SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
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School of Science and Humanities

Department of Physics

UNIT 1-Introduction about Nano Materials-SPHA7404

SPHA7404	NANO MATERIALS AND APPLICATIONS	L	T	P	Credits	Total Marks
		3	0	0	3	100

COURSE OBJECTIVE

- To provide the fundamental knowledge of nano materials, their synthesis and fabrication, properties and applications. Also to motivate the students to pursue research in the field of nanomaterials.

UNIT 1 INTRODUCTION ABOUT NANO MATERIALS 12 Hrs.

Classification of Nano structured materials – Present and potential with significant technological impact – Industrial in nano materials – Fullerenes and nano tubes – Metals and inorganic – Fundamental issues in nano materials.

UNIT 2 NANO MATERIALS SYNTHESIS AND PROCESSING 12 Hrs.

Mechanical grinding – Wet chemical synthesis if nano materials – Sol-gel process – Liquid solid reactions – Gas phase synthesis of nano materials – Gas condensation processing (GPC) – Chemical vapour condensation (CVC) – cold plasma methods–Plasma CVD – Sputtered plasma processing – Microwave plasma processing – Laser ablation – vapour liquid – solid growth – Particle precipitation aided CVD – gas phase synthesis method.

UNIT 3 SYNTHESIS METHODS OF NANO COMPOSITES 12 Hrs.

Bio-metic process – film – printing mechanism nano particles – dispersion of nano particles – stabilization of nano particles – application of nano materials.

UNIT 4 MECHANICAL PROPERTIES 12 Hrs.

Ceramics – Strengthening and toughening mechanism – reduction in processing flow size – R-curve effects – crack deflection – Thermal expansion mismatch – Average internal stresses – local stress distribution.

UNIT 5 OPTICAL PROPERTIES 12 Hrs.

Classical optics – absorption of light in materials – Electronic absorption – lattice absorption – phonons radiative and non-radiative recombination – dynamic Maxwell – garnet equation – application of laser crystals – electrical rectification – powder laser.

Course Outcomes:

Upon successful completion of this course, students should be able to:

CO1: Understand the fundamental of nanomaterials and their applications.
CO2: Synthesize nanomaterials using various physical and chemical methods.
CO3: Prepare nanocomposites and study their potential applications.
CO4: Understand the mechanical properties of nanomaterials.
CO5: Acquire knowledge on the optical properties of nanomaterials.

INTRODUCTION TO NANOMATERIALS

1. Introduction

Nanomaterials are cornerstones of nanoscience and nanotechnology. 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. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

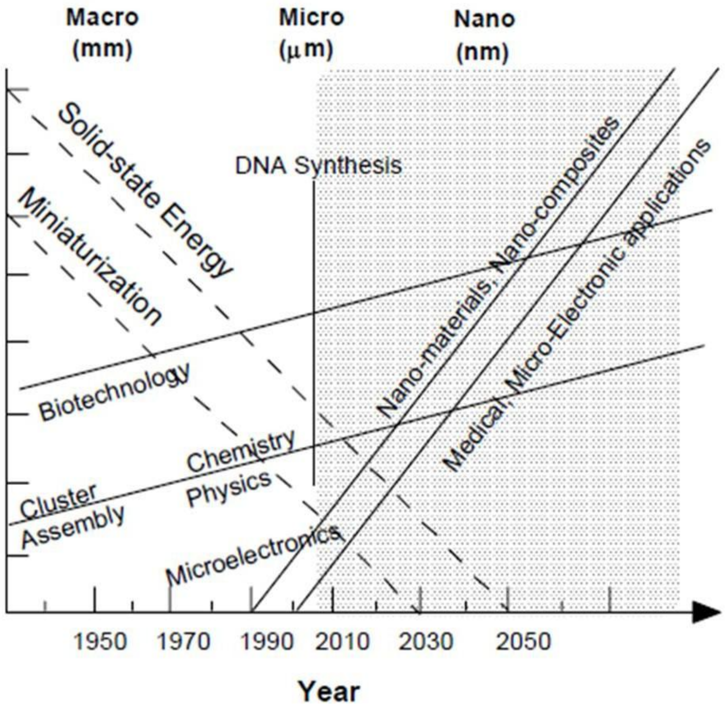


Fig. 1.1. Evolution of science and technology and the future

1.1. What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Fig. 1.2. Nanomaterial (For example: Carbon nanotube)

1.2. Where are nanomaterials found?

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.

Engineered nanomaterials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. 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.

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites 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 butyl-rubber/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.

1.3 Advances in Nanomaterials

The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans. The scientific story of nanomaterials however began much later. One of the first scientific report is the colloidal gold particles synthesised by Michael Faraday as early as 1857. 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.

Nanosized amorphous silica particles have found large-scale applications in many every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibers and catalyst supports. In the 1960s and 1970's 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 biocorrosion 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 superlattice 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 superlattice are present, as has been shown by the fabrication of synthetic samples.

Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials 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. e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

1.4 Classification of Nanomaterials

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).

According to Siegel, Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

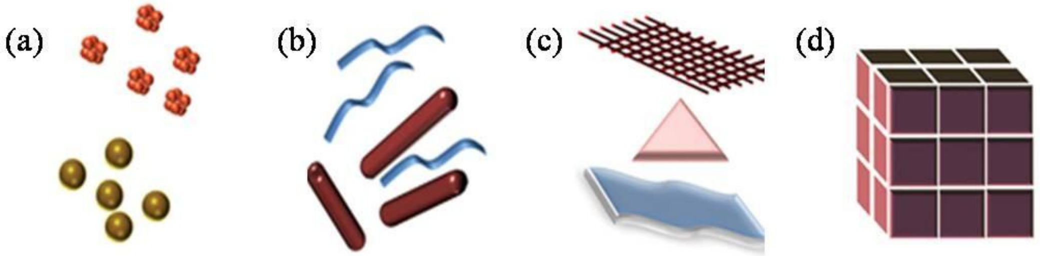


Fig. 1.3. Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

Nanomaterials are materials which are characterized by an ultra fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayers), two (ultrafine-grained overlayers or buried layers), and three (nanophase materials consisting of equiaxed nanometer sized grains) as shown in the above figure 3.

1.5 Why are nanomaterials important?

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

(i) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

(ii) Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

(iii) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

(iv) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

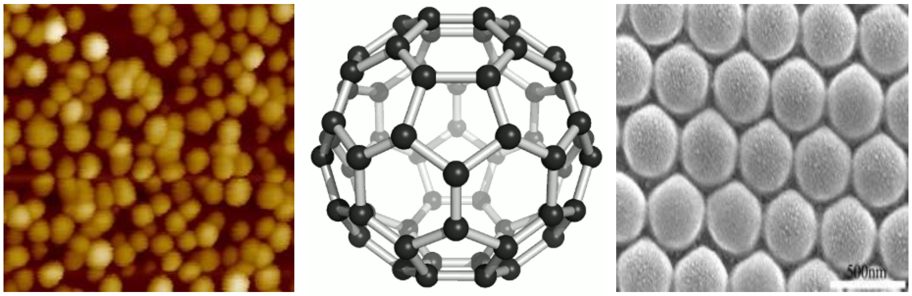
(v) Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantio selective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.

(vi) Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NOx, CO, CO2, CH4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO2) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

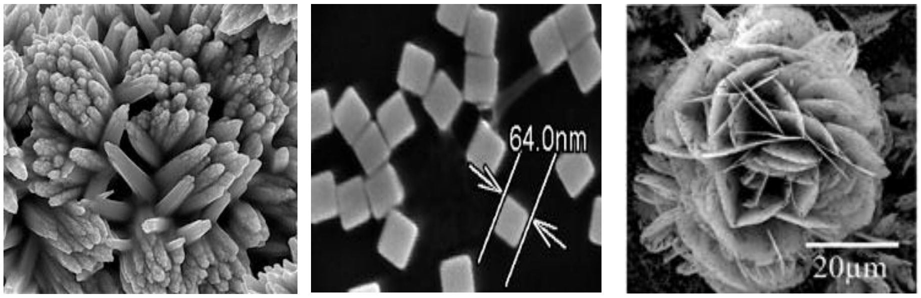
(vii) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

1.6 Examples of Nanomaterials

Nanomaterials (gold, carbon, metals, meta oxides and alloys) with variety of morphologies (shapes) are depicted in Fig. 4.



Au nanoparticle Buckminsterfullerene FePt nanosphere



Titanium nanoflower Silver nanocubes SnO2 nanoflower

Fig 1.4. Nanomaterials with a variety of morphologies

1.7 Present and potential with significant technological impact

The impact of nanotechnology extends from its medical, ethical, mental, legal and environmental applications, to fields such as engineering, biology, chemistry, computing, materials science, and communications.

Major benefits of nanotechnology include improved manufacturing methods, water purification systems, energy systems, physical enhancement, nanomedicine, better food production methods, nutrition and large-scale infrastructure auto-fabrication. Nanotechnology's reduced size may allow for automation of tasks which were previously inaccessible due to physical restrictions, which in turn may reduce labor, land, or maintenance requirements placed on humans.

(i)Health impact

The health impacts of nanotechnology are the possible effects that the use of nanotechnological materials and devices will have on human health. As nanotechnology is an emerging field, there is great debate regarding to what extent nanotechnology will benefit or pose risks for human health. Nanotechnology's health impacts can be split into two aspects: the potential for nanotechnological innovations to have medical applications to cure disease, and the potential health hazards posed by exposure to nanomaterials.

In regards to the current global pandemic, researchers, engineers and medical professionals are using an extremely developed collection of nano science and nanotechnology approaches to explore the ways it could potentially help the medical, technical, and scientific communities to help fight the pandemic.

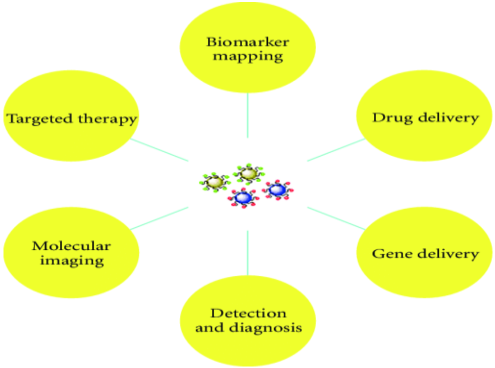


Fig 1.5. Multi directional applications of Nano medicine

(ii) Environmental Impact

The environmental impact of nanotechnology is the possible effects that the use of nanotechnological materials and devices will have on the environment. As nanotechnology is an emerging field, there is debate regarding to what extent industrial and commercial use of nanomaterials will affect organisms and ecosystems.

Nanotechnology's environmental impact can be split into two aspects: the potential for nanotechnological innovations to help improve the environment, and the possibly novel type of pollution that nanotechnological materials might cause if released into the environment.

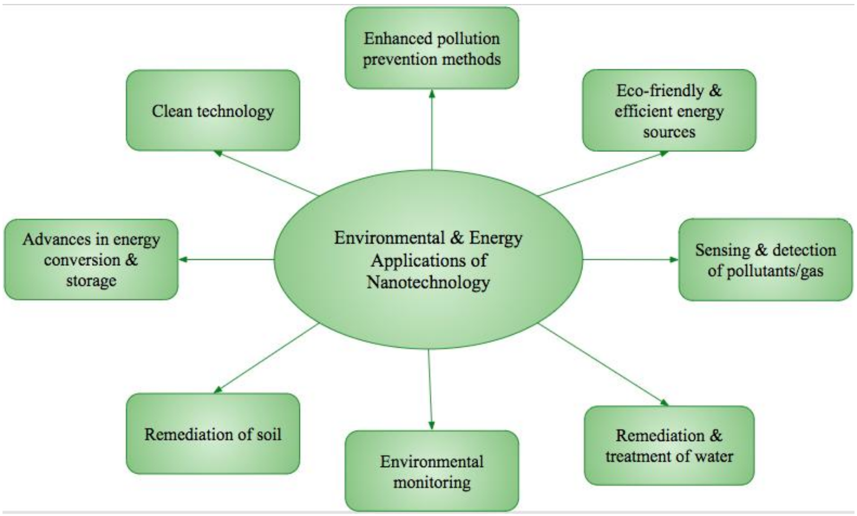


Fig 1.6 Multi directional Environmental applications of nano particle

(iii) Social Impact

Beyond the toxicity risks to human health and the environment which are associated with first-generation nanomaterials, nanotechnology has broader societal impact and poses broader social challenges. Social scientists have suggested that nanotechnology's social issues should be understood and assessed not simply as "downstream" risks or impacts. Rather, the challenges should be factored into "upstream" research and decision-making in order to ensure technology development that meets social objectives.

Societal impact is how institutions, organization, businesses or individuals actions affect the surrounding society. The social implications of any new technology can be felt by people directly incorporated with organization or individual or people in different societies and countries.

The societal impacts of new technologies are easy to identify but hard to measure or predict. Nanotechnology will have significant social impacts in the areas of military applications, intellectual property issues, as well as having an effect on labor and the balance between citizens and governments.

Fig 1.7 Multi directional societal applications of nano particle

1.8 Industrial in nano materials

Nanotechnology is impacting the field of consumer goods, several products that incorporate nanomaterials are already in a variety of items; many of which people do not even realize contain nanoparticles, products with novel functions ranging from easy-to-clean to scratch-resistant. Examples of those car bumpers are made lighter, clothing is more stain repellant, sunscreen is more radiation resistant, synthetic bones are stronger, cell phone screens are lighter weight, glass packaging for drinks leads to a longer shelf-life, and balls for various sports are made more durable. Using nanotech, in the mid-term modern textiles will become "smart", through embedded "wearable electronics", such novel products have also a promising potential especially in the field of cosmetics, and has numerous potential applications in heavy industry. Nanotechnology is predicted to be a main driver of technology and business in this century and holds the promise of higher performance materials, intelligent systems and new production methods with significant impact for all aspects of society.

(i) Food:

A complex set of engineering and scientific challenges in the food and bioprocessing industry for manufacturing high quality and safe food through efficient and sustainable means can be solved through nanotechnology. Bacteria identification and food quality monitoring using biosensors; intelligent, active, and smart food packaging systems; nanoencapsulation of bioactive food compounds are few examples of emerging applications of nanotechnology for the food industry. Nanotechnology can be applied in the production, processing, safety and packaging of food. A nanocomposite coating process could improve food packaging by placing anti-microbial agents directly on the surface of the coated film. Nanocomposites could increase or decrease gas permeability of different fillers as is needed for different products. They can also improve the mechanical and heat-resistance properties and lower the oxygen transmission rate. Research is being performed to apply nanotechnology to the detection of chemical and biological substances for sensanges in foods.

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Nano-foods

New foods are among the nanotechnology-created consumer products coming onto the market at the rate of 3 to 4 per week, according to the Project on Emerging Nanotechnologies (PEN), based on an inventory it has drawn up of 609 known or claimed nano-products. On PEN's list are three foods—a brand of canola cooking oil called Canola Active Oil, a tea called Nanotea and a chocolate diet shake called Nanoceuticals Slim Shake Chocolate. According to company information posted on PEN's Web site, the canola oil, by Shemen Industries of Israel, contains an additive called "nanodrops" designed to carry vitamins, minerals and phytochemicals through the digestive system and urea[The shake, according to U.S. manufacturer RBC Life Sciences Inc., uses cocoa infused "NanoClusters" to enhance the taste and health benefits of cocoa without the need for extra sugar.

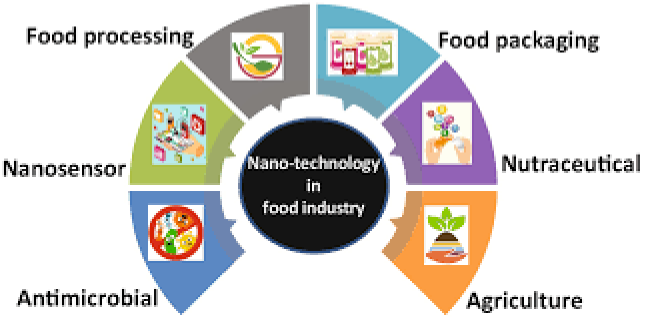


Fig 1.8 Nano materials uses in Food industry

(ii)Consumer goods

Surfaces and coatings

The most prominent application of nanotechnology in the household is self-cleaning or "easy-to-clean" surfaces on ceramics or glasses. Nanoceramic particles have improved the smoothness and heat resistance of common household equipment such as the flat iron.

The first sunglasses using protective and anti-reflective ultrathin polymer coatings are on the market. For optics, nanotechnology also offers scratch resistant surface coatings based on nanocomposites. Nano-optics could allow for an increase in precision of pupil repair and other types of laser eye surgery.

Textiles

The use of engineered nanofibers already makes clothes water- and stain-repellent or wrinkle-free. Textiles with a nanotechnological finish can be washed less frequently and at lower temperatures. Nanotechnology has been used to integrate tiny carbon particles membrane and guarantee full-surface protection from electrostatic charges for the wearer. Many other applications have been developed by research institutions such as the Textiles Nanotechnology Laboratory at Cornell University, and the UK's Dstl and its spin out company

Cosmetics

One field of application is in sunscreens. The traditional chemical UV protection approach suffers from its poor long-term stability. A sunscreen based on mineral nanoparticles such as titanium oxide offer several advantages. Titanium oxide nanoparticles have a comparable UV protection property as the bulk material, but lose the cosmetically undesirable whitening as the particle size is decreased

Sports

Nanotechnology may also play a role in sports such as soccer, football, and baseball. Materials for new athletic shoes may be made in order to make the shoe lighter (and the athlete faster). Baseball bats already on the market are made with carbon nanotubes that reinforce the resin, which is said to improve its performance by making it lighter.

Fig 1.9 Nano materials in consumer goods

(ii) Aerospace vehicle manufactures

Lighter and stronger materials will be of immense use to aircraft manufacturers, leading to increased performance. Spacecraft will also benefit, where weight is a major factor. Nanotechnology might thus help to reduce the size of equipment and thereby decrease fuel-consumption required to get it airborne. Hang gliders may be able to halve their weight while increasing their strength and toughness through the use of nanotech materials.

(iii) Catalysis

Chemical catalysis benefits especially from nanoparticles, due to the extremely large surface-to-volume ratio. The application potential of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photocatalytic devices. Catalysis is also important for the production of chemicals. For example, nanoparticles with a distinct chemical surrounding (ligands), or specific optical properties.

(iv) Construction

Nanotechnology has the potential to make construction faster, cheaper, safer, and more varied. Automation of nanotechnology construction can allow for the creation of structures from advanced homes to massive skyscrapers much more quickly and at much lower cost. In the near future, Nanotechnology can be used to sense cracks in foundations of architecture and can send nanobots to repair them.

Nanotechnology in construction involves using nanoparticles such as alumina and silica. Manufacturers are also investigating the methods of producing nano-cement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics, high strength composites and electronic applications.

1.9 Fullerenes and Nano tubes

The first fullerene was discovered by Harold Kroto, Richard Smalley and Robert Curl in 1985 by using a laser to vaporise graphite rods in an atmosphere of helium gas. The fullerenes (allotropes of carbon) are graphene sheets rolled into tubes or spheres. It is a cage like molecule composed of 60 carbon atoms (C60) joined together by single and double bonds to form a hollow sphere with 20 hexagonal and 12 pentagonal faces (a design that resembles a football). It was named as buckminsterfullerene or buckyball after the name of American architect Buckminster Fuller, the inventor of the geodesic dome. The structure of fullerene (C60) is shown in Fig. 10.

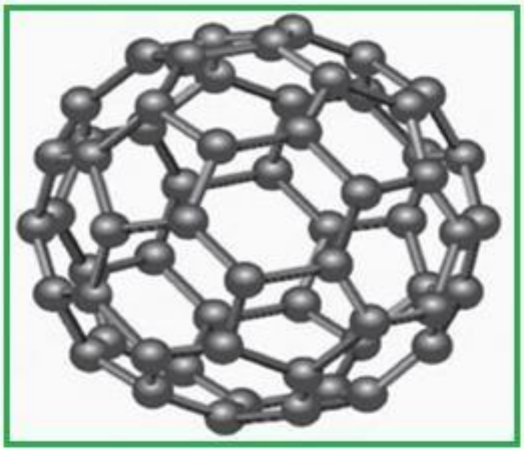


Fig. 1.10 Fullerene (C_{60})

Applications

The recent research has suggested that fullerence has many uses, including medical applications, superconductors, fiber-optics, etc. Some of the important applications are listed as follows:

- Fullerenes (C60) and their derivatives have potential antiviral activity, and may be used for the treatment of HIV-infection.
- They have potential medicinal applications as they can bind specific antibiotics and target certain types of cancer cells such as melanoma.
- They are used as biological antioxidants.
- They are also used as potential photosensitizers in photodynamic therapy and catalysts for hydrogenation.
- Fullerenes incorporated with sulphides of tungsten and molybdenum exhibit excellent solid-lubricant properties.

Nanotubes

The carbon nanotubes (elongated form of fullerenes) were identified in 1991 by Iijima Sumio of Japan. A carbon nanotube is a tube-shaped material, made up of carbon, having a diameter ranging from < 1 nm to 50 nm. Simply we can say, carbon nanotubes (CNTs) are cylinders of one or more layers of graphene (lattice). Carbon nanotubes show a unique combination of stiffness, strength, and tenacity compared to other fibre materials. Thermal and electrical conductivity are also very high as comparable to other conductive materials. Carbon nanotubes may be categorized as follows:

- **Single-wall nanotubes (SWNT):** These may be zigzag, armchair and chiral depending on the manner in which the grapheme sheets are rolled.
- **Multi-wall nanotubes (MWNT):** It consists of several single walled nanotubes with different diameters. A multi-wall nanotube is shown in Fig. 11.

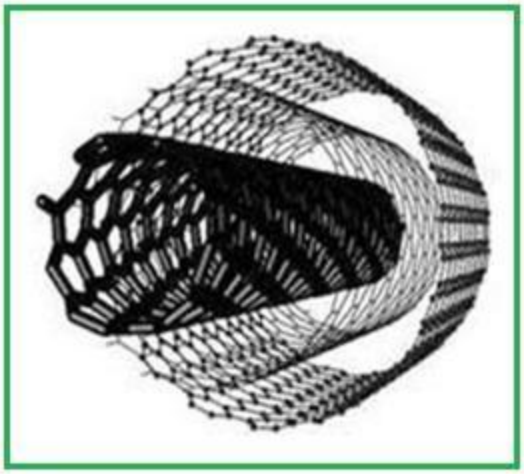


Fig.1.11: Multi-walled nanotube

Applications

Carbon nanotube technology can be used for a wide range of new and existing applications, which are as follows:

- Nanotubes can potentially replace indium tin oxide in solar cells to generate photocurrent.
- SWNTs are used in transistors and solar panels.

- MWNTs are used in lithium ion batteries to enhance cycle life.
- Parallel CNTs have been used to create loudspeakers.
- CNTs can serve as a multifunctional coating material.
- CNTs can be used to produce nanowires.
- CNTs are also used for applications in energy storage, automotive parts, boat hulls, water filters, thin-film electronics coatings, ultra-capacitors, biosensors for harmful gases, extra strong fibers, etc.

1.10. Metals and inorganic nanoparticle:

(i) Metal nanoparticle

Nanomaterials have unique properties due to their small dimensions (1–100 nm). ... The first category of nanomaterial comprises the pure form of metal-based nanoparticles, which are also called metal nanoparticles (e.g., silver, copper, gold, titanium, platinum, zinc, magnesium, iron)

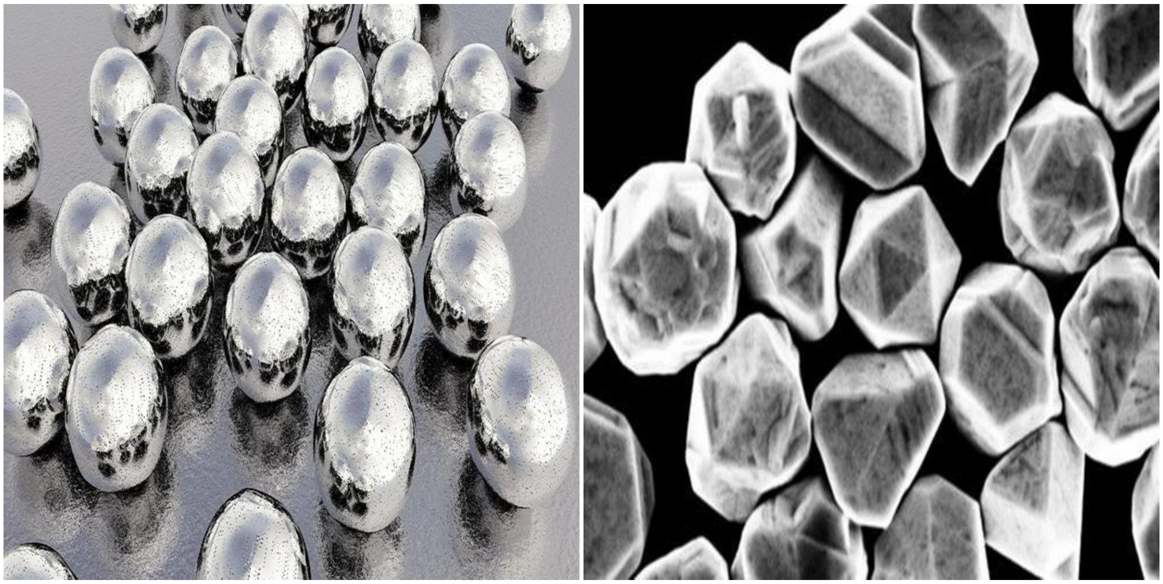


Fig. 12: Metal nano particle

- Metal nanoparticles are usually defined as particles of metal atoms with diameters between 1 nm and about a few hundreds of nanometers. Particles with sizes below 1 nm are classified as clusters.

- Metal nanoparticles possess unique electronic, optical, and chemical properties compared to the bulk metal
- These are metal based materials that we commonly regarded as quantum dots, nanogold, nanosilver and oxides with metal bases.
- Titanium dioxide is one such example.

Properties:

- Good mechanical strengths,
- high surface area,
- low melting point,
- Good optical properties & magnetic properties.
- Catalysts which are used in metallic nanoparticles are selective and highly active, has long lifetime for many chemical reactions.
- Noble metallic nanoparticles, such as AuNPs, AgNPs, PtNPs, offer high stability, easy chemical synthesis and tuneable surface functionalization.

Metal oxide nanoparticles

These metal oxide nanoparticles are chemically stable (have no adverse effects) and are used in a variety of different applications such as adsorption, photocatalytic activities, antibacterial and antifungal activities. Metal oxides are well-known materials for the sensor and biosensor applications.

Applications

Noble metal nanoparticles (Ag, Au, Pt) have been used for several biomedical applications such as anticancer, radiotherapy enhancement, drug delivery, thermal ablation, antibacterial, diagnostic assays, antifungal, gene delivery, and many others.

(ii) Inorganic nanomaterial

An inorganic nanomaterial (NM) can comprise a metal or non-metal element, or take the form of an oxide, hydroxide or phosphate compound. These materials are essential to our societies and find many applications, including in electronics, photonics, chemical sensors and biosensors, and biomedical devices.

Example: Gold nano, Quantum dots

Properties:

- non-toxic,
- hydrophilic,
- biocompatible and highly stable compared to organic materials
- Size, shape, specific surface area, aspect ratio.
- Agglomeration/aggregation state.
- Size distribution.
- Surface morphology/topography.
- Structure, including crystallinity and defect structure.
- Solubility.

1.11 . Fundamental issues in nano materials

Instability of the particles - Retaining the active metal nanoparticles is highly challenging, as the kinetics associated with nanomaterials is rapid. In order to retain nanosize of particles, they are encapsulated in some other matrix. Nanomaterials are thermodynamically metastable and lie in the region of high-energy local-minima. Hence they are prone to attack and undergo transformation. These include poor corrosion resistance, high solubility, and phase change of nanomaterials. This leads to deterioration in properties and retaining the structure becomes challenging.

Fine metal particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

Impurity - Because nanoparticles are highly reactive, they inherently interact with impurities as well. In addition, encapsulation of nanoparticles becomes necessary when they are synthesized in a solution (chemical route). The stabilization of nanoparticles occurs because of a non-reactive species engulfing the reactive nano-entities. Thereby, these secondary impurities become a part of the synthesized nanoparticles, and synthesis of pure nanoparticles becomes highly difficult. Formation of oxides, nitrides, etc can also get aggravated from the impure environment/ surrounding while synthesizing nanoparticles. Hence retaining high purity in nanoparticles can become a challenge hard to overcome.

Biologically harmful - Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominant owing to their high surface area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver/blood could also prove to be harmful.

Difficulty in synthesis, isolation and application - It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecule/material.

Hence free nanoparticles are hard to be utilized in isolation, and they have to be interacted for intended use via secondary means of exposure. Grain growth is inherently present in nanomateirals during their processing. The finer grains tend to merge and become bigger and stable grains at high temperatures and times of processing.

Recycling and disposal - There are no hard-and-fast safe disposal policies evolved for nanomaterials. Issues of their toxicity are still under question, and results of exposure experiments are not available. Hence the uncertainty associated with affects of nanomaterials is yet to be assessed in order to develop their disposal policies.

Unit 11-Nano Materials Synthesis and Processing-SPHA7404

2.Nanomaterial - synthesis and processing

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the 'bottom up' or the 'top down' approaches (Fig. 5) to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

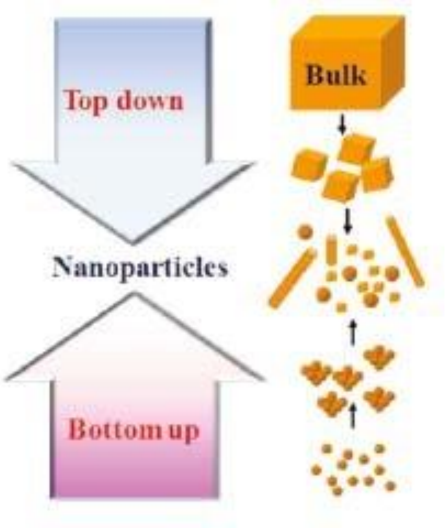


Fig. 2.1. Schematic illustration of the preparative methods of nanoparticles.

2.1Methods for creating nanostructures

There are many different ways of creating nanostructures: of course, macromolecules or nanoparticles or buckyballs 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.

2.1.1. Mechanical grinding

Mechanical attrition is a typical example of ‘top down’ method of synthesis of nanomaterials, where the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials. The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications. Similarly, the serious problems that are usually cited are;

1. contamination from milling media and/or atmosphere, and
2. to consolidate the powder product without coarsening the nanocrystalline microstructure.

In fact, the contamination problem is often given as a reason to dismiss the method, at least for some materials. Here we will review the mechanisms presently believed responsible for formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders, and mechanical crystallisation of amorphous materials. The two important problems of contamination and powder consolidation will be briefly considered.

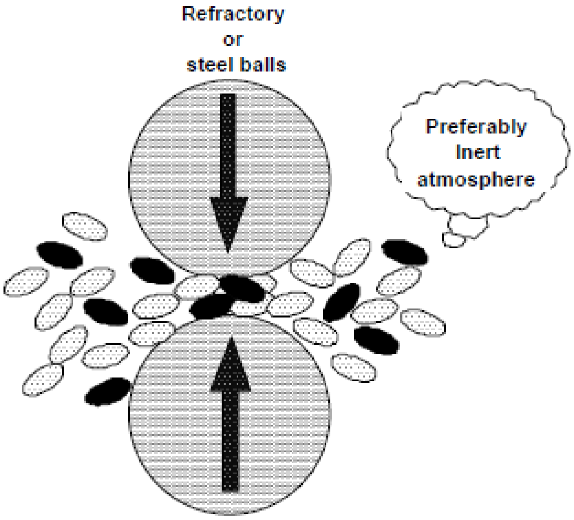


Fig. 2.2. Schematic representation of the principle of mechanical milling

Mechanical milling is typically achieved using high energy shaker, planetary ball, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanoparticles are produced by the shear action during grinding.

Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles be handled in an appropriate vacuum system or glove box. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed. Based on the energy of the milling process and thermodynamic properties of the constituents the alloy can be rendered amorphous by this processing.

2.1.2 Wet Chemical Synthesis of Nanomaterials

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

2.1.3 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. 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:

MOR + H_2O → MOH + ROH (hydrolysis) MOH
+ ROM → M-O-M + ROH (condensation)

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.

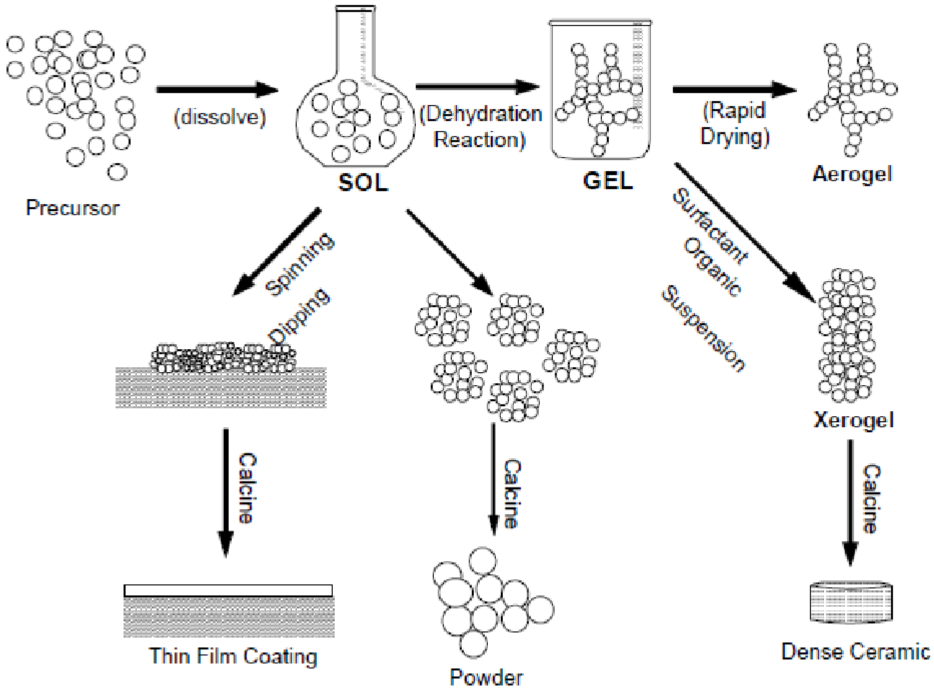


Fig. 2.3. Schematic representation of sol-gel process of synthesis of nanomaterials.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. 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 viscocity of the solution.
3. 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.

4. 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 super critical conditions, the product is an *aerogel*.
5. Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800^0C.
6. Densification and decomposition of the gels at high temperatures ($T>800^0$C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic 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.

2.1.4 Gas Phase synthesis of nanomaterials

The gas-phase synthesis methods are of increasing interest because they allow elegant way to control process parameters in order to be able to produce size, shape and chemical composition controlled nanostructures. Before we discuss a few selected pathways for gas-phase formation of nanomaterials, some general aspects of gas-phase synthesis needs to be discussed. In conventional chemical vapour deposition (CVD) synthesis, gaseous products either are allowed to react homogeneously or heterogeneously depending on a particular application.

1. In homogeneous CVD, particles form in the gas phase and diffuse towards a cold surface due to thermophoretic forces, and can either be scrapped of from the cold surface to give nano-powders, or deposited onto a substrate to yield what is called ***'particulate films'***.
2. In heterogeneous CVD, the solid is formed on the substrate surface, which catalyses the reaction and a dense film is formed.

In order to form nanomaterials several modified CVD methods have been developed. Gas phase processes have inherent advantages, some of which are noted here:

- An excellent control of size, shape, crystallinity and chemical composition
- Highly pure materials can be obtained
- Multicomonent systems are relatively easy to form
- Easy control of the reaction mechanisms

Most of the synthesis routes are based on the production of small clusters that can aggregate to form nano particles (condensation). Condensation occurs only when the vapour is supersaturated and in these processes homogeneous nucleation in the gas phase is utilised to form particles. This can be achieved both by physical and chemical methods.

a.Furnace

The simplest fashion to produce nanoparticles is by heating the desired material in a heat-resistant crucible containing the desired material. This method is appropriate only for materials that have a high vapour pressure at the heated temperatures that can be as high

as 2000°C. Energy is normally introduced into the precursor by arc heating, electron- beam heating or Joule heating. The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound). To carry out reactive synthesis, materials with very low vapour pressure have to be fed into the furnace in the form of a suitable precursor such as organometallics, which decompose in the furnace to produce a condensable material. The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. In case a compound is being synthesized, these precursors react in the gas phase and form a compound with the material that is separately injected in the reaction chamber. The clusters would continue to grow if they remain in the supersaturated region. To control their size, they need to be rapidly removed from the supersaturated environment by a carrier gas. The cluster size and its distribution are controlled by only three parameters:

1) the rate of evaporation (energy input),
2) the rate of condensation (energy removal), and
3) the rate of gas flow (cluster removal).

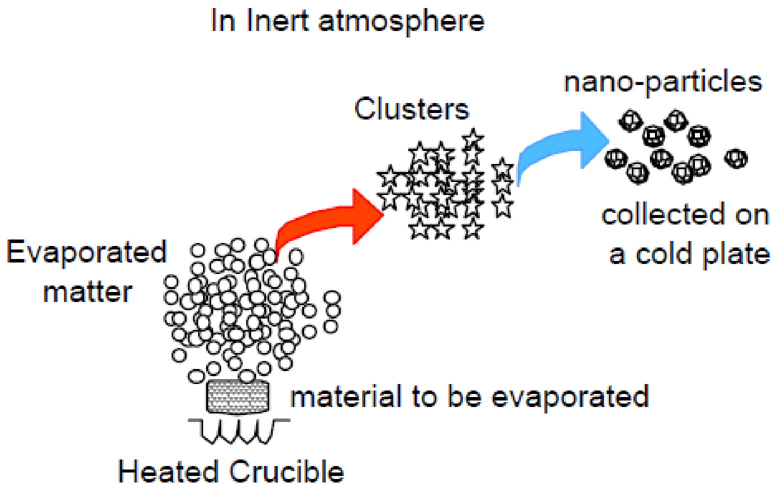


Fig. 2.4. Schematic representation of gas phase process of synthesis of single phase nanomaterials from a heated crucible

Because of its inherent simplicity, it is possible to scale up this process from laboratory (mg/day) to industrial scales (tons/day).

b.Flame assisted ultrasonic spray pyrolysis

In this process, precusrsors are nebulized and then unwanted components are burnt in a flame to get the required material, eg. ZrO_2 has been obtained by this method from a precursor of $Zr(CH_3\ CH_2\ CH_2O)_4$. Flame hydrolysis that is a variant of this process is used for the manufacture of fused silica. In the process, silicon tetrachloride is heated in an oxy-hydrogen flame to give a highly dispersed silica. The resulting white amorphous powder consists of spherical particles with sizes in the range 7-40 nm. The combustion flame synthesis, in which the burning of a gas mixture, e.g. acetylene and oxygen or hydrogen and oxygen, supplies the energy to initiate the pyrolysis of precursor compounds, is widely used for the industrial production of powders in large quantities, such as carbon black, fumed silica and titanium dioxide. However, since the gas pressure during the reaction is high, highly agglomerated powders are produced which is disadvantageous for subsequent processing. The basic idea of low pressure combustion flame synthesis is to extend the pressure range to the pressures used in gas phase synthesis and thus to reduce or avoid the agglomeration. Low pressure flames have been extensively used by aerosol scientists to study particle formation in the flame.

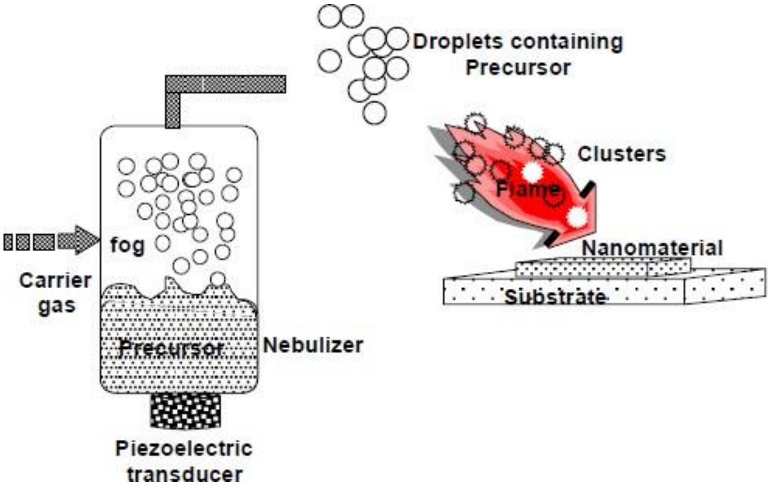


Fig. 2.5. Flame assisted ultrasonic spray pyrolysis

A key for the formation of nanoparticles with narrow size distributions is the exact control of the flame in order to obtain a flat flame front. Under these conditions the thermal history, i.e. time and temperature, of each particle formed is identical and narrow distributions result. However, due to the oxidative atmosphere in the flame, this synthesis process is limited to the formation of oxides in the reactor zone.

2.1.5 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.

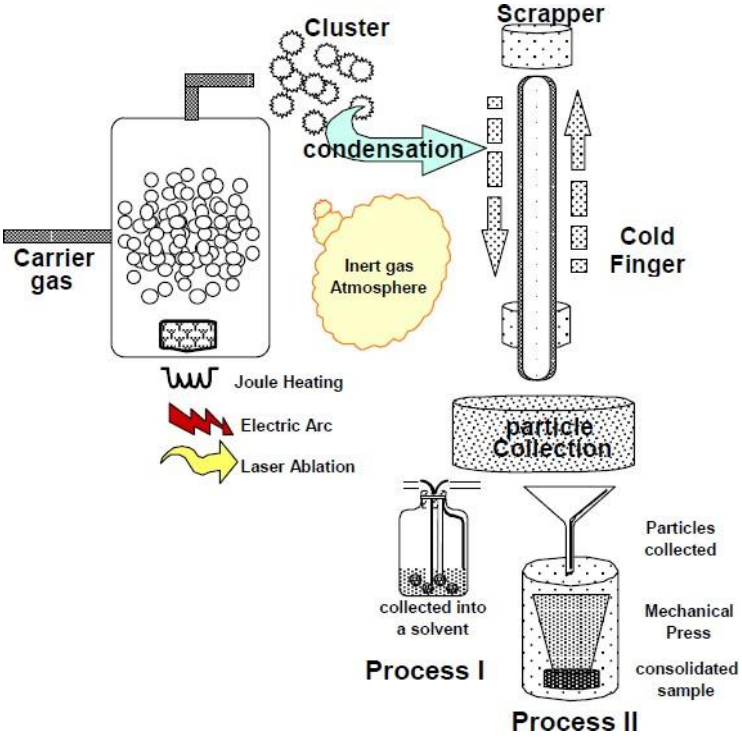


Fig. 2.6. Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.

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. Lognormal 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.

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. Subsequenly, 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 postoxidation of primary nanoparticles of a pure metal (e.g. Ti to TiO2) or a suboxide (e.g. ZrO to ZrO2). 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 CeO2 or ZrO2. 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.

2.1.6 **Chemical Vapour Condensation (CVC)**

As shown schematically in Figure, the evaporative source used in 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.

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. Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesised. Additionally, more complex oxides such as $BaTiO_3$ 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-ZrO_2 coated with n-Al_2O_3 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.

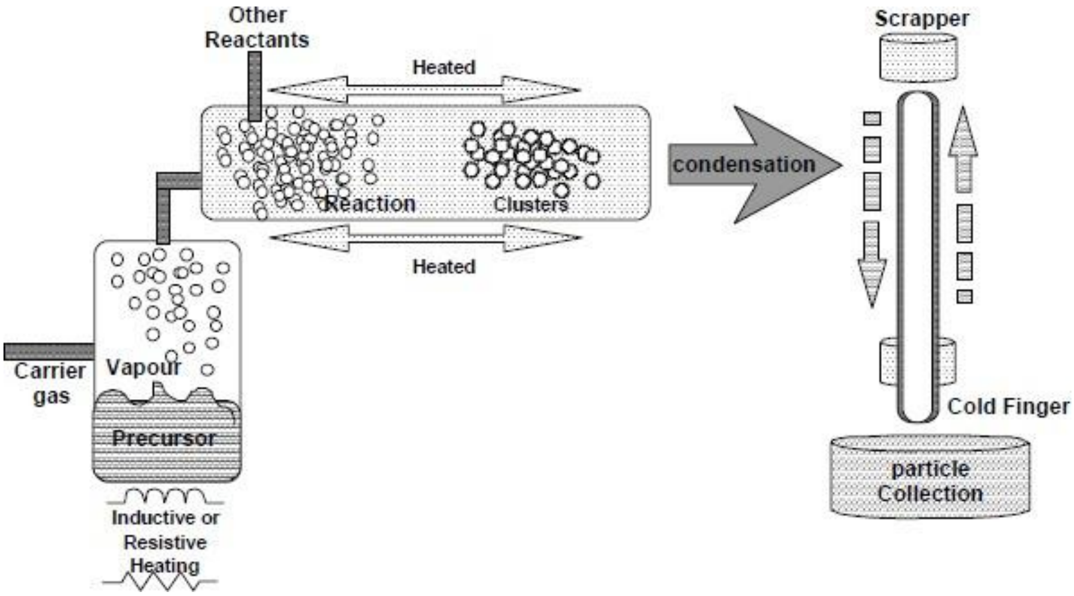


Fig. 2.7. A schematic of a typical CVC reactor

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.

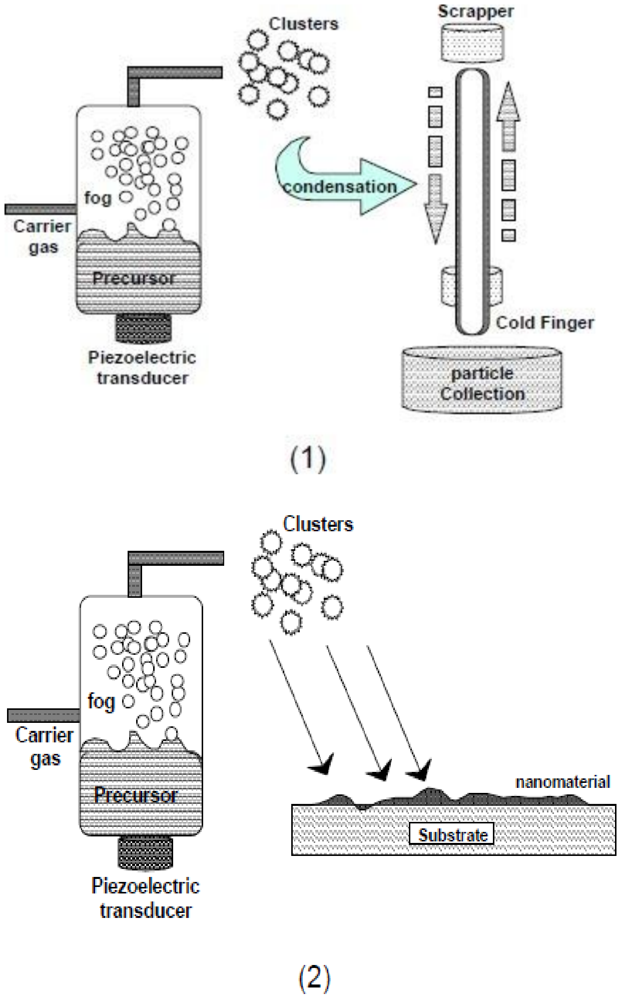
2.1.7 Sputtered Plasma Processing:

In this method is yet again a variation of the gas-condensation method excepting the fact that the source material is a sputtering target and this target is sputtered using rare gases and the constituents are allowed to agglomerate to produce nanomaterial. Both dc (direct current) and rf (radio-frequency) sputtering has been used to synthesize nanoparticles. Again reactive sputtering or multitarget sputtering has been used to make alloys and/or oxides, carbides, nitrides of materials. This method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal.

2.1.8 Microwave Plasma Processing

This technique is similar to the previously discussed CVC method but employs plasma instead of high temperature for decomposition of the metal organic precursors. The method uses microwave plasma in a 50 mm diameter reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor such as a chloride compound is introduced into the front end of the reactor. Generally, the microwave cavity is designed as a single mode cavity using the TE10 mode in a WR975 waveguide with a frequency of 0.915 GHz. The major advantage of the plasma assisted pyrolysis in contrast to the thermal activation is the low temperature reaction which reduces the tendency for agglomeration of the primary particles. This is also true in the case of plasma-CVD processes. Additionally, it has been shown that by introducing another precursor into a second reaction zone of the tubular reactor, e.g. by splitting the microwave guide tubes, the primary particles can be coated with a second phase. For example, it has been demonstrated that ZrO**2** nanoparticles can be coated by Al2O3. In this case the inner ZrO2 core is crystalline, while the Al2O3 coating is amorphous. The reaction sequence can be reversed with the result that an amorphous Al2O3 core is coated with crystalline ZrO2. While the formation of the primary particles occurs by homogeneous nucleation, it can be easily estimated using gas reaction kinetics that the coating on the primary particles grows heterogeneously and that homogeneous nucleation of nanoparticles originating from the second compound has a very low probability.

2.1.9 Particle precipitation aided CVD:



(1)

(2)

Fig. 2.8. Schematic representation of (1) nanoparticle, and (2) particulate film formation

In another variation of this process, colloidal clusters of materials are used to prepare nanoparticles. The CVD reaction conditions are so set that particles form by condensation in the gas phase and collect onto a substrate, which is kept under a different condition that allows heterogeneous nucleation. By this method both nanoparticles and particulate films can be prepared. An example of this method has been used to form nanomaterials eg. SnO2, by a method called pyrosol deposition process, where clusters of tin hydroxide are transformed into small aerosol droplets, following which they are reacted onto a heated glass substrate.

2.1.10. Laser ablation

Laser ablation has been extensively used for the preparation of nanoparticles and particulate films. In this process a laser beam is used as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications. The small dimensions of the particles and the possibility to form thick films make this method quite an efficient tool for the production of ceramic particles and coatings and also an ablation source for analytical applications such as the coupling to induced coupled plasma emission spectrometry, ICP, the formation of the nanoparticles has been explained following a liquefaction process which generates an aerosol, followed by the cooling/solidification of the droplets which results in the formation of fog. The general dynamics of both the aerosol and the fog favours the aggregation process and micrometer-sized fractal-like particles are formed. The laser spark atomizer can be used to produce highly mesoporous thick films and the porosity can be modified by the carrier gas flow rate. ZrO_2 and SnO_2 nanoparticulate thick films were also synthesized successfully using this process with quite identical microstructure. Synthesis of other materials such as lithium manganate, silicon and carbon has also been carried out by this technique..

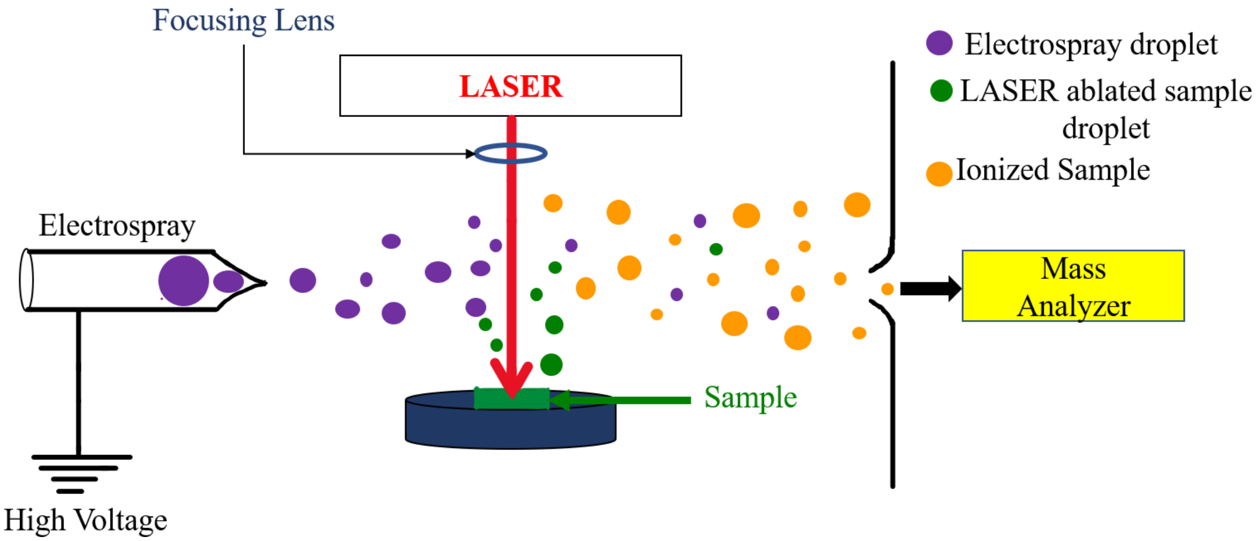


Fig. 2.8. Schematic representation of Laser ablation method

UNIT -III-Synthesis Methods of Nano Composites-SPHA7404

Bio-metic process

The need for biosynthesis of nanoparticles rose as the physical and chemical processes were costly. So in the search of for cheaper pathways for nanoparticle synthesis, scientists used microorganisms and then plant extracts for synthesis. Nature has devised various processes for the synthesis of nano- and micro- length scaled inorganic materials which have contributed to the development of relatively new and largely unexplored area of research based on the biosynthesis of nanomaterials.

Biosynthesis of nanoparticles is a kind of bottom up approach where the main reaction occurring is reduction/oxidation. The microbial enzymes or the plant phytochemicals with anti oxidant or reducing properties are usually responsible for reduction of metal compounds into their respective nanoparticles.

The three main steps in the preparation of nanoparticles that should be evaluated from a green chemistry perspective are the choice of the solvent medium used for the synthesis, the choice of an environmentally benign reducing agent and the choice of a non toxic material for the stabilization of the nanoparticles. Most of the synthetic methods reported to date rely heavily on organic solvents. This is mainly due to the hydrophobicity of the capping agents used Synthesis using bio-organisms is compatible with the green chemistry principles: the bio-organism is (i) eco-friendly as are (ii) the reducing agent employed and (iii) the capping agent in the reaction. Often chemical synthesis methods lead to the presence of some toxic chemical species adsorbed on the surface that may have adverse effects in medical applications. This is not an issue when it comes to biosynthesized nanoparticles as they are eco friendly and biocompatible for pharmaceutical applications.

Use of organisms to synthesize nanoparticles

Biomimetics refers to applying biological principles for materials formation. One of the primary processes in biomimetics involves bioreduction. Initially bacteria were used to synthesize nanoparticles and this was later succeeded with the use of fungi, actinomycetes and more recently plants.

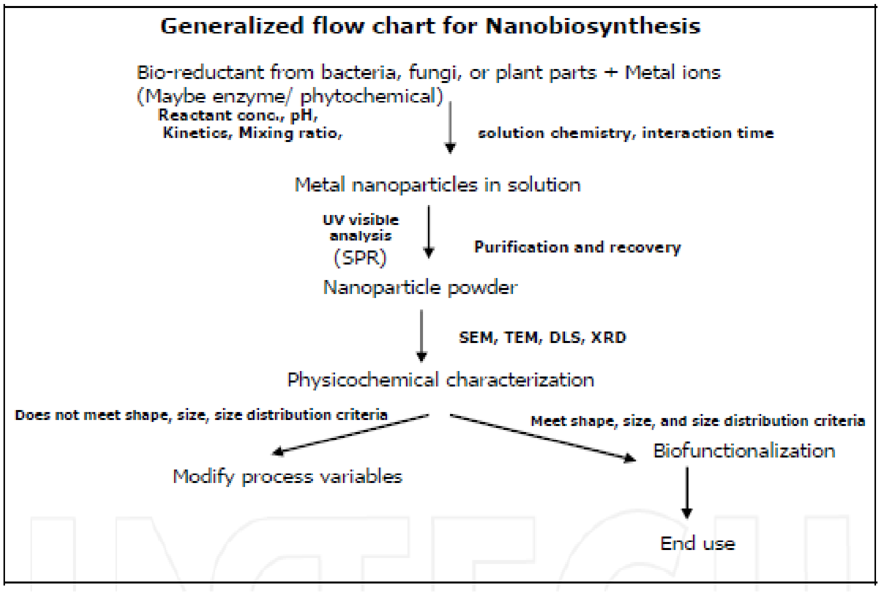


Fig 3.1 Flowchart denoting the biosynthesis or nanoparticle

Materials and Methods

The natural compound or organisms, such as plant extract, fungi, and bacteria, act as reluctant and stabilizing agents, which could be considered as an alternative for the synthesis of inorganic nanoparticles . The medicinal plants are a good source of biosynthesis of metal nanoparticles.

(i)Use of plants to synthesize nanoparticles

The advantage of using plants for the synthesis of nanoparticles is that they are easily available, safe to handle and possess a broad variability of metabolites that may aid in reduction.

A number of plants are being currently investigated for their role in the synthesis of nanoparticles. Gold nanoparticles with a size range of 2- 20 nm have been synthesized using the live alfa alfa plants. Nanoparticles of silver, nickel, cobalt, zinc and copper have also been synthesized inside the live plants of Brassica juncea (Indian mustard), Medicago sativa (Alfa alfa) and Heliantus annus (Sunflower). Certain plants are known to accumulate higher concentrations of metals compared to others and such plants are termed as hyperaccumulators. Of the plants investigated, Brassica juncea had better metal accumulating ability and later assimilating it as nanoparticles. Silver in bulk form carries antimicrobial potential . However, in a reduced state, the antimicrobial potential gets enhanced for silver nanoparticles . The biological and chemical syntheses of silver nanoparticles have been widely studied for their therapeutic potential. The way in which the metal nanoparticle has gained interest, the various methods evolving in terms of less toxic chemical involvement, cost-effectiveness, and stability of nanoparticles are a prime area of interest . The natural extracts contain active biomolecules which generally helps in reducing and binding of nanomaterials with specific receptors cell of the bacterial membrane . These natural compounds may be rich in flavonoids, aldehydes, amides, polysaccharides, etc. The multidrug resistance of bacteria against bactericides and antibiotics is very common nowadays due to the development of resistant strains. Some natural compounds act as antimicrobial agents, and hence there is a need to develop novel ways of formulating biomaterials is an upcoming field of attraction.

Preparation of leave extract:

For preparing, the aqueous extracellular solution of plant leaves, 5 g of freshly collected plant leaves of were cut chopped into appropriate size (~ 1 cm×1 cm), and were taken to 250ml conical flask and washed several times with distilled water. After this, 100ml distilled water was added to the flask containing freshly chopped and washed plant leaves followed by the boiling at 60 ^{0}C for 15minutes. The obtained crude extract was filtered through Whatman filter paper no.1, and the supernatant was stored at 4 ^{o}C and used within a week.

Fig 3.2 Biological synthesis of nanoparticle using leave extract

Synthesis and physico-chemical optimization of silver nanoparticles :

To obtain optimum conditions for maximum synthesis, the plant filtrate was used as a reducing and stabilizing agent for 1mM AgNO3. In a typical optimization route, silver nanoparticles formed by the reduction of Ag^{+} ions to Ag^{0}. The process involved with the addition of 5ml filtrate to 30ml of 10^{-3}M AgNO3 solution in a 250ml flask and kept on a rotary shaker (120rpm) at 30 ^{0}C . The nanoparticle synthesis was optimized by varying the different parameters.

Purification of silver nanoparticles

To remove the non-AgNPs components along with a maximal recovery of AgNPs colloids from the synthesized solution, an optimal centrifugation process was obtained based at 10,000 rpm for 10 min. The supernatant was collected and frozen at −70 ^{0}C for 45 min for 2 days using Lyophilizer (Micro Modulyo 230 freeze dryer, Thermo Electron Corporation, India). The lyophilized nanoparticles were stored desiccated at 4 ^{0}C.

Recently gold nanoparticles have been synthesized using the extracts of Magnolia kobus and Diopyros kaki leaf extracts. The effect of temperature on nanoparticle formation was investigated and it was reported that polydisperse particles with a size range of 5- 300nm was obtained at lower temperature while a higher temperature supported the formation of smaller and spherical particles.

While fungi and bacteria require a comparatively longer incubation time for the reduction of metal ions, water soluble phytochemicals do it in a much lesser time. Therefore compared to bacteria and fungi, plants are better candidates for the synthesis of nanoparticles. Taking use of plant tissue culture techniques and downstream processing procedures, it is possible to synthesize metallic as well as oxide nanoparticles on an industrial scale once issues like the metabolic status of the plant etc. are properly addressed.

(ii) Use of bacteria to synthesize nanoparticles

The use of microbial cells for the synthesis of nanosized materials has emerged as a novel approach for the synthesis of metal nanoparticles. Although the efforts directed towards the biosynthesis of nanomaterials are recent, the interactions between microorganisms and metals have been well documented and the ability of microorganisms to extract and/or accumulate metals is employed in commercial biotechnological processes such as bioleaching and bioremediation. Bacteria are known to produce inorganic materials either intra cellularly or extra cellularly. Microorganisms are considered as a potential biofactory for the synthesis of nanoparticles like gold, silver and cadmium sulphide. Some well known examples of bacteria synthesizing inorganic materials include magnetotactic bacteria (synthesizing magnetic nanoparticles) and S layer bacteria which produce gypsum and calcium carbonate layers. Some microorganisms can survive and grow even at high metal ion concentration due to their resistance to the metal. The mechanisms involve: efflux systems, alteration of solubility and toxicity via reduction or oxidation, biosorption, bioaccumulation, extra cellular complexation or precipitation of metals and lack of specific metal transport systems. For e.g. Pseudomonas stutzeri AG 259 isolated from silver mines has been shown to produce silver nanoparticles.

Many microorganisms are known to produce nanostructured mineral crystals and metallic nanoparticles with properties similar to chemically synthesized materials, while exercising strict control over size, shape and composition of the particles. Examples include the formation of magnetic nanoparticles by magnetotactic bacteria, the production of silver nanoparticles within the periplasmic space of Pseudomonas stutzeri and the formation of palladium nanoparticles using sulphate reducing bacteria in the presence of an exogenous electron donor

Though it is widely believed that the enzymes of the organisms play a major role in the bioreduction process, some studies have indicated it otherwise. Studies indicate that some microorganisms could reduce silver ions where the processes of bioreduction were probably non enzymatic. For e.g. dried cells of Bacillus megaterium D01, Lactobacillus sp. A09 were shown to reduce silver ions by the interaction of the silver ions with the groups on the microbial cell wall. Silver nanoparticles in the size range of 10- 15 nm were produced by treating dried cells of Corynebacterium sp. SH09 with diammine silver complex. The ionized carboxyl group of amino acid residues and the amide of peptide chains were the main groups trapping $(Ag(NH_3)_{2+})$ onto the cell wall and some reducing groups such as aldehyde and ketone were involved in subsequent bioreduction. But it was found that the reaction progressed slowly and could be accelerated in the presence of OH_-.

In the case of bacteria, most metal ions are toxic and therefore the reduction of ions or the formation of water insoluble complexes is a defense mechanism developed by the bacteria to overcome such toxicity .

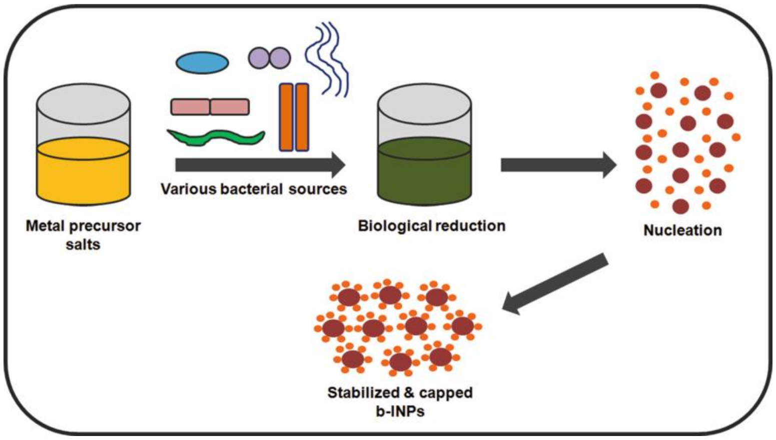


Fig 3.3 Biological synthesis of nanoparticle using bacteria

(ii) Use of actinomycetes to synthesize nanoparticles

prokaryotes such as bacteria. Even though they are classified as prokaryotes, they were originally designated as ray fungi. Focus on actinomycetes has primarily centred on their exceptional ability to produce secondary metabolites such as antibiotics. It has been observed that a novel alkalothermophilic actinomycete, Thermomonospora sp. synthesized gold nanoparticles extracellularly when exposed to gold ions under alkaline conditions. In an effort to elucidate the mechanism or the processes favouring the formation of nanoparticles with desired features, studied the formation of monodisperse gold nanoparticles by Thermomonospora sp. and concluded that extreme biological conditions such as alkaline and slightly elevated temperature conditions were favourable for the formation of monodisperse particles. Based on this hypothesis, alkalotolerant actinomycete Rhodococcus sp. has been used for the intracellular synthesis of monodisperse gold nanoparticles. In this study it was observed that the concentration of nanoparticles were more on the cytoplasmic membrane. This could have been due to the reduction of metal ions by the enzymes present in the cell wall and on the cytoplasmic membrane but not in the cytosol. The metal ions were also found to be non toxic to the cells which continued to multiply even after the formation of the nanoparticles.

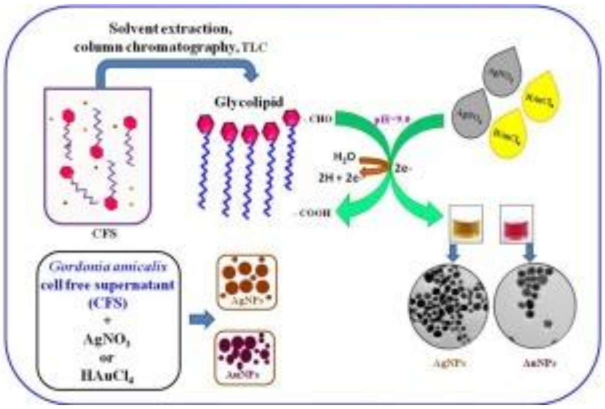


Fig 3.3 Biological synthesis of nanoparticle using actinomycete

iv. Use of fungi to synthesize nanoparticles

Fungi have been widely used for the biosynthesis of nanoparticles and the mechanistic aspects governing the nanoparticle formation have also been documented for a few of them. In addition to monodispersity, nanoparticles with well defined dimensions can be obtained using fungi. Compared to bacteria, fungi could be used as a source for the production of large amount of nanoparticles. This is due to the fact that fungi secrete more amounts of proteins which directly translate to higher productivity of nanoparticle formation .

Yeast, belonging to the class ascomycetes of fungi has shown to have good potential for the synthesis of nanoparticles. Gold nanoparticles have been synthesized intracellularly using the fungi Instead of fungi culture, isolated proteins from them have also been used successfully in nanoparticles production. Nanocrystalline zirconia was produced at room temperature by cationic proteins while were similar to silicatein secreted by F. oxysporum

The use of specific enzymes secreted by fungi in the synthesis of nanoparticles appears promising. Understanding the nature of the biogenic nanoparticle would be equally important. This would lead to the possibility of genetically engineering microorganisms to over express specific reducing molecules and capping agents and thereby control the size and shape of the biogenic nanoparticles.

Microbiological methods generate nanoparticles at a much slower rate than that observed when plant extracts are used. This is one of the major drawbacks of biological synthesis of nanoparticles using microorganisms and must be corrected if it must compete with other methods.

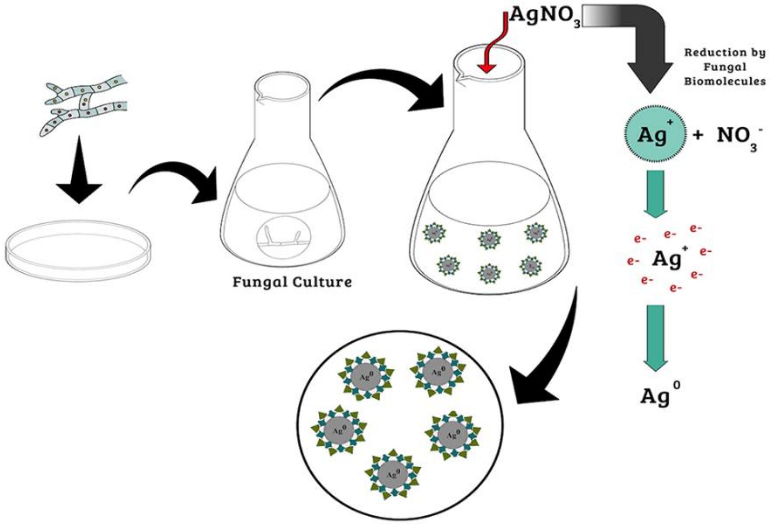


Fig 3.4 Biological synthesis of nanoparticle using fungi

3.2 Printing Mechanism Nano Particles

Printing is a process for reproducing text and images

For centuries, printing of texts and graphics on flat (two-dimensional) substrates such as textiles and paper has been an essential enabling technology for the cultural development of mankind. Only recently has this technique been considered as a valuable tool for the processing of functional nanomaterials, for example, in the electronics and biomedical industries. This property provides new possibilities for advanced light control at the nanoscale. The simultaneous excitation of both electric and magnetic dipoles within a single nanoparticle generates a strongly anisotropic scattering pattern.

For electronics manufacturing, for example, printing has some decisive advantages compared with the more traditional approaches of semiconductor processing. First of all, printing is an additive process, meaning that functional materials are deposited only where needed and can be used much more efficiently than with subtractive techniques, which tend to produce a lot of waste. In addition, printing can be carried out at atmospheric pressure, making high-vacuum technologies obsolete, which also contributes to significant savings on production costs. A third advantage is the selectivity of printing, making multi material applications such as multicolor lighting or printed thin-film transistors possible. Since in the graphics printing industry, many 2D printing technologies have already been developed toward roll-to-roll processing, commercial mass production of nanomaterial-based printed electronics devices in a continuous manufacturing mode is also within reach.

A wide variety of 2D printing technologies has been applied for the processing of functional nanomaterials, which can be subdivided into two different groups: noncontact or digital (maskless) printing technologies (without physical contact between printing equipment and substrate) and contact (mask-based) printing technologies (with physical contact). In noncontact printing, droplets or jets of the functional ink are generated at a (small) distance from the substrate and transferred onto it by a pressure pulse that propels them across the interspace. Contact printing typically makes use of a predetermined pattern, embedded as a mask in a drum or screen, which is repeatedly replicated on the substrate by directly touching it. Typical examples for noncontact techniques are inkjet printing (IJP) and laser-induced forward transfer (LIFT), and examples of contact technologies are offset, flexo, gravure, screen, and microcontact printing.

3D Printing:

The action or process of making a physical object from a three-dimensional digital model, typically by laying down many thin layers of a material in succession.

There are three broad types of 3D printing technology; **sintering**, **melting**, and **stereolithography**.

- **Sintering** is a technology where the material is heated, but not to the point of melting, to create high resolution items. Metal powder is used for direct metal laser sintering while thermoplastic powders are used for selective laser sintering.
- **Melting** methods of 3D printing include powder bed fusion, electron beam melting and direct energy deposition, these use lasers, electric arcs or electron beams to print objects by melting the materials together at high temperatures.
- **Stereolithography** utilises photopolymerization to create parts. This technology uses the correct light source to interact with the material in a selective manner to cure and solidify a cross section of the object in thin layers.

Process of 3D printing:

  - It is a method of converting a virtual 3D model into physical object.
  - Where a 3D object is created by laying down successive layers of material.(Additive Manufacturing)

- You only need a printer ,raw material and software to tell the printer what to print.
- Step 1: cad file Is created
- Step 2 :The cad file is exported to 3d printing machine.
- Step 3: Layer by layer
- Step 4: Actual object

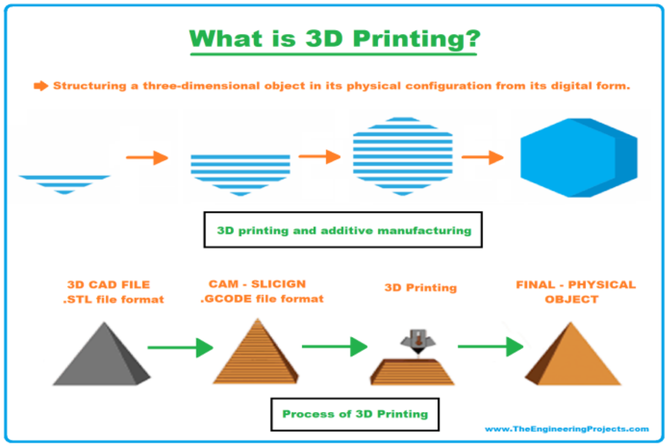


Fig 3.5 Process of 3D printing

Use of nanoparticle for printing mechanism

- Nanoparticles can have unique optical properties. Silicon nanoparticles, for example, provide strong electric and magnetic dipole responses within the visible range. This property provides new possibilities for advanced light control at the nanoscale.
- Inks with nano-particles and structures can be used in most printing processes including printed electronics.
- Noncontact printing technologies typically deposit the ink in the formof free flying droplets formed at some distance from the substrate. The two most important noncontact printing technologies are IJP and LIFT . Whereas IJP is a well-established technology, LIFT is a rather new development specifically aimed at high-resolution printing of high-viscous and solid materials. Aerosol patterning is another type of noncontact printing . Heat is used to create airborne nanoparticles that are directed to a substrate via a confined jet. An annulus of air is used to control the dimensions of the deposited material.
- Inkjet inks require small particles in their formulation especially for dyes and

pigments, and thus benefit greatly from nanotechnology. Researchers state that the inkjet printing technology is growing side by side with the development of nanomaterials.

Advantages

- Rapid prototyping
- Clean process, wastage of material is negligible
- Complex shape can be produced
- Easy to use
- Reduce design complexity
- Cheap

Disadvantages

- Process is slow
- Components do not have enough strength
- Cost of raw materials
- d printers are still expensive
- Misuse technology

Ink jet printing

- Inkjet printing is a type of computer printing that recreates a digital image by propelling droplet of link onto paper, plastic or other substrate. inkjet printers are the most commonly used type of printer and range from small inexpensive consumer models to expensive professional machine.
- A piezo electric crystal creates an acoustic waves as it vibrates within gun body and causes the stream of liquid to break into droplet at regular intervals :64000 to 165000 droplets per second may be achieved.
- The ink droplets are subjects subjected to an electrostatic field created by charging electrode as form the field varies according to the degree of drop deflection desired. The results in a controlled variable electrostatic charge on each droplet. Charged droplets are separated by one or more unchanged guard droplets to minimize electrostatic repulsion between neighboring droplets.

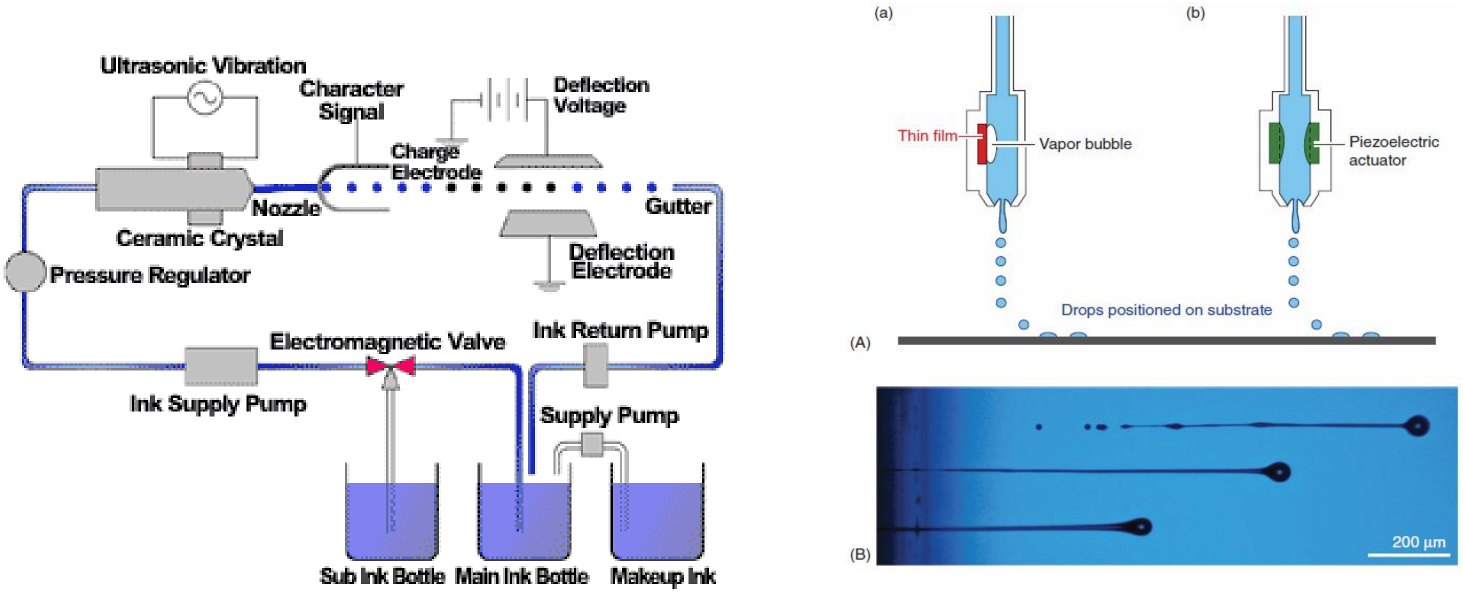


Fig 3.5 Process of inkjet printer

Advantages of inkjet printers:

1) Low cost
2) High quality of output, capable of printing fine and smooth details
3) Capable of printing in vivid color, good for printing pictures
4) Easy to use
5) Reasonably fast
6) Quieter than dot matrix printer
7) No warm up time

Disadvantages of inkjet printers:

1) Print head is less durable, prone to clogging and damage
2) Expensive replacement ink cartridges
3) Not good for high volume printing

4) Printing speed is not as fast as laser printers

5) Ink bleeding, ink carried sideways causing blurred effects on some papers

6) Aqueous ink is sensitive to water, even a small drop of water can cause blurring

7) Cannot use highlighter marker on inkjet printouts

Laser-Induced Forward Transfer:

For the nanoparticle printing process, femtosecond laser pulses are applied to generate and transfer single nanoparticles from a donor substrate to another receiver substrate. In this respect, thin films, as well as bulkmaterials, can be used as donormaterials. In both cases, the irradiation by tightly focused femtosecond laser pulses results in the controlled melting of a defined volume and nanoparticle ejection.

It has been shown that femtosecond laser printing can be applied to controlled fabrication of metal (Au, Ag, Cu, Fe, etc.) and semiconductor (Si, Ge, etc.) nanoparticles with precisely adjustable radii between 100 and 800 nm and their accurate positioning on a desired substrate

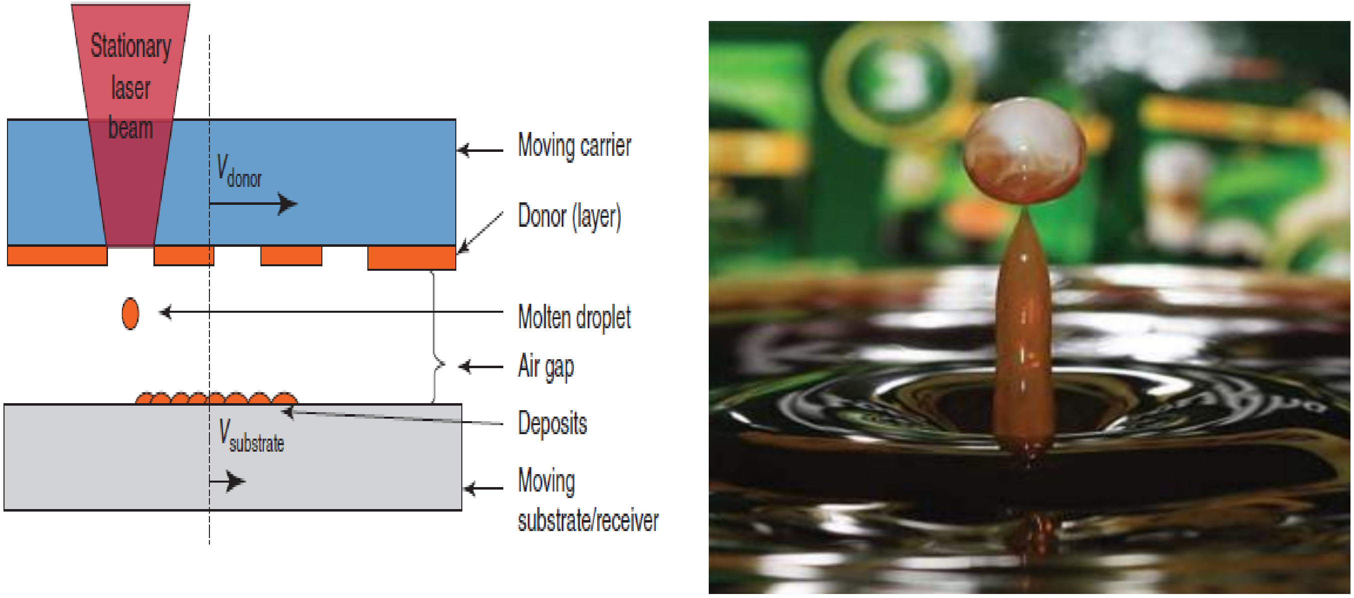


Fig 3.6 Process of Laser printer

Working:

For the nanoparticle printing process, which is described in this chapter, femtosecond laser pulses are applied to generate and transfer single nanoparticles from a donor substrate to another receiver substrate. In this respect, thin films, as well as bulkmaterials, can be used as donormaterials. In both cases, the irradiation by tightly focused femtosecond laser pulses results in the controlled melting of a defined volume and nanoparticle ejection.

Advantages:

- Better for Large Printing Volume:
- Excellent Speed:
- Reliable and Durable:
- Less Expensive per Print:
- Best Quality and Accurate Output:
- Noise Emission:

Disadvantages

- More Expensive:
- High Cost Toners:
- Less Portability:
- Poor Graphics Output:
- More Power Consumption:
- Health Problem:
- Need Quality Paper:

3.3 Dispersion of nano particles

Recently, the technological innovation of low-cost and large-scale synthesis process of nanoparticles with less than 100 nm in diameter is developing, and various kinds of nanoparticles are applied as the raw materials in the different fields, for example, cosmetic, medical supplies, catalysts, pigments, toner, and ink. Because the commercial products in such fields are colloidal suspension with relatively low solid content or powdery condition, it is rather easy to apply nanoparticles for commercial product. On the contrary, for the application of functional properties of nanoparticles to new materials, it is difficult to produce the final commercial products. Nanoparticles are expected to be raw materials for many kinds of new functional materials, for example, nanodevice with high-density circuit and wiring in use of nanoparticles, two-dimensional high-density nanodot memory element, and hybrid composite materials with high-density packed nanoparticles. For the commercial implementation of such materials, it needs to develop many kinds of nanoparticle processing. For nanometer-scaled devices, it is necessary to develop nanoparticle dispersion in suspension without aggregation, nanoparticles assemble on the circuit, and drying and sintering technology to cause neither disconnection nor deformation.

Dispersing means to distribute evenly. Dispersing nanoparticles is intriguing because the resulting composition is not only a mixture but a microscopically homogeneous composition with respect to e.g. optical, mechanical, electrical, or magnetic properties. Nanoparticle technology as enabling technology is therefore a tool usable in many different industries.

Dispersing nanoparticles of high refractive index into optical coatings can increase the refractive index of the layer and thus allows coating of high refractive index lenses without interference effects. The quality of dispersion destines the transparency. Mineral UV absorbers provide safe and sustainable protection from UV degradation, for the human skin as well as for wooden buildings and plastic parts. Apart from transparency, efficiency is controlled by the state of dispersion. Catalysts need to be in contact with the reaction partner. Dispersing catalytically active metal oxides increase the accessible surface area and thus the activity. Nanoparticles are used to render printing substrates suitable for photo-quality ink-jet printing. The particle dispersion can only be applied if the viscosity of the coating composition is low. In all these cases, the dispersion process including chemical modification is the key element. In addition it is important to note that the ultimate goal comprises the stable functional colloid in the final product formulation. Whereas the production of a nanoparticle dispersion in water or a solvent may be a difficult task in itself, dispersing nanoparticles in complex roduct formulations is even more challenging. The interaction with the additional components has to be taken into account when processing nanoparticles; this is also true if pre-dispersing int o a solvent is used as first step.

We produce customized dispersions of nanoparticles in aqueous, organic, and resinous formulations by combining our chemical and mechanical competences.

Example: Here dispersion means to form an homogenous solution of silver nanoparticles. nanoparticles have high surface area hence it tends to get agglomerated. Citrate act has capping agent, which caps the silver nanoparticles to prevent agglomeration and forms homogenous suspension.

Fig 3.7 Normal and Dispersed silver nanoparticle

Essentially synthesis of nano particles and using bottom up as well as top down approaches and we briefly indicated some characterization techniques that are used to follow the efficiency of these processes. Synthesis nano particle, how do keep them in their nano form. So dispersion is an important consideration in colloidal suspensions as well as composite materials. So particle dispersion needs to happen in fluids as in solids.

Agglomeration accelerated by:

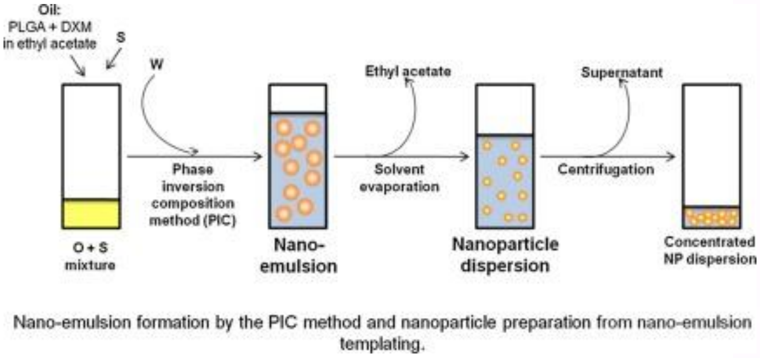
Higher Temp,
Longer time,
Small size,
Viscosity is lower

Methods of dispersion in suspensions and composites

Stirring-Magnetic stirrer-Particle or uniformly distributed and dispersed

Orbital shaking-A centrifugal force-Which can again prevent particles from becoming dispersed.

Sonication-In addition to providing high cavitation intensity for fragmenting particles ,the fields associated with sonication can also keep the particle well dispersed solution



Nano-emulsion formation by the PIC method and nanoparticle preparation from nano-emulsion templating.

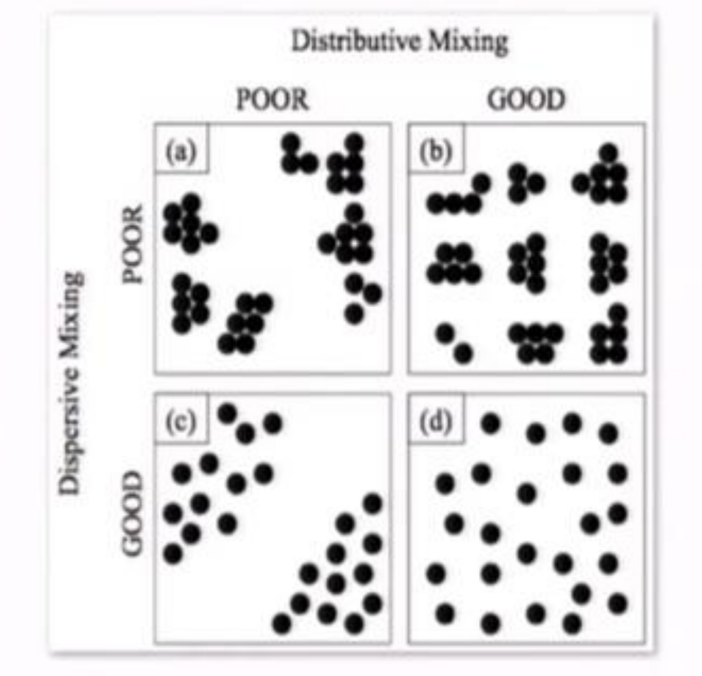


Fig 3.8 Dispersed and Distributed nanoparticle

3.4 Stabilization of nano particles

The term "nanoparticle stability" is widely used to describe the preservation of a particular nanostructure property ranging from aggregation, composition, crystallinity, shape, size, and surface chemistry. ... The stability of solution-phase nanoparticles are also impacted by aggregation state.

The stabilization of nanoparticles in concentrated aqueous suspensions is required in many manufacturing technologies and industrial products. Nanoparticles are commonly stabilized through the adsorption of a dispersant layer around the particle surface. The formation of a dispersant layer (adlayer) of appropriate thickness is crucial for the stabilization of suspensions containing high nanoparticle concentrations. Thick adlayers result in an excessive excluded volume around the particles, whereas thin adlayers lead to particle agglomeration. Both effects reduce the maximum concentration of nanoparticles in the suspension. However, conventional dispersants do not allow for a systematic control of the adlayer thickness on the particle surface. In this study, we synthesized dispersants with a molecular architecture that enables better control over the particle adlayer thickness. By tailoring the chemistry and length of these novel dispersants, we were able to prepare fluid suspensions (viscosity < 1 Pa.s at 100 s-1) with more than 40 vol % of 65-nm alumina particles in water, as opposed to the 30 vol % achieved with a state-of-the-art dispersing agent. This remarkably high concentration facilitates the fabrication of a wide range of products and intermediates in materials technology, cosmetics, pharmacy, and in all other areas where concentrated nanoparticle suspensions are required. On the basis of the proposed molecular architecture, one can also envisage other similar molecules that could be successfully applied for the functionalization of surfaces for biosensing, chromatography, medical imaging, drug delivery, and aqueous lubrication, among others.

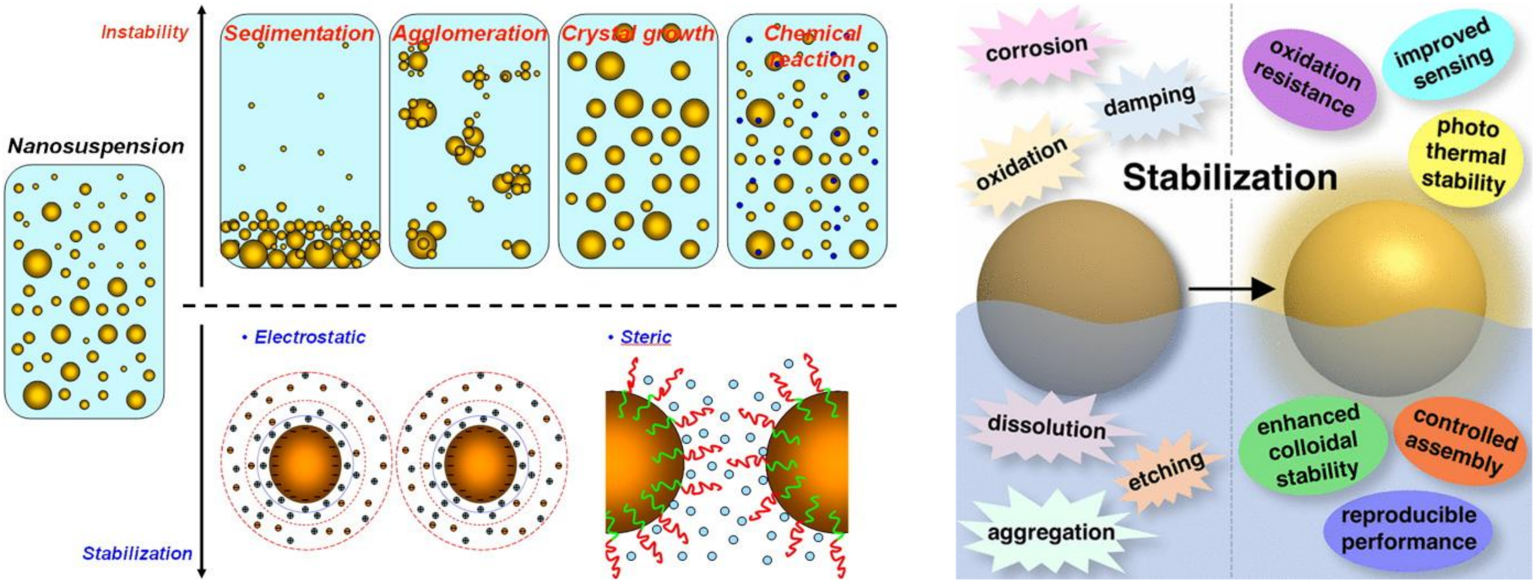


Fig 3.9 Stabilization of nanoparticle

Example: In the citrate reduction method, citrate anions reduce metal ions to atoms and stabilize clustered atoms, resulting in colloidal nanoparticles. Citrate-stabilized metal nanoparticles have played a crucial role as a fundamental material in a number of gold nanoparticle-based plasmonic applications.

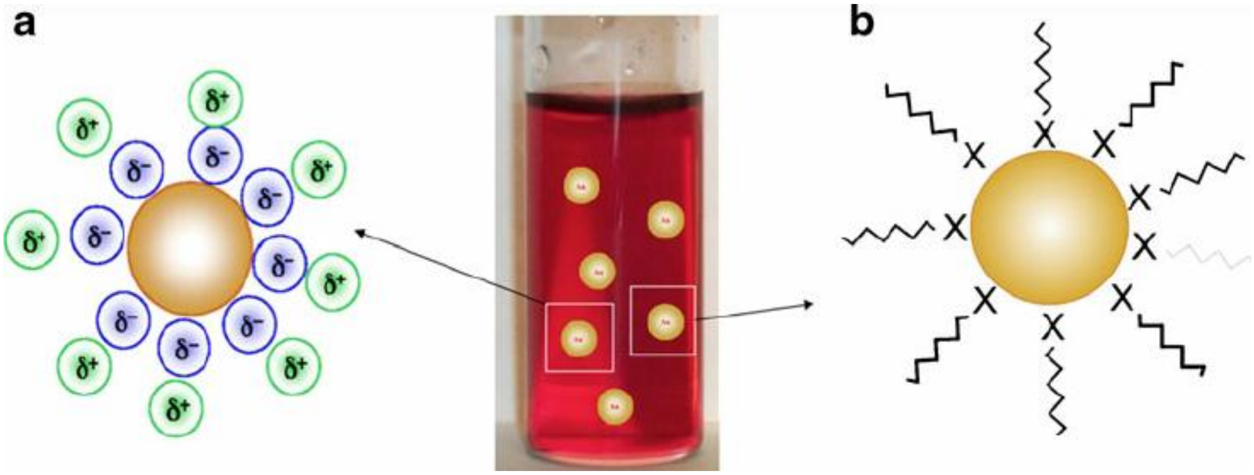


Fig 3.10 Stabilization of Gold nanoparticle

Stabilization method:

Essentially, NPs can be stabilized by steric, electrostatic or both effects.

steric stabilization

The **adsorption of large molecules on** the nanoparticle surface that includes surfactant or polymers to prevent aggregation is called steric stabilization. Due to increase of concentration of adsorbed molecules, there is an increase of osmotic repulsive force that enhances the stability of nanostructured particles

electrostatic stabilization

Electrostatic stabilization of Colloids is the mechanism in which the attraction van der Waals forces are **counterbalanced** by the repulsive Coulomb forces acting between the negatively charged colloidal particles.

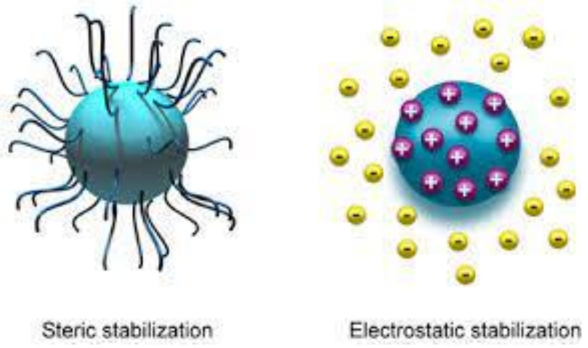


Fig 3.11 Steric, electrostatic stabilization

3.6 **Application of nanomaterials**

Nanomaterials having wide range of applications in the field of electronics, fuel cells, batteries,agriculture, food industry, and medicines, etc... It is evident that nanomaterials split their conventional counterparts because of their superior chemical, physical, and mechanical properties and of their exceptional formability.

Fig 3.6 Applications of nanomaterials

Next-Generation Computer Chips

- The microelectronics sector has paid special attention to miniaturization, which involves reducing the size of circuits like transistors, capacitors, and resistors. A considerable reduction in their size enables microprocessors developed using these parts, to operate much faster, thus allowing computations at much greater speeds.
- However, there are a number of technical obstacles to achieving these advancements, such as the lack of ultrafine precursors to make these parts, inadequate dissipation of huge amounts of heat generated by these microprocessors because of faster speeds, poor mean time to failures (poor reliability), etc.
- Nanomaterials help the industry to overcome these obstacles by offering manufacturers materials with better thermal conductivity, nanocrystalline starting materials, ultra-high-purity materials, and longer-lasting, durable interconnections (connections between different parts in the microprocessors).

Catalysis

Higher surface area available with the nanomaterial counterparts, nano-catalysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that it is utilized as a solid-fuel in rocket propulsion, whereas the bulk aluminum is widely used in utensils. Nano-aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activity, and can very well be utilized in manipulating the rate-controlling step.

Better Insulation Materials

Nanocrystalline materials manufactured by the sol-gel method give rise to foam-like structures known as “aerogels.” In spite of being extremely lightweight and porous, these aerogels can hold loads equal to 100 times their weight. Aerogels are made up of continuous 3D networks of particles with air (or any other fluid, such as a gas) trapped at their interstices.

Since aerogels are porous and include air trapped at the interstices, they are used for insulation in homes, offices, etc. This considerably reduces the cooling and heating bills, thus saving power and decreasing the associated environmental pollution.

They are also being employed as materials for “smart” windows, which darken when the sun is very bright (same as in changeable lenses in sunglasses and prescription spectacles), and lighten when the sun is not shining very brightly.

Phosphors for High-Definition TV &Low cost panel displays

The resolution of a monitor or television is subject to the size of the pixel. These pixels are fundamentally composed of materials known as “phosphors,” which glow when struck by a stream of electrons within the cathode ray tube (CRT). The resolution enhances with a reduction in the pixel size or the phosphors.

Nanocrystalline zinc selenide, cadmium sulfide, zinc sulfide, and lead telluride prepared through the sol-gel methods are potential materials for enhancing the resolution of monitors. The use of nanophosphors is intended to lower the cost of these displays to make personal computers and high-definition televisions (HDTVs) affordable for an average household in the United States.

Tougher and Harder Cutting Tools

Cutting tools made of nanocrystalline materials like carbides of tantalum, tungsten, and titanium, are a lot harder, much more erosion-resistant and wear-resistant, and last longer than their traditional (large-grained) equivalents. They also allow the manufacturer to machine several materials much faster, thereby boosting productivity and largely minimizing manufacturing costs.

Moreover, miniaturizing microelectronic circuits necessitates microdrills (drill bits having diameters lesser than the thickness of an average human hair [100 µm]) with improved edge retention and much better wear resistance. Nanocrystalline carbides are being used in these micro drills since they are much harder, stronger, and wear-resistant.

Elimination of Pollutants

Nanocrystalline materials have very large grain boundaries corresponding to their grain size. Therefore, they are very active with regards to their physical, chemical, and mechanical properties. Owing to their improved chemical activity, nanomaterials can be employed as catalysts to react with toxic and noxious gases such as nitrogen oxide and carbon monoxide, in power generation equipment and automobile catalytic converters, to avoid environmental pollution caused when gasoline and coal are burnt.

High Energy Density Batteries

Traditional and rechargeable batteries are used in nearly all applications that necessitate electric power. These applications include laptop computers, automobiles, toys, electric vehicles, personal stereos, cordless phones, cellular phones, watches, and next-generation electric vehicles (NGEV) that reduce environmental pollution. The energy density (storage capacity) of these batteries is very low, necessitating frequent recharging. The life of traditional and rechargeable batteries is also low.

Nanocrystalline materials produced using sol-gel methods have a foam-like (aerogel) structure that can store significantly more energy than their traditional equivalents. Hence, they are highly suitable for separator plates in batteries. Moreover, nickel-metal hydride (Ni-MH) batteries made of nanocrystalline nickel and metal hydrides have been predicted to necessitate much lesser recharging and to last considerably longer because of their large grain boundary (surface) area and improved chemical, physical, and mechanical properties.

High-Power Magnets

A magnet’s strength is measured in terms of saturation magnetization and coercivity values. These values will increase when there is a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains) of the grains. It has been demonstrated that magnets made of nanocrystalline yttrium-samarium-cobalt grains have highly uncommon magnetic properties because of their extremely large surface area.

Common applications for these high-power rare-earth magnets include ultra-sensitive analytical instruments, quieter submarines, land-based power generators, automobile alternators, motors for ships, and magnetic resonance imaging (MRI) in medical diagnostics.

High-Sensitivity Sensors

When carbon monoxide is present, the oxygen atoms in zirconium oxide react with the carbon in carbon monoxide to reduce zirconium oxide partially. This reaction activates a modification in the sensor’s characteristics, such as capacitance and conductivity (or resistivity).

The rate and the degree of this reaction are significantly increased by a decrease in the grain size. Therefore, sensors made of nanocrystalline materials are highly sensitive to variations in their environment. Common applications for sensors made using nanocrystalline materials are ice detectors on aircraft wings, smoke detectors, automobile engine performance sensors, etc

Nanowires for junctionless transistors

Transistors are made so tiny to reduce the size of sub assemblies of electronic systems and make smaller and smaller devices, but it is difficult to create high-quality junctions. In particular, it is very difficult to change the doping concentration of a material over distances shorter than about 10 nm. Researchers have succeeded in making the junctionless transistor having nearly ideal electrical properties. It could potentially operate faster and use less power than any conventional transistor on the market today. The device consists of a silicon nanowire in which current flow is perfectly controlled by a silicon gate that is separated from the nanowire by a thin insulating layer. The entire silicon nanowire is heavily n-doped, making it an excellent conductor. However, the gate is p-doped and its presence has the effect of depleting the number of electrons in the region of the nanowire under the gate. The device also has near-ideal electrical properties and behaves like the most perfect of transistors without suffering from current leakage like conventional devices and operates faster and using less energy.

Sun-screen lotion

Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO_2 provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO_2) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

Water treatment

The application of nanomaterials in water and wastewater treatment has drawn wide attention. Due to their small sizes and thus large specific surface areas, nanomaterials have strong adsorption capacities and reactivity. Heavy metals , organic pollutants , inorganic anions , and bacteria have been reported to be successfully removed by various kinds of nanomaterials . In recent years, photocatalytic degradation by metal oxide nanoparticles such as TiO_2 has been successfully applied in the contaminant degradation in water and wastewater. TiO_2 has been a highly researched material because of its non-toxicity, chemical stability, commercial availability, high photoactivity, etc. At the presence of light and catalyst, contaminants can be gradually oxidized into low molecular weight intermediate products and eventually transformed into CO_2, H_2O, and anions such as NO_3^-, PO_4^{3-} and Cl^-.

Nanomedicine

The properties of silver nanoparticles such as broad-acting and potent antibacterial activity are widely investigated. A wide range of nanosilver applications has emerged in consumer products ranging from disinfecting medical devices and home appliances to water treatments, as well as in nanomedicine.

Unit 4-Mechanical Properties-SPHA7404

4.1 Ceramics

Ceramic nanoparticle is a type of nanoparticle that is composed of ceramics, which are generally classified as inorganic, heat-resistant, nonmetallic solids that can be made of both metallic and nonmetallic compounds. The material offers unique properties. Macroscale ceramics are brittle and rigid and break upon impact. However, Ceramic nanoparticles take on a larger variety of functions, including dielectric, ferroelectric, piezoelectric, pyroelectric, ferromagnetic, magnetoresistive, superconductive and electro-optical.

Ceramic nanoparticle were discovered in the early 1980s. They were formed using a process called sol-gel which mixes nanoparticles within a solution and gel to form the nanoparticle. Later methods involved sintering (pressure and heat). The material is so small that it has basically no flaws. Larger scale materials have flaws that render them brittle.

In 2014 researchers announced a lasering process involving polymers and ceramic particles to form a nanotruss. This structure was able to recover its original form after repeated crushing.

Ceramic nanoparticles have been used as drug delivery mechanism in several diseases including bacterial infections, glaucoma, and most commonly, chemotherapy deliver in cancer.

Example: TiO_2, Al_2O_3, SiO_2

Synthesis :

Sol-gel

One process for making nanoceramics varies is the sol-gel process, also known as chemical solution deposition. This involves a chemical solution, or the sol, made of nanoparticles in liquid phase and a precursor, usually a gel or polymer, made of molecules immersed in a solvent. The sol and gel are mixed to produce an oxide material which are generally a type of ceramic. The excess products (a liquid solvent) are evaporated. The particles desires are then heated in a process called densification to produce a solid product. This method could also be applied to produce a nanocomposite by heating the gel on a thin film to form a nanoceramic layer on top of the film.

Two-photon lithography

This process uses a laser technique called two-photon lithography to etch out a polymer into a three-dimensional structure. The laser hardens the spots that it touches and leaves the rest unhardened. The unhardened material is then dissolved to produce a "shell". The shell is then coated with ceramic, metals, metallic glass, etc. In the finished state, the nanotruss of ceramic can be flattened and revert to its original state.

Sintering

In another approach sintering was used to consolidate nanoceramic powders using high temperatures. This resulted in a rough material that damages the properties of ceramics and requires more time to obtain an end product. This technique also limits the possible final geometries. Microwave sintering was developed to overcome such problems. Radiation is produced from a magnetron, which produces electromagnetic waves to vibrate and heat the powder. This method allows for heat to be instantly transferred across the entire volume of material instead of from the outside in.[1]

The nanopowder is placed in an insulation box composed of low insulation boards to allow the microwaves to pass through it. The box increases temperature to aid absorption. Inside the boxes are suspectors that absorb microwaves at room temperature to initialize the sintering process. The microwave heats the suspectors to about 600 °C, sufficient to trigger the nanoceramics to absorb the microwaves.

Properties

Ceramic nanoparticle have unique properties because of their size and molecular structure.

- The bulk behavior of materials can be changed dramatically when they are made from nanoscale building blocks - for example, the hardness and strength of a material can be greatly enhanced by consolidating ceramic materials from nanoscale particles – with the size of the building block affecting the properties of the final product.
- Nanoceramics are very strong and show substantial resistance against compression and bending. Their strength is similar to that of steel, and most ceramics maintain their

strength at high temperatures. However, their brittleness is the biggest technical barrier preventing their practical employment, especially in load-bearing applications.

- Traditional brittle materials can be made more ductile by reducing the size of the grain used in making it, so a nanoceramics' physical and mechanical strength is dependent on the size of the particle used to make them. When constructed from nanoparticles, ceramics can be superplastically deformed at a modest temperature before being heat treated at a higher temperature for high-temperature strengthening.
- Nanoceramics are relatively inert, and where reactivity does occur it is where coordinatively unsaturated and defect sites occur. Some ceramics – those that are iron-based, or made with nickel, barium and chromium – have metallic properties and exhibit a high resistance to demagnetization.
- The term ceramics incorporates electrically conducting, insulating and semiconducting materials such as chromium oxide, aluminum oxide and silicon carbide. Many electrical properties are particle-size and composition dependent: electrical resistance and dielectric constant for some systems increases as a result of small particle size, for example.

Nanotruss

Ceramic nanoparticle is more than 85% air and is very light, strong, flexible and durable. The fractal nanotruss is a nanostructure architecture made of alumina, or aluminum oxide. Its maximum compression is about 1 micron from a thickness of 50 nanometers. After its compression, it can revert to its original shape without any structural damage.

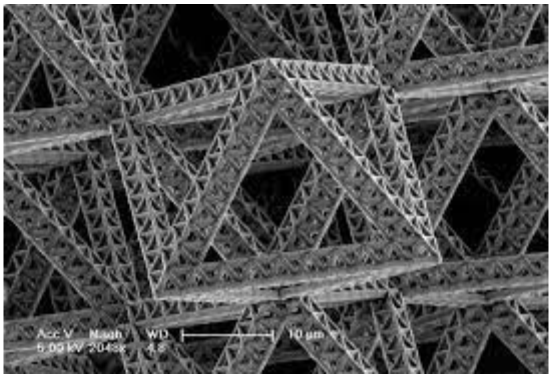


Fig 4.1 Nano scale truss work

Uses

- One of the main uses of nanoceramics has been in biomedicine and medical technology, particularly in bone repair. Bioactive ceramics closely match the properties of bone and can act as a nanoscaffold to help support bone regrowth.

- It has also been suggested that nanoceramics might find uses in energy supply and storage, communications, transportation systems, aerospace and construction. They have also found use in electronics as insulators, semiconductors, conductors and magnets.

- Nanoceramics might also find a use in armor to replace the stiff, tough layers of woven fiber which absorbs impact. A hard body armor is under development that includes ceramic inserts and steel or titanium panels that could offer greater protection against blunt trauma and high velocity ammunition. The inserts could absorb kinetic energy of the projectile and dissipate it in a localized shattering of the ceramic insert.

4.2 Strengthening and toughening mechanism

Structural ceramics exhibit several excellent properties, such as high thermal resistance, good chemical stability, and mechanical strength. However, ceramics have a low fracture toughness because of their ionic and covalent bonds, hence the plastic deformation of structural ceramics due to dislocation movement is extremely limited. To overcome the inherent brittleness of ceramics, a new material design concept must be developed .

Basic microstructures in nanocomposites are classified into three types: intra-type, inter-type, and nano/nanotype. With respect to mechanical properties such as strength and fracture toughness, the most important structure is an intra-type nanostructure where dispersed particles are embedded within the matrix grains.

Toughening mechanism

Crack extension resistance in polycrystalline ceramics with R-curve behavior is expressed as

$$\mathbf{K_R(\Delta a)=Ki+\Delta K_R(\Delta a)}$$

where **$K_R(\Delta a)$** represents the fracture toughness of the material exhibiting R-curve behavior, **Ki** is the intrinsic fracture toughness, and **$\Delta K_R(\Delta a)$**is the extrinsic increase in the fracture toughness after a certain extension from the initial crack tip, **(Δa).**

A schematic diagram explaining crack extension resistances in polycrystalline ceramics with rising R-curve behavior is shown in Fig4.2 .Comparison of Eq. and Fig indicates that the intrinsic fracture toughness, Ki, is related to the energy required to create the damaged FPZ at the crack tip, and that **ΔK_R** is caused by the shielding effects of bridging in a process zone wake. Thus, there are two mechanisms for improving the fracture toughness in polycrystalline ceramics. One mechanism is the process zone toughening mechanism which creates a damaged zone in front of a crack tip. Therefore, to improve the intrinsic fracture toughness, the fracture energy consumed in the process zone must be increased. The other mechanism is the crack-surface bridging toughening mechanism operating in a process zone wake which produces an extrinsic increase in crack resistance after a certain extension of the crack from the initial crack length. The toughening mechanism in nanocomposites is mainly the process zone toughening mechanism .

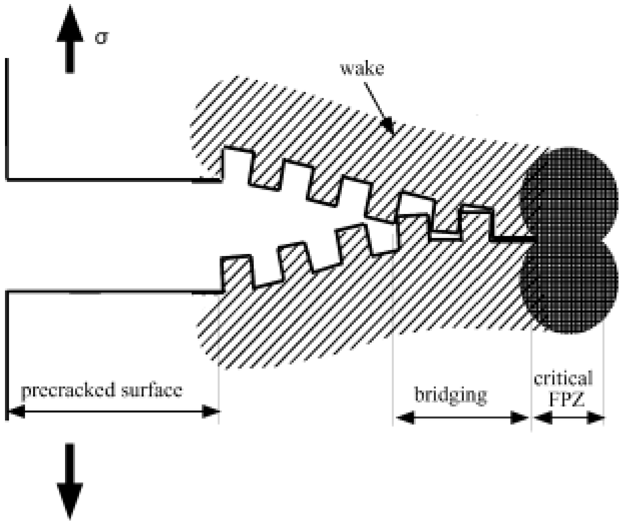


Fig 4.2 Schematic diagram of a frontal process zone and briding in polycrystalline ceramics with R-Curve behaviour

Fig 4.3 shows a schematic illustration of the toughening mechanism of nanocomposites . Dispersed dislocations within the matrix grains after annealing for alumina/silicon carbide nanocomposites are described in this figure. In a matrix grain, sub-grain boundaries or dislocation networks are generated around the nano-sized silicon carbide particles and the sessile dislocations are dispersed in the matrix, shown in Fig. 4.3(A). In this situation, when the tip of a propagating large crack reaches this area, these sessile dislocations in the matrix will operate as nano-crack nuclei in the vicinity of the propagating crack tip, shown in Fig. 4.3(B). The highly stressed state in the FPZ is then released by nano-crack nucleation, and the nano-cracks expand the FPZ size, enhancing the intrinsic fracture toughness of the materials.

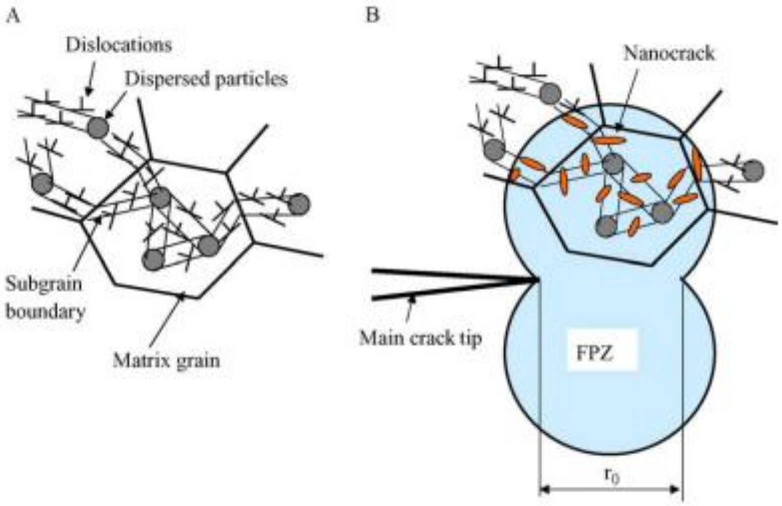


Fig 4.3.Schematics description of the toughening mechanism in nano composites (A) Intra type nano structure after annealing(B) FPZ creation

Strengthening mechanism

The grains and grain boundaries of sintered alumina contain tensile residual stresses resulting from anisotropic thermal expansion, Young's modulus along the crystal axes, and crystallographic misorientation across the grain boundaries. Therefore, in the sintered polycrystalline alumina, it is conceivable that the large crack along a grain boundary created by the synergetic effects of both residual stresses and processing defects, will be equivalent to the grain size of the material and that the weakest crack generated along a boundary in the specimen will dominate the strength of the specimen. The fracture toughness of grain boundaries is usually lower than that within the grains. Hence, polycrystalline alumina ceramics exhibit a mainly intergranular fracture mode, as schematically shown in Fig. 4.4 (A) shows the scanning electron microscopy (SEM) observation of the fracture surface of monolithic alumina.

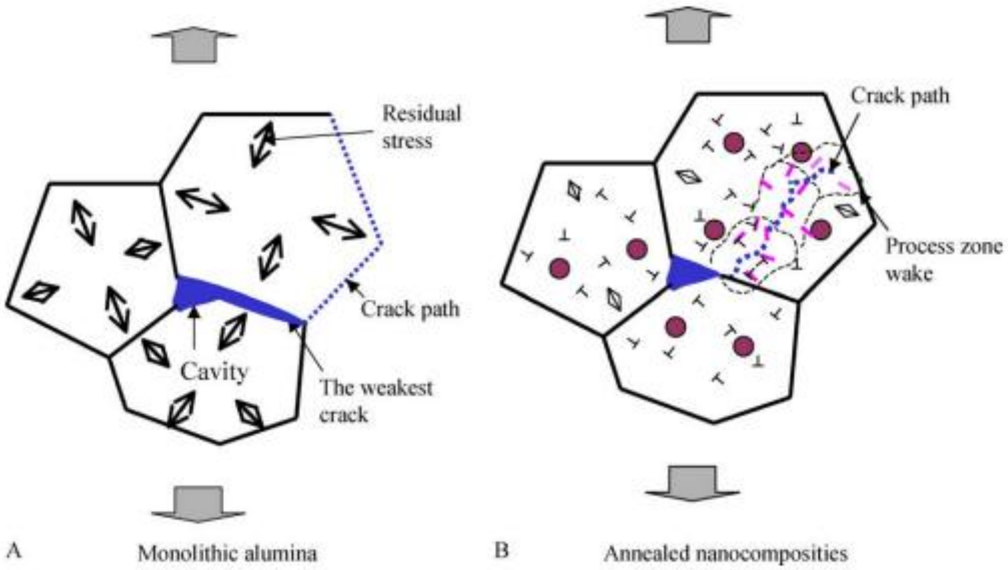


Fig 4.4.Schematics description of the Strengthening mechanism in nano composites

Nanocomposites, however, will yield dislocations around the particles, and the dislocations release residual stresses in the matrix. Consequently, the defect size along the grain boundaries is reduced in nanocompsoites, as shown in Fig. 4.4 (B). Also, the dislocations are difficult to move in ceramics at room temperature, serve as origins of small stress concentrations, and create nano-cracks around the propagating crack tip. These nano-cracks slightly reduce the strength of the alumina matrix, while reduction of both the residual stresses along the grain boundaries and the strength in the matrix are attributable to a change in the fracture mode from that of the intergranular fracture in monolithic alumina to that of the transgranular fracture in nanocomposites. Also, the fracture surface of the transgranular mode of nanocomposites is not a simple planar cleavage plane. Several steps are frequently observed on the surface and are likely to be evidence of nano-cracking in the FPZ wake.

Reduction of both the defect size along the grain boundaries and the tensile residual stresses in the matrix grains by dislocations result in improvement of the strength of nanocomposites. Several mechanical properties of nanocomposites are also improved for the same reason, such as hardness, wear resistance, creep resistance, and thermal shock resistance. reported drastic changes in the abrasive wear surfaces between monolithic alumina and nanocomposites, where the surface of monolithic alumina showed grain pullout. The nanocomposites, however, showed ground or abraded surfaces because of the improved strength along the grain boundaries.

4.3 Reduction in processing flow size

Ceramics have low fracture toughness because of their ionic and covalent bonds hence, the plastic deformation in structural ceramics due to dislocation movement is extremely limited, particularly at room temperature. Therefore, the FPZ ahead of a crack tip is considered to be composed of many micro-cracks or nano-cracks rather than dislocations as in metals . Although the critical size of the FPZ is considered to be an important factor for assessing toughening mechanisms, there is no direct means of measuring the critical size of the FPZ.

Recently, we proposed a novel technique for estimating the critical size of the FPZ in ceramics using a single-edge V-notched beam (SEVNB) method on the basis of the local fracture criterion. The local fracture criterion states that a crack will propagate when the stress at the characteristic distance from the crack tip reaches the critical value . Fig. 4.5 shows the stress distribution on the r-axis ahead of a crack tip when the crack length is long enough compared to the critical FPZ size, r_0, that is to say, linear fracture mechanics is applicable in this case. The stress intensity approximation can be adopted for the stress at r_0. If the characteristic distance is equal to the critical frontal process zone size, as shown in Fig. 4.5,

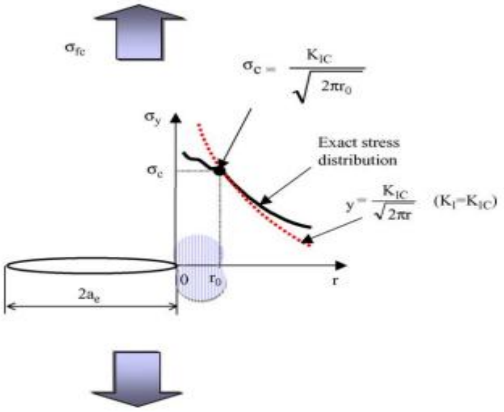
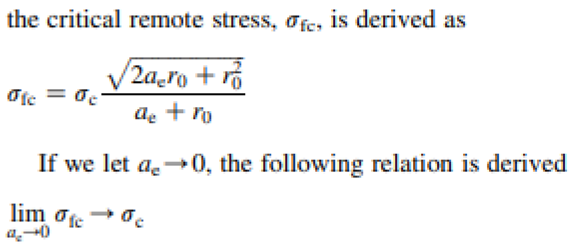


Fig 4.5 critical frontal process zone size


the critical remote stress, σ_{fc}, is derived as

$$\sigma_{fc} = \sigma_c \frac{\sqrt{2a_e r_0 + r_0^2}}{a_e + r_0}$$

If we let $a_e \rightarrow 0$, the following relation is derived

$$\lim_{a_e \rightarrow 0} \sigma_{fc} \rightarrow \sigma_c$$

The value of sc is, therefore, considered to be the strength of the infinite plate with no artificial crack. However, actual materials have inherent cracks and the weakest crack dominates the strength. The difference between the strength of actual materials and the value of sc is then considered to be the difference between their effective volumes, where the effective volume is the critical FPZ size.

4.4 R-curve effects

The nature of the applied driving force curve relative to the material's R-curve determines the stability of a given crack. The usage of R-curves in fracture analysis is a more complex, but more comprehensive failure criteria compared to the common failure criteria that fracture occurs when G>Gc, Where Gc is simply a constant value called the critical energy release rate. An R-curve based failure analysis takes into account the notion that a material's resistance to fracture is not necessarily constant during crack growth.

R-curves can alternatively be discussed in terms of stress intensity factors rather than energy release rates where the R-curves can be expressed as the fracture toughness as a function of crack length.

Types of R-Curves:

Flat R-Curves

The simplest case of a material's crack resistance curve would be materials which exhibit a "flat R-curve". In materials with flat R-curves, as a crack propagates, the resistance to further crack propagation remains constant Physically, the independence of GR from Δa is indicative that in these materials the phenomena which are energetically costly during crack propagation do not evolve during crack propagation. This tends to be an accurate model for perfectly brittle materials such as ceramics, in which the principal energetic cost of fracture is the development of new free surfaces on the crack faces. The character of the energetic cost of the creation of new surfaces remains largely unchanged regardless of how long the crack has propagated from its initial length.

Rising R-Curves

Another category of R-curve that is common in real materials is a "rising R-curve" In materials with rising R-curves, as a crack propagates, the resistance to further crack propagation increases, and it requires a higher and higher applied G in order to achieve each subsequent increment of crack extension s such, it can be technically challenging in these materials in practice to define a single value to quantify resistance to fracture.

Falling R-Curves

While far less common, some materials can exhibit falling R-curves In some cases, the material may initially exhibit rising R-curve behavior, reach a steady-state condition, and then transition into falling R-curve behavior. In a falling R-curve regime, as a crack propagates, the resistance to further crack propagation drops, and it requires less and less applied G in order to achieve each subsequent increment of crack extension . Materials experiencing these conditions would exhibit highly unstable crack growth as soon as any initial crack began to propagate.

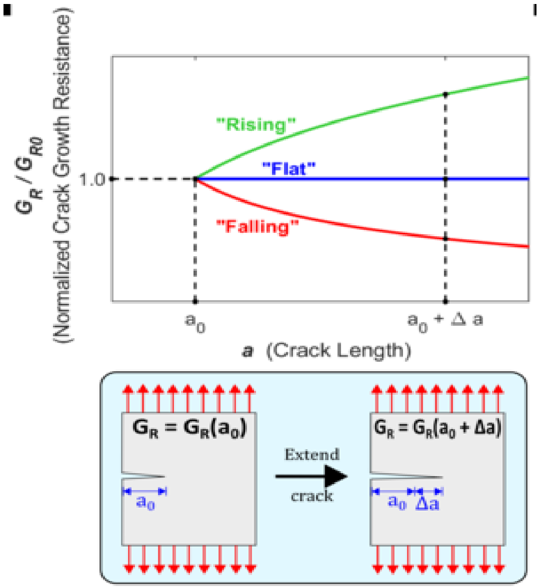


Fig 4.6 R Three canonical R curve types

Effect of size and Shape:

Size and geometry also plays a role in determining the shape of the R curve. A crack in a thin sheet tends to produce a steeper R curve than a crack in a thick plate because there is a low degree of stress triaxiality at the crack tip in the thin sheet while the material near the tip of the crack in the thick plate may be in plane strain. The R curve can also change at free boundaries in the structure. Thus, a wide plate may exhibit a somewhat different crack growth resistance behavior than a narrow plate of the same material. Ideally, the R curve, as well as other measures of fracture toughness, is a property only of the material and does not depend on the size or shape of the cracked body. Much of fracture mechanics is predicated on the assumption that fracture toughness is a material property.

Testing:

ASTM evolved a standard practice for determining R-curves to accommodate the widespread need for this type of data. While the materials to which this standard practice can be applied are not restricted by strength, thickness or toughness, the test specimens must be of sufficient size to remain predominantly elastic throughout the test. The size requirement is to ensure the validity of the linear elastic fracture mechanics calculations. Specimens of standard proportions are required, but size is variable, adjusted for yield strength and toughness of the material considered.

ASTM Standard E561 covers the determination of R-curves using a middle cracked tension panel [M(T)], compact tension [C(T)], and crack-line-wedge-loaded [C(W)] specimens. While the C(W) specimen had gained substantial popularity for collecting KR curve data, many organizations still conduct wide panel, center cracked tension tests to obtain fracture toughness data. As with the plane-strain fracture toughness standard, ASTM E399, the planar dimensions of the specimens are sized to ensure that nominal elastic conditions are met. For the M(T) specimen, the width (W) and half crack size (a) must be chosen so that the remaining ligament is below net section yielding at failure.

4.5 Crack deflection

In polycrystalline ceramics, the crack can propagate in an intergranular way. The associated irreversible work per unit area is 2γ-γgb. where γ is the surface energy of material and γgb is the grain boundary energy. Though the irreversible work is decreased because of grain boundary energy, the fracture area is increased in intergranular crack propagation. Moreover, Mode II crack can be caused by deflection from normal fracture plane during intergranular crack propagation, which furtherly improves the toughness of ceramics. As a result, the ceramics with intergranular fracture shows a higher toughness than that with transgranular fracture. when it fractures intergranularly. Crack deflection mechanisms bring about increased toughness in ceramics exhibiting abnormal grain growth (AGG). The heterogeneous microstructures produced by AGG form materials that can be considered as “in-situ composites” or “self-reinforced materials.

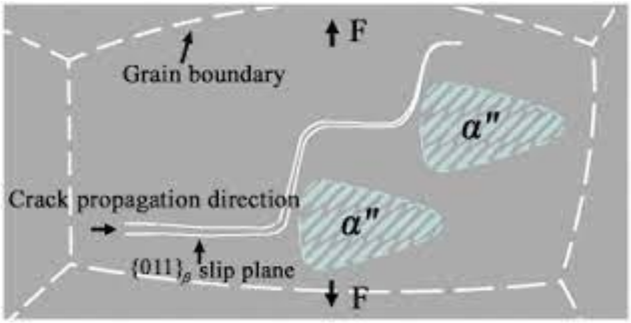


Fig 4.7 Crack deflection

4.6 Thermal expansion mismatch

Metal fillers (solders and brazes) can join a wide variety of materials, including aluminum, copper, stainless steel, refractory metals with aluminum oxide, aluminum nitride, silicon carbide and other oxide, nitrides and carbides… However, the success of bonding ceramic to metals depends on the exact ceramic and metal materials and the joined assembly size and geometry. This discussion is based on the coefficient of thermal expansion (CTE) mismatch of the materials being joined. Materials expand at different rates depending on the composition (atomic elements), structure (atomic arrangement) and thermal properties. A material’s volume will change equation based on the relationship and when derived to any linear dimension, the relationship of the increase of length per unit length per °C (or °F) is established that leads to the linear expansion relation.

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \frac{\Delta L}{L} = \alpha_L \Delta T$$

So with CTE being a major concern when ceramic:metal bonding, the design consideration are:

- CTE of the ceramic and metal… selecting lower CTE metals can be one solution.
- Size and geometry of joint… smaller joints and joints that are symmetric can offset strains.
- Bonding temperature… when bonding at lower temperatures, accumulated stresses are lower.

When making ceramic:metal bonds, outside of adhesive or glass bonding, brazing and soldering are the most common bonding methods to create connections or hermetic seals. Braze filler metals melt above 450 C where soldering filler metals melt below 450 C. From a CTE perspective solder joints would create less stressed joints when ceramic:metal bonding. But many times an assembly is subjected to service temperatures above the remelt temperature of solders or the solders may not be compatible with the service atmosphere so braze filler metals bonding above 850 C are used.

Lower filler metals such as **S-Bond active solders**, can bond aluminum to ceramic using low temperature. In solder joining, unlike brazing (over 450C) the component parts require heating to ~ 250 °C. Looking at the CTE values in the table below, a 12” plate of Aluminum will grow by almost 0.060” while the 12” plate of aluminum oxide will only grow by about 1/10 that amount with a CTE of 4.4 ppm for Alumina vs. the 23 ppm for Aluminum. Thus the alumina plate only grows at 250°C by about 0.010”… so upon cooling, the aluminum will try to return to length, by 0.060” where the alumina will only return, upon being bonded at 250°C by 0.010” setting up a strain difference to bending of the assemble plates, as seen in the figures above.

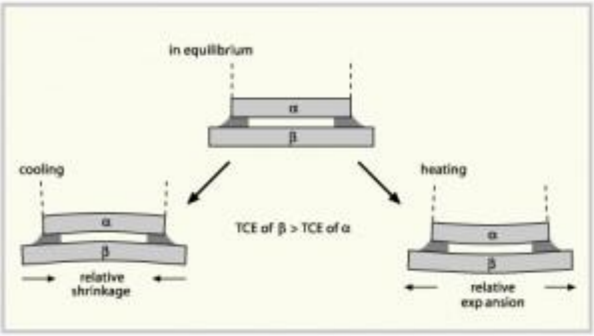


Fig 4.8 Thermal expansion mismatch of ceramics

So when ceramic:metal bonding CTE mismatch must be taken into their assembly designs by some of the following techniques.

1. Using better matched CTE materials (e.g. ceramic to Kovar).
2. Using multi-layers to over a distance accommodate CTE.
3. Bond smaller areas/components or make a mosaic breaking the larger CTE materials into smaller pieces.
4. Stiffening a design to resist bowing (may still fracture joint).
5. Use lower temperature joining processes, such as exothermic materials that only heat the joint areas, a recent commercially developed nanofoil has been developed and can reheat and solder joints via a patented NanoBond process.
6. Use design analytical modelling to better understand CTE mismatch and how it may be mitigated by design and/or process or filler metal material selections.

4.7 Average internal stresses & local stress distribution

Internal stress is stress that comes from within us and is often the most common cause of stress. We often worry about things we cannot control (e.g. whether we are going to lose our job) and we actually put ourselves into situations which we know will cause us stress.

The idea of stress considered in §3.1 is not difficult to conceptualise since objects interacting with other objects are encountered all around us. A more difficult concept is the idea of forces and stresses acting inside a material, “within the interior where neither eye nor experiment can reach” as Euler put it. It took many great minds working for centuries on this question to arrive at the concept of stress we use today, an idea finally brought to us by Augustin Cauchy, who presented a paper on the subject to the Academy of Sciences in Paris, in 1822.

Internal Stress

Consider first a long slender block of material subject to equilibrating forces F at its ends, Fig. 4.9.1a. If the complete block is in equilibrium, then any sub-division of the block must be in equilibrium also. By imagining the block to be cut in two, and considering free-body diagrams of each half, as in Fig. 4.9.1b, one can see that forces F must be acting within the block so that each half is in equilibrium. Thus external loads create internal forces; internal forces represent the action of one part of a material on another part of the same material across an internal surface. We can take it that a uniform stress σ = F / A acts over this interior surface, Fig. 4.9.1b.

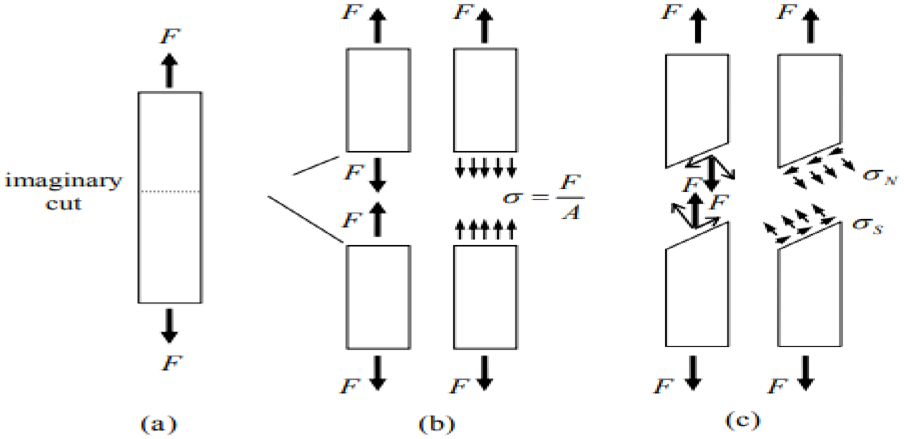


Fig 4.9 Internal stress

Note that, if the internal forces were not acting over the internal surfaces, the two halfblocks of Fig. 4.9.1b would fly apart; one can thus regard the internal forces as those required to maintain material in an un-cut state. If the internal surface is at an incline, as in Fig. 4.9.1c, then the internal force required for equilibrium will not act normal to the surface. There will be components of the force normal and tangential to the surface, and thus both normal (σ N) and shear (σ S) stresses must arise. Thus, even though the material is subjected to a purely normal load, internal shear stresses develop.

Unit-V- Optical Properties-SPHA7404

5.Introduction:

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine.

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures.

Classical optics is divided into two main branches: geometrical (or ray) optics and physical (or wave) optics. In geometrical optics, light is considered to travel in straight lines, while in physical optics, light is considered as an electromagnetic wave.

5.1 Classical optics

Classical optics is divided into two main branches: geometrical (or ray) optics and physical (or wave) optics. In geometrical optics, light is considered to travel in straight lines, while in physical optics, light is considered as an electromagnetic wave. Geometrical optics can be viewed as an approximation of physical optics that applies when the wavelength of the light used is much smaller than the size of the optical elements in the system being modelled.

Non-linear optics and non-linear optical properties:

The non-linear optics deals with the “intense light”, which upon interaction with material changes its optical properties. Unlike linear optical systems the non-linear optical systems does not follow superposition principle (i.e. A +B# X+Y). As a result of non-linear effect the incident light undergoes a change in optical properties like polarization, frequency, phase or path of incident light because the polarization density of medium responds non-linearly to the electric field of light. This behaviour is observed when the optical electric field strength of light is very high and comparable to that of intra-atomic electric field. In this case, the induced polarization is given by Eq.

$$P=\chi^{(1)} \cdot E+\chi^{(2)} \cdot E2+\chi^{(3)} \cdot E3+\cdots$$

χ(1) is the linear polarization susceptibility of materials which is applicable forlenses. χ(2) and χ(3) are non-linear polarization susceptibilities of the materials,which defines second order effects like a second harmonic generation and third order effects such as third harmonic generation, stimulated Raman scattering, four wave mixing and intensity dependence of the index of refraction. In non-linear optics, the light does not follow superposition principle. At high irradiance many molecules are excited to a high energy state, which are excited further to another higher energy states (the first excited state act on a low energy state for a high energy states). This causes vibrations at all frequencies corresponding to energy differences between populated states which, upon mixing, generate light with different frequency.

The non-linear properties of materials are susceptible to change at higher powersinducing nonlinear effects like self-focusing, solitons and high-harmonic generation.The most common non-linear processes involves second harmonic generation, thirdharmonic generation, optical parametric amplification, optical rectification, opticalKerr effect, multi photon absorption and cross polarised wave generation .

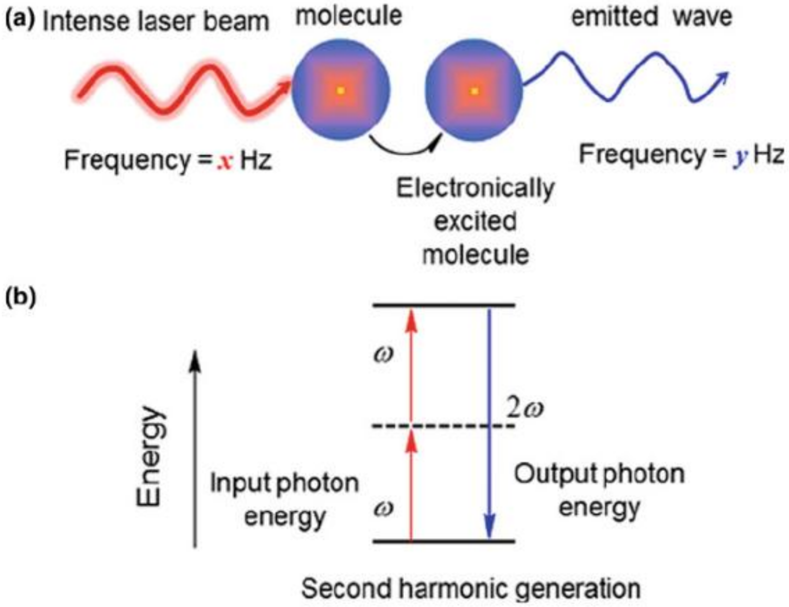


Fig 5.1 Presentation of Nonlinar optics system

5.2 Absorption of light in materials

Those who can remember sitting through elementary science class might recall learning that with all matter, light is absorbed and converted into energy. In the case of plants, this process is known as photosynthesis. However, they are by no means the only species or objects that do this.

In truth, all objects, living or inorganic are capable of absorbing light. In all cases, absorption depends on the electromagnetic frequency of the light being transmitted (i.e. the color) and the nature of the atoms of the object. If they are complementary, light will be absorbed; if they are not, then the light will be reflected or transmitted. In most cases, these processes occur simultaneously and to varying degrees, since light is usually transmitted at various frequencies. Therefore most objects will selectively absorb light while also transmitting and/or reflecting some of it. Wherever absorption occurs, heat energy is generated.

As already noted, absorption depends upon the state of an objects electrons. All electrons are known to vibrate at specific frequencies, what is commonly known as their natural frequency. When light, in the form of photons, interacts with an atom with the same natural frequency, the electrons of that atom will become excited and set into a natural vibrational motion. During this vibration, the electrons of the atom interact with neighboring atoms in such a way as to convert this vibrational energy into thermal energy. Subsequently, the light energy is not to be seen again, hence why absorption is differentiated from reflection and transmission. And since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies of visible light.

By relying on this method, physicists are able to determine the properties and material composition of an object by seeing which frequencies of light it is able to absorb. Whereas some materials are opaque to some wavelengths of light, they transparent to others. Wood, for example, is opaque to all forms of visible light. Glass and water, on the other hand, are opaque to ultraviolet light, but transparent to visible light.

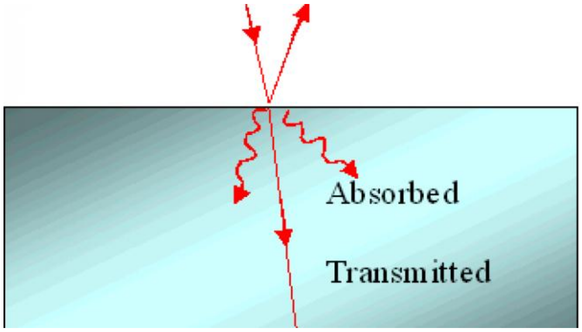


Fig 5.2 Light absorption materials

Ultimately, absorption of electromagnetic radiation requires the generation of the opposite field, in other words, the field which has the opposite coefficient in the same mode. A good demonstration of this is color. If a material or matter absorbs light of certain wavelengths (or colors) of the spectrum, an observer will not see these colors in the reflected light. On the other hand if certain wavelengths of colors are reflected from the material, an observer will see them and see the material in those colors. For example, the leaves of green plants contain a pigment called chlorophyll, which absorbs the blue and red colors of the spectrum and reflects the green. Leaves therefore appear green, whereas reflected light often appears to the naked eye to be refracted into several colors of the spectrum (i.e. a rainbow effect).

5.3 Electronic absorption

In conductors, absorption due to the presence of a cloud of free electrons or holes is continuous, with a magnitude that increases approximately as the square of the incident wavelength. Overlapping valence and conduction bands provide high reflectivity but prohibit transparency throughout the entire infrared. As the electron energy bands become separated in semiconductors however, the extent to which free electron carriers cause absorption becomes dependent upon the size of the energy gap at any given temperature, and the absence of impurities.

The electronic absorption processes at the higher frequency end of the infrared spectrum caused by band-to-band or band-to-exciton (electron in an electrostatically attracted combination with a hole) transitions can be divided into four main categories for semiconductor materials;

1. Intrinsic absorption, where in a pure semiconductor transitions between full valence bands and empty conduction bands are free to occur.
2. Extrinsic absorption, where transitions occur between the valence or conduction band and donor or acceptor sites in the band gap.
3. Free carrier absorption in which transitions occur within any one energy band, and
4. Localised energy states caused by defects or impurities, where electrons or holes may be excited into a higher energy state.

At frequencies close to the electronic absorption edge, a change in the bandgap (E_g) of the crystal by a fraction of an electron volt can change the absorption coefficient (α) by nearly four orders of magnitude. By measurement of the spectral position and profile of the absorption edge, values for the energy band-gap (E_g) can be determined, together with other general information about the energy states either side of the forbidden band responsible for electrical conduction. However, the estimation of the energy gap from the absorption edge is not a straightforward for the following reason;

As the momentum of a photon (h/λ) is very small compared to the crystal momentum (h/a), where a is the lattice constant, the photon-absorption process should conserve the momentum of the electron. However, the absorption coefficient (α) for a given photon energy hf is proportional to the probability ($P_{i,f}$) for the transition from the initial state (n_i) to the final state (n_f) , the density of electrons in the initial state, and also to the density of available final states. These processes must be summed for all the possible transitions between states that are separated by an energy difference equal to hf,

$$\alpha_{(hf)} = \sum_{i}^{f} P_{i,f} n_i n_f$$

Therefore both the exact positioning and shape of the electronic absorption edge cannot easily be predicted or modelled through solid state theory without detailed knowledge of all the allowed & forbidden, direct & indirect transitions available, together with knowledge of the density of electrons as given by the product of the density of states and the Fermi-Dirac function, with the probability of an electron level possessing an electron given by:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}$$

where, E is the energy level, E_f is the Fermi-energy level, k is Boltzmann' s constant and T is the absolute temperature. The following figure illustrates the various electronic absorption energy band transitions available in a typical semiconductor material.

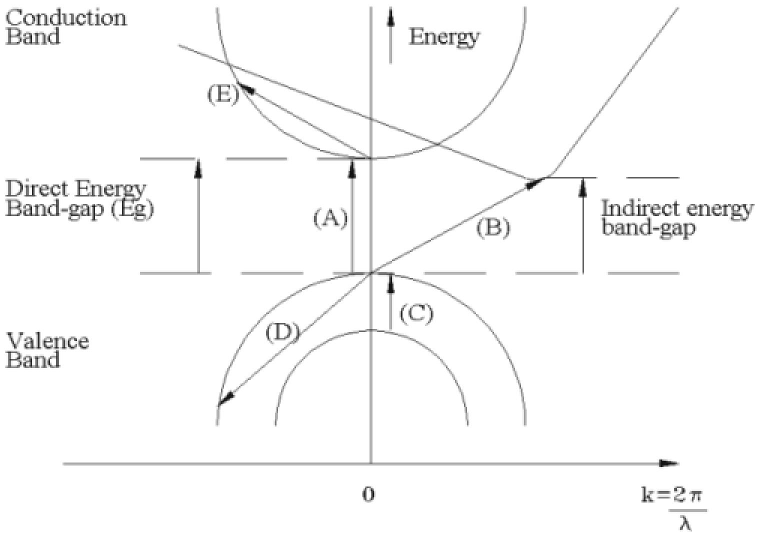


Fig 5.3 Electronic absorption

Electronic absorption energy band transitions

- Direct valence to conduction band transitions (constant *k* vector)
- Indirect valence to conduction band transitions aided by photon/phonon coupling interactions
- Inter-valence band transitions
- Valence band free-carrier transitions aided by impurities or photon/phonon interactions
- Conduction band free-carrier transitions aided by impurities or photon/phonon interactions

Optical materials that are opaque in the visible, because of comparatively small bandgaps (≤ 1.25eV), are arbitrarily classified as infrared semiconductors whilst materials of larger bandgap, and whose lattice absorption is present in the far-infrared are insulators.

5.4 Lattice absorption

The conductive properties of many materials that are suitable for use as optical substrates can provide a good indication of the expected spectral performance, as the systematic tendencies in the electrical properties tend to parallel the optical behaviour. Insulator materials show some regions of transparency, either in the near or far-infrared, whilst good electrical and thermal conductors exhibit a continuous background of electronic absorption over the whole infrared region.

All of the resonant absorption processes involved in an infrared material can be explained by the same common principal. At particular frequencies the incident radiation is allowed to propagate through the crystal lattice producing the observed transparency, other frequencies however, are forbidden when the incident radiation is at resonance with any of the properties of the lattice material, and as such are transferred as thermal energy, exciting the atoms or electrons. The resonant vibrational absorption characteristics created by the lattice are highly complex, consisting of several types of fundamental vibrations. In order that a mode of vibration can absorb, a mechanism for coupling the vibrational motion to the electromagnetic radiation must exist.

Transfer of electromagnetic radiation from the incident medium to the material is in the form of a couple, where the lattice vibration produces an oscillating dipole moment which can be driven by the oscillating electric field (E) of the radiation. In order for the total transfer of energy to be complete, the following three conditions must be satisfied;

- the conservation of energy is maintained,
- the conservation of momentum is maintained, and
- a coupling mechanism between the material and the incident medium is present.

The conservation of momentum is governed by the relationship between de Broglie's particle/wave duality, from the photon and phonon momenta, where the photon momentum is $P = h/\lambda$. The phonon momentum in the crystal is given by $P = h/a$, where α is the lattice constant for the unit cell. When $\lambda=a$, the conservation of momentum is preserved between the incident photon and thermal phonon, resulting in complete absorption of the incident radiation by the lattice. However, the photon has a low momentum when compared to the momentum of a phonon, therefore two or more photons are required to satisfy the conservation of momentum and produce total absorption.

The coupling mechanism between the incident photon and the lattice phonon is produced by a change of state in the electric dipole moment *(M)* of the crystal. A dipole moment arises when two equal and opposite charges are situated a very short distance apart, and is the product of either of the charges with the distance between them. Thus energy absorbed from the radiation will be converted into vibrational motion of the atoms. In simple gas molecules this gives rise to a characteristic spectral absorption band, as the many molecules form a large number of coupled dipole moments.

In more complex lattice structures, in order for a mode of vibration to absorb any incident radiation, the basic mechanism for coupling must be present. Three different coupled absorption mechanisms exist;

1. Reststrahl absorption, this only occurs in ionic crystals and is caused by the creation of single phonons in the lattice.
2. Multi-phonon absorption which occurs when two or more phonons simultaneously interact and produce an electric moment with which the incident radiation may couple.
3. Defect induced one phonon absorption, which in a pure crystal is where the creation of a single phonon is not accompanied by a transitional change of state in dipole moment that can act as a couple, but is induced by the existence of a crystal defect or impurity to aid the coupling mechanism.

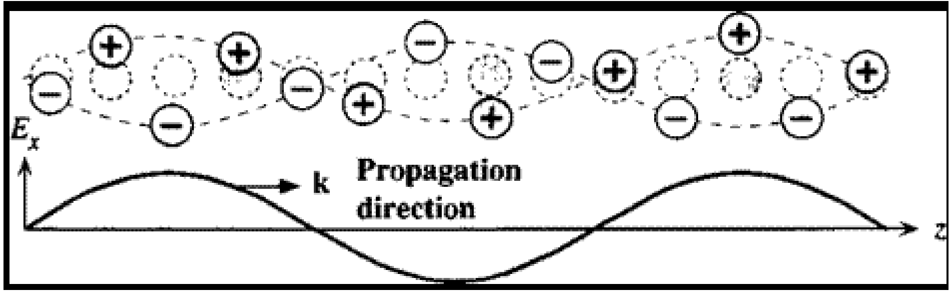


Fig 5.4 Lattice absorption through a crystal

5.5 phonons radiative and non-radiative recombination

In the solid-state physics of semiconductors, **carrier generation** and **carrier recombination** are processes by which mobile charge carriers (electrons and electron holes) are created and eliminated. Carrier generation and recombination processes are fundamental to the operation of many optoelectronic semiconductor devices, such as photodiodes, light-emitting diodes and laser diodes. They are also critical to a full analysis of p-n junction devices such as bipolar junction transistors and p-n junction diodes.

The **electron–hole pair** is the fundamental unit of generation and recombination in inorganic semiconductors, corresponding to an electron transitioning between the valence band and the conduction band where generation of electron is a transition from the valence band to the conduction band and recombination leads to a reverse transition.

Radiative recombination is the mechanism responsible for photoemission in semiconductor light emitting diodes and is mainly associated with band to band recombination as a result of the high energy differences associated with a complete band gap transition. Direct band to band recombination is only possible in materials with extremely low defect concentrations due to the fact that strain fields in the crystal structure will alter atomic interaction distances and strengths. This difference is directly related to electron interaction density in the material which, according to the band theory of semiconductors, will alter the band structure of the material. Direct band gap Extrinsic semiconductors, like GaAs, are manufactured to have little to no crystalline defects so to prevent the creation of defect levels within the band gap.

When radiative recombination occurs, the photon emitted has a characteristic energy similar to the band gap of the material and therefore will have a very weak interaction with the material. Therefore allowing for photons emitted within the sample through radiative recombination events to escape.

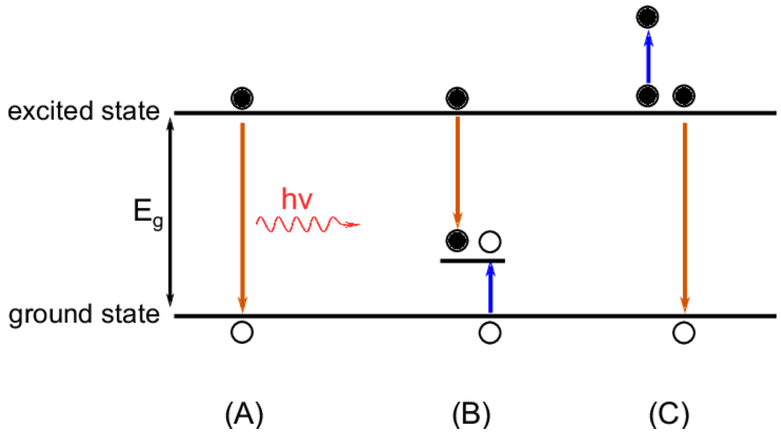


Fig 5.5- Sources of recombination losses: radiative recombination (A), non-radiative recombination via trap state (B) and Auger recombination (C).

Non-Radiative Recombination

Non-radiative recombination is a process in phosphors and semiconductors, whereby charge carriers recombine releasing phonons instead of photons. Non-radiative recombination in optoelectronics and phosphors is an unwanted process, lowering the light generation efficiency and increasing heat losses.

Non-radiative life time is the average time before an electron in the conduction band of a semiconductor recombines with a hole. It is an important parameter in optoelectronics where radiative recombination is required to produce a photon; if the non-radiative life time is shorter than the radiative, a carrier is more likely to recombine non-radiatively. This results in low internal quantum efficiency.

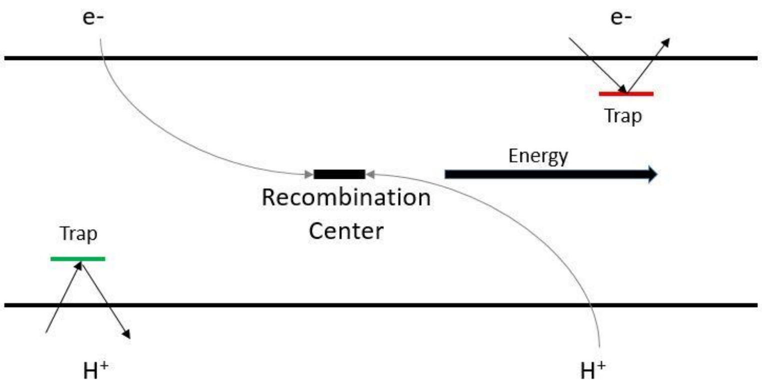


Fig 5.6- Non radiative recombination

5.6 Dynamic Maxwell – garnet equation

In 1904, Maxwell Garnett developed a simple but immensely successful homogenization theory . As any such theory, it aims to approximate a complex electromagnetic medium such as a colloidal solution of gold microparticles in water with a homogeneous effective medium. The Maxwell Garnett mixing formula gives the permittivity of this effective medium (or, simply, the effective permittivity) in terms of the permittivities and volume fractions of the individual constituents of the complex medium.

A closely related development is the Lorentz molecular theory of polarization. This theory considers a seemingly different physical system: a collection of point-like polarizable atoms or molecules in vacuum. The goal is, however, the same: compute the macroscopic dielectric permittivity of the medium made up by this collection of molecules. A key theoretical ingredient of the Lorentz theory is the so-called local field correction, and this ingredient is also used in the Maxwell Garnett theory.

The two theories mentioned above seem to start from very different first principles. The Maxwell Garnett theory starts from the macroscopic Maxwell's equations, which are assumed to be valid on a fine scale inside the composite. The Lorentz theory does not assume that the macroscopic Maxwell's equations are valid locally. The molecules cannot be characterized by macroscopic quantities such as permittivity, contrary to small inclusions in a composite. However, the Lorentz theory is still macroscopic in nature. It simply replaces the description of inclusions in terms of the internal field and polarization by a cumulative characteristic called the polarizability. Within the approximations used by both theories, the two approaches are mathematically equivalent.

Maxwell Garnett Mixing Formula

We are now ready to derive the Maxwell Garnett mixing formula. We will start with the simple case of small spherical particles in vacuum. This case is conceptually very close to the Lorentz molecular theory of polarization. Of course, the latter operates with "molecules," but the only important physical characteristic of a molecule is its polarizability, α. A small inclusion in a composite can also be characterized by its polarizability. Therefore, the two models are almost identical.

Consider spherical particles of radius a and permittivity ϵ that are distributed in vacuum either on a lattice or randomly but uniformly on average. The specific volume per one particle is v, and the volume fraction of inclusions is f=(4π/3)(a3/v). The effective permittivity of such a medium can be computed by applying Eq. directly. The only thing that we will do is substitute the appropriate expression for α, which in the case considered is given by Eq.. We then have

$$\epsilon_{\mathrm{MG}} = \frac{1 + 2f\frac{\epsilon-1}{\epsilon+2}}{1 - f\frac{\epsilon-1}{\epsilon+2}} = \frac{1 + \frac{1+2f}{3}(\epsilon - 1)}{1 + \frac{1-f}{3}(\epsilon - 1)}.$$

This is the Maxwell Garnett mixing formula (hence the subscript MG) for small inclusions in vacuum. We emphasize that, unlike in the Lorentz theory of polarization, ϵMG is the effective permittivity of a composite, not the usual permittivity of a natural material.

Next, we remove the assumption that the background medium is vacuum, which is not realistic for composites. Let the host medium have the permittivity ϵh and the inclusions have the permittivity ϵi. The volume fraction of inclusions is still equal to f. We can obtain the required generalization by making the substitutions ϵMG→ϵMG/ϵh and ϵ→$\epsilon i/\epsilon h$, which yields

$$\epsilon_{\mathrm{MG}} = \epsilon_h \frac{1 + 2f\frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}}{1 - f\frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}} = \epsilon_h \frac{\epsilon_h + \frac{1+2f}{3}(\epsilon_i - \epsilon_h)}{\epsilon_h + \frac{1-f}{3}(\epsilon_i - \epsilon_h)}.$$

5.7 Application of laser crystals

Laser crystals are optical crystals – typically single crystals (monocrystalline optical materials) – which are used as gain media for solid-state lasers. In most cases, they are doped with either trivalent rare earth ions or transition metal ions. These ions enable the crystal to amplify light at the laser wavelength via stimulated emission, when energy is supplied to the crystal via absorption of pump light (→ *optical pumping*).

Compared with doped glasses, crystals usually have higher transition cross sections, a smaller absorption and emission bandwidth, a higher thermal conductivity, and possibly birefringence. (The article on laser glasses discusses the differences in more detail.) In some cases, monocrystalline laser materials may be replaced with ceramic laser gain media, which have a fine polycrystalline structure.

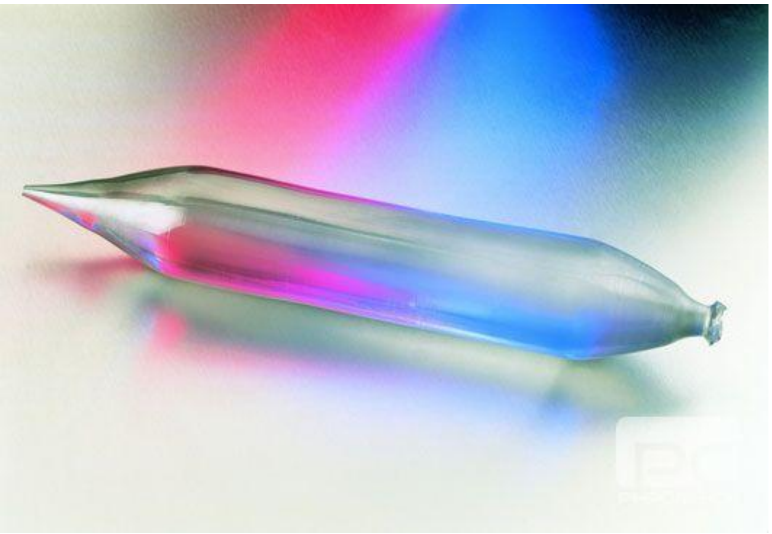


Fig 5.7- Laser crystal

Applications :

Biomedical sensing: small size, low cost, and low power consumption offer a variety of advantages in biomedical sensing applications. Potentially, liquid-crystal lasers could form the basis for "lab on a chip" devices that provide immediate readings without sending a sample away to a separate lab.

Medical: low emission power limits such medical procedures as cutting during surgeries, but liquid-crystal lasers show potential to be used in microscopy techniques and in vivo techniques such as photodynamic therapy.

Display screens: liquid-crystal-laser-based displays offer most of the advantages of standard liquid-crystal displays, but the low spectral spread gives more precise control over color. Individual elements are small enough to act as single pixels while retaining high brightness and color definition. A system in which each pixel is a single spatially tuned device could avoid the sometimes long relaxation times of dynamic tuning, and could emit any color using spatial addressing and the same monochromatic pumping source.

Environmental sensing: using a material with a helical pitch highly sensitive to temperature, electric field, magnetic field, or mechanical strain, color shift of the output laser provides a simple, direct measurement of environmental conditions.

5.8 Electrical rectification

Electro-optic rectification (EOR), also referred to as optical rectification, is a non-linear optical process that consists of the generation of a quasi-DC polarization in a non-linear medium at the passage of an intense optical beam. For typical intensities, optical rectification is a second-order phenomenon[1] which is based on the inverse process of the electro-optic effect. It was reported for the first time in 1962,[2] when radiation from a ruby laser was transmitted through potassium dihydrogen phosphate (KDP) and potassium dideuterium phosphate (KD_dP) crystals.

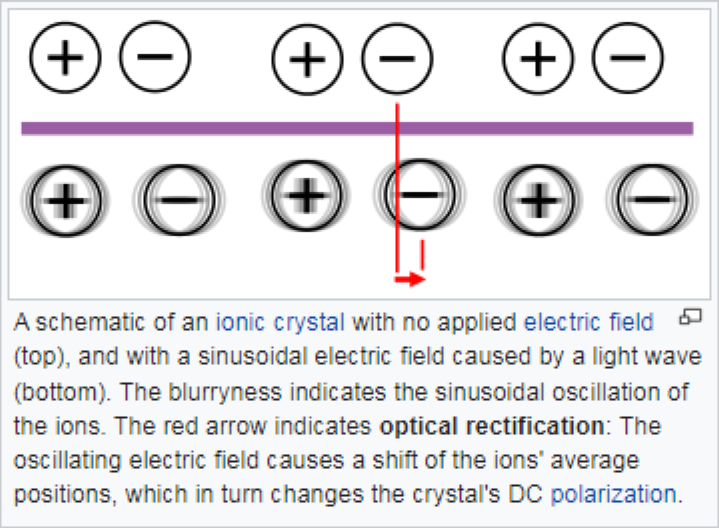
Optical rectification can be intuitively explained in terms of the symmetry properties of the non-linear medium: in the presence of a preferred internal direction, the polarization will not reverse its sign at the same time as the driving field. If the latter is represented by a sinusoidal wave, then an average DC polarization will be generated.

Optical rectification is analogous to the electric rectification effect produced by diodes, wherein an AC signal can be converted ("rectified") to DC. However, it is not the same thing. A diode can turn a sinusoidal electric field into a DC current, while optical rectification can turn a sinusoidal electric field into a DC polarization, but not a DC current. On the other hand, a changing polarization is a kind of current. Therefore, if the incident light is getting more and more intense, optical rectification causes a DC current, while if the light is getting less and less intense, optical rectification causes a DC current in the opposite direction. But again, if the light intensity is constant, optical rectification cannot cause a DC current.

When the applied electric field is delivered by a femtosecond-pulse-width laser, the spectral bandwidth associated with such short pulses is very large. The mixing of different frequency components produces a beating polarization, which results in the emission of electromagnetic waves in the terahertz region. The EOR effect is somewhat similar to a classical electrodynamic emission of radiation by an accelerating/decelerating charge, except that here the charges are in a bound dipole form and the THz generation depends on the second order susceptibility of the nonlinear optical medium. A popular material for generating radiation in the 0.5–3 THz range (0.1 mm wavelength) is zinc telluride.

Optical rectification also occurs on metal surfaces by similar effect as surface second harmonic generation. The effect is however influenced e. g. by nonequilibrium electron excitation and generally it manifests in a more complicated way.

Similar to other nonlinear optical processes, optical rectification is also reported to become enhanced when surface plasmons are excited on a metal surface.



A schematic of an ionic crystal with no applied electric field (top), and with a sinusoidal electric field caused by a light wave (bottom). The blurryness indicates the sinusoidal oscillation of the ions. The red arrow indicates **optical rectification**: The oscillating electric field causes a shift of the ions' average positions, which in turn changes the crystal's DC polarization.

Fig 5.8 Optical rectification

5.9 Powder laser

Metal additive manufacturing is "the process of joining materials to make objects from 3D computer-aided design (CAD) model data, usually layer upon layer, as opposed to subtractive manufacturing technologies."1 Metal additive manufacturing has a number of modalities, including material extrusion, material jetting, material droplet printing, binder jetting, sheet lamination, powder bed fusion, and directed energy deposition.2 Most current metal additive manufacturing systems are of the powder bed fusion type.2 In the powder bed fusion process, thin layers of powder are applied to a build plate and an energy source (a laser or electron beam) is used to fuse the powder at locations specified by the model of desired geometry. When one layer is completed, a new layer of powder is applied and the process is repeated until a 3D part is produced. The powder bed fusion process is alternately known as selective laser sintering (SLS), selective laser melting (SLM), direct metal laser sintering (DMLS), direct metal laser melting (DMLM), and electron beam melting (EBM).3 Current metal powder bed fusion additive manufacturing systems tend to use melting as opposed to sintering to build full-density parts

Metal laser powder bed fusion additive manufacturing systems have designs similar to that illustrated in Fig. 5.9 They are composed of powder delivery and energy delivery systems. The powder delivery system comprises a piston to supply powder, a coater to create the powder layer, and a piston that holds the fabricated part. The energy delivery system is made up of a laser (usually a single-mode continuous wave Ytterbium fiber laser operating at 1075 nm wavelength) and a scanner system with optics that enable the delivery of a focused spot to all points of the build platform. A flow of gas (usually nitrogen or argon) passes over the powder bed with the intention to (a) protect the part from oxygen and (b) to clear any “spatter” and metal fumes that are created from the laser path. Some systems have an in situ process monitoring capability that can image the melt pool using a high-speed camera or a temperature sensor that is inline with the laser system.

During production, the laser executes a scanning or exposure strategy. The strategies associated with the laser path are characterized by the length, direction, and separation (hatch spacing) of neighboring scan vectors. A detailed discussion of scanning strategies is beyond the scope of this paper, but a list of scanning strategies has been compiled Scanning strategies can affect the properties of the part including density, mechanical properties, and residual stress. Residual stress is one of several important material responses that need to be optimized for laser-based additively manufactured parts. A part can be fabricated within tolerances only to have residual stress-induced distortions put the part out of tolerance when removed from the build plate. Residual stresses can also cause a part’s connection to support structures to fail or result in surface deformations that can damage the coater or inhibit the coater’s motion

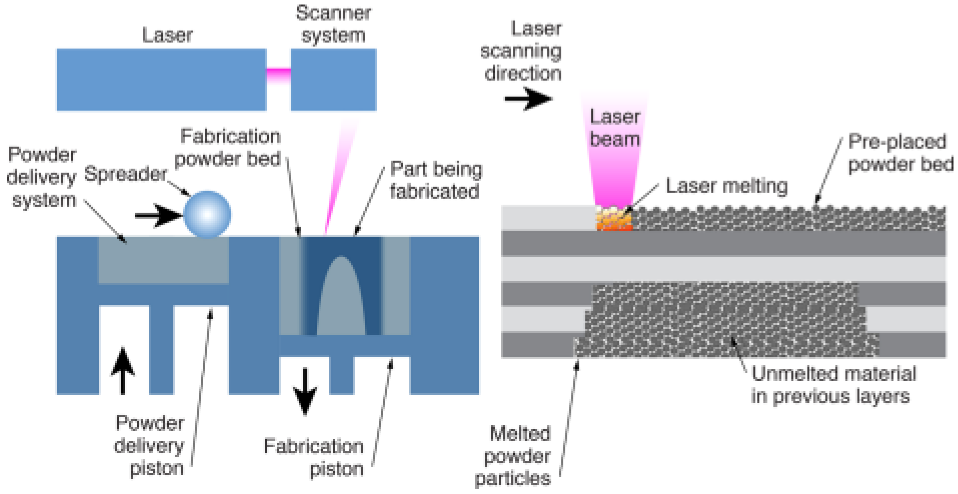


Fig 5.8 Laser powder bed fusion

Advantages

- Reduced material wastage and cost (superior buy-to-fly ratio)
- Improved production development times
- Enablement of rapid prototyping and low volume production
- Capable of building functionally graded parts
- Fully customised parts on a batch by batch basis, eliminating fixed designs
- Good resolution when compared to other additive manufacturing processes
- Efficient recycling of un-melted powder
- Ability to join many material grades, including ceramics, glass, plastics, metals and alloys
- Elimination of the need for machining fixtures

T EXT / REFERENCE BOOKS

1. C.M. Srivastava & C. Srinivasan, Science of Engineering materials, 1st reprinting, Willey eastern limited, 1991.
2. S. K. Hijra choudhury and A.K. Hajr choudhury, Material science and process, J.K. Publishers, 1986.
3. Bhushan, B., Luo, D., Schricker, S.R., Sigmund, W, Zauscher, S. Handbook of Nanomaterials Properties, 1st Edn, Springer.
4. Giri, P. K., Goswami, D. K., Perumal, A., Advanced Nanomaterials and Nanotechnology, Springer, 2013.
5. Lumban Gaol, Ford, Webb, Jeffrey, X, Recent Trends in Nanotechnology and Materials Science, Springer, 2014.