. Several phenomena are responsible for sonochemistry and specifically the production or modification of nanomaterials during ultrasonic irradiation. The most notable effects are consequences of acoustic cavitation (the formation, growth, and implosive collapse of bubbles), and can be categorized as primary sonochemistry (gas-phase chemistry occurring inside collapsing bubbles),

secondary sonochemistry (solution-phase chemistry occurring outside the bubbles), and physical modifications (caused by high-speed jets or shock waves derived from bubble collapse).



Hydrodynamic Cavitation

A systematic study was made on the synthesis of nanocalcite using a hydrodynamic cavitation reactor. The effects of various parameters such as diameter and geometry of orifice, CO_2 flow rate, and $\text{Ca}(\text{OH})_2$ concentration were investigated. It was observed that the orifice diameter and its geometry had significant effect on the carbonation process. The reaction rate was significantly faster than that observed in a conventional carbonation process. The particle size was significantly affected by the reactor geometry. The results showed that an orifice with 5 holes of 1 mm size resulted in the particle size reduction to 37 nm.



Titanium dioxide nanoparticles

Titanium dioxide nanoparticles, also called ultrafine titanium dioxide or nanocrystalline titanium dioxide or microcrystalline titanium dioxide, are particles of titanium dioxide (TiO_2) with diameters less than 100 nm. Ultrafine TiO_2 is used in sunscreens due to its ability to block UV radiation while remaining transparent on the skin. It is in rutile crystal structure and coated with silica or/and alumina to prevent photocatalytic phenomena. The health risks of ultrafine

TiO₂ from dermal exposure on intact skin are considered extremely low^[1], and it is considered safer than other substances used for UV protection.

Nanosized particles of titanium dioxide tend to form in the metastable anatase phase, due to the lower surface energy of this phase, relative to the equilibrium rutile phase^[2]. Surfaces of ultrafine titanium dioxide in the anatase structure have photocatalytic sterilizing properties, which make it useful as an additive in construction materials, for example in antifogging coatings and self-cleaning windows.

Properties

Of the three common TiO₂ polymorphs (crystal forms), TiO₂ nanoparticles are produced in the rutile and anatase forms. Unlike larger TiO₂ particles, TiO₂ nanoparticles are transparent rather than white. Ultraviolet (UV) absorption characteristics are dependent from the crystal size of titanium dioxide and ultrafine particles has strong absorption against both UV-A (320-400 nm) and UV-B (280-320 nm) radiation^[3]. Light absorption in the UV occurs because of the presence of strongly bound excitons^[4]. The wavefunction of these excitons has a two-dimensional character and extends on the {001} plane.

TiO₂ nanoparticles have photocatalytic activity^{[5]:82[6]} It is n-type semiconductor and its band gap between the valence and the conductivity bands is wider than of many other substances. The photocatalysis of TiO₂ is a complex function of the physical characteristics of the particles. Doping TiO₂ with certain atoms its photocatalytic activity could be enhanced.^[7] In contrast, pigment-grade TiO₂ usually has a median particle size in the 200–300 nm range.^{[5]:1–2} Because TiO₂ powders contain a range of sizes, they may have a fraction of nanoscale particles even if the average particle size is larger.^[8] In turn ultrafine particles usually form agglomerates and particle size could be much larger than crystal size.

Synthesis

Most manufactured nanoscale titanium dioxide is synthesized by the sulfate process, the chloride process or the sol-gel process.^[9] In the sulfate process, anatase or rutile TiO₂ is produced by digesting ilmenite (FeTiO₃) or titanium slag with sulfuric acid. Ultrafine anatase form is precipitated from sulfate solution and ultrafine rutile from chloride solution. In the chloride process, natural or synthetic rutile is chlorinated at temperatures of 850–1000 °C, and the titanium tetrachloride is converted to the ultrafine anatase form by vapor-phase oxidation.^{[5]:1–2}

It is not possible to convert pigmentary TiO₂ to ultrafine TiO₂ by grinding. Ultrafine titanium dioxide could be obtained by different kind of processes as precipitation method, gas-phase reaktion, sol-gel method, and atomic layer deposition method.

Uses

Ultrafine TiO₂ is believed to be one of the three most produced nanomaterials, along with silicon dioxide nanoparticles and zinc oxide nanoparticles.^{[8][10][11]} It is the second most advertised nanomaterial in consumer products, behind silver nanoparticles.^[12] Due to its long use as a commodity chemical, TiO₂ can be considered a "legacy nanomaterial."^{[13][14]}

Ultrafine TiO₂ is used in sunscreens due to its ability to block UV radiation while remaining transparent on the skin.^[15] TiO₂ particles used in sunscreens typically have sizes in the range 5–50 nm.^[3]

Ultrafine TiO₂ is used in housing and construction as an additive to paints, plastics, cements, windows, tiles, and other products for its UV absorption and photocatalytic sterilizing properties, for example in antifogging coatings and self-cleaning windows.^[6] Engineered TiO₂ nanoparticles are also used in light-emitting diodes and solar cells.^{[5]:82} In addition, the photocatalytic activity of TiO₂ can be used to decompose organic compounds in wastewater.^[3] TiO₂ nanoparticle products are sometimes coated with silica or alumina, or doped with another metal for specific applications.^{[5]:2[9]}

Zinc Oxide Nanoparticles

Zinc oxide nanoparticles are nanoparticles of zinc oxide (ZnO) that have diameters less than 100 nanometers. They have a large surface area relative to their size and high catalytic activity. The exact physical and chemical properties of zinc oxide nanoparticles depend on the different ways they are synthesized. Some possible ways to produce ZnO nano-particles are laser ablation, hydrothermal methods, electrochemical depositions, sol–gel method, chemical vapor deposition, thermal decomposition, combustion methods, ultrasound, microwave-assisted combustion method, two-step mechanochemical–thermal synthesis, anodization, coprecipitation, electrophoretic deposition, and precipitation processes using solution concentration, pH, and washing medium. ZnO is a wide-bandgap semiconductor with an energy gap of 3.37 eV at room temperature.^[1]

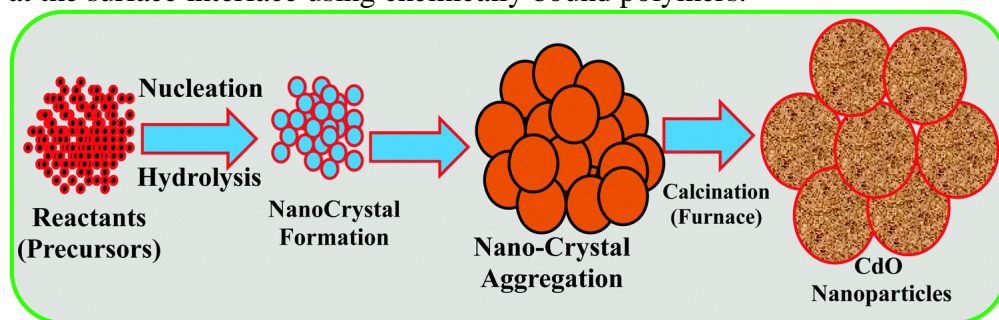
ZnO nanoparticles are believed to be one of the three most produced nanomaterials, along with titanium dioxide nanoparticles and silicon dioxide nanoparticles.^{[2][3][4]} The most common use of ZnO nanoparticles is in sunscreen. They are used because they reflect ultraviolet light, but are small enough to be transparent to visible light.^[5] They are also being investigated to kill harmful microorganisms in packaging,^[6] and in UV-protective materials such as textiles.^[7] Many companies do not label products that contain nanoparticles, making it difficult to make statements about production and pervasiveness in consumer products.^[8]

Since ZnO nanoparticles are a relatively new material, there is concern over the potential hazards they can cause. Because they are very tiny, nanoparticles generally can travel throughout the body, and have been shown in animal studies to penetrate the placenta, blood–brain barrier, individual cells, and their nuclei. Tissues can absorb them easily due to their size which makes it difficult to detect them. However, human skin is an effective barrier to ZnO nanoparticles, for example when used as a sunscreen, unless abrasions occur. ZnO nanoparticles may enter the system from accidental ingestion of small quantities when putting on sunscreen. When sunscreen is washed off, the ZnO nanoparticles can leach into runoff water and travel up the food chain. As of 2011 there were no known human illnesses resulting from any engineered nanoparticles.^[5]

Cadmium Oxide Nanoparticles

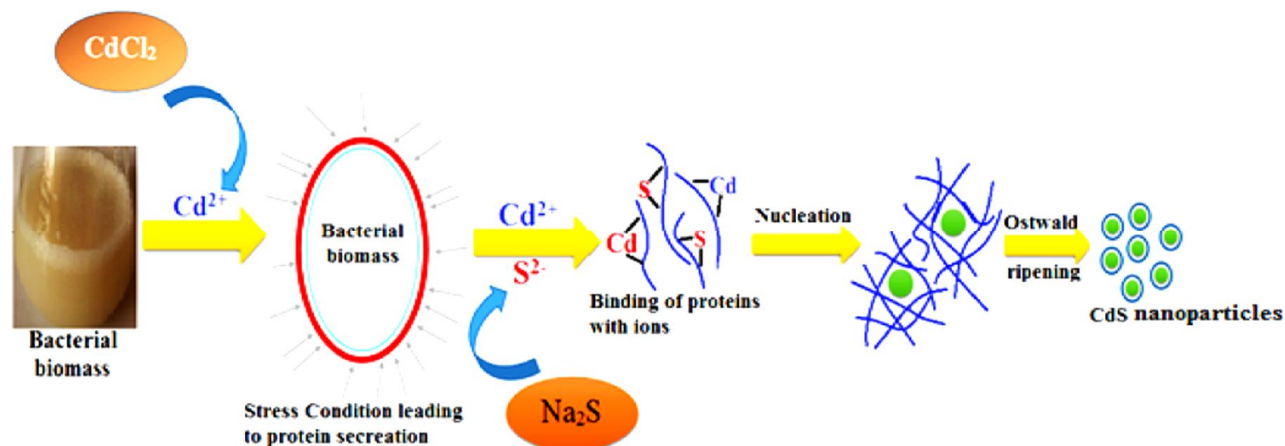
Cadmium Oxide (CdO) Nanopowder or Nanoparticles, nanodots or nanocrystals are spherical or faceted high surface area oxide magnetic nanostructured particles. Nanoscale Cadmium Oxide Particles are typically 20-80 nanometers (nm) with specific surface area (SSA)

in the 10 - 50 m²/g range and also available with an average particle size of 100 nm range with a specific surface area of approximately 7- 10 m²/g. Nano Cadmium Oxide Particles are also available in ultra high purity and high purity, transparent, and coated and dispersed forms. They are also available as a dispersion through the AE Nanofluid production group. Nanofluids are generally defined as suspended nanoparticles in solution either using surfactant or surface charge technology. Nanofluid dispersion and coating selection technical guidance is also available. Other nanostructures include nanorods, nanowhiskers, nanohorns, nanopyramids and other nanocomposites. Surface functionalized nanoparticles allow for the particles to be preferentially adsorbed at the surface interface using chemically bound polymers.



CdS Nanomaterials

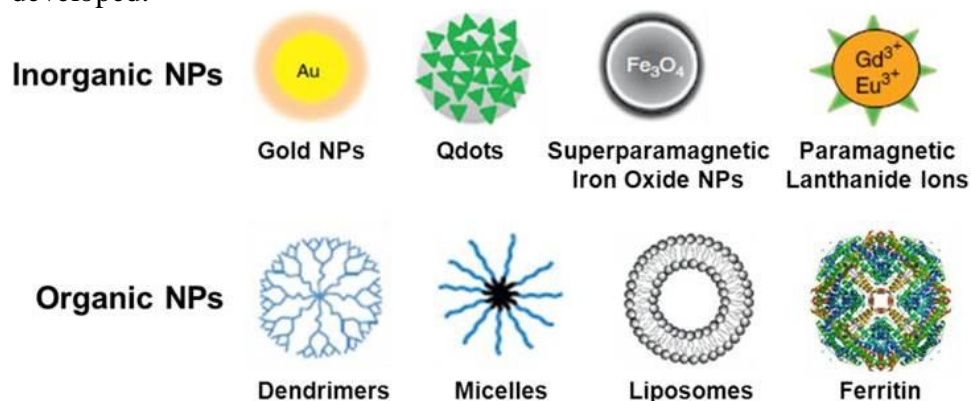
The CdS nanoparticles of different sizes are synthesized by a simple chemical method. Here, CdS nanoparticles are grown through the reaction of solution of different concentration of CdCl₂ with H₂S. X-ray diffraction pattern confirms nano nature of CdS and has been used to determine the size of particle. Optical absorption spectroscopy is used to measure the energy band gap of these nanomaterials by using Tauc relation. Energy band gap ranging between 3.12 eV to 2.47 eV have been obtained for the samples containing the nanoparticles in the range of 2.3 to 6.0 nm size.



Organic Nanomaterials

There is a growing interest in the development of organic nanomaterials for biomedical applications. An increasing number of studies focus on the uses of nanomaterials with organic structure for regeneration of bone, cartilage, skin or dental tissues. Solid evidence has been found for several advantages of using natural or synthetic organic nanostructures in a wide variety of

dental fields, from implantology, endodontics, and periodontics, to regenerative dentistry and wound healing. Most of the research is concentrated on nanoforms of chitosan, silk fibroin, synthetic polymers or their combinations, but new nanocomposites are constantly being developed.



Discover a new generation of organic nanomaterials and their applications Recent developments in nanoscience and nanotechnology have given rise to a new generation of functional organic nanomaterials with controlled morphology and well-defined properties, which enable a broad range of useful applications.

The main groups of organic nanocarriers are liposomes, micelles, protein/peptide based and dendrimers. Protein/peptide based nanocarriers are amorphous (non-crystalline) materials generally conjugated to the therapeutic agent and is often further functionalised with other molecules. Micelles and liposomes are formed by amphiphilic (both hydrophilic and hydrophobic parts), micelles form monolayers whereas liposomes form bilayers. Lastly, dendrimer nanocarriers are tree-like structures which have a starting atom core (eg. nitrogen) and other elements are added through a series of chemical reactions resulting in a spherical branching structure. This final structure is not unlike blood hemoglobin and albumin macromolecules.

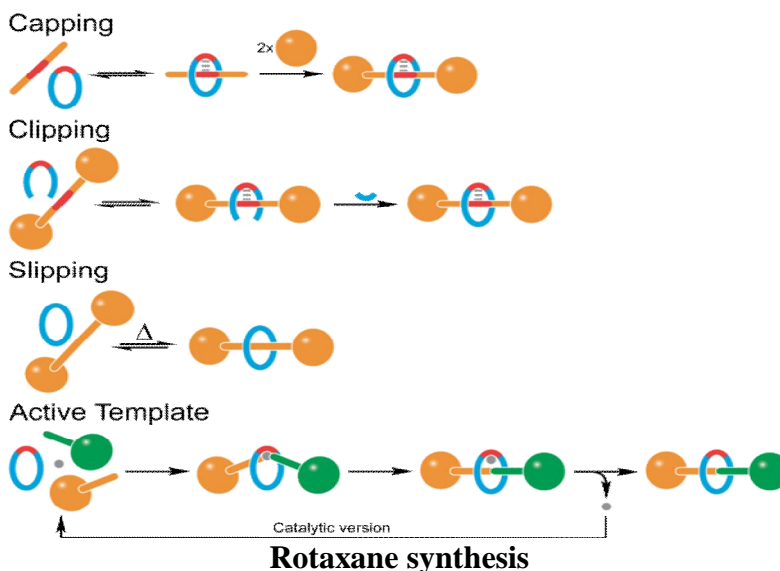
These vesicular nanocarriers can be used to trap both hydrophobic and hydrophilic drugs and even small nanoparticles inside the aqueous/lipid core. This provides protection for drugs and facilitates significant drug loading – minimising toxicity and increasing blood circulation time (increasing possibility that the drug will reach the therapeutic target from avoiding opsonisation).

Rotaxane

A rotaxane is a mechanically interlocked molecular architecture consisting of a "dumbbell shaped molecule" which is threaded through a "macrocycle" (see graphical representation). The name is derived from the Latin for wheel (rota) and axle (axis). The two components of a rotaxane are kinetically trapped since the ends of the dumbbell (often called stoppers) are larger than the internal diameter of the ring and prevent dissociation (unthreading) of the components since this would require significant distortion of the covalent bonds.

Much of the research concerning rotaxanes and other mechanically interlocked molecular architectures, such as catenanes, has been focused on their efficient synthesis or their utilization

as artificial molecular machines. However, examples of rotaxane substructure have been found in naturally occurring peptides, including: cystine knot peptides, cyclotides or lasso-peptides such as microcin J25.



Potential applications

Molecular machines

Rotaxane-based molecular machines have been of initial interest for their potential use in molecular electronics as logic molecular switching elements and as molecular shuttles.^{[12][13]} These molecular machines are usually based on the movement of the macrocycle on the dumbbell. The macrocycle can rotate around the axis of the dumbbell like a wheel and axle or it can slide along its axis from one site to another. Controlling the position of the macrocycle allows the rotaxane to function as a molecular switch, with each possible location of the macrocycle corresponding to a different state. These rotaxane machines can be manipulated both by chemical^[14] and photochemical inputs.^[15] Rotaxane based systems have also been shown to function as molecular muscles.^{[16][17]} In 2009, there was a report of a "domino effect" from one extremity to the other in a Glycorotaxane Molecular Machine. In this case, the ⁴C₁ or ¹C₄ chair-like conformation of the mannopyranoside stopper can be controlled, depending on the localization of the macrocycle.^[18] In 2012, unique pseudo-macrocycles consisting of double-lasso molecular machines (also called rotamacrocycles) were reported in Chem. Sci. These structures can be tightened or loosened depending on pH. A controllable jump rope movement was also observed in these new molecular machines.^[19]

Ultrastable dyes

Potential application as long-lasting dyes is based on the enhanced stability of the inner portion of the dumbbell-shaped molecule.^{[20][21]} Studies with cyclodextrin-protected rotaxane azo dyes established this characteristic. More reactive squaraine dyes have also been shown to have enhanced stability by preventing nucleophilic attack of the inner squaraine moiety.^[22] The enhanced stability of rotaxane dyes is attributed to the insulating effect of the macrocycle, which is able to block interactions with other molecules.

Nanorecording

In a nanorecording application,^[23] a certain rotaxane is deposited as a Langmuir–Blodgett film on ITO-coated glass. When a positive voltage is applied with the tip of a scanning tunneling microscope probe, the rotaxane rings in the tip area switch to a different part of the dumbbell and the resulting new conformation makes the molecules stick out 0.3 nanometer from the surface. This height difference is sufficient for a memory dot. It is not yet known how to erase such a nanorecording film.

Catenane

A catenane is a mechanically-interlocked molecular architecture consisting of two or more interlocked macrocycles, i.e. a molecule containing two or more intertwined rings. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles. Catenane is derived from the Latin *catena* meaning "chain". They are conceptually related to other mechanically interlocked molecular architectures, such as rotaxanes, molecular knots or molecular Borromean rings. Recently the terminology "mechanical bond" has been coined that describes the connection between the macrocycles of a catenane. Catenanes have been synthesised in two different ways: statistical synthesis and template-directed synthesis.

Synthesis

There are two primary approaches to the organic synthesis of catenanes. The first is to simply perform a ring-closing reaction with the hope that some of the rings will form around other rings giving the desired catenane product. This so-called "statistical approach" led to the first successful synthesis of a catenane; however, the method is highly inefficient, requiring high dilution of the "closing" ring and a large excess of the pre-formed ring, and is rarely used.

The second approach relies on supramolecular preorganization of the macrocyclic precursors utilizing hydrogen bonding, metal coordination, hydrophobic effect, or coulombic interactions. These non-covalent interactions offset some of the entropic cost of association and help position the components to form the desired catenane upon the final ring-closing. This "template-directed" approach, together with the use of high-pressure conditions, can provide yields of over 90%, thus improving the potential of catenanes for applications. An example of this approach used bis-bipyridinium salts which form strong complexes threaded through crown ether bis(*para*-phenylene)-34-crown-10.^[3]

Template directed syntheses are mostly performed under kinetic control, when the macrocyclization (catenation) reaction is irreversible. More recently, the groups of Sanders and Otto have shown that dynamic combinatorial approaches using reversible chemistry can be particularly successful in preparing new catenanes of unpredictable structure.^[4] The thermodynamically controlled synthesis provides an error correction mechanism; even if a macrocycle closes without forming a catenane it can re-open and yield the desired interlocked structure later. The approach also provides information on the affinity constants between different macrocycles thanks to the equilibrium between the individual components and the catenanes, allowing a titration-like experiment.^[5]

Properties and applications

A particularly interesting property of many catenanes is the ability of the rings to rotate with respect to one another. This motion can often be detected and measured by NMR spectroscopy, among other methods. When molecular recognition motifs exist in the finished catenane (usually those that were used to synthesize the catenane), the catenane can have one or more thermodynamically preferred positions of the rings with respect to each other (recognition sites). In the case where one recognition site is a switchable moiety, a mechanical molecular switch results. When a catenane is synthesized by coordination of the macrocycles around a metal ion, then removal and re-insertion of the metal ion can switch the free motion of the rings on and off.

If there are more than one recognition sites it is possible to observe different colors depending on the recognition site the ring occupies and thus it is possible to change the color of the catenane solution by changing the preferred recognition site.^[6] Switching between the two sites may be achieved by the use of chemical, electrochemical or even visible light based methods.

Catenanes have been synthesized incorporating many functional units, including redox-active groups (e.g. viologen, TTF=tetrathiafulvalene), photoisomerizable groups (e.g. azobenzene), fluorescent groups and chiral groups.^[7] Some such units have been used to create molecular switches as described above, as well as for the fabrication of molecular electronic devices and molecular sensors.